CHEMICAL ENGINEERING DESIGN

PRINCIPLES, PRACTICE AND ECONOMICS OF PLANT AND PROCESS DESIGN

GAVIN TOWLER
RAY SINNOTT

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Ray Sinnott began his career in design and development with several major companies, including DuPont and John Brown. He later joined the Chemical Engineering Department at the University of Wales, Swansea, UK, publishing the first edition of Chemical Engineering Design in 1983. He is a Chartered Engineer, Eur. Ing. and Fellow of the Institute of Chemical Engineers.

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Preface

This book was first published as Volume 6 of the *Chemical Engineering* series edited by Coulson and Richardson. It was originally intended to be a standalone design textbook for undergraduate design projects that would supplement the other volumes in the Coulson and Richardson series. Emphasis was placed on the practice of process and equipment design, while the reader was referred to the other volumes in the series and other chemical engineering textbooks for details of the fundamental principles underlying the design methods.

In adapting this book for the North American market, we have followed the same philosophy, seeking to create a comprehensive guide to process plant design that could be used as part of the typical chemical engineering curriculum, while providing references to more detailed and specialized texts wherever necessary. The design procedures can be used without the need for reference to the other books, research papers, or websites cited.

We recognize that chemical engineers work in a very diverse set of industries, and many of these industries have their own design conventions and specialized equipment. We have attempted to include examples and problems from a broad range of process industries, but where space or our lack of expertise in the subject has limited coverage of a particular topic, references to design methods available in the general literature are provided.

In writing this book, we have drawn on our experience of the industrial practice of process design, as well as our experience teaching design at the University of Wales Swansea, University of Manchester, and Northwestern University. Since the book is intended to be used in practice and not just as a textbook, our aim has been to describe the tools and methods that are most widely used in industrial process design. We have deliberately avoided describing idealized conceptual methods developed by researchers that have not yet gained wide currency in industry. The reader can find good descriptions of these methods in the research literature and in more academic textbooks.

Standards and codes of practice are an essential part of engineering; therefore, the relevant North American standards are cited. The codes and practices covered by these standards will be applicable to other countries. They will be covered by equivalent national standards in most developed countries, and in some cases the relevant British, European, or International standards have also been cited. Brief summaries of important U.S. and Canadian safety and environmental legislation have been given in the relevant chapters. The design engineer should always refer to the original source references of laws, standards, and codes of practice, as they are updated frequently.

All of the costs and examples have been put on a U.S. basis, and examples have been provided in both metric and conventional units. Where possible, the terminology used in the U.S. engineering and construction industry has been used.

Most industrial process design is carried out using commercial design software. Extensive reference has been made to commercial process and equipment design software throughout the book. Many of the commercial software vendors provide licenses of their software for educational purposes at nominal fees. We strongly recommend that students be introduced to commercial software at as early a stage in their education as possible. The use of academic design and costing software should be discouraged. Academic programs usually lack the quality control and support required by industry, and the student is unlikely to use such software after graduation. All computer-aided design tools must be used with some discretion and engineering judgment on the part of the designer. This judgment mainly comes from experience, but we have tried to provide helpful tips on how to best use computer tools.

The art and practice of design cannot be learned from books. The intuition and judgment necessary to apply theory to practice will come only from practical experience. We trust that this book will give its readers a modest start on that road.

Ray Sinnott
Gavin Towler

How to Use This Book

This book has been written primarily for students in undergraduate courses in chemical engineering and has particular relevance to their senior design projects. It should also be of interest to new graduates working in industry who find they need to broaden their knowledge of unit operations and design. Some of the earlier chapters of the book can also be used in introductory chemical engineering classes and by other disciplines in the chemical and process industries.

As a Senior Design Course Textbook

Chapters 1 to 9 and 14 cover the basic material for a course on process design and include an explanation of the design method, including considerations of safety, costing, and materials selection. Chapters 2, 3, and 8 contain a lot of background material that should have been covered in earlier courses and can be quickly skimmed as a reminder. If time is short, Chapters 4, 6, and 9 deserve the most emphasis. Chapters 10 to 13 cover equipment selection and design, including mechanical aspects of equipment design. These important subjects are often neglected in the chemical engineering curriculum. The equipment chapters can be used as the basis for a second course in design or as supplementary material in a process design class.

As an Introductory Chemical Engineering Textbook

The material in Chapters 1, 2, 3, and 6 does not require any prior knowledge of chemical engineering and can be used as an introductory course in chemical engineering. Much of the material in Chapters 7, 9, 10, and 14 could also be used in an introductory class. There is much to be said for introducing design at an early point in the chemical engineering curriculum, as it helps the students have a better appreciation of the purpose of their other required classes, and sets the context for the rest of the syllabus. Students starting chemical engineering typically find the practical applications of the subject far more fascinating than the dry mathematics they are usually fed. An appreciation of economics, optimization, and equipment design can dramatically improve a student's performance in other chemical engineering classes.

If the book is used in an introductory class, then it can be referred to throughout the curriculum as a guide to design methods.

Supplementary Material

Many of the calculations described in the book can be performed using spreadsheets. Templates of spreadsheet calculations and equipment specification sheets are available in Microsoft Excel format online and can be downloaded by all readers of this book from http://books.elsevier.com/companions.

Resources for Instructors

Supplementary material is available for registered instructors who adopt *Chemical Enginering Design* as a course text. Please visit http://textbooks.elsevier.com for information and to register for access to the following resources.

Lecture Slides

Microsoft PowerPoint presentations to support most of the chapters are available free of charge to instructors who adopt this book. To preview PDF samples of the slides please register with the site above. A complete set of slides on CD, in customizable PowerPoint format, will be sent to qualifying adopters on request.

Image Bank

A downloadable image bank of artwork from the book to use in lecture presentations is available.

Instructor's Manual

A full solutions manual with worked answers to the exercises in the main text is available for download.

Acknowledgments

As in my prefaces to the earlier editions of this book, I would like to acknowledge my debt to those colleagues and teachers who have assisted me in a varied career as a professional engineer. I would particularly like to thank Professor J. F. Richardson for his help and encouragement with earlier editions of this book. Also, my wife, Muriel, for her help with the typescripts of the earlier editions.

Eur. Ing. R. K. Sinnott
Coed-y-bryn, Wales

I would like to thank the many colleagues at UOP and elsewhere who have worked with me, shared their experience, and taught me all that I know about design. Particular thanks are due to Dr. Rajeev Gautam for allowing me to pursue this project and to Dick Conser, Peg Stine, and Dr. Andy Zarchy for the time they spent reviewing my additions to Ray's book and approving the use of examples and figures drawn from UOP process technology. My contribution to this book would not have been possible without the love and support of my wife, Caroline, and our children Miranda, Jimmy, and Johnathan.

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We are grateful to Aspen Technology Inc. and Honeywell Inc. for permission to include the screen shots that were generated using their software to illustrate the process simulation and costing examples. Laurie Wang of Honeywell also provided valuable review comments. The material safety data sheet in Appendix I is reproduced with permission of Fischer Scientific Inc. Aspen Plus®, Aspen Kbase, Aspen ICARUS, and all other AspenTech product names or logos are trademarks or registered trademarks of Aspen Technology Inc. or its subsidiaries in the United States and/or in other countries. All rights reserved.

The supplementary material contains images of processes and equipment from many sources. We would like to thank the following companies for permission to use these images: Alfa-Laval, ANSYS, Aspen Technology, Bete Nozzle, Bos-Hatten Inc., Chemineer, Dresser, Dresser-Rand, Enardo Inc., Honeywell, Komax Inc., Riggins Company, Tyco Flow Control Inc., United Value Inc., UOP LLC, and The Valve Manufacturer's Association.

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1 INTRODUCTION TO DESIGN

Chapter Contents

Key Learning Objectives

- How design projects are carried out and documented in industry
- Why engineers in industry use codes and standards and build margins into their designs
- How to improve a design using optimization methods
- Why experienced design engineers very rarely use rigorous optimization methods in industrial practice

1.1. INTRODUCTION

This chapter is an introduction to the nature and methodology of the design process and its application to the design of chemical manufacturing processes.

1.2. NATURE OF DESIGN

This section is a general discussion of the design process. The subject of this book is chemical engineering design, but the methodology described in this section applies equally to other branches of engineering.

Chemical engineering has consistently been one of the highest paid engineering professions. There is a demand for chemical engineers in many sectors of industry, including the traditional processing industries: chemicals, polymers, fuels, foods, pharmaceuticals, and paper, as well as other sectors such as electronic materials and devices, consumer products, mining and metals extraction, biomedical implants, and power generation.

The reason that companies in such a diverse range of industries value chemical engineers so highly is the following:

> *Starting from a vaguely defined problem statement such as a customer need or a set of experimental results, chemical engineers can develop an understanding of the important underlying physical science relevant to the problem and use this understanding to create a plan of action and set of detailed specifications which, if implemented, will lead to a predicted financial outcome.*

The creation of plans and specifications and the prediction of the financial outcome if the plans were implemented is the activity of chemical engineering design.

Design is a creative activity, and as such can be one of the most rewarding and satisfying activities undertaken by an engineer. The design does not exist at the start of the project. The designer begins with a specific objective or customer need in mind and, by developing and evaluating possible designs, arrives at the best way of achieving that objective—be it a better chair, a new bridge, or for the chemical engineer, a new chemical product or production process.

When considering possible ways of achieving the objective, the designer will be constrained by many factors, which will narrow down the number of possible designs. There will rarely be just one possible solution to the problem, just one design. Several alternative ways of meeting the objective will normally be possible, even several best designs, depending on the nature of the constraints.

These constraints on the possible solutions to a problem in design arise in many ways. Some constraints will be fixed and invariable, such as those that arise from physical laws, government regulations, and standards. Others will be less rigid and can be relaxed by the designer as part of the general strategy for seeking the best design. The constraints that are outside the designer's influence can be termed the external constraints. These set the outer boundary of possible designs, as shown in Figure 1.1. Within this boundary there will be a number of plausible designs bounded by the other

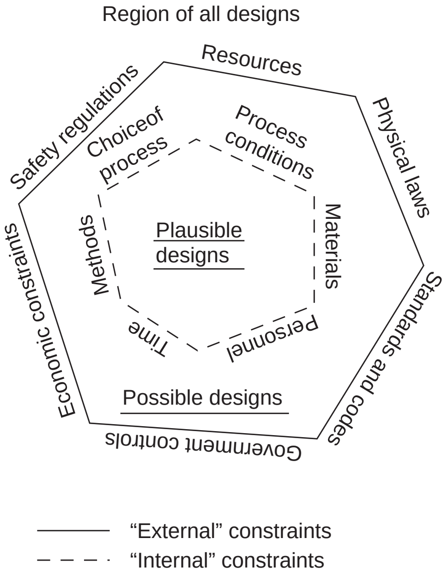

Figure 1.1. Design constraints.

constraints, the internal constraints, over which the designer has some control, such as choice of process, choice of process conditions, materials, and equipment.

Economic considerations are obviously a major constraint on any engineering design: plants must make a profit. Process costing and economics are discussed in Chapter 6.

Time will also be a constraint. The time available for completion of a design will usually limit the number of alternative designs that can be considered.

The stages in the development of a design, from the initial identification of the objective to the final design, are shown diagrammatically in Figure 1.2. Each stage is discussed in the following sections.

Figure 1.2 shows design as an iterative procedure; as the design develops, the designer will be aware of more possibilities and more constraints, and will be constantly seeking new data and ideas, and evaluating possible design solutions.

1.2.1. The Design Objective (The Need)

All design starts with a perceived need. In the design of a chemical process, the need is the public need for the product, creating a commercial opportunity, as foreseen by the sales and marketing organization. Within this overall objective, the designer will recognize subobjectives, the requirements of the various units that make up the overall process.

Before starting work, the designer should obtain as complete, and as unambiguous, a statement of the requirements as possible. If the requirement (need) arises from outside the design group, from a customer or from another department, then the designer will have to elucidate the real requirements through discussion. It is important to distinguish between the needs that are "must haves" and those that are "should

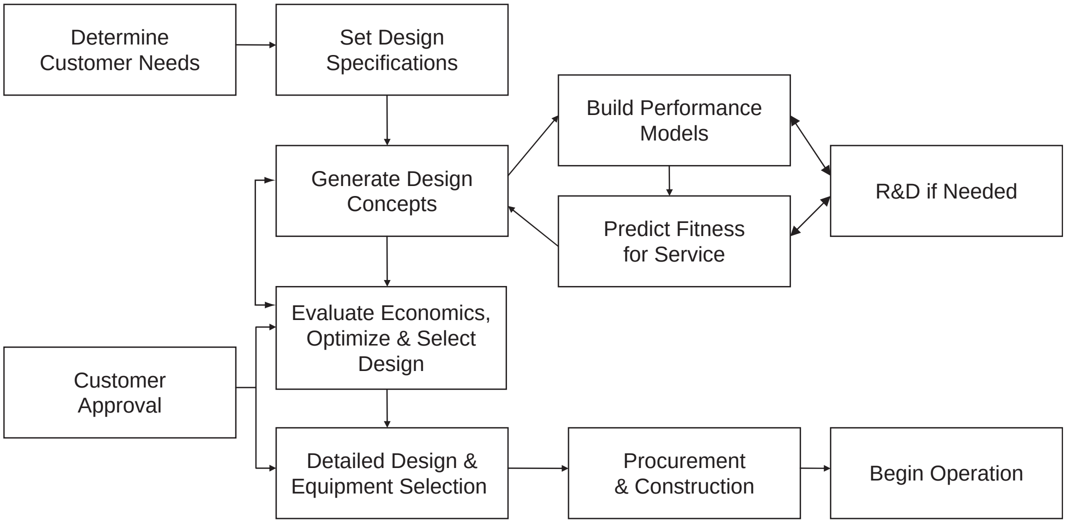

Figure 1.2. The design process.

haves.'' The ''should haves'' are those parts of the initial specification that may be thought desirable, but that can be relaxed if required as the design develops. For example, a particular product specification may be considered desirable by the sales department, but may be difficult and costly to obtain, and some relaxation of the specification may be possible, producing a saleable but cheaper product. Whenever possible, the designer should always question the design requirements (the project and equipment specifications) and keep them under review as the design progresses. It is important for the design engineer to work closely with the sales or marketing department or with the customer directly, to have as clear as possible an understanding of the customer's needs.

When writing specifications for others, such as for the mechanical design or purchase of a piece of equipment, the design engineer should be aware of the restrictions (constraints) that are being placed on other designers. A well-thought-out, comprehensive specification of the requirements for a piece of equipment defines the external constraints within which the other designers must work.

1.2.2. Setting the Design Basis

The most important step in starting a process design is translating the customer need into a design basis. The design basis is a more precise statement of the problem that is to be solved. It will normally include the production rate and purity specifications of the main product, together with information on constraints that will influence the design, such as

1. The system of units to be used.
2. The national, local or company design codes that must be followed.
3. Details of raw materials that are available.

4. Information on potential sites where the plant might be located, including climate data, seismic conditions, and infrastructure availability. Site design is discussed in detail in Chapter 14.
5. Information on the conditions, availability, and price of utility services such as fuel (gas), steam, cooling water, process air, process water, and electricity, that will be needed to run the process.

The design basis must be clearly defined before design can be begun. If the design is carried out for a client, then the design basis should be reviewed with the client at the start of the project. Most companies use standard forms or questionnaires to capture design basis information. A sample template is given in Appendix G and can be downloaded in MS Excel format from the online material at http://books.elsevier.com/companions.

1.2.3. Generation of Possible Design Concepts

The creative part of the design process is the generation of possible solutions to the problem for analysis, evaluation, and selection. In this activity, most designers largely rely on previous experience—their own and that of others. It is doubtful if any design is entirely novel. The antecedents of most designs can usually be easily traced. The first motor cars were clearly horse-drawn carriages without the horse, and the development of the design of the modern car can be traced step by step from these early prototypes. In the chemical industry, modern distillation processes have developed from the ancient stills used for rectification of spirits, and the packed columns used for gas absorption have developed from primitive, brushwood-packed towers. So, it is not often that a process designer is faced with the task of producing a design for a completely novel process or piece of equipment.

Experienced engineers usually prefer the tried-and-tested methods, rather than possibly more exciting but untried novel designs. The work that is required to develop new processes and the cost are usually underestimated. Commercialization of new technology is difficult and expensive, and few companies are willing to make multimillion dollar investments in technology that is not well proven (known as ‘‘me third’’ syndrome). Progress is made more surely in small steps; however, when innovation is wanted, previous experience, through prejudice, can inhibit the generation and acceptance of new ideas (known as ‘‘not invented here’’ syndrome).

The amount of work, and the way it is tackled, will depend on the degree of novelty in a design project. Development of new processes inevitably requires much more interaction with researchers and collection of data from laboratories and pilot plants.

Chemical engineering projects can be divided into three types, depending on the novelty involved:

A. Modifications, and additions, to existing plant; usually carried out by the plant design group.
B. New production capacity to meet growing sales demand and the sale of established processes by contractors. Repetition of existing designs, with only minor design changes, including designs of vendors’ or competitors’ processes carried out to understand whether they have a compellingly better cost of production.

C. New processes, developed from laboratory research, through pilot plant, to a commercial process. Even here, most of the unit operations and process equipment will use established designs.

The majority of process designs are based on designs that previously existed. The design engineer very seldom sits down with a blank sheet of paper to create a new design from scratch, an activity sometimes referred to as "process synthesis." Even in industries such as pharmaceuticals, where research and new product development are critically important, the types of processes used are often based on previous designs for similar products, so as to make use of well-understood equipment and smooth the process of obtaining regulatory approval for the new plant.

The first step in devising a new process design will be to sketch out a rough block diagram showing the main stages in the process and to list the primary function (objective) and the major constraints for each stage. Experience should then indicate what types of unit operations and equipment should be considered. The steps involved in determining the sequence of unit operations that constitute a process flowsheet are described in Chapter 4.

The generation of ideas for possible solutions to a design problem cannot be separated from the selection stage of the design process; some ideas will be rejected as impractical as soon as they are conceived.

1.2.4. Fitness Testing

When design alternatives are suggested, they must be tested for fitness of purpose. In other words, the design engineer must determine how well each design concept meets the identified need. In the field of chemical engineering, it is usually prohibitively expensive to build several designs to find out which one works best (a practice known as "prototyping," which is common in other engineering disciplines). Instead, the design engineer builds a mathematical model of the process, usually in the form of computer simulations of the process, reactors, and other key equipment. In some cases, the performance model may include a pilot plant or other facility for predicting plant performance and collecting the necessary design data. In other cases, the design data can be collected from an existing full-scale facility or can be found in the chemical engineering literature.

The design engineer must assemble all of the information needed to model the process so as to predict its performance against the identified objectives. For process design this will include information on possible processes, equipment performance, and physical property data. Sources of process information and physical properties are reviewed in Chapter 8.

Many design organizations will prepare a basic data manual, containing all the process "know-how" on which the design is to be based. Most organizations will have design manuals covering preferred methods and data for the more frequently used design procedures. The national standards are also sources of design methods and data. They are also design constraints, as new plants must be designed in accordance with the national standards. If the necessary design data or models do not exist, then research and development work is needed to collect the data and build new models.

Once the data has been collected and a working model of the process has been established, then the design engineer can begin to determine equipment sizes and costs. At this stage it will become obvious that some designs are uneconomical and they can be rejected without further analysis. It is important to make sure that all of the designs that are considered are fit for the service, i.e., meet the customer's "must have" requirements. In most chemical engineering design problems, this comes down to producing products that meet the required specifications. A design that does not meet the customer's objective can usually be modified until it does so, but this always adds extra costs.

1.2.5. Economic Evaluation, Optimization, and Selection

Once the designer has identified a few candidate designs that meet the customer objective, then the process of design selection can begin. The primary criterion for design selection is usually economic performance, although factors such as safety and environmental impact may also play a strong role. The economic evaluation usually entails analyzing the capital and operating costs of the process to determine the return on investment, as described in Chapter 6.

The economic analysis of the product or process can also be used to optimize the design. Every design will have several possible variants that make economic sense under certain conditions. For example, the extent of process heat recovery is a trade-off between the cost of energy and the cost of heat exchangers (usually expressed as a cost of heat exchange area). In regions where energy costs are high, designs that use a lot of heat exchange surface to maximize recovery of waste heat for reuse in the process will be attractive. In regions where energy costs are low, it may be more economical to burn more fuel and reduce the capital cost of the plant. The mathematical techniques that have been developed to assist in the optimization of plant design and operation are discussed briefly in Section 1.9.

When all of the candidate designs have been optimized, the best design can be selected. Very often, the design engineer will find that several designs have very close economic performance, in which case the safest design or that which has the best commercial track record will be chosen. At the selection stage an experienced engineer will also look carefully at the candidate designs to make sure that they are safe, operable, and reliable, and to ensure that no significant costs have been overlooked.

1.2.6. Detailed Design and Equipment Selection

After the process or product concept has been selected, the project moves on to detailed design. Here the detailed specifications of equipment such as vessels, exchangers, pumps, and instruments are determined. The design engineer may work with other engineering disciplines, such as civil engineers for site preparation, mechanical engineers for design of vessels and structures, and electrical engineers for instrumentation and control.

Many companies engage specialist Engineering, Procurement, and Construction (EPC) companies, commonly known as contractors, at the detailed design stage.

The EPC companies maintain large design staffs that can quickly and competently execute projects at relatively low cost.

During the detailed design stage there may still be some changes to the design, and there will certainly be ongoing optimization as a better idea of the project cost structure is developed. The detailed design decisions tend to focus mainly on equipment selection though, rather than on changes to the flowsheet. For example, the design engineer may need to decide whether to use a U-tube or a floating-head exchanger, as discussed in Chapter 12, or whether to use trays or packing for a distillation column, as described in Chapter 11.

1.2.7. Procurement, Construction, and Operation

When the details of the design have been finalized, the equipment can be purchased and the plant can be built. Procurement and construction are usually carried out by an EPC firm unless the project is very small. Because they work on many different projects each year, the EPC firms are able to place bulk orders for items such as piping, wire, valves, etc., and can use their purchasing power to get discounts on most equipment. The EPC companies also have a great deal of experience in field construction, inspection, testing, and equipment installation. They can therefore normally contract to build a plant for a client cheaper (and usually also quicker) than the client could build it on its own.

Finally, once the plant is built and readied for startup, it can begin operation. The design engineer will often then be called upon to help resolve any startup issues and teething problems with the new plant.

1.3. THE ANATOMY OF A CHEMICAL MANUFACTURING PROCESS

The basic components of a typical chemical process are shown in Figure 1.3, in which each block represents a stage in the overall process for producing a product from the raw materials. Figure 1.3 represents a generalized process; not all the stages will be needed for any particular process, and the complexity of each stage will depend on the nature of the process. Chemical engineering design is concerned with the selection and arrangement of the stages and the selection, specification, and design of the equipment required to perform the function of each stage.

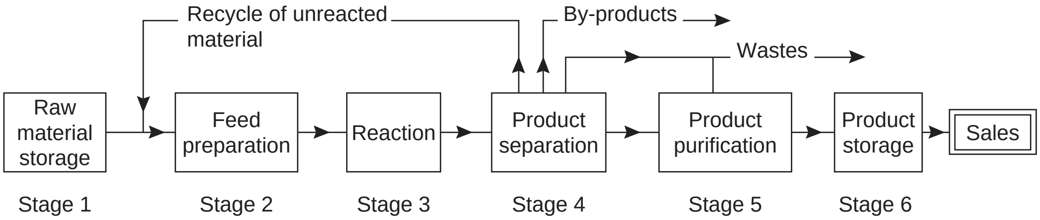

Figure 1.3. Anatomy of a chemical process.

Stage 1. Raw material storage: Unless the raw materials (also called feed stocks or feeds) are supplied as intermediate products (intermediates) from a neighboring plant, some provision will have to be made to hold several days' or weeks' worth of storage to smooth out fluctuations and interruptions in supply. Even when the materials come from an adjacent plant, some provision is usually made to hold a few hours' or even days' worth of inventory to decouple the processes. The storage required depends on the nature of the raw materials, the method of delivery, and what assurance can be placed on the continuity of supply. If materials are delivered by ship (tanker or bulk carrier), several weeks' stocks may be necessary, whereas if they are received by road or rail, in smaller lots, less storage will be needed.

Stage 2. Feed preparation: Some purification and preparation of the raw materials will usually be necessary before they are sufficiently pure, or in the right form, to be fed to the reaction stage. For example, acetylene generated by the carbide process contains arsenic and sulfur compounds, and other impurities, which must be removed by scrubbing with concentrated sulfuric acid (or other processes) before it is sufficiently pure for reaction with hydrochloric acid to produce dichloroethane. Feed contaminants that can poison process catalysts, enzymes, or micro-organisms must be removed. Liquid feeds need to be vaporized before being fed to gas-phase reactors and solids may need crushing, grinding, and screening.

Stage 3. Reaction: The reaction stage is the heart of a chemical manufacturing process. In the reactor the raw materials are brought together under conditions that promote the production of the desired product; almost invariably, some byproducts will also be formed, either through the reaction stoichiometry, by side reactions, or from reactions of impurities present in the feed.

Stage 4. Product separation: After the reactor(s) the products and byproducts are separated from any unreacted material. If in sufficient quantity, the unreacted material will be recycled to the reaction stage or to the feed purification and preparation stage. The byproducts may also be separated from the products at this stage. In fine chemical processes there are often multiple reaction steps, each followed by one or more separation steps.

Stage 5. Purification: Before sale, the main product will often need purification to meet the product specifications. If produced in economic quantities, the byproducts may also be purified for sale.

Stage 6. Product storage: Some inventory of finished product must be held to match production with sales. Provision for product packaging and transport is also needed, depending on the nature of the product. Liquids are normally dispatched in drums and in bulk tankers (road, rail, and sea); solids in sacks, cartons, or bales.

The amount of stock that is held will depend on the nature of the product and the market.

Ancillary Processes

In addition to the main process stages shown in Figure 1.3, provision must be made for the supply of the services (utilities) needed, such as process water, cooling water, compressed air, and steam. Facilities are also needed for maintenance, firefighting, offices and other accommodation, and laboratories; see Chapter 14.

1.3.1. Continuous and Batch Processes

Continuous processes are designed to operate 24 hours a day, 7 days a week, throughout the year. Some downtime will be allowed for maintenance and, for some processes, catalyst regeneration. The plant attainment or operating rate is the percentage of the available hours in a year that the plant operates, and is usually between 90 and 95%.

$$\text{Attainment } \% = \frac{\text{hours operated}}{8760} \times 100$$

Batch processes are designed to operate intermittently, with some, or all, of the process units being frequently shut down and started up. It is quite common for batch plants to use a combination of batch and continuous operations. For example, a batch reactor may be used to feed a continuous distillation column.

Continuous processes will usually be more economical for large-scale production. Batch processes are used when some flexibility is wanted in production rate or product specifications.

The advantages of batch processing are

A. Batch processing allows production of multiple different products or different product grades in the same equipment.
B. In a batch plant, the integrity of a batch is preserved as it moves from operation to operation. This can be very useful for quality control purposes.
C. The production rate of batch plants is very flexible, as there are no turn-down issues when operating at low output.
D. Batch plants are easier to clean and maintain sterile operation.
E. Batch processes are easier to scale up from chemist's recipes.
F. Batch plants have low capital for small production volumes. The same piece of equipment can often be used for several unit operations.

The drawbacks of batch processing are

A. The scale of production is limited.
B. It is difficult to achieve economies of scale by going to high production rates.
C. Batch-to-batch quality can vary, leading to high production of waste products or off-spec product.
D. Recycle and heat recovery are harder, making batch plants less energy efficient and more likely to produce waste byproducts.

E. Asset utilization is lower for batch plants, as the plant almost inevitably is idle part of the time.
F. The fixed costs of production are much higher for batch plants on a $/unit mass of product basis.

Choice of Continuous versus Batch Production

Given the higher fixed costs and lower plant utilization of batch processes, batch processing usually makes sense only for products that have high value and are produced in small quantities. Batch plants are commonly used for

- Food products
- Pharmaceutical products such as drugs, vaccines, and hormones
- Personal care products
- Specialty chemicals

Even in these sectors, continuous production is favored if the process is well understood, the production volume is large, and the market is competitive.

1.4. THE ORGANIZATION OF A CHEMICAL ENGINEERING PROJECT

The design work required in the engineering of a chemical manufacturing process can be divided into two broad phases.

Phase 1: Process design, which covers the steps from the initial selection of the process to be used, through to the issuing of the process flowsheets and includes the selection, specification, and chemical engineering design of equipment. In a typical organization, this phase is the responsibility of the Process Design Group, and the work is mainly done by chemical engineers. The process design group may also be responsible for the preparation of the piping and instrumentation diagrams.

Phase 2: Plant design, including the detailed mechanical design of equipment; the structural, civil, and electrical design; and the specification and design of the ancillary services. These activities will be the responsibility of specialist design groups, having expertise in the whole range of engineering disciplines.

Other specialist groups will be responsible for cost estimation, and the purchase and procurement of equipment and materials.

The sequence of steps in the design, construction and startup of a typical chemical process plant is shown diagrammatically in Figure 1.4, and the organization of a typical project group is shown in Figure 1.5. Each step in the design process will not be as neatly separated from the others as is indicated in Figure 1.4, nor will the sequence of events be as clearly defined. There will be a constant interchange of information between the various design sections as the design develops, but it is clear that some steps in a design must be largely completed before others can be started.

A project manager, often a chemical engineer by training, is usually responsible for the coordination of the project, as shown in Figure 1.5.

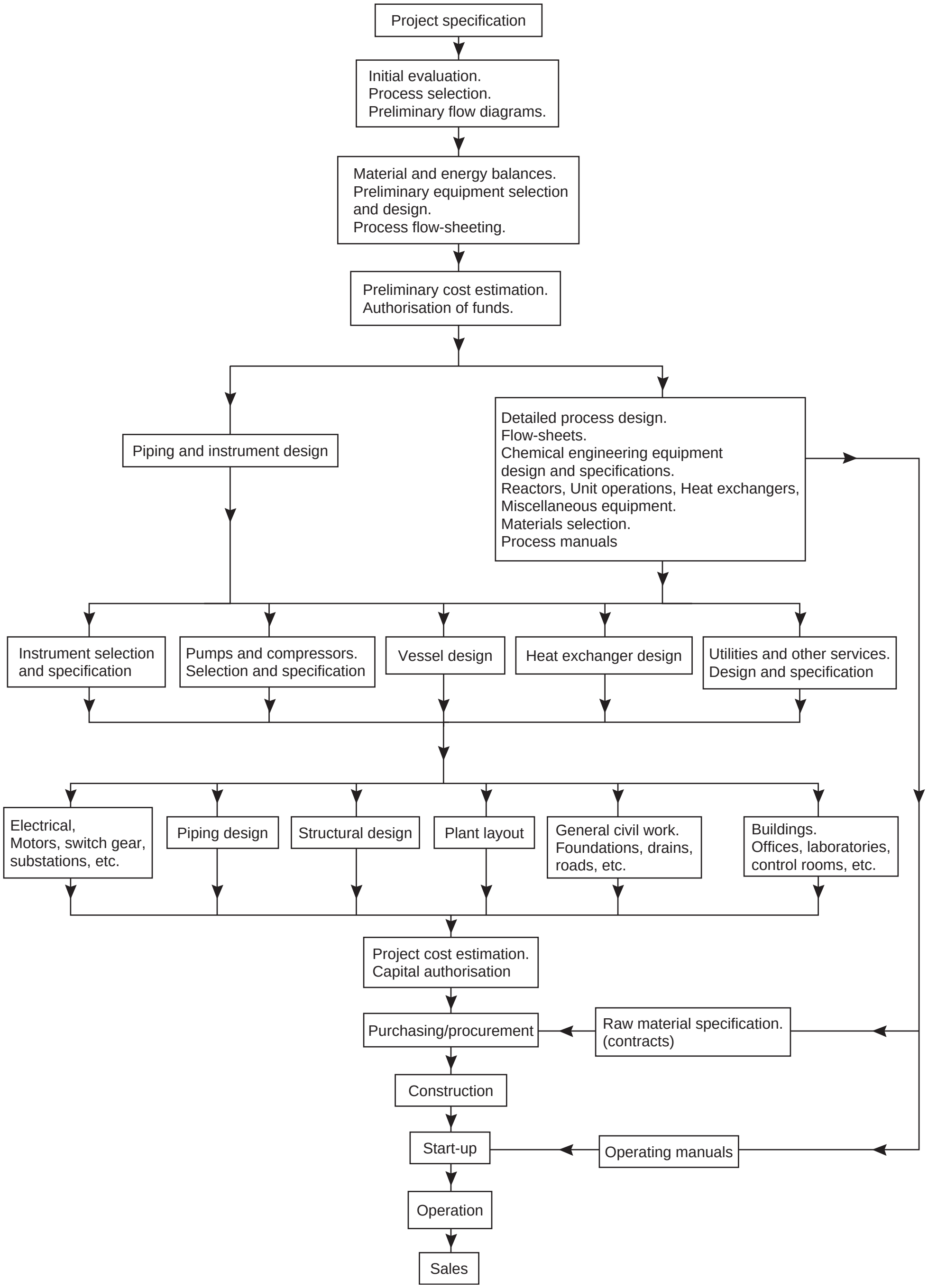

Figure 1.4. The structure of a chemical engineering project.

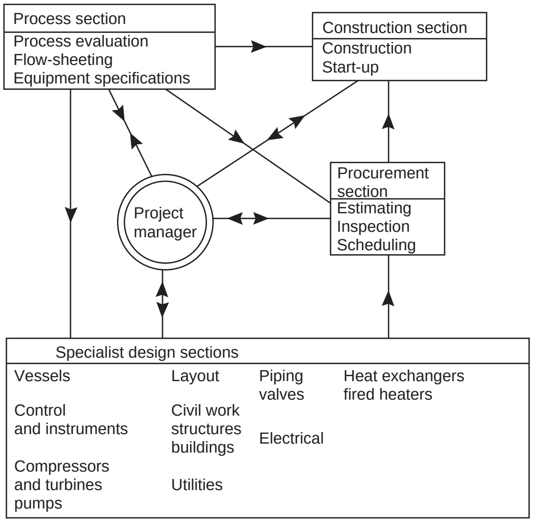

Figure 1.5. Project organization.

As was stated in Section 1.2.1, the project design should start with a clear specification defining the product, capacity, raw materials, process, and site location. If the project is based on an established process and product, a full specification can be drawn up at the start of the project. For a new product, the specification will be developed from an economic evaluation of possible processes, based on laboratory research, pilot plant tests and product market research.

Some of the larger chemical manufacturing companies have their own project design organizations and carry out the whole project design and engineering, and possibly construction, within their own organization. More usually, the design and construction, and possibly assistance with startup, are entrusted to one of the international Engineering, Procurement, and Construction contracting firms.

The technical "know-how" for the process could come from the operating company or could be licensed from the contractor or a technology vendor. The operating company, technology provider, and contractor will work closely together throughout all stages of the project.

On many modern projects, the operating company may well be a joint venture between several companies. The project may be carried out between companies based in different parts of the world. Good teamwork, communications, and project management are therefore critically important in ensuring that the project is executed successfully.

1.5. PROJECT DOCUMENTATION

As shown in Figure 1.5 and described in Section 1.4, the design and engineering of a chemical process requires the cooperation of many specialist groups. Effective cooperation depends on effective communications, and all design organizations have formal procedures for handling project information and documentation. The project documentation will include

1. General correspondence within the design group and with
    - Government departments
    - Equipment vendors
    - Site personnel
    - The client
2. Calculation sheets
    - Design calculations
    - Cost estimates
    - Material and energy balances
3. Drawings
    - Flowsheets
    - Piping and instrumentation diagrams
    - Layout diagrams
    - Plot/site plans
    - Equipment details
    - Piping diagrams (isometrics)
    - Architectural drawings
    - Design sketches
4. Specification sheets
    - The design basis
    - Feed and product specifications
    - An equipment list
    - Sheets for equipment, such as heat exchangers, pumps, heaters, etc.
5. Health, Safety and Environmental information:
    - Materials safety data sheets (MSDS forms)
    - HAZOP or HAZAN documentation (see Chapter 9)
    - Emissions assessments and permits
6. Purchase orders
    - Quotations
    - Invoices

All documents are assigned a code number for easy cross-referencing, filing, and retrieval.

Calculation Sheets

The design engineer should develop the habit of setting out calculations so that they can be easily understood and checked by others. It is good practice to include on calculation sheets the basis of the calculations, and any assumptions and approximations made, in sufficient detail for the methods, as well as the arithmetic, to be checked. Design calculations are normally set out on standard sheets. The heading at the top of each sheet should include the project title and identification number, the revision number and date and, most importantly, the signature (or initials) of the person who checked the calculation. A template calculation sheet is given in Appendix G and can be downloaded in MS Excel format from the online material at http://books.elsevier.com/companions.

Drawings

All project drawings are normally drawn on specially printed sheets, with the company name, project title and number, drawing title and identification number, drafter's name and person checking the drawing, clearly set out in a box in the bottom-right corner. Provision should also be made for noting on the drawing all modifications to the initial issue.

Drawings should conform to accepted drawing conventions, preferably those laid down by the national standards. The symbols used for flowsheets and piping and instrument diagrams are discussed in Chapters 4 and 5. In most design offices, computer-aided design (CAD) methods are now used to produce the drawings required for all the aspects of a project: flowsheets, piping and instrumentation, mechanical and civil work. While the released versions of drawings are usually drafted by a professional, the design engineer will often need to mark up changes to drawings or make minor modifications to flowsheets, so it is useful to have some proficiency with the drafting software.

Specification Sheets

Standard specification sheets are normally used to transmit the information required for the detailed design, or purchase, of equipment items, such as heat exchangers, pumps, columns, pressure vessels, etc.

As well as ensuring that the information is clearly and unambiguously presented, standard specification sheets serve as check lists to ensure that all the information required is included.

Examples of equipment specification sheets are given in Appendix G. These specification sheets are referenced and used in examples throughout the book. Blank templates of these specification sheets are available in MS Excel format in the online material at http://books.elsevier.com/companions. Standard worksheets are also often used for calculations that are commonly repeated in design.

Process Manuals

Process manuals are usually prepared by the process design group to describe the process and the basis of the design. Together with the flowsheets, they provide a complete technical description of the process.

Operating Manuals

Operating manuals give the detailed, step-by-step instructions for operation of the process and equipment. They would normally be prepared by the operating company personnel, but may also be issued by a contractor or technology licensor as part of the technology transfer package for a less-experienced client. The operating manuals are used for operator instruction and training and for the preparation of the formal plant operating instructions.

1.6. CODES AND STANDARDS

The need for standardization arose early in the evolution of the modern engineering industry; Whitworth introduced the first standard screw thread to give a measure of interchangeability between different manufacturers in 1841. Modern engineering standards cover a much wider function than the interchange of parts. In engineering practice they cover

1. Materials, properties, and compositions.
2. Testing procedures for performance, compositions, and quality.
3. Preferred sizes; for example, tubes, plates, sections, etc.
4. Methods for design, inspection, and fabrication.
5. Codes of practice for plant operation and safety.

The terms *standard* and *code* are used interchangeably, though *code* should really be reserved for a code of practice covering, say, a recommended design or operating procedure; and *standard* for preferred sizes, compositions, etc.

All of the developed countries and many of the developing countries have national standards organizations, which are responsible for the issue and maintenance of standards for the manufacturing industries and for the protection of consumers. In the United States, the government organization responsible for coordinating information on standards is the National Bureau of Standards; standards are issued by federal, state, and various commercial organizations. The principal ones of interest to chemical engineers are those issued by the American National Standards Institute (ANSI), the American Petroleum Institute (API), the American Society for Testing Materials (ASTM), the American Society of Mechanical Engineers (ASME) (pressure vessels and pipes), the National Fire Protection Association (NFPA; safety), and the Instrumentation, Systems and Automation Society (ISA; process control). Most Canadian provinces apply the same standards used in the United States. The preparation of the standards is largely the responsibility of committees of persons from the appropriate industry, the professional engineering institutions, and other interested organizations.

The International Organization for Standardization (ISO) coordinates the publication of international standards. The European countries used to maintain their own national standards, but these are now being superseded by common European standards.

Lists of codes and standards and copies of the most current versions can be obtained from the national standards agencies or by subscription from commercial websites such as I.H.S. (www.ihs.com).

As well as the various national standards and codes, the larger design organizations will have their own (in-house) standards. Much of the detail in engineering design work is routine and repetitious, and it saves time and money, and ensures conformity between projects, if standard designs are used whenever practicable.

Equipment manufacturers also work to standards to produce standardized designs and size ranges for commonly used items, such as electric motors, pumps, heat exchangers, pipes, and pipe fittings. They will conform to national standards, where they exist, or to those issued by trade associations. It is clearly more economic to produce a limited range of standard sizes than to have to treat each order as a special job.

For the designer, the use of a standardized component size allows for the easy integration of a piece of equipment into the rest of the plant. For example, if a standard range of centrifugal pumps is specified, the pump dimensions will be known, and this facilitates the design of the foundation plates, pipe connections, and the selection of the drive motors: standard electric motors would be used.

For an operating company, the standardization of equipment designs and sizes increases interchangeability and reduces the stock of spares that must be held in maintenance stores.

Though there are clearly considerable advantages to be gained from the use of standards in design, there are also some disadvantages. Standards impose constraints on the designer. The nearest standard size will normally be selected on completing a design calculation (rounding up), but this will not necessarily be the optimum size; though as the standard size will be cheaper than a special size, it will usually be the best choice from the point of view of initial capital cost. The design methods given in the codes and standards are, by their nature, historical, and do not necessarily incorporate the latest techniques.

The use of standards in design is illustrated in the discussion of the pressure vessel design in Chapter 13. Relevant design codes and standards are cited throughout the book.

1.7. DESIGN FACTORS (DESIGN MARGINS)

Design is an inexact art; errors and uncertainties arise from uncertainties in the design data available and in the approximations necessary in design calculations. Experienced designers include a degree of over-design known as a "design factor," "design margin," or "safety factor," to ensure that the design that is built meets product specifications and operates safely.

In mechanical and structural design, the design factors used to allow for uncertainties in material properties, design methods, fabrication, and operating loads are well established. For example, a factor of around 4 on the tensile strength, or about 2.5 on the 0.1% proof stress, is normally used in general structural design. The recommended design factors are set out in the codes and standards. The selection of design factors in mechanical engineering design is illustrated in the discussion of pressure vessel design in Chapter 13.

Design factors are also applied in process design to give some tolerance in the design. For example, the process stream average flows calculated from material balances are usually increased by a factor, typically 10%, to give some flexibility in process operation. This factor will set the maximum flows for equipment, instrumentation, and piping design. Where design factors are introduced to give some contingency in a process design, they should be agreed upon within the project organization and clearly stated in the project documents (drawings, calculation sheets, and manuals). If this is not done, there is a danger that each of the specialist design groups will add its own "factor of safety," resulting in gross and unnecessary over-design. Companies often specify design factors in their design manuals.

When selecting the design factor, a balance has to be made between the desire to make sure the design is adequate and the need to design to tight margins to remain competitive. Greater uncertainty in the design methods and data requires the use of bigger design factors.

1.8. SYSTEMS OF UNITS

Most of the examples and equations in this book use SI units; however, in practice the design methods, data, and standards that the designer will use are often only available in the traditional scientific and engineering units. Chemical engineering has always used a diversity of units, embracing the scientific CGS and MKS systems and both the American and British engineering systems. Those engineers in the older industries will also have had to deal with some bizarre traditional units, such as degrees Twaddle or degrees API for density and barrels for quantity. Although almost all of the engineering societies have stated support for the adoption of SI units, this is unlikely to happen worldwide for many years. Furthermore, much useful historic data will always be in the traditional units, and the design engineer must know how to understand and convert this information. In a globalized economy, engineers are expected to use different systems of units even within the same company, particularly in the contracting sector where the choice of units is at the client's discretion. Design engineers must therefore have a familiarity with SI, metric, and customary units, and a few of the examples and many of the exercises are presented in customary units.

It is usually the best practice to work through design calculations in the units in which the result is to be presented; but, if working in SI units is preferred, data can be converted to SI units, the calculation made, and the result converted to whatever units are required. Conversion factors to the SI system from most of the scientific and engineering units used in chemical engineering design are given in Appendix D.

Some license has been taken in the use of the SI system. Temperatures are given in degrees Celsius (°C); degrees Kelvin are used only when absolute temperature is required in the calculation. Pressures are often given in bar (or atmospheres) rather than in Pascals (N/m^2), as this gives a better feel for the magnitude of the pressures. In technical calculations the bar can be taken as equivalent to an atmosphere, whatever definition is used for atmosphere. The abbreviations bara and barg are often used to denote bar absolute and bar gauge, analogous to psia and psig when the pressure is expressed in pound force per square inch. When bar is used on its own, without qualification, it is normally taken as absolute.

For stress, N/mm^2 have been used, as these units are now generally accepted by engineers, and the use of a small unit of area helps to indicate that stress is the intensity of force at a point (as is also pressure). The corresponding traditional unit for stress is the ksi or thousand pounds force per square inch. For quantity, kmol are

TABLE 1.1. Approximate Conversions Between Customary Units and SI Units

Quantity	Customary Unit	SI Unit Approx.	Exact
Energy	1 Btu	1 kJ	1.05506
Specific enthalpy	1 Btu/lb	2 kJ/kg	2.326
Specific heat capacity	1 Btu/lb°F	4 kJ/kg°C	4.1868
Heat transfer coeff.	1 Btu/ft2h°F	6 W/m^2 °C	5.678
Viscosity	1 centipoise	1 mNs/m^2	1.000
	1 lbf/ft h	0.4 mNs/m^2	0.4134
Surface tension	1 dyne/cm	1 mN/m	1.000
Pressure	1 lbf/in^2 (psi)	7 kN/m^2	6.894
	1 atm	1 bar 10^5 N/m^2	1.01325
Density	1 lb/ft^3	16 kg/m^3	16.0185
	1 g/cm^3	1 kg/m^3	
Volume	1 US gal	3.8×10^{-3} m^3	3.7854×10^{-3}
Flow rate	1 US gal/min	0.23 m^3/h	0.227

Note:
1 U.S. gallon = 0.84 imperial gallons (UK)
1 barrel (oil) = 42 U.S. gallons ≈ 0.16 m^3 (exact 0.1590)
1 kWh = 3.6 MJ

generally used in preference to mol, and for flow, kmol/h instead of mol/s, as this gives more sensibly sized figures, which are also closer to the more familiar lb/h.

For volume and volumetric flow, m^3 and m^3/h are used in preference to m^3/s, which gives ridiculously small values in engineering calculations. Liters per second are used for small flow rates, as this is the preferred unit for pump specifications.

Where, for convenience, other than SI units have been used on figures or diagrams, the scales are also given in SI units, or the appropriate conversion factors are given in the text. Where equations are presented in customary units, a metric equivalent is generally given.

Some approximate conversion factors to SI units are given in Table 1.1. These are worth committing to memory, to give some feel for the units for those more familiar with the traditional engineering units. The exact conversion factors are also shown in the table. A more comprehensive table of conversion factors is given in Appendix D.

1.9. OPTIMIZATION

Optimization is an intrinsic part of design: the designer seeks the best, or optimum, solution to a problem.

Many design decisions can be made without formally setting up and solving a mathematical optimization problem. The design engineer will often rely on a combination of experience and judgment, and in some cases the best design will be immediately obvious. Other design decisions have such a trivial impact on process costs that it makes more sense to make a close guess at the answer than to properly set up and solve the optimization problem. In every design though, there will be several problems that require rigorous optimization. This section introduces the techniques for formulating and solving optimization problems, as well as some of the pitfalls that are commonly encountered in optimization.

In this book, the discussion of optimization will, of necessity, be limited to a brief overview of the main techniques used in process and equipment design. Chemical engineers working in industry use optimization methods for process operations far more than they do for design, as discussed in Section 1.9.11. Chemical engineering students would benefit greatly from more classes in operations research methods, which are generally part of the Industrial Engineering curriculum. These methods are used in almost every industry for planning, scheduling, and supply-chain management: all critical operations for plant operation and management. There is an extensive literature on operations research methods and several good books on the application of optimization methods in chemical engineering design and operations. A good overview of operations research methods is given in the classic introductory text by Hillier and Lieberman (2002). Applications of optimization methods in chemical engineering are discussed by Rudd and Watson (1968), Stoecker (1989), Biegler et al. (1997), Edgar and Himmelblau (2001), and Diwekar (2003).

1.9.1. The Design Objective

An optimization problem is always stated as the maximization or minimization of a quantity called the objective. For chemical engineering design projects, the objective should be a measure of how effectively the design meets the customer's needs. This will usually be a measure of economic performance. Some typical objectives are given in Table 1.2.

The overall corporate objective is usually to maximize profits, but the design engineer will often find it more convenient to use other objectives when working on subcomponents of the design. The optimization of subsystems is discussed in more detail in Section 1.9.4.

The first step in formulating the optimization problem is to state the objective as a function of a finite set of variables, sometimes referred to as the decision variables:

$$z = f(x_1, x_2, x_3, \ldots, x_n) \tag{1.1}$$

where

z = objective
$x_1, x_2, x_3, \ldots, x_n$ = decision variables

This function is called the objective function. The decision variables may be independent, but they will usually be related to each other by many constraint equations. The optimization problem can then be stated as maximization or minimization of the objective function subject to the set of constraints. Constraint equations are discussed in the next section.

TABLE 1.2. Typical Design Optimization Objectives

Maximize	Minimize
Project net present value	Project expense
Return on investment	Cost of production
Reactor productivity per unit volume	Total annualized cost
Plant availability (time on stream)	Plant inventory (for safety reasons)
Process yield of main product	Formation of waste products

Design engineers often face difficulties in formulating the objective function. Some of the economic objectives that are widely used in making investment decisions lead to intrinsically difficult optimization problems. For example, discounted cash flow rate of return (DCFROR) is difficult to express as a simple function and is highly nonlinear, while net present value (NPV) increases with project size and is unbounded unless a constraint is set on plant size or available capital. Optimization is therefore often carried out using simple objectives such as "minimize cost of production." Health, safety, environmental, and societal impact costs and benefits are difficult to quantify and relate to economic benefit. These factors can be introduced as constraints, but few engineers would advocate building a plant in which every piece of equipment was designed for the minimum legally permissible safety and environmental performance.

An additional complication in formulating the objective function is the quantification of uncertainty. Economic objective functions are generally very sensitive to the prices used for feeds, raw materials, and energy, and also to estimates of project capital cost. These costs and prices are forecasts or estimates and are usually subject to substantial error. Cost estimation and price forecasting are discussed in Sections 6.3 and 6.4. There may also be uncertainty in the decision variables, either from variation in the plant inputs, variations introduced by unsteady plant operation, or imprecision in the design data and the constraint equations. Optimization under uncertainty is a specialized subject in its own right and is beyond the scope of this book. See Chapter 5 of Diwekar (2003) for a good introduction to the subject.

1.9.2. Constraints and Degrees of Freedom

The constraints on the optimization are the set of equations that bound the decision variables and relate them to each other.

If we write **x** as a vector of n decision variables, then we can state the optimization problem as

$$\begin{aligned} &\text{Optimize (Max. or Min.) } z = f(\mathbf{x}) \\ &\text{subject to (s.t.):} \quad \mathbf{g}(\mathbf{x}) \leq \mathbf{0} \\ &\qquad\qquad\qquad\quad\ \mathbf{h}(\mathbf{x}) = \mathbf{0} \end{aligned} \tag{1.2}$$

where

z = the scalar objective
$f(\mathbf{x})$ = the objective function
$\mathbf{g}(\mathbf{x})$ = a m_i vector of inequality constraints
$\mathbf{h}(\mathbf{x})$ = a m_e vector of equality constraints

The total number of constraints is $m = m_i + m_e$.

Equality constraints arise from conservation equations (mass, mole, energy, and momentum balances) and constitutive relations (the laws of chemistry and physics, correlations of experimental data, design equations, etc.). Any equation that is introduced into the optimization model that contains an equal (=) sign will become an equality constraint. Many examples of such equations can be found throughout this book.

Inequality constraints generally arise from the external constraints discussed in Section 1.2: safety limits, legal limits, market and economic limits, technical limits set by design codes and standards, feed and product specifications, availability of resources, etc. Some examples of inequality constraints might include

$$\text{Main product purity} \geq 99.99\,\text{wt\%}$$

$$\text{Feed water content} \leq 20\,\text{ppmw}$$

$$\text{NO}_x \text{ emissions} \leq 50\,\text{kg/yr}$$

$$\text{Production rate} \leq 400{,}000 \text{ metric tons per year}$$

Maximum design temperature for ASME Boiler and Pressure Vessel Code Section VIII Division 2 $\leq 900°\text{F}$

$$\text{Investment capital} \leq \$50\,\text{MM (50 million dollars)}$$

The effect of constraints is to limit the parameter space. This can be illustrated using a simple two-parameter problem:

$$\begin{aligned} \text{Max. } & z = x_1^2 + 2x_2^2 \\ \text{s.t. } & x_1 + x_2 = 5 \\ & x_2 \leq 3 \end{aligned}$$

The two constraints can be plotted on a graph of x_1 vs. x_2, as in Figure 1.6.

In the case of this example, it is clear by inspection that the set of constraints does not bound the problem. In the limit $x_1 \to \infty$, the solution to the equality constraint is $x_2 \to -\infty$, and the objective function gives $z \to \infty$, so no maximum can be found. Problems of this kind are referred to as "unbounded." For this problem to have a solution, we need an additional constraint of the form

$$x_1 \leq a \text{ (where } a > 2)$$

$$x_2 \geq b \text{ (where } b < 3)$$

or

$$h(x_1, x_2) = 0$$

to define a closed search space.

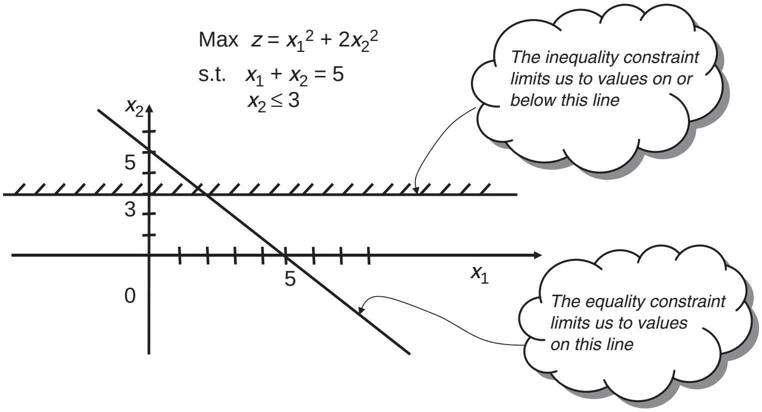

Figure 1.6. Constraints on a simple optimization problem.

It is also possible to overconstrain the problem. For example, if we set the problem

$$\begin{aligned} \text{Max.} \quad & z = {x_1}^2 + 2{x_2}^2 \\ \text{s.t.} \quad & x_1 + x_2 = 5 \\ & x_2 \leq 3 \\ & x_1 \leq 1 \end{aligned}$$

In this case, it can be seen from Figure 1.7 that the feasible region defined by the inequality constraints does not contain any solution to the equality constraint. The problem is therefore infeasible as stated.

Degrees of Freedom

If the problem has n variables and m_e equality constraints, then it has $n - m_e$ degrees of freedom. If $n = m_e$ then there are no degrees of freedom and the set of m_e equations can be solved for the n variables. If $m_e > n$, then the problem is

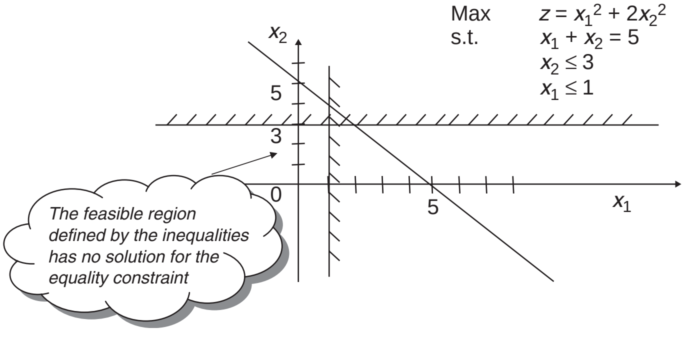

Figure 1.7. An over-constrained problem.

overspecified. In most cases, however, $m_e < n$ and $n - m_e$ is the number of parameters that can be independently adjusted to find the optimum.

When inequality constraints are introduced into the problem, they generally set bounds on the range over which parameters can be varied and hence reduce the space in which the search for the optimum is carried out. Very often, the optimum solution to a constrained problem is found to be at the edge of the search space, i.e., at one of the inequality constraint boundaries. In such cases, that inequality constraint becomes equal to zero and is said to be "active." It is often possible to use engineering insight and understanding of chemistry and physics to simplify the optimization problem. If the behavior of a system is well understood, then the design engineer can decide that an inequality constraint is likely to be active. Converting the inequality constraint into an equality constraint reduces the number of degrees of freedom by one and makes the problem simpler.

This can be illustrated by a simple reactor optimization example. The size and cost of a reactor are proportional to residence time, which decreases as temperature is increased. The optimal temperature is usually a trade-off between reactor cost and the formation of byproducts in side reactions; but if there were no side reactions, then the next constraint would be the maximum temperature allowed by the pressure vessel design code. More expensive alloys might allow for operation at higher temperatures. The variation of reactor cost with temperature will look something like Figure 1.8, where T_A, T_B, and T_C are the maximum temperatures allowed by the vessel design code for alloys A, B, and C, respectively.

The design engineer could formulate this problem in several ways. It could be solved as three separate problems, one corresponding to each alloy, each with a constraint on temperature $T < T_{alloy}$. The design engineer would then pick the solution that gave the best value of the objective function. The problem could also be formulated as a mixed integer nonlinear program with integer variables to determine the selection of alloy and set the appropriate constraint (see Section 1.9.10). The design engineer could also recognize that alloy A costs a lot less than alloy B, and the higher alloys give only a relatively small extension in the allowable temperature range. It is clear that cost decreases with temperature, so the optimum temperature will be T_A for alloy A and

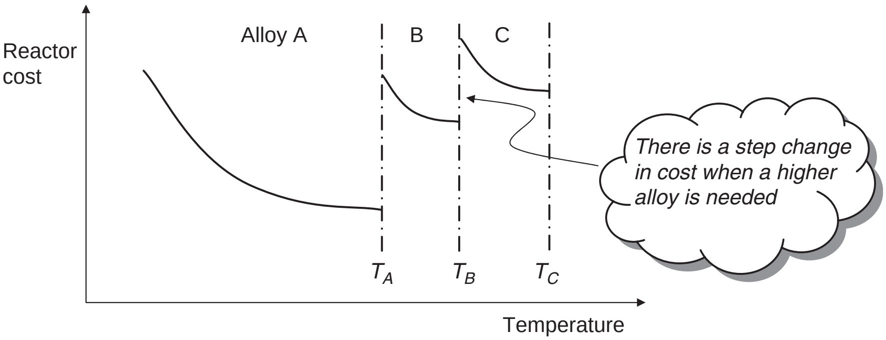

Figure 1.8. Variation of reactor cost with temperature.

T_B for alloy B. Unless the design engineer is aware of some other effect that has an impact on cost as temperature is increased, it is safe to write $T = T_A$ as an equality constraint and solve the resulting problem. If the cost of alloy B is not excessive, then it would be prudent to also solve the problem with $T = T_B$, using the cost of alloy B.

The correct formulation of constraints is the most important step in setting up an optimization problem. Inexperienced engineers are often unaware of many constraints and consequently find "optimal" designs that are dismissed as unfeasible by more experienced designers.

1.9.3. Trade-Offs

If the optimal value of the objective is not at a constraint limit, then it will usually be determined by a trade-off between two or more effects. Trade-offs are very common in design, because better performance in terms of increased purity, increased recovery, or reduced energy or raw materials use usually comes at the expense of higher capital expense, operating expense, or both. The optimization problem must capture the trade-off between cost and benefit.

A well-known example of a trade-off is the optimization of process heat recovery. A high degree of heat recovery requires close temperature approaches in the heat exchangers (see Section 3.17), which leads to high capital cost as the exchangers require more surface area. If the minimum temperature approach is increased, then the capital cost is reduced but less energy is recovered. We can plot the capital cost and energy cost against the minimum approach temperature, as shown schematically in Figure 1.9. If the capital cost is annualized (see Section 6.7), then the two costs can be added to give a total cost. The optimum value of the approach temperature, $\Delta T_{optimum}$, is then given by the minimum point in the total cost curve.

Some common trade-offs encountered in design of chemical plants include

- More separations equipment and operating cost vs. lower product purity;
- More recycle costs vs. increased feed use and waste formation;
- More heat recovery vs. cheaper heat exchange network;
- Higher reactivity at high pressure vs. more expensive reactors and higher compression costs;

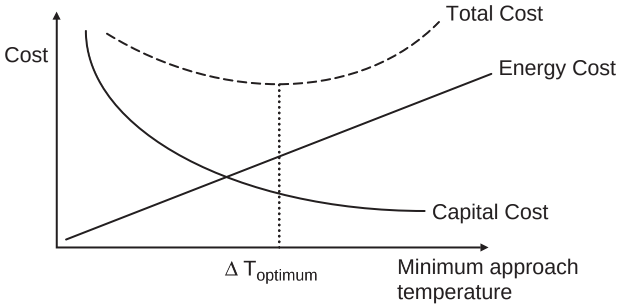

Figure 1.9. The capital-energy trade-off in process heat recovery.

- Fast reactions at high temperature vs. product degradation;
- Marketable byproducts vs. more plant expense;
- Cheaper steam and electricity vs. more off-site capital cost.

Stating an optimization problem as a trade-off between two effects is often useful in conceptualizing the problem and interpreting the optimal solution. For example, in the case of process heat recovery, it is usually found that the shape of the total cost curve in Figure 1.9 is relatively flat over the range $15°C < \Delta T_{optimum} < 40°C$. Knowing this, most experienced designers would not worry about finding the value of $\Delta T_{optimum}$, but would instead select a value for the minimum temperature approach within the range 15°C to 40°C, based on knowledge of the customer's preference for high energy efficiency or low capital expense.

1.9.4. Problem Decomposition

The task of formally optimizing the design of a complex processing plant involving several hundred variables, with complex interactions, is formidable, if not impossible. The task can be reduced by dividing the process into more manageable units, identifying the key variables and concentrating work where the effort involved will give the greatest benefit. Subdivision and optimization of the subunits rather than the whole will not necessarily give the optimum design for the whole process. The optimization of one unit may be at the expense of another. For example, it will usually be satisfactory to optimize the reflux ratio for a fractionating column independently of the rest of the plant; but if the column is part of a separation stage following a reactor, in which the product is separated from the unreacted materials, then the design of the column will interact with, and may well determine, the optimization of the reactor design. Care must always be taken to ensure that subcomponents are not optimized at the expense of other parts of the plant.

1.9.5. Optimization of a Single Decision Variable

If the objective is a function of a single variable, x, the objective function $f(x)$ can be differentiated with respect to x to give $f'(x)$. Any stationary points in $f(x)$ can then be found as the solutions of $f'(x) = 0$. If the second derivative of the objective function is greater than zero at a stationary point, then the stationary point is a local minimum. If the second derivative is less than zero, then the stationary point is a local maximum; and if it is equal to zero, then it is a saddle point. If x is bounded by constraints, then we must also check the values of the objective function at the upper and lower limiting constraints. Similarly, if $f(x)$ is discontinuous, then the value of $f(x)$ on either side of the discontinuity should also be checked.

This procedure can be summarized as the following algorithm:

$$\begin{aligned} \text{Min.} \quad & z = f(x) \\ \text{s.t.} \quad & x \geq x_L \\ & x \leq x_U \end{aligned} \tag{1.3}$$

1. Solve $f' = \frac{df(x)}{dx} = 0$ to find values of x_S.
2. Evaluate $f'' = \frac{d^2 f(x)}{dx^2}$ for each value of x_S. If $f'' > 0$, then x_S corresponds to a local minimum in $f(x)$.
3. Evaluate $f(x_S)$, $f(x_L)$, and $f(x_U)$.
4. If the objective function is discontinuous, then evaluate $f(x)$ on either side of the discontinuity, x_{D1} and x_{D2}.
5. The overall optimum is the value from the set (x_L, x_S, x_{D1}, x_{D2}, x_U) that gives the lowest value of $f(x)$.

This is illustrated graphically in Figure 1.10a for a continuous objective function. In Figure 1.10a, x_L is the optimum point, even though there is a local minimum at x_{S1}. Figure 1.10b illustrates the case of a discontinuous objective function. Discontinuous functions are quite common in engineering design, arising, for example, when changes in temperature or pH cause a change in metallurgy. In Figure 1.10b the optimum is at x_{D1}, even though there is a local minimum at x_S.

If the objective function can be expressed as a differentiable equation, then it is usually also easy to plot a graph like those in Figure 1.10 and quickly determine whether the optimum lies at a stationary point or a constraint.

1.9.6. Search Methods

In design problems, the objective function very often cannot be written as a simple equation that is easily differentiated. This is particularly true when the objective function requires solving large computer models, possibly using several different programs and requiring several minutes, hours, or days to converge a single solution. In such cases, the optimum is found using a search method. The concept of search methods is most easily explained for single variable problems, but search methods are at the core of the solution algorithms for multivariable optimization as well.

Unrestricted Search

If the decision variable is not bounded by constraints, then the first step is to determine a range in which the optimum lies. In an unrestricted search we make an

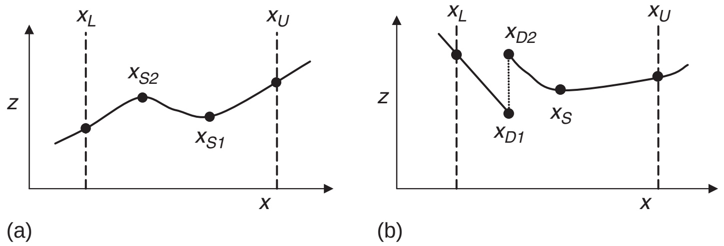

Figure 1.10. (a, b) Optimization of a single variable between bounds.

initial guess of x and assume a step size, h. We then calculate $z_1 = f(x)$, $z_2 = f(x+h)$, and $z_3 = f(x-h)$. From the values of z_1, z_2, and z_3, we determine the direction of search that leads to improvement in the value of the objective, depending on whether we wish to minimize or maximize z. We then continue increasing (or decreasing) x by successive steps of h until the optimum is passed.

In some cases, it may be desirable to accelerate the search procedure, in which case the step size can be doubled at each step. This gives the sequence $f(x + h)$, $f(x + 3h)$, $f(x + 7h)$, $f(x + 15h)$, etc.

Unrestricted searching is a relatively simple method of bounding the optimum for problems that are not constrained. In engineering design problems, it is almost always possible to state upper and lower bounds for every parameter, so unrestricted search methods are not widely used in design.

Once a restricted range that contains the optimum has been established, then restricted range search methods can be used. These can be broadly classified as direct methods that find the optimum by eliminating regions in which it does not lie, and indirect methods that find the optimum by making an approximate estimate of $f'(x)$.

Regular Search (Three-Point Interval Search)

The three-point interval search starts by evaluating $f(x)$ at the upper and lower bounds, x_L and x_U, and at the center point $(x_L + x_U)/2$. Two new points are then added in the midpoints between the bounds and the center point, at $(3x_L + x_U)/4$ and $(x_L + 3x_U)/4$, as shown in Figure 1.11. The three adjacent points with the lowest values of $f(x)$ (or the highest values for a maximization problem) are then used to define the next search range.

By eliminating two of the four quarters of the range at each step, this procedure reduces the range by half each cycle. To reduce the range to a fraction ε of the initial range therefore takes n cycles, where $\varepsilon = 0.5^n$. Since each cycle requires calculating $f(x)$ for two additional points, the total number of calculations is $2n = 2 \log \varepsilon / \log 0.5$.

The procedure is terminated when the range has been reduced sufficiently to give the desired precision in the optimum. For design problems, it is usually not necessary to specify the optimal value of the decision variables to high precision, so ε is usually not a very small number.

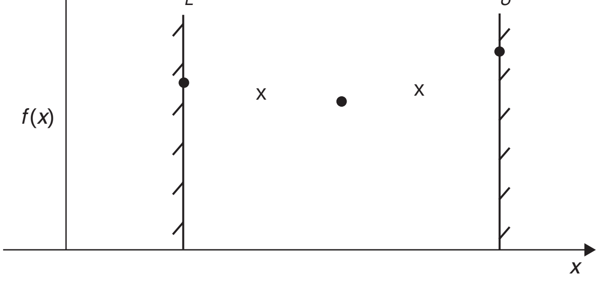

Figure 1.11. Regular search.

Golden-Section Search

The golden-section search, sometimes called the golden-mean search, is as simple to implement as the regular search, but is more computationally efficient if $\varepsilon < 0.29$. In the golden-section search, only one new point is added at each cycle.

The golden-section method is illustrated in Figure 1.12. We start by evaluating $f(x_L)$ and $f(x_U)$ corresponding to the upper and lower bounds of the range, labeled *A* and *B* in the figure. We then add two new points, labeled *C* and *D*, each located a distance ωAB from the bounds *A* and *B*, i.e., located at $x_L + \omega(x_U - x_L)$ and $x_U - \omega(x_U - x_L)$. For a minimization problem, the point that gives the highest value of $f(x)$ is eliminated. In Figure 1.12, this is point *B*. A single new point, *E*, is added, such that the new set of points *AECD* is symmetric with the old set of points *ACDB*.

For the new set of points to be symmetric with the old set of points, $AE = CD = \omega AD$.

But we know $DB = \omega AB$, so $AD = (1 - \omega)AB$ and $CD = (1 - 2\omega)AB$

so
$$(1 - 2\omega) = \omega(1 - \omega)$$
$$\omega = \frac{3 \pm \sqrt{5}}{2}$$

Each new point reduces the range to a fraction $(1 - \omega) = 0.618$ of the original range. To reduce the range to a fraction ε of the initial range therefore requires $n = \log \varepsilon / \log 0.618$ function evaluations.

The number $(1 - \omega)$ is known as the golden mean. The significance of this number has been known since ancient times. Livio (2002) gives a very entertaining account of its history and occurrence in art, architecture, music, and nature.

Quasi-Newton Method

Newton's method is a super-linear indirect search method that seeks the optimum by solving $f'(x)$ and $f''(x)$ and searching for where $f'(x) = 0$. The value of x at step $k + 1$ is calculated from the value of x at step k using

$$x_{k+1} = x_k - \frac{f'(x_k)}{f''(x_k)} \tag{1.4}$$

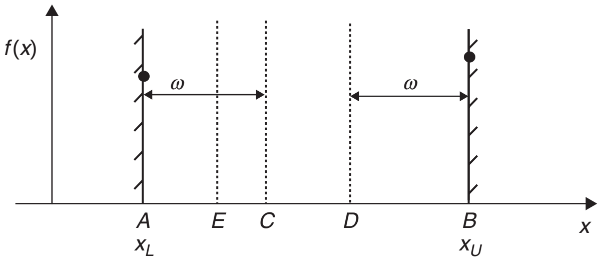

Figure 1.12. Golden-section search.

and the procedure is repeated until $(x_{k+1} - x_k)$ is less than a convergence criterion or tolerance, ε.

If we do not have explicit formulae for $f'(x)$ and $f''(x)$, then we can make a finite difference approximation about a point, in which case

$$x_{k+1} = x_k - \frac{[f(x_k + h) - f(x_k - h)]/2h}{[f(x_k + h) - 2f(x) + f(x_k - h)]/h^2} \tag{1.5}$$

Care is needed in setting the step size, h, and the tolerance for convergence, ε. The Quasi-Newton method generally gives fast convergence unless $f''(x)$ is close to zero, in which case convergence is poor.

All of the methods discussed in this section are best suited for unimodal functions, i.e., functions with no more than one maximum or minimum within the bounded range.

1.9.7. Optimization of Two or More Decision Variables

A two-variable optimization problem can be stated as

$$\begin{aligned} \text{Min.} \quad & z = f(x_1, x_2) \\ \text{s.t.} \quad & h(x_1, x_2) = 0 \\ & g(x_1, x_2) \leq 0 \end{aligned} \tag{1.6}$$

For simplicity, all problems will be stated as minimization problems from here on. A maximization problem can be rewritten as Min. $z = -f(x_1, x_2)$.

With two parameters, we can plot contour lines of z on a graph of x_1 vs. x_2 and hence get a visual representation of the behavior of z. For example, Figure 1.13 shows a schematic of a contour plot for a function that exhibits a local minimum of <30 at about (4,13) and a global minimum of <10 at about (15,19). Contour plots are useful

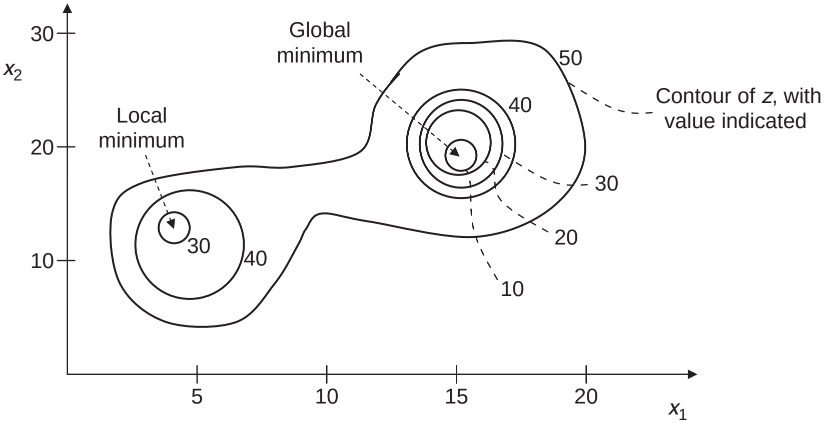

Figure 1.13. Optimization of two decision variables.

for understanding some of the key features of multivariable optimization that become apparent as soon as we consider more than one decision variable.

Convexity

Constraint boundaries can also be plotted in the (x_1, x_2) parameter space, as illustrated in Figure 1.14. If the constraints are not linear, then there is a possibility that the feasible region may not be convex. A convex feasible region, illustrated in Figure 1.14a, is one in which any point on a straight line between any two points inside the feasible region also lies within the feasible region. This can be stated mathematically as

$$\begin{gathered} x = \alpha x_a + (1 - \alpha)x_b \in \mathrm{FR} \\ \forall x_a, x_b \in \mathrm{FR},\ 0 < \alpha < 1 \end{gathered} \tag{1.7}$$

where

x_a, x_b = any two points belonging to the feasible region
FR = the set of points inside the feasible region bounded by the constraints
α = a constant

If any two points in the feasible region can be found such that some point on a straight line between them lies outside the feasible region, then the feasible region is nonconvex, as illustrated in Figure 1.14b.

The importance of convexity is that problems with a convex feasible region are more easily solved to a global optimum. Problems with nonconvex feasible regions are prone to convergence to local minima.

Searching in Two Dimensions

The procedures for searching in two dimensions are mostly extensions of the methods used for single variable line searches:

1. Find an initial solution (x_1, x_2) inside the feasible region.
2. Determine a search direction.
3. Determine step lengths δx_1 and δx_2.
4. Evaluate $z = f(x_1 + \delta x_1, x_2 + \delta x_2)$.
5. Repeat steps 2 to 4 until convergence.

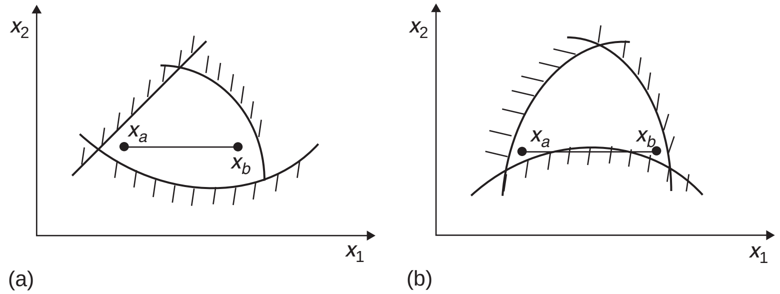

Figure 1.14. Convexity for a two-variable problem. (a) Convex feasible region. (b) Non-convex feasible region.

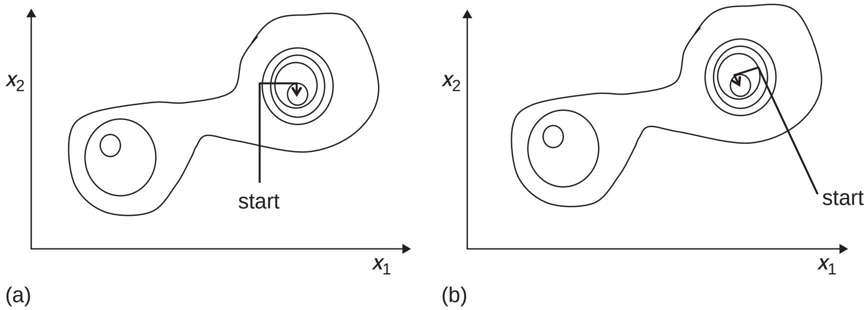

Figure 1.15. Search methods. (a) Univariate search. (b) Steepest descent.

If x_1 and x_2 are varied one at a time, then the method is known as a univariate search and is the same as carrying out successive line searches. If the step length is determined so as to find the minimum with respect to the variable searched, then the calculation steps toward the optimum, as shown in Figure 1.15a. This method is simple to implement, but can be very slow to converge. Other direct methods include pattern searches such as the factorial designs used in statistical design of experiments (see, for example, Montgomery, 2001), the EVOP method (Box, 1957) and the sequential simplex method (Spendley et al., 1962).

Indirect methods can also be applied to problems with two or more decision variables. In the steepest descent method (also known as the gradient method), the search direction is along the gradient at point (x_1, x_2), i.e., orthogonal to the contours of $f(x_1, x_2)$. A line search is then carried out to establish a new minimum point where the gradient is re-evaluated. This procedure is repeated until the convergence criterion is met, as shown in Figure 1.15b.

Problems in Multivariable Optimization

Some common problems that are encountered in multivariable optimization can be described for a two-variable problem and are illustrated in Figure 1.16. In Figure 1.16a, the shape of the contours is such that a univariate search would be very slow to converge. Using an indirect method such as steepest descent would be more appropriate in this case. Figure 1.16b shows the problem of convergence to a local optimum. In this scenario, different answers are obtained for different initial solutions. This problem can be overcome by using pattern searches with a larger grid or by using probabilistic methods such as simulated annealing or genetic algorithms that introduce some possibility of moving away from a local optimum. An introduction to probabilistic methods is given in Diwekar (2003). Probabilistic methods are also useful when faced with a nonconvex feasible region, as pictured in Figure 1.16c.

Multivariable Optimization

When there are more than two decision variables, it is much harder to visualize the parameter space, but the same issues of initialization, convergence, convexity, and local

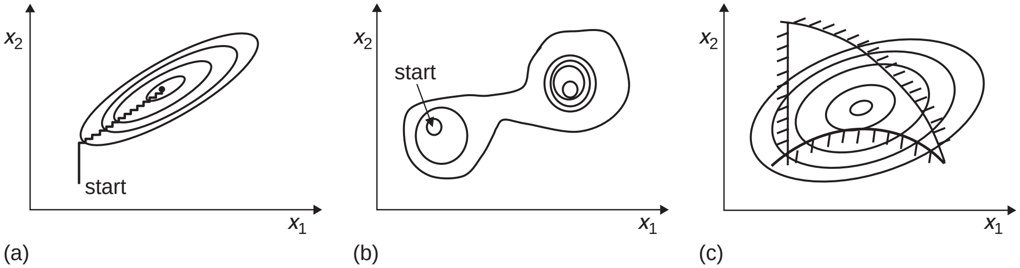

Figure 1.16. Common problems in multivariable optimization. (a) Slow convergence. (b) Convergence to local optimum. (c) Non-convex feasible region.

optima are faced. The solution of large multivariable optimization problems is at the core of the field of operations research. Operations research methods are widely used in industry, particularly in manufacturing facilities, as discussed in Section 1.9.11.

The following sections give only a cursory overview of this fascinating subject. Readers who are interested in learning more should refer to Hillier and Lieberman (2002) and the other references cited in Section 1.10.

1.9.8. Linear Programming

A set of continuous linear constraints always defines a convex feasible region. If the objective function is also linear and $x_i > 0$ for all x_i, then the problem can be written as a linear program (LP). A simple two-variable illustration of a linear program is given in Figure 1.17.

Linear programs always solve to a global optimum. The optimum must lie on the boundary at an intersection between constraints, which is known as a *vertex* of the feasible region. The inequality constraints that intersect at the optimum are said to be active and have $h(\mathbf{x}) = 0$, where $\mathbf{x}$ is the vector of decision variables.

Many algorithms have been developed for solution of linear programs, of which the most widely used are based on the SIMPLEX algorithm developed by Dantzig

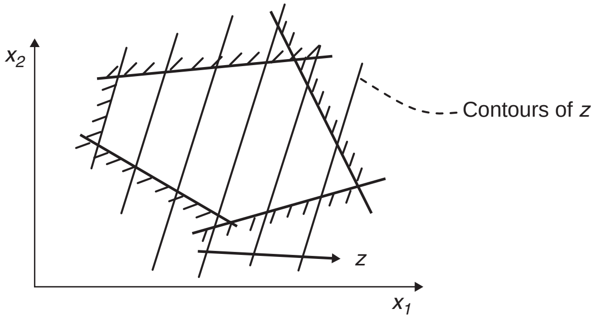

Figure 1.17. A linear program.

(1963). The SIMPLEX method introduces slack and surplus variables to transform the inequality constraints into equalities. For example, if

$$x_1 + x_2 - 30 \leq 0$$

we can introduce a slack variable, S_1, and write

$$x_1 + x_2 - 30 + S_1 = 0$$

The resulting set of equalities is solved to obtain a feasible solution, in which some of the slack and surplus variables will be zero, corresponding to active constraints. The algorithm then searches the vertices of the feasible region, increasing the objective at each step until the optimum is reached. Details of the SIMPLEX method are given in most optimization or operations research textbooks. See, for example, Hillier and Lieberman (2002) or Edgar and Himmelblau (2001). There have been many improvements to the SIMPLEX algorithm over the years, but it is still the method used in most commercial solvers.

Some problems that can occur in solving linear programs are illustrated in Figure 1.18. In Figure 1.18a, the contours of the objective function are exactly parallel to one of the constraints. The problem is said to be degenerate and has an infinite number of solutions along the line of that constraint. Figure 1.18b shows a problem where the feasible region is unbounded. This situation does not usually occur in engineering design unless the problem has been badly formulated. The situation in Figure 1.18c is more common, in which the problem is overconstrained and there is no feasible region.

Linear programming can be used to solve very large problems, with thousands of variables and constraints. The method is widely used in operations, particularly in optimization of oil refineries and petrochemical plants. It is used a lot less in design, as design problems almost inevitably contain many nonlinear equations.

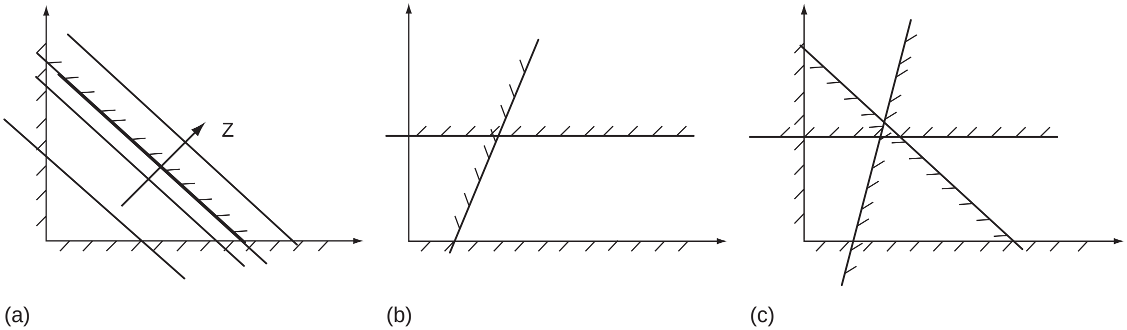

Figure 1.18. Problems in linear programming. (a) Objective function parallel to a constraint (degenerate problem). (b) Feasible region unbounded. (c) No feasible region.

1.9.9. Nonlinear Programming

When the objective function and/or the constraints are nonlinear, then the optimization must be solved as a nonlinear program (NLP). Three main methods are used for solving an NLP.

Successive Linear Programming (SLP)

In successive linear programming, $f(\mathbf{x})$, $\mathbf{g}(\mathbf{x})$, and $\mathbf{h}(\mathbf{x})$ are linearized at an initial point. The resulting LP is solved to give an initial solution, and $f(\mathbf{x})$, $\mathbf{g}(\mathbf{x})$, and $\mathbf{h}(\mathbf{x})$ are linearized again at the new point. The procedure is then repeated until convergence. If the new point is outside the feasible region, then the nearest point lying inside the feasible region is used.

With SLP there is no guarantee of convergence or global optimality. The method is widely used, nonetheless, as it is a simple extension of linear programming. It should be noted that whenever discontinuous linear functions are used to approximate a nonlinear function, then the problem behaves like an SLP. There is no guarantee of convexity or convergence to the optimal solution.

Successive Quadratic Programming (SQP)

The SQP algorithm is similar to SLP, but instead approximates $f(\mathbf{x})$ as a quadratic function and uses quadratic programming methods that give faster convergence than SLP. SQP works well for highly nonlinear problems with relatively few variables, for example, optimizing a process simulation or the design of a single piece of equipment. Biegler et al. (1997) suggest SQP is the best method for problems with fewer than 50 variables and where the gradients must be found numerically.

Reduced Gradient Method

Reduced gradient methods are related to the SIMPLEX algorithm. The method linearizes the constraints and introduces slack and surplus variables to transform the inequalities into equalities. The n-dimensional vector $\mathbf{x}$ is then partitioned into $n - m$ independent variables, where m is the number of constraints. A search direction is determined in the space of the independent variables, and a quasi-Newton method is used to determine an improved solution of $f(\mathbf{x})$ that still satisfies the nonlinear constraints. If all the equations are linear, this reduces to the SIMPLEX method (Wolfe, 1962). Various algorithms have been proposed, using different methods for carrying out the search and returning to a feasible solution, for example, the generalized reduced gradient (GRG) algorithm (Abadie and Guigou, 1969) and the MINOS algorithm (Murtagh and Saunders, 1978, 1982).

Reduced gradient methods are particularly effective for sparse problems with a large number of variables. A problem is said to be sparse if each constraint involves only a few of the variables. This is a common situation in design problems, where many of the constraints are written in terms of only one or two variables. Reduced gradient methods also work better when many of the constraints are linear, as less computational time is spent linearizing constraints and returning the solution to the feasible region. Because of the decomposition of the problem, fewer calculations are required per iteration, particularly if analytical expressions for the gradients are known (which is usually not the case in design). The reduced gradient method is often used in optimizing large spreadsheet models.

All of the nonlinear programming algorithms can suffer from the convergence and local optima problems described in Section 1.9.7. Probabilistic methods such as simulated annealing and genetic algorithms can be used if it is suspected that the feasible region is nonconvex or multiple local optima are present.

1.9.10. Mixed Integer Programming

Many of the decisions faced in operations involve discrete variables. For example, if we need to ship 3.25 trucks of product from plant A to plant B each week, we could send 3 trucks for 3 weeks and then 4 trucks in the fourth week, or we could send 4 trucks each week, with the fourth truck only one-quarter filled, but we cannot send 3.25 trucks every week. Some common operational problems involving discrete variables include

- *Production scheduling:* Determine the production schedule and inventory to minimize the cost of meeting demand. This is particularly important for batch plants, when the plant can make different products.
- *Transshipment problems and supply chain management:* Satisfy demands at different producing plants and sales destinations from different supply points, warehouses, and production facilities.
- *Assignment problems:* Schedule workers to different tasks.

Discrete variables are also sometimes used in process design, for example, the number of trays or the feed tray of a distillation column, and in process synthesis, to allow selection between flowsheet options, as described later.

Discrete decisions are addressed in operations research by introducing integer variables. When integer variables are introduced, a linear program becomes a mixed-integer linear program (MILP), and a nonlinear program becomes a mixed-integer nonlinear program (MINLP). Binary integer variables are particularly useful, as they can be used to formulate rules that enable the optimization program to choose between options. For example, if we define y as a binary integer variable such that

$$\begin{array}{ll} \text{if } y = 1 & \text{a feature exists in the optimal solution, and} \\ \text{if } y = 0 & \text{the feature does not exist in the optimal solution,} \end{array}$$

then we can formulate constraint equations such as:

$$\sum_{i=1}^{n} y_i = 1 \qquad \text{choose only one of } n \text{ options}$$

$$\sum_{i=1}^{n} y_i \leq m \qquad \text{choose at most } m \text{ of } n \text{ options}$$

$$\sum_{i=1}^{n} y_i \geq m \qquad \text{choose at least } m \text{ of } n \text{ options}$$

$$y_k - y_j \leq 0 \qquad \text{if item } k \text{ is selected, item } j \text{ must be selected, but not vice versa}$$

$$\left.\begin{array}{l} g_1(x) - My \leq 0 \\ g_2(x) - M(1-y) \leq 0 \\ M \text{ is a large scalar value} \end{array}\right\} \quad \text{either } g_1(x) \leq 0 \text{ or } g_2(x) \leq 0$$

The last rule listed here can be used to select between alternative constraints.

Mixed-Integer Programming Algorithms

Although integer variables are convenient for problem formulation, if too many integer variables are used, the number of options explodes in a combinatorial manner and solution becomes difficult. MILP problems can be solved efficiently using methods such as the "branch and bound" algorithm. The branch and bound method starts by treating all integer variables as continuous and solving the resulting LP or NLP to give a first approximation. All integer variables are then rounded to the nearest integer to give a second approximation. The problem is then partitioned into two new integer problems for each integer variable that had a nonintegral solution in the first approximation. In one branch a constraint is added that forces the integer variable to be greater than or equal to the next highest integer, while in the other branch a constraint is added that forces the variable to be equal to or less than the next lowest integer. For example, if a variable was found to have an optimal value $y = 4.4$ in the first approximation, then the new constraints would be $y \geq 5$ in one branch and $y \leq 4$ in the other. The branched problems are then solved to give new first approximations, and the branching procedure is repeated until an integer solution is found.

When an integer solution is found, it is used to set a bound on the value of the objective. For example, in a minimization problem, the optimal solution must be less than or equal to the bound set by this integral solution. Consequently, all branches with greater values of the objective can be discarded, as forcing the variables in these branches to integer values will lead to deterioration in the objective rather than improvement. The procedure then continues branching on all the nonintegral integer variables from each first approximation, and setting new bounds each time an improved integer solution is found, until all of the branches have been bounded and the optimal solution has been obtained. See Hillier and Lieberman (2002) or Edgar and Himmelblau (2001) for details of the algorithm and examples of its application.

The branch and bound method can be used for MINLP problems, but it requires solving a large number of NLP problems and is, therefore, computationally intensive. Instead, methods such as the Generalized Benders' Decomposition and Outer Approximation algorithms are usually preferred. These methods solve a master MILP problem to initialize the discrete variables at each stage and then solve an NLP subproblem to optimize the continuous variables. Details of these methods are given in Biegler et al. (1997) and Diwekar (2003).

Superstructure Optimization

Binary integer variables can be used to formulate optimization problems that choose between flowsheet options. For example, consider the problem of selecting a reactor. We can set up a unit cell consisting of a well-mixed reactor, a plug-flow reactor and a

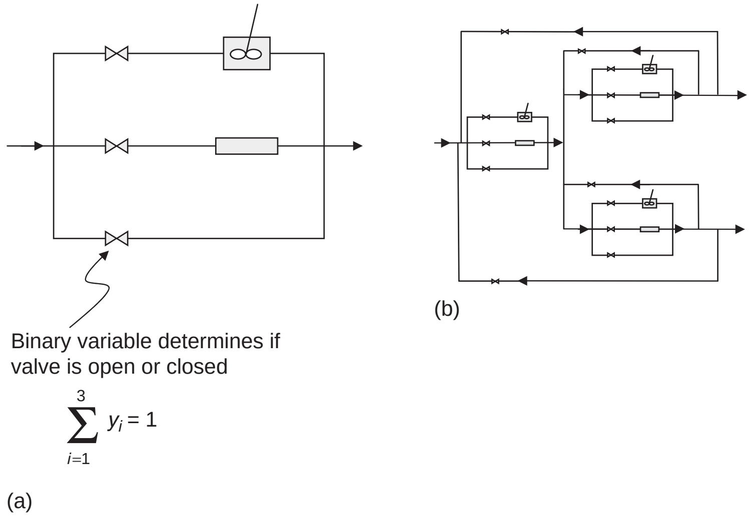

Figure 1.19. Application of integer programming to reactor design. (a) Unit cell of reactor options. (b) Superstructure of unit cells and recycles.

bypass in parallel, each with a valve upstream, as illustrated in Figure 1.19a. If a binary variable is used to describe whether the valve is open or closed and a constraint is introduced such that only one of the valves is open, then the optimization will select the best option. A set of such unit cells can be built into a superstructure, incorporating additional features such as recycles, as shown schematically in Figure 1.19b. A more rigorous superstructure that encompasses other options such as side-stream feeds to the PFR was developed by Kokossis and Floudas (1990).

The optimization of such a superstructure can identify reactor networks or mixing arrangements that would not be intuitively obvious to the design engineer. Similar superstructure formulations have been proposed for other process synthesis problems such as distillation column sequencing, design of heat exchange networks, and design of site utility systems. Biegler et al. (1997) give an excellent overview of the use of superstructure-based methods in process synthesis.

1.9.11. Optimization in Industrial Practice

Optimization of Process Operations

Perhaps not surprisingly, operations research methods are widely used in process operations. Few manufacturing plants do not use LP or MILP tools for planning and scheduling. Supply chain management is very important to economic performance and is usually carried out using large MILP models. The models used in industry for these purposes are often not very sophisticated, but proper formulation of constraints and the ability to solve robustly with a large number of variables are usually more important features of tools for these applications.

Optimization of Batch and Semicontinuous Processes

In batch operation, there will be periods when product is being produced, followed by nonproductive periods when the product is discharged and the equipment prepared for the next batch. The rate of production will be determined by the total batch time, productive plus nonproductive periods.

$$\text{Batches per year} = \frac{8760 \times \text{plant attainment}}{\text{batch cycle time}} \tag{1.8}$$

where the ‘‘plant attainment’’ is the fraction of the total hours in a year (8760) that the plant is in operation.

$$\text{Annual production} = \text{quantity produced per batch} \times \text{batches per year.}$$

$$\text{Cost per unit of production} = \frac{\text{annual cost of production}}{\text{annual production rate}} \tag{1.9}$$

With many batch operations, the production rate decreases during the production period; for example, batch reactors and plate and frame filter presses. There is then an optimum batch size, or optimum cycle time, that gives the minimum cost per unit of production.

For some continuous processes, the period of continuous production will be limited by gradual changes in process conditions. Examples include the deactivation of catalysts or the fouling of heat exchange surfaces. Production is lost during the periods when the plant is shut down for catalyst renewal or equipment clean-up. As with batch processes, there is an optimum cycle time to give the minimum production cost. The optimum time between shutdowns can be found by determining the relationship between cycle time and cost per unit of production (the objective function) and using one of the optimization techniques outlined in this section to find the minimum.

With discontinuous processes, the period between shutdowns will usually be a function of equipment size. Increasing the size of critical equipment will extend the production period, but at the expense of increased capital cost. The designer must strike a balance between the savings gained by reducing the nonproductive period and the increased investment required.

In some batch plants, several trains of identical equipment are operated in a sequence that allows some degree of heat recovery or enables downstream equipment to operate continuously. In this type of plant the time allowed for each operation in the sequence is optimized so that an overall schedule for the plant can be developed. Scheduling of batch processes is described in Biegler et al. (1997).

Optimization in Process Design

Few, if any, industrial designs are rigorously optimized. This is because

A. The cost of building rigorous models of reactor kinetics and hydraulics that give accurate prediction of byproduct yields is usually not justified. The amount of time available for the project is usually insufficient for such models to be built.

B. The uncertainty in the forecasts of future prices is usually so large that it dominates most differences between design alternatives.
C. Regardless of the quality of the tools used, or the experience of the estimator, it is usually impossible to make a capital cost estimate within ±15% without completing a substantial amount of design work (see Chapter 6). Many design decisions are thus made on the basis of sketchy cost estimates. The cost of going back and revisiting these design decisions at a later stage in the project when more design detail is available is usually not justified.
D. Criteria such as safety, operability, reliability, and flexibility are of vital importance in process design. These features make the design more robust to variations in the design assumptions and operating requirements. A safe, operable, and reliable plant will often require more expense above the cost of the "optimal" design. This extra expense is difficult to trade off against the non-financial benefits of having a process that is easier to run.
E. In most cases there are several "near optimal" designs. The difference between the values of the objective obtained for each of these is often not statistically significant, given the errors in prices, cost estimates, and yields.

In industrial process design, optimization usually involves carrying out sufficient analysis to be certain that the design is reasonably close to the optimum. The most important things for the design engineer to understand are

A. What are the constraints on the design?
B. Which constraints are hard (inviolable) and which are soft (can be modified)?
C. Where are the discontinuities in cost? For example, what conditions cause a change to a more costly metallurgy or a different design code?
D. What are the main design trade-offs?
E. How does the objective function vary with the main process parameters?
F. What are the major cost components of the process (both capital and operating costs), and what radical changes could be made to the process to reduce these costs?

Experienced design engineers usually think through these questions carefully, to satisfy themselves that their design is "good enough." Only very occasionally do they formulate an optimization problem and solve it rigorously.

Example 1.1

Optimize the design of a distillation column to separate 225 metric tons per hour of an equimolar mixture of benzene, toluene, ethylbenzene, paraxylene, and orthoxylene with minimum total annualized cost. The feed is a saturated liquid at 330 kPa. The recovery of toluene in the distillate should be greater than 99%, and the recovery of ethylbenzene in the bottoms should be greater than 99%.

Solution

The first step is to determine the design factor. If we assume a design factor of 10%, then the equipment should be designed for a flow rate of 248 metric tons per hour (te/h). This flow rate is used in simulating the process for the purpose of sizing equipment, but energy consumption must be based on the reboiler and condenser duties expected for a 225 te/h feed rate.

This is a single distillation column, which is easy to model in any of the commercial simulation programs. UniSim^{TM} Process Design (Honeywell Inc.) was used for the purpose of this example. The simulation was set up using the component recoveries of toluene and ethylbenzene as column specifications, which gave rapid convergence. Tray sizing calculations were run using the UniSim^{TM} tray sizing utility. A tray spacing of 0.61 m (2 feet) was assumed, and other tray parameters were left at the UniSim^{TM} default values. Two meters were added to the column height to allow space for a sump and demister. Sieve trays were used and the stage efficiency was assumed to be 80%.

To optimize the design, we need to formulate an objective function. The distillation column has the following cost components:

- *Capital costs:* Column shell, internals, condenser, receiver drum, reboiler, pumps, piping, instrumentation, structure, foundations, etc.
- *Operating costs:* Cost of heating for the reboiler and cost of cooling for the condenser.

The purchased equipment costs can be estimated based on information from the process simulation using the cost correlations given in Section 6.3. The column shell is a pressure vessel and the design can be completed using the methods given in Chapter 13. The details of how to complete these calculations are not important here, but Example 13.2 and Example 6.2 provide detailed explanations of the method followed. Carbon steel construction was assumed. The purchased equipment costs can be converted into an installed capital cost by multiplying by an installation factor. For the purposes of this example, the installation factor can be assumed to be 4.0 (see Section 6.3.3). The installed capital costs can be converted into an annual capital charge by dividing by 3, using a rule of thumb that is developed in Section 6.7.6.

The operating costs are simple to estimate from the condenser and reboiler duties if the cost of energy is known. For this example, the cost of heat is taken as \$5.5/GJ and the cost of cooling is \$0.2/GJ.

The objective function can then be written as

$$\begin{aligned}\text{Min.: Total annualized cost (TAC)} &= \text{cost of heating} + \text{cost of cooling} \\ &\quad + \text{annualized capital cost} \\ &= 5.5Q_r + 0.2Q_c \\ &\quad + (4/3)\ (\Sigma \text{ purchased equipment costs})\end{aligned}$$

where:

Q_r = annual reboiler energy consumption (GJ/yr)
Q_c = annual condenser energy consumption (GJ/yr)

The optimization problem is strictly a MINLP, as we need to consider discrete variables (number of trays, feed tray) as well as continuous variables (reflux ratio, reboiler duty, etc.). This problem is actually relatively easy to formulate and solve rigorously, but instead we will step through the calculation to illustrate how an experienced industrial designer would approach the problem.

Table 1.3 gives the results of several iterations of the optimization.

A. To begin, we need to find a feasible solution. As an initial guess, we can use 40 trays with the feed on tray 20. The column converges with a reflux ratio of 3.34 and diameter 5.49 m. This is large but not unreasonable for such a high flow rate. When we look at the components of the total annualized cost, the capital is contributing \$0.8 MM/yr and energy is contributing \$8.6 MM/yr, so the costs are dominated by energy cost. It is clear that adding more stages and reducing the reflux ratio will reduce the total cost. (If capital costs were dominating, then we would reduce the number of stages.) There is no upper hard constraint on column height, but there is a soft constraint. At the time of writing, there are only 14 cranes in the world that can lift a column taller than 80 m. There are 48 cranes that can lift a column up to 60 m. We can therefore expect that the cost of lifting a column >60 m height will go up as it becomes more expensive to rent the necessary equipment for installation. We can start by assuming a soft constraint that the maximum height must be less than 60 m.

B. Using 90 trays with feed on tray 45 gives a reflux ratio of 2.5 and diameter 4.42 m. The column height is 56 m, which allows some space for vessel supports and clearance for piping at the column base and still comes in under the 60 m target. The capital cost increases to \$0.95 MM/yr, while energy cost is reduced to \$6.96 MM/yr, giving a total annualized cost of \$7.91 MM/yr and savings of \$1.5 MM/yr relative to the initial design.

C. We should explore whether going to an even taller column would make sense. We can investigate this by increasing the installation factor from 4 to 5 for the column shell to allow for the higher cost of using one of the larger cranes. If we increase the number of trays to 120, the column height is 75 m, which will give a total height of close to 80 m when installed. The total annualized cost increases to \$8.2 MM/yr, so we can conclude that it is probably not economical

TABLE 1.3. Optimization Results

Iteration Number	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Number of trays	40	90	120	70	80	76	84	80	80
Feed tray	20	45	60	35	40	38	42	27	53
Column height (m)	26.4	56.9	75.2	44.7	50.8	48.4	53.2	50.8	50.8
Column diameter (m)	5.49	4.42	4.42	4.42	4.42	4.42	4.42	4.42	4.57
Reflux ratio	3.34	2.50	2.48	2.57	2.52	2.54	2.51	2.48	2.78
Reboiler duty, Q_r (GJ)	34.9	28.3	28.2	28.8	28.5	28.6	28.4	28.2	30.4
Condenser duty, Q_c (GJ)	33.9	27.3	27.2	27.8	27.5	27.6	27.4	27.2	29.4
Annualized capital cost (MM\$/yr)	0.82	0.95	1.25	0.83	0.89	0.87	0.91	0.89	0.94
Annual energy cost (MM\$/yr)	8.59	6.96	6.93	7.10	7.01	7.04	6.99	6.93	7.50
Total annualized cost (MM\$/yr)	9.41	7.91	8.18	7.93	7.900	7.905	7.904	7.82	8.44

to go to a total height above 60 m. We can notice though that the reflux ratio didn't change much when we added extra trays. This suggests that we are getting close to minimum reflux. It might therefore be worth backing off from the maximum column height constraint to see if there is an optimum number of trays.

D. Adding a design with 70 trays and feed on tray 35 (roughly halfway between 40 and 90) gives reflux ratio 2.57 and total annualized cost $7.94 MM/yr. This is not an improvement on the 90-tray design, so the optimum must be between 70 and 90 trays.

E. A design with 80 trays and feed on tray 80 (halfway between 70 and 90) gives reflux ratio 2.52 and total annualized cost $7.900 MM/yr. This is better than 70 or 90 trays. If we wanted to proceed further to establish the optimum, we could continue reducing the search space using a regular search until we get to the optimum number of trays. Instead, an experienced designer would note that the difference in cost within the range examined ($0.03 MM/yr) is relatively small compared with the error in the capital cost estimate (±30%, or $0.29 MM/yr). Since the optimum appears to be fairly flat with respect to number of trays over the range 70 to 90, it is reasonable to take the optimum as 80 trays. (As a confirmation, iterations 6 and 7, with 76 and 84 trays indicate that the optimum indeed lies at 80 ± 2 trays).

F. Having fixed the number of trays at 80, we should now optimize the feed tray. We start by adding two new points, with the feed trays at trays 27 and 53. These give total annualized costs of $7.82 MM/yr and $8.43 MM/yr, respectively. The minimum cost is given by the lower bound on feed tray location. If we try a higher feed tray (say, tray 26), the UniSim^{TM} tray sizing utility gives a warning "head loss under downcomers is too large." We could overcome this warning by modifying the tray design, but once again we can notice that the annualized cost savings that we have gained by optimizing the feed tray ($0.08 MM/yr) is small compared to the error in the capital cost, so the design with feed tray 27 is close enough to optimum.

The column design is thus set at 80 trays, with feed on tray 27, giving a column 50.8 m high and 4.42 m diameter.

The solution obtained is "good enough" but is not rigorously optimal. Several possible variations in flow scheme were not considered. For example, we could have examined use of feed preheat, intermediate stage condensers or reboilers, or more efficient column internals such as high-efficiency trays or structured packing. The column cost may also be reduced if different diameters or different internals were used in the rectifying and stripping sections. In the broader context of the process, it may be possible to supply the heat required for the reboiler using heat recovered from elsewhere in the process, in which case the cost of energy will be reduced and the capital energy trade-off will be altered. In the overall process context, we could also question whether the column needs such high recoveries of toluene and ethylbenzene, since the high recoveries clearly lead to a high reflux rate and column energy cost.

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1.11. NOMENCLATURE

		Dimensions in **\$MLTθ**
a	A constant	—
b	A constant	—
$f(x)$	General function of x	—
$f'(x)$	First derivative of function of x with respect to x	—
$f''(x)$	Second derivative of function of x with respect to x	—
FR	The set of points contained in a feasible region	—
$\mathbf{g}(\mathbf{x})$	A m_i vector of inequality constraints	—
$g(x)$	General inequality constraint equation in x	—
$\mathbf{h}(\mathbf{x})$	A m_e vector of equality constraints	—
$h(x)$	General equality constraint equation in x	—
h	Step length in a search algorithm	—

		Dimensions in **\$MLTθ**
M	A large scalar constant	—
m	Number of constraints	—
m_e	Number of equality constraints	—
m_i	Number of inequality constraints	—
n	Number of variables	—
Q_c	Condenser duty in distillation	$\mathbf{ML^2T^{-3}}$
Q_r	Reboiler duty in distillation	$\mathbf{ML^2T^{-3}}$
$S_1, S_2 \ldots$	Slack and surplus variables	—
T	Temperature	$\boldsymbol{\theta}$
T_{alloy}	Maximum allowed temperature for an alloy	$\boldsymbol{\theta}$
T_A, T_B, T_C	Maximum allowed temperature for alloys A, B, and C	$\boldsymbol{\theta}$
U	Overall heat transfer coefficient	$\mathbf{MT^{-3}}\boldsymbol{\theta}^{-1}$
$\mathbf{x}$	A vector of *n* decision variables	—
$x_1, x_2 \ldots$	Continuous variables	—
$y_1, y_2 \ldots$	Integer (discrete) variables	—
z	The objective (in optimization)	—
α	A constant between 0.0 and 1.0	—
ε	Fraction of search range or tolerance for convergence	—
ΔT	Temperature difference	$\boldsymbol{\theta}$
$\Delta T_{optimum}$	The optimal minimum temperature approach in heat recovery	$\boldsymbol{\theta}$
$\delta x_1, \delta x_2$	Small increments in x_1 and x_2	—
ω	Ratio used in golden section search (= 0.381966)	—
Suffixes		
D1	lower side of a discontinuity	
D2	upper side of a discontinuity	
i	i^th^ variable	
j	j^th^ variable	
k	k^th^ iteration	
L	lower bound	
S	stationary point	
U	upper bound	

1.12. PROBLEMS

1.1. Develop project plans for the design and construction of the following processes. Use Figure 1.2 as a guide to the activities that must occur. Estimate the overall time required from launching the project to the start of operation.

- **i.** A petrochemical process using established technology, to be built on an existing site;
- **ii.** A process for full-scale manufacture of a new drug, based on a process currently undergoing pilot plant trials;
- **iii.** A novel process for converting cellulose waste to fuel products;
- **iv.** A spent nuclear fuel reprocessing facility;
- **v.** A solvent recovery system for an electronics production facility.

1.2. You are the project manager of a team that has been asked to complete the design of a chemical plant up to the stage of design selection. You have three engineers available (plus yourself), and the work must be completed in 10 weeks. Develop a project plan and schedule of tasks for each engineer. Be sure to allow sufficient time for equipment sizing, costing, and optimization. What intermediate deliverables would you specify to ensure that the project stays on track?

1.3. A separator divides a process stream into three phases: a liquid organic stream, a liquid aqueous stream, and a gas stream. The feed stream contains three components, all of which are present to some extent in the separated steams. The composition and flow rate of the feed stream are known. All the streams will be at the same temperature and pressure. The phase equilibrium constants for the three components are available.

- **i.** How many design variables must be specified in order to calculate the output stream compositions and flow rates?
- **ii.** How would you optimize these variables if the objective of the separator was to maximize recovery of condensable components into the organic liquid stream? What constraints might limit the attainable recovery?

1.4. A rectangular tank with a square base is constructed from 5 mm steel plates. If the capacity required is 8 cubic meters, determine the optimum dimensions if the tank has

- **i.** A closed top.
- **ii.** An open top.

1.5. Estimate the optimum thickness of insulation for the roof of a house given the following information. The insulation will be installed flat on the attic floor. Overall heat transfer coefficient for the insulation as a function of thickness, U values (see Chapter 12):

thickness, mm	0	25	50	100	150	200	250
U, $Wm^{-2}K^{-1}$	20	0.9	0.7	0.3	0.25	0.20	0.15

The cost of insulation, including installation, is $120/m^3. Capital charges (see Chapter 6) are 20% per year. The cost of fuel, allowing for the efficiency of the heating system is $8/GJ. The cost of cooling is $5/GJ. Average temperatures for any region of the United States or Canada can be found online at www.weather.com (under the Averages tab). Assume the house is heated or cooled to maintain an internal temperature in the range 70 to 80°F.

Note: The rate at which heat is being lost or gained is given by $U \times \Delta T$, W/m^2, *where* U *is the overall coefficient and* ΔT *is the temperature difference; see Chapter 12.*

1.6. What is the optimum practical shape for an above-ground dwelling, to minimize the heat losses through the building fabric? When is (or was) this optimum shape used? Why is this optimum shape seldom used in richer societies?

1.7. Hydrogen is manufactured from methane by either steam reforming (reaction with steam) or partial oxidation (reaction with oxygen). Both processes are endothermic. What reactor temperature and pressure would you expect to be optimal for these processes? What constraints might apply?

1.8. Ethylene and propylene are valuable monomers. A key step in the recovery of these materials is fractionation of the olefin from the corresponding paraffin (ethane or propane). These fractionation steps require refrigeration of the overhead condenser and very large distillation columns with many stages. Raising the pressure at which the column operates improves the performance of the refrigeration system but increases the number of stages needed. Formulate the objective function for optimizing the recovery of ethylene from an ethylene-ethane mixture. What are the key constraints? What will be the main trade-offs?

1.9. If you had to design a plant for pasteurizing milk, what constraints would you place on the design?

1.10. A catalytic process was designed to make 150 metric tons per year of product with a net profit of \$0.25/lb of product. The catalyst for the process costs \$10/lb and it takes 2 months to shut down the process, empty the old catalyst, reload fresh catalyst, and restart the process. The feed and product recovery and purification sections can be pushed to make as much as 120% of design basis capacity. The reactor section is sized with sufficient catalyst to make 100% of design basis when operated with fresh catalyst at 500°F. The reactor can be operated at temperatures only up to 620°F, for safety reasons. The reactor weight hourly space velocity (lb of product per hour per lb of catalyst) is given by the equation

$$\text{WHSV} = 4.0 \times 10^6 \exp\left(\frac{-8000}{T}\right) \exp\left(-8.0 \times 10^5 \times t \times T\right)$$

where

t = time on stream in months
T = temperature

Find the optimal temperature versus time profile for the reactor and determine how long the process should be operated before the catalyst is changed out. (Hint: The initial temperature does not have to be 500°F.)

1.11. The following portfolio of investment projects has been proposed for a company for next year:

Project	Net Present Value (MM$)	Cost (MM$)
A	100	61
B	60	28
C	70	33
D	65	30
E	50	25
F	50	17
G	45	25
H	40	12
I	40	16
J	30	10

i. Develop a spreadsheet optimization program to select the optimal portfolio of projects to maximize total portfolio net present value (NPV), given a total budget of $100 million. (This is a simple MILP.)

ii. How would the portfolio and NPV change if the budget was increased to $110 million?

iii. Because of corporate cost-cutting, the budget is reduced to $80 million. Which projects are now funded and what is the new NPV?

iv. Based on your answers to parts (i) to (iii), can you draw any conclusions on which projects are likely to be funded regardless of the financial situation?

v. Can you see any problems with this project selection strategy? If so, how would you recommend they should be addressed?

2 FUNDAMENTALS OF MATERIAL BALANCES

Chapter Contents

Key Learning Objectives

- How to use mass balances to understand process flows
- How to select a system boundary and design basis
- How to estimate reactor and process yields

2.1. INTRODUCTION

Material balances are the basis of process design. A material balance taken over the complete process will determine the quantities of raw materials required and products produced. Balances over individual process units set the process stream flows and compositions, and provide the basic equations for sizing equipment.

A good understanding of material balance calculations is essential in process design. In this chapter the fundamentals of the subject are covered, using simple examples to illustrate each topic. Practice is needed to develop expertise in handling what can often become very involved calculations. More examples and a more detailed discussion of the subject can be found in the numerous specialist books written on material and energy balance computations. Several suitable texts are listed in the ‘‘Bibliography’’ section at the end of this chapter.

For complex processes, material balances are usually completed using process simulation software, as described in Chapter 4. Significant time and effort can be wasted in process simulation if the fundamentals of material and energy balances are not properly understood. Careful attention must be paid to selecting the best basis and boundaries for material and energy balances; to predicting yields; and to understanding recycle, purge, and bypass schemes. Shorthand calculations, of the type illustrated in this chapter, should always be used to check process simulation results. Short calculations can also be used to accelerate convergence of flowsheet simulations by providing good initial estimates of recycle and make-up streams.

Material balances are also useful tools for the study of plant operation and troubleshooting. They can be used to check performance against design, to extend the often limited data available from the plant instrumentation, to check instrument calibrations, and to locate sources of material loss. Material balances are essential to obtaining high-quality data from laboratory or pilot plants.

2.2. THE EQUIVALENCE OF MASS AND ENERGY

Einstein showed that mass and energy are equivalent. Energy can be converted into mass, and mass into energy. They are related by Einstein’s equation:

$$E = mc^2 \tag{2.1}$$

where

E = energy, J,
m = mass, kg,
c = the speed of light *in vacuo*, 3×10^8 m/s.

The loss of mass associated with the production of energy is significant only in nuclear reactions. Energy and matter are always considered to be separately conserved in chemical reactions.

2.3. CONSERVATION OF MASS

The general conservation equation for any process system can be written as

$$\text{Material out} = \text{Material in} + \text{Generation} - \text{Consumption} - \text{Accumulation}$$

For a steady-state process, the accumulation term is zero. Except in nuclear processes, mass is neither generated nor consumed; but if a chemical reaction takes place, a particular chemical species may be formed or consumed in the process. If there is no chemical reaction, the steady-state balance reduces to

$$\text{Material out} = \text{Material in}$$

A balance equation can be written for each separately identifiable species present, elements, compounds, or radicals; and for the total material. Balances can be written for mass or for number of moles.

Example 2.1

2000 kg of a 5% slurry of calcium hydroxide in water is to be prepared by diluting a 20% slurry. Calculate the quantities required. The percentages are by weight.

Solution

Let the unknown quantities of the 20% slurry and water be X and Y, respectively.

Material balance on $Ca(OH)_2$

$$\overset{In}{X\frac{20}{100}} = \overset{Out}{2000 \times \frac{5}{100}} \tag{a}$$

Balance on water

$$X\frac{(100-20)}{100} + Y = 2000\frac{(100-5)}{100} \tag{b}$$

From equation (a), $X = 500$ kg.

Substituting into equation (b) gives $Y = \underline{\underline{1500\,\text{kg}}}$

Check material balance on total quantity:

$$X + Y = 2000$$
$$500 + 1500 = 2000, \text{ correct}$$

2.4. UNITS USED TO EXPRESS COMPOSITIONS

When a composition is specified as a percentage, it is important to state clearly the basis: weight, molar, or volume.

The abbreviations w/w, wt%, and %wt are used for mass (weight) basis. Volume basis is usually abbreviated vol%, LV%, or v/v.

Example 2.2

Technical grade hydrochloric acid has a strength of 28% w/w. Express this as a mole fraction.

Solution

Basis of calculation 100 kg of 28% w/w acid.

$$\begin{aligned}
&\text{Molecular mass: water 18, HCl 36.5}\\
\text{Mass HCl} &= 100 \times 0.28 = 28\,\text{kg}\\
\text{Mass water} &= 100 \times 0.72 = 72\,\text{kg}\\
\text{kmol HCl} &= \frac{28}{36.5} = 0.77\\
\text{kmol water} &= \frac{72}{18} \quad = 4.00\\
\text{Total mols} &\qquad\quad = 4.77\\
\text{mol fraction HCl} &= \frac{0.77}{4.77} = 0.16\\
\text{mol fraction water} &= \frac{4.00}{4.77} = 0.84\\
\text{Check total} &\qquad\quad\ \ 1.00
\end{aligned}$$

Within the accuracy needed for technical calculations, volume fractions can be taken as equivalent to mole fractions for gases, up to moderate pressures (say 25 bar).

Trace quantities are often expressed as parts per million (ppm). The basis, weight or volume, needs to be stated, for example, ppmw or ppmv.

$$\text{ppm} = \frac{\text{quantity of component}}{\text{total quantity}} \times 10^6$$

Note: 1 ppm = 10^{-4}percent.

Minute quantities are sometimes quoted in parts per billion (ppb). This refers to an American billion (10^9), not a UK billion (10^{12}).

2.5. STOICHIOMETRY

The stoichiometric equation for a chemical reaction states unambiguously the number of molecules of the reactants and products that take part, from which the quantities can be calculated. The equation must balance.

With simple reactions it is usually possible to balance the stoichiometric equation by inspection, or by trial-and-error calculations. If difficulty is experienced in balancing complex equations, the problem can always be solved by writing a balance for each element present. The procedure is illustrated in Example 2.3.

Example 2.3

Write out and balance the overall equation for the manufacture of vinyl chloride from ethylene, chlorine, and oxygen.

Solution

Method: Write out the equation using letters for the unknown number of molecules of each reactant and product. Make a balance on each element. Solve the resulting set of equations.

$$A(C_2H_4) + B(Cl_2) + C(O_2) = D(C_2H_3Cl) + E(H_2O)$$

Balance on carbon

$$2A = 2D, \ A = D$$

on hydrogen

$$4A = 3D + 2E$$

$$\text{substituting } D = A \text{ gives } E = \frac{A}{2}$$

on chlorine

$$2B = D, \qquad \text{hence} \qquad B = \frac{A}{2}$$

on oxygen

$$2C = E, \qquad C = \frac{E}{2} = \frac{A}{4}$$

putting $A = 1$, the equation becomes

$$C_2H_4 + 1/2Cl_2 + 1/4O_2 = C_2H_3Cl + 1/2H_2O$$

multiplying through by the largest denominator to remove the fractions

$$4C_2H_4 + 2Cl_2 + O_2 = 4C_2H_3Cl + 2H_2O$$

2.6. CHOICE OF SYSTEM BOUNDARY

The conservation law holds for the complete process and any subdivision of the process. The system boundary defines the part of the process being considered. The flows into and out of the system are those crossing the boundary and must balance with material generated or consumed within the boundary.

Any process can be divided up in an arbitrary way to facilitate the material balance calculations. The judicious choice of the system boundaries can often greatly simplify what would otherwise be difficult and tortuous calculations.

No hard and fast rules can be given on the selection of suitable boundaries for all types of material balance problems. Selection of the best subdivision for any particular process is a matter of judgment, and depends on insight into the structure of the problem, which can only be gained by practice. The following general rules serve as a guide:

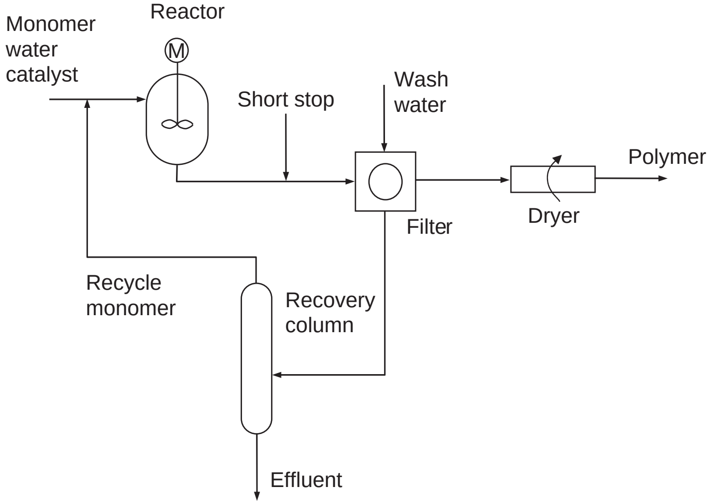
1. With complex processes, first take the boundary around the complete process and if possible calculate the flows in and out. Raw materials in, products and byproducts out.
2. Select the boundaries to subdivide the process into simple stages and make a balance over each stage separately.
3. Select the boundary around any stage so as to reduce the number of unknown streams to as few as possible.
4. As a first step, include any recycle streams within the system boundary (see Section 2.14).

Example 2.4

The diagram shows the main steps in a process for producing a polymer. From the following data, calculate the stream flows for a production rate of 10,000 kg/h.

Reactor selectivity for polymer	100%
slurry polymerization	20 wt% monomer/water
conversion	90% per pass
catalyst	1 kg/1000 kg monomer
short stopping agent	0.5 kg/1000 kg unreacted monomer

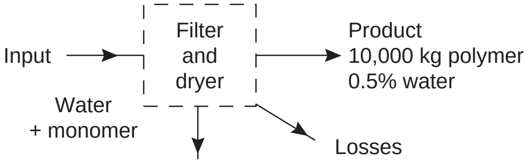
Filter wash water approx. 1 kg/1 kg polymer
Recovery column yield 98% (percentage recovered)
Dryer feed ~5% water, product specification 0.5% H_2O
Polymer losses in filter and dryer ~1%



Solution

Only those flows necessary to illustrate the choice of system boundaries and method of calculation are given in the solution.

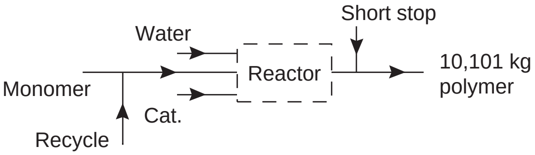
Basis: 1 hour
Take the first system boundary around the filter and dryer.



With 1% loss, polymer entering subsystem

$$= \frac{10{,}000}{0.99} = \underline{\underline{10{,}101\,\text{kg}}}$$

Take the next boundary around the reactor system; the feeds to the reactor can then be calculated.



At 90% conversion per pass, monomer feed $= \dfrac{10{,}101}{0.9} = \underline{\underline{11{,}223\,\text{kg}}}$

Unreacted monomer $= 11{,}223 - 10{,}101 = \underline{\underline{1122\,\text{kg}}}$

Short-stop, at 0.5 kg/1000 kg unreacted monomer $= 1122 \times 0.5 \times 10^{-3} = \underline{\underline{0.6\,\text{kg}}}$

Catalyst, at 1 kg/1000 kg monomer $= 11{,}223 \times 1 \times 10^{-3} = \underline{\underline{11\,\text{kg}}}$

Let water feed to reactor be F_1, then for 20% monomer

$$0.2 = \frac{11{,}223}{F_1 + 11{,}223}$$

$$F_1 = \frac{11{,}223(1 - 0.2)}{0.2} = \underline{\underline{44{,}892\,\text{kg}}}$$

Now consider filter-dryer subsystem again.

Water in polymer to dryer, at 5% (neglecting polymer loss)

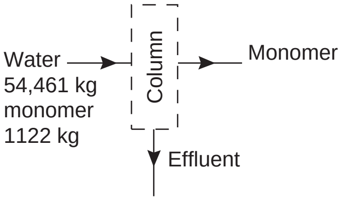
$$= \frac{10{,}101 \times 0.05}{0.95} = \underline{\underline{532\,\text{kg}}}$$

Balance over reactor-filter-dryer subsystem gives flows to recovery column.

$$\text{water, } 44{,}892 + 10{,}101 - 532 = \underline{\underline{54{,}461\,\text{kg}}}$$

$$\text{monomer, unreacted monomer} = \underline{\underline{1122\,\text{kg}}}$$

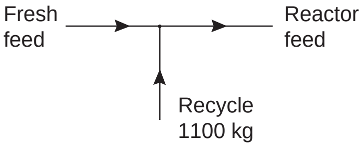
Now consider recovery system



With 98% recovery, recycle to reactor

$$= 0.98 \times 1122 = \underline{\underline{1100\,\text{kg}}}$$

Composition of effluent is 23 kg monomer, 54,461 kg water.
Consider reactor monomer feed



Balance around tee gives fresh monomer required

$$= 11{,}223 - 1100 = \underline{\underline{10{,}123\,\text{kg}}}$$

Note that this 12-line calculation would have required setting up a recycle and three stream-adjusts in a process simulator, illustrating that simple problems can often be solved more easily by hand or spreadsheet calculations if the boundaries for mass balances are chosen carefully.

2.7. CHOICE OF BASIS FOR CALCULATIONS

The choice of the basis for a calculation often determines whether the calculation proves to be simple or complex. As with the choice of system boundaries, no all-embracing rules or procedures can be given for the selection of the right basis for any problem. The selection depends on judgment gained by experience. Some guide rules are

A. Time: Choose the time basis in which the results are to be presented; for example kg/h, metric tons/y, unless this leads to very large or very small numbers, where rounding errors can become problematic.
B. For batch processes, use one batch.
C. Choose as the mass basis the stream flow for which most information is given.
D. It is often easier to work in moles, rather than weight, even when no reaction is involved.
E. For gases, if the compositions are given by volume, use a molar basis, remembering that volume fractions are equivalent to mole fractions up to moderate pressures.

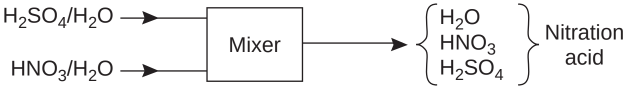
2.8. NUMBER OF INDEPENDENT COMPONENTS

A balance equation can be written for each independent component. Not all the components in a material balance will be independent.

Physical Systems, No Reaction

If there is no chemical reaction, the number of independent components is equal to the number of distinct chemical species present.

Consider the production of a nitration acid by mixing 70% nitric and 98% sulfuric acid. The number of distinct chemical species is three: water, sulfuric acid, nitric acid.



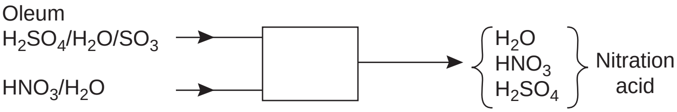
Chemical Systems, Reaction

If the process involves chemical reaction, the number of independent components is not necessarily equal to the number of chemical species, as some may be related by the chemical equation. In this situation the number of independent components can be calculated by the following relationship:

$$\text{Number of independent components} = \text{Number of chemical species} - \text{Number of independent chemical equations} \tag{2.2}$$

Example 2.5

If nitration acid is made up using oleum in place of the 98% sulfuric acid, there will be four distinct chemical species: sulfuric acid, sulfur trioxide, nitric acid, water. The sulfur trioxide will react with the water producing sulfuric acid, so there are only three independent components.



Solution

Reaction equation $SO_3 + H_2O \rightarrow H_2SO_4$	
No. of chemical species	4
No. of reactions	1
No. of independent equations	3

2.9. CONSTRAINTS ON FLOWS AND COMPOSITIONS

It is obvious, but worth emphasizing, that the sum of the individual component flows in any stream cannot exceed the total stream flow. Also, the sum of the individual molar or weight fractions must equal 1. Hence, the composition of a stream is completely defined if all but one of the component concentrations are given.

The component flows in a stream (or the quantities in a batch) are completely defined by any of the following:

A. Specifying the flow (or quantity) of each component.
B. Specifying the total flow (or quantity) and the composition.
C. Specifying the flow (or quantity) of one component and the composition.

Example 2.6

The feed stream to a reactor contains ethylene 16%, oxygen 9%, nitrogen 31%, and hydrogen chloride. If the ethylene flow is 5000 kg/h, calculate the individual component flows and the total stream flow. All percentages are by weight.

Solution

$$\text{Percentage HCl} = 100 - (16 + 9 + 31) = 44$$

$$\text{Percentage ethylene} = \frac{5000}{\text{total}} \times 100 = 16$$

$$\text{hence total flow} = 5000 \times \frac{100}{16} = \underline{\underline{31{,}250\ \text{kg/h}}}$$

$$\text{so, oxygen flow} = \frac{9}{100} \times 31{,}250 = \underline{\underline{2813\ \text{kg/h}}}$$

$$\text{nitrogen} = 31{,}250 \times \frac{31}{100} = \underline{\underline{9687\ \text{kg/h}}}$$

$$\text{hydrogen chloride} = 31{,}250 \times \frac{44}{100} = \underline{\underline{13{,}750\ \text{kg/h}}}$$

General rule: The ratio of the flow of any component to the flow of any other component is the same as the ratio of the compositions of the two components.

The flow of any component in Example 2.6 could have been calculated directly from the ratio of the percentage to that of ethylene and the ethylene flow.

$$\text{Flow of hydrogen chloride} = \frac{44}{16} \times 5000 = \underline{\underline{13{,}750\ \text{kg/h}}}$$

2.10. GENERAL ALGEBRAIC METHOD

Simple material-balance problems involving only a few streams and with a few unknowns can usually be solved by simple, direct methods. The relationship between the unknown quantities and the information given can usually be clearly seen. For more complex problems, and for problems with several processing steps, a more formal algebraic approach can be used. The procedure is tedious if the calculations have to be done manually, but should result in a solution to even the most intractable problems, providing sufficient information is given for the problem to have a solution.

Algebraic symbols are assigned to all the unknown flows and compositions. Balance equations are then written around each subsystem for the independent components (chemical species or elements).

Material-balance problems are particular examples of the general design problem discussed in Chapter 1. The unknowns are compositions or flows, and the relating equations arise from the conservation law and the stoichiometry of the reactions. For any problem to have a unique solution, it must be possible to write the same number of independent equations as there are unknowns.

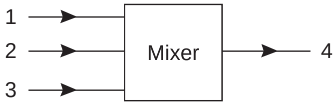
Consider the general material balance problem where there are N_s streams each containing N_c independent components. Then the number of variables, N_v, is given by

$$N_v = N_c \times N_s \tag{2.3}$$

If N_e independent balance equations can be written, then the number of variables, N_d, that must be specified for a unique solution, is given by

$$N_d = (N_s \times N_c) - N_e \tag{2.4}$$

Consider a simple mixing problem:



Let F_n be the total flow in stream n, and $x_{n,m}$ the concentration of component m in stream n. Then the general balance equation can be written

$$F_1x_{1,m} + F_2x_{2,m} + F_3x_{3,m} = F_4x_{4,m} \tag{2.5}$$

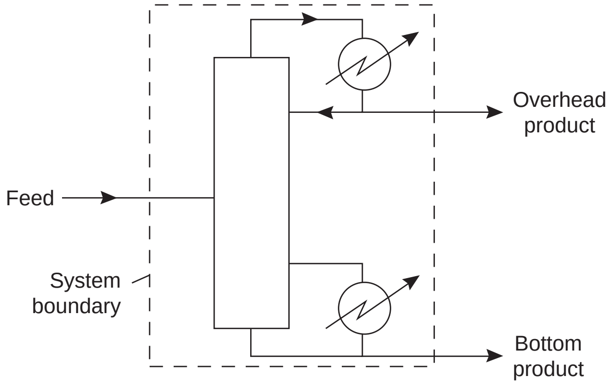
A balance equation can also be written for the total of each stream:

$$F_1 + F_2 + F_3 = F_4 \tag{2.6}$$

but this could be obtained by adding the individual component equations, and so is not an additional independent equation. There are m independent equations, the number of independent components.

This problem has $4m$ variables and m independent balance equations. There will be a unique solution to the problem if we specify $3m$ variables, for example, the molar flows of all m components in the three feeds or in two feeds and the product.

Consider a separation unit, such as a distillation column, that divides a process stream into two product streams. Let the feed rate be 10,000 kg/h; composition benzene 60%, toluene 30%, xylenes 10%.



There are three streams—feed, overheads, and bottoms—and three independent components in each stream.

Number of variables (component flow rates) = 9

Number of independent material balance equations = 3

Number of variables to be specified for a unique solution = 9 − 3 = 6

Three variables are specified; the feed flow and composition fixes the flow of each component in the feed.

Number of variables to be specified by designer = 6 − 3 = 3. Any three component flows can be chosen.

Normally the top composition and flow or the bottom composition and flow would be chosen.

If the primary function of the column is to separate the benzene from the other components, the maximum toluene and xylenes in the overheads would be specified (say, at 5 kg/h and 3 kg/h) and the loss of benzene in the bottoms also specified (say, at not greater than 5 kg/h). Three flows are specified, so the other flows can be calculated.

Benzene in overheads = benzene in feed – benzene in bottoms.

$$0.6 \times 10{,}000 - 5 = \underline{\underline{5995\,\text{kg/h}}}$$

Toluene in bottoms = toluene in feed – toluene in overheads

$$0.3 \times 10{,}000 - 5 = \underline{\underline{2995\,\text{kg/h}}}$$

Xylenes in bottoms = xylenes in feed – xylenes in overheads

$$0.1 \times 10{,}000 - 3 = \underline{\underline{997\,\text{kg/h}}}$$

2.11. TIE COMPONENTS

In Section 2.9 it was shown that the flow of any component was in the same ratio to the flow of any other component as the ratio of the concentrations of the two components. If one component passes unchanged through a process unit, it can be used to tie the inlet and outlet compositions.

This technique is particularly useful in handling combustion calculations where the nitrogen in the combustion air passes through unreacted and is used as the tie component. This is illustrated in Example 2.8.

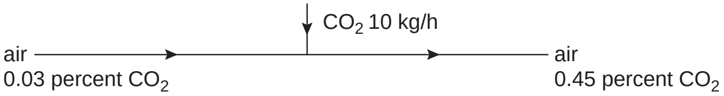
This principle is also often used in experiments to measure the flow of a process stream by introducing a measured flow of some easily analyzed, compatible, and inert material.

Example 2.7

Carbon dioxide is added at a rate of 10 kg/h to an air stream and the air is sampled at a sufficient distance downstream to ensure complete mixing. If the analysis shows 0.45% v/v CO_2, calculate the air-flow rate.

Solution

Normal carbon dioxide content of air is 0.03%.



Basis: kmol/h, as percentages are by volume.

$$\text{kmol/h } CO_2 \text{ introduced} = \frac{10}{44} = 0.2273$$

Let X be the air flow.
Balance on CO_2, the tie component

$$\begin{aligned}
&CO_2 \text{ in} = 0.0003X + 0.2273\\
&CO_2 \text{ out} = 0.0045X\\
&X(0.0045 - 0.0003) = 0.2273\\
&X = 0.2273/0.0042 = 54\,\text{kmol/h}\\
&\quad = 54 \times 29 = \underline{\underline{1560\,\text{kg/h}}}
\end{aligned}$$

Example 2.8

In a test on a furnace fired with natural gas (composition 95% methane, 5% nitrogen), the following flue gas analysis was obtained: carbon dioxide 9.1%, carbon monoxide 0.2%, oxygen 4.6%, nitrogen 86.1%, all percentages by volume.

Calculate the percentage excess air flow (percentage above stoichiometric).

Solution

$$\text{Reaction: } CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Note: The flue gas analysis is reported on a dry basis, any water formed having been condensed out. Nitrogen is the tie component.

Basis: 100 mol, dry flue gas; as the analysis of the flue gas is known, the moles of each element in the flue gas (flow out) can be easily calculated and related to the flow into the system.

Let the quantity of fuel (natural gas) per 100 mol dry flue gas be X.

Balance on carbon, moles in fuel = moles in flue gas

$$0.95X = 9.1 + 0.2, \text{ hence } X = 9.79\,\text{mol}$$

Balance on nitrogen (composition of air O_2 21%, N_2 79%):

Let Y be the flow of air per 100 mol dry flue gas.

$$N_2 \text{ in air} + N_2 \text{ in fuel} = N_2 \text{ in flue gas}$$
$$0.79Y + 0.05 \times 9.79 = 86.1, \text{ hence } Y = 108.4\,\text{mol}$$

Stoichiometric air: From the reaction equation 1 mol methane requires 2 mol oxygen,

$$\text{so, stoichiometric air} = 9.79 \times 0.95 \times 2 \times \frac{100}{21} = 88.6\,\text{mol}$$

$$\text{Percentage excess air} = \frac{(\text{air supplied} - \text{stoichiometric air})}{\text{stoichiometric air}} \times 100$$
$$= \frac{108.4 - 88.6}{88.6} = \underline{\underline{22 \text{ percent}}}$$

Note that we simplified the problem by neglecting the carbon dioxide present in the ambient air. From Example 2.7, this is 0.03%, i.e., 108.4 × 0.00003 = 0.0325 mol per 100 mol of dry flue gas, or roughly one-third of one percent error. This does not significantly affect the calculation of the percentage excess air.

2.12. EXCESS REAGENT

In industrial reactions the components are seldom fed to the reactor in exact stoichiometric proportions. A reagent may be supplied in excess to promote the desired reaction, to maximize the use of an expensive reagent, or to ensure complete reaction of a reagent, as in combustion.

The percentage excess reagent is defined by the following equation:

$$\text{Percent excess} = \frac{\text{quantity supplied} - \text{stoichiometric}}{\text{stoichiometric quantity}} \times 100 \tag{2.7}$$

It is necessary to state clearly to which reagent the excess refers.

Example 2.9

To ensure complete combustion, 20% excess air is supplied to a furnace burning natural gas. The gas composition (by volume) is methane 95%, ethane 5%.

Calculate the moles of air required per mole of fuel.

Solution

Basis: 100 mol gas, as the analysis is volume percentage.

$$\text{Reactions:}\quad \begin{aligned} &CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \\ &C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O \end{aligned}$$

Stoichiometric moles of O_2 required $= 95 \times 2 + 5 \times 3.5 = 207.5$

With 20% excess, moles of O_2 required $= 207.5 \times 1.2 = 249$

Moles of air (21% O_2) $= 249 \times 100/21 = 1185.7$

Air per mole of fuel $= 1185.7/100 = \underline{\underline{11.86\,\text{mol}}}$

2.13. CONVERSION, SELECTIVITY, AND YIELD

It is important to distinguish between conversion and yield. Conversion is to do with reactants; yield with products.

Conversion

Conversion is a measure of the fraction of the reagent that reacts.

To optimize reactor design and minimize byproduct formation, the conversion of a particular reagent is often less than 100%. If more than one reactant is used, the reagent on which the conversion is based must be specified.

Conversion is defined by the following expression:

$$\begin{aligned} \text{Conversion} &= \frac{\text{amount of reagent consumed}}{\text{amount supplied}} \\ &= \frac{(\text{amount in feed stream}) - (\text{amount in product stream})}{(\text{amount in feed stream})} \qquad (2.8) \end{aligned}$$

This definition gives the total conversion of the particular reagent to all products.

Example 2.10

In the manufacture of vinyl chloride (VC) by the pyrolysis of dichloroethane (DCE), the reactor conversion is limited to 55% to reduce carbon formation, which fouls the reactor tubes.

Calculate the quantity of DCE fed to the reactor to produce 5000 kg/h of VC.

Solution

Basis: 5000 kg/h VC (the required quantity).

$$\text{Reaction: } C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$$

Molar weights: DCE 99, VC 62.5

$$\text{kmol/h VC produced} = \frac{5000}{62.5} = 80$$

From the stoichiometric equation, 1 kmol DCE produces 1 kmol VC. Let X be DCE feed in kmol/h:

$$\text{Percent conversion} = 55 = \frac{80}{X} \times 100$$

$$X = \frac{80}{0.55} = \underline{\underline{145.5\,\text{kmol/h}}}$$

In this example, the small loss of DCE to carbon and other products has been neglected. All the DCE reacted has been assumed to be converted to VC.

Selectivity

Selectivity is a measure of the efficiency of the reactor in converting reagent to the desired product. It is the fraction of the reacted material that was converted into the desired product. If no byproducts are formed, then the selectivity is 100%. If side reactions occur and byproducts are formed, then the selectivity decreases. Selectivity is always expressed as the selectivity of feed A for product B and is defined by the following equation:

$$\begin{aligned}\text{Selectivity} &= \frac{\text{moles of B formed}}{\text{moles of B that could have been formed if all A reacted to give B}}\\ &= \frac{\text{moles of B formed}}{\text{moles of A consumed} \times \text{stoichiometric factor}} \qquad (2.9)\end{aligned}$$

$$\begin{aligned}\text{Stoichiometric factor} = {} & \text{moles of B produced per mole of A reacted}\\ & \text{in the reaction stoichiometric equation}\end{aligned}$$

Selectivity is usually improved by operating the reactor at low conversion. At high conversion, the reactor has low concentrations of at least one reagent and high concentrations of products, so reactions that form byproducts are more likely to occur.

Reagents that are not converted in the reactor can be recovered and recycled. Reagents that become converted to byproducts usually cannot be recovered, and the byproducts must be purified for sale or else disposed as waste (see Section 6.4.8).

The optimum reactor conditions thus usually favor low reactor conversion to give high selectivity for the desired products when all of these costs are taken into account.

Yield

Yield is a measure of the performance of a reactor or plant. Several different definitions of yield are used, and it is important to state clearly the basis of any yield numbers. This is often not done when yields are quoted in the literature, and judgment must be used to decide what was intended.

The yield of product B from feed A is defined by

$$\text{Yield} = \frac{\text{moles of B formed}}{\text{moles of A supplied} \times \text{stoichiometric factor}} \qquad (2.10)$$

For a reactor, the yield is the product of conversion and selectivity:

$$\text{Reaction yield} = \text{Conversion} \times \text{Selectivity}$$

$$= \frac{\text{moles A consumed}}{\text{moles A supplied}} \times \frac{\text{moles B formed}}{\text{moles A consumed} \times \text{stoichiometric factor}} \tag{2.11}$$

With industrial reactors, it is necessary to distinguish between "Reaction yield" (chemical yield), which includes only chemical losses to side products; and the overall "Reactor yield," which also includes physical losses, such as losses by evaporation into vent gas.

If the conversion is near 100%, it may not be worth separating and recycling the unreacted material; the overall reactor yield would then include the loss of unreacted material. If the unreacted material is separated and recycled, the overall yield *taken over the reactor and separation step* would include any physical losses from the separation step.

Plant yield is a measure of the overall performance of the plant and includes all chemical and physical losses.

Plant yield (applied to the complete plant or any stage)

$$= \frac{\text{moles of product produced}}{\text{moles of reagent supplied to the process} \times \text{stoichiometric factor}} \tag{2.12}$$

Where more than one reagent is used, or product produced, it is essential that product and reagent to which the yield refers is clearly stated.

The plant yield of B from A is the product of the reactor selectivity of feed A for product B and the separation efficiency (recovery) of each separation step that handles product B or reagent A.

Example 2.11

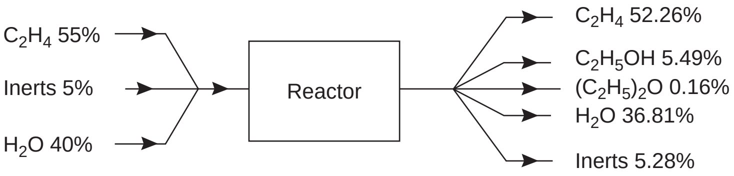
In the production of ethanol by the hydrolysis of ethylene, diethyl ether is produced as a byproduct. A typical feed stream composition is 55% ethylene, 5% inerts, 40% water; and product stream: 52.26% ethylene, 5.49% ethanol, 0.16% ether, 36.81% water, 5.28% inerts. Calculate the selectivity of ethylene for ethanol and for ether.

Solution

$$\text{Reactions:} \quad C_2H_4 + H_2O \rightarrow C_2H_5OH \tag{a}$$

$$2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O \tag{b}$$

Basis: 100 moles feed (easier calculation than using the product stream)



Note: The flow of inerts will be constant, as they do not react; and it can thus be used to calculate the other flows from the compositions.

Feed stream	ethylene	55 mol
	inerts	5 mol
	water	40 mol

Product stream

$$\text{ethylene} = \frac{52.26}{5.28} \times 5 = 49.49\,\text{mol}$$

$$\text{ethanol} = \frac{5.49}{5.28} \times 5 = 5.20\,\text{mol}$$

$$\text{ether} = \frac{0.16}{5.28} \times 5 = 0.15\,\text{mol}$$

$$\text{Amount of ethylene reacted} = 55.0 - 49.49 = 5.51\,\text{mol}$$

$$\text{Selectivity of ethylene for ethanol} = \frac{5.20}{5.51 \times 1.0} \times 100 = \underline{\underline{94.4\%}}$$

As 1 mol of ethanol is produced per mol of ethylene, the stoichiometric factor is 1.

$$\text{Selectivity of ethylene for ether} = \frac{0.15}{5.51 \times 0.5} \times 100 = \underline{\underline{5.44\%}}$$

The stoichiometric factor is 0.5, as 2 mol of ethylene produce 1 mol of ether.

Note that the conversion of ethylene, to all products, is given by

$$\text{Conversion} = \frac{\text{mols fed} - \text{mols out}}{\text{mols fed}} = \frac{55 - 49.49}{55} \times 100$$
$$= \underline{\underline{10\text{ percent}}}$$

The selectivity based on water could also be calculated but is of no real interest, as water is relatively inexpensive compared with ethylene. Water is clearly fed to the reactor in considerable excess.

The yield of ethanol based on ethylene is

$$\text{Reaction yield} = \frac{5.20}{55 \times 1.0} \times 100 = \underline{\underline{9.45\%}}$$

Example 2.12

In the chlorination of ethylene to produce dichloroethane (DCE), the conversion of ethylene is reported as 99.0%. If 94 mol of DCE are produced per 100 mol of ethylene reacted, calculate the selectivity and the overall yield based on ethylene. The unreacted ethylene is not recovered.

Solution

$$\text{Reaction: } C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$$

The stoichiometric factor is 1.

$$\text{Selectivity} = \frac{\text{moles DCE produced}}{\text{moles ethylene reacted} \times 1} \times 100$$

$$= \frac{94}{100} \times 100 = \underline{\underline{94\%}}$$

$$\text{Overall yield (including physical losses)} = \frac{\text{moles DCE produced}}{\text{moles ethylene fed} \times 1} \times 100$$

Therefore, 99 moles of ethylene are reacted for 100 moles fed, so

$$\text{Overall yield} = \frac{94}{100} \times \frac{99}{100} = \underline{\underline{93.1\%}}$$

Note that we get the same answer by multiplying the selectivity (0.94) and conversion (0.99).

The principal byproduct of this process is trichloroethane.

Sources of Conversion, Selectivity, and Yield Data

If there is minimal byproduct formation, then the reactor costs (volume, catalyst, heating, etc.) can be traded off against the costs of separating and recycling unconverted reagents to determine the optimal reactor conversion. More frequently, the selectivity of the most expensive feeds for the desired product is less than 100%, and byproduct costs must also be taken into account. The reactor optimization then requires a relationship between reactor conversion and selectivity, not just for the main product, but for all the byproducts that are formed in sufficient quantity to have an impact on process costs.

In simple cases, when the number of byproducts is small, it may be possible to develop a mechanistic model of the reaction kinetics that predicts the rate of formation of the main product and byproducts. If such a model is fitted to experimental data over a suitably wide range of process conditions, then it can be used for process optimization. The development of reaction kinetics models is described in most reaction engineering textbooks. See, for example, Levenspiel (1998), Froment and Bischoff (1990), and Fogler (2005).

In cases in which the reaction quickly proceeds to equilibrium, the yields are easily estimated as the equilibrium yields. Under these circumstances, the only possibilities for process optimization are to change the temperature, pressure, or feed composition, so as to obtain a different equilibrium mixture. The calculation of reaction equilibrium is easily carried out using commercial process simulation programs.

When the number of components or reactions is too large, or the mechanism is too complex to deduce with statistical certainty, then response surface models can be used instead. Methods for the statistical design of experiments can be applied, reducing the amount of experimental data that must be collected to form a statistically meaningful correlation of selectivity and yield to the main process parameters. See Montgomery (2001) for a good introduction to the statistical design of experiments.

In the early stages of design, the design engineer will often have neither a response surface, nor a detailed mechanistic model of the reaction kinetics. Few companies are prepared to dedicate a laboratory or pilot plant and the necessary staff to collecting reaction kinetics data until management has been satisfied that the process under investigation is economically attractive. A design is thus needed before the necessary data set has been collected. Under such circumstances, the design engineer must select the optimal reactor conditions from whatever data are available. This initial estimate of reactor yield may come from a few data points collected by a chemist or taken from a patent or research paper. The use of data from patents is discussed in Section 8.2. For the purposes of completing a design, only a single estimate of reactor yield is needed. Additional yield data taken over a broader range of process conditions give the designer greater ability to properly optimize the design.

2.14. RECYCLE PROCESSES

Processes in which a flow stream is returned (recycled) to an earlier stage in the processing sequence are frequently used. If the conversion of a valuable reagent in a reaction process is appreciably less than 100%, the unreacted material is usually separated and recycled. The return of reflux to the top of a distillation column is an example of a recycle process in which there is no reaction.

In mass balance calculations the presence of recycle streams makes the calculations more difficult.

Without recycle, the material balances on a series of processing steps can be carried out sequentially, taking each unit in turn; the calculated flows out of one unit become the feeds to the next. If a recycle stream is present, then at the point where the recycle is returned, the flow will not be known as it will depend on downstream flows not yet calculated. If the recycle flow is not known, the sequence of calculations cannot be continued to the point where the recycle flow can be determined.

Two approaches to the solution of recycle problems are possible:

A. The cut-and-try ("tear") method. The recycle stream flows can be estimated and the calculations continued to the point where the recycle is calculated. The estimated flows are then compared with those calculated, and a better estimate is made. The procedure is continued until the difference between the estimated and the calculated flows is within an acceptable tolerance.

B. The formal, algebraic method. The presence of recycle implies that some of the mass balance equations must be solved simultaneously. The equations are set up with the recycle flows as unknowns and solved using standard methods for the solution of simultaneous equations.

With simple problems that have only one or two recycle loops, the calculation can often be simplified by the careful selection of the basis of calculation and the system boundaries. This is illustrated in Examples 2.4 and 2.13.

The solution of more complex material balance problems involving several recycle loops is discussed in Chapter 4.

Example 2.13

The block diagram shows the main steps in the balanced process for the production of vinyl chloride from ethylene. Each block represents a reactor and several other processing units. The main reactions are

Block A, chlorination

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2, \quad \text{yield on ethylene 98 percent}$$

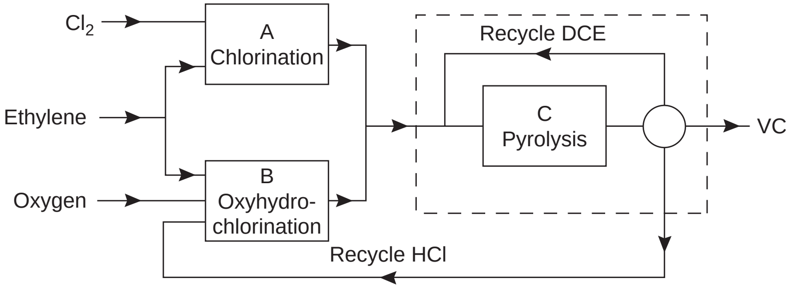
Block B, oxyhydrochlorination

$$C_2H_4 + 2HCl + 0.5O_2 \rightarrow C_2H_4Cl_2 + H_20 \quad \text{yields: on ethylene 95\%, on HCl 90\%}$$

Block C, pyrolysis

$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl, \quad \text{yields: on DCE 99 percent, on HCl 99.5 percent}$$

The HCl from the pyrolysis step is recycled to the oxyhydrochlorination step. The flow of ethylene to the chlorination and oxyhydrochlorination reactors is adjusted so that the production of HCl is in balance with the requirement. The conversion in the pyrolysis reactor is limited to 55%, and the unreacted dichloroethane (DCE) is separated and recycled.



Using the yield figures given, and neglecting any other losses, calculate the flow of ethylene to each reactor and the flow of DCE to the pyrolysis reactor, for a production rate of 12,500 kg/h vinyl chloride (VC).

Solution

Molecular weights: vinyl chloride 62.5, DCE 99.0, HCl 36.5.

$$\text{VC per hour} = \frac{12{,}500}{62.5} = 200\,\text{kmol/h}$$

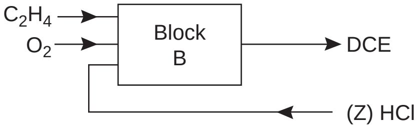
Draw a system boundary around each block, enclosing the DCE recycle within the boundary of step C.

Let the flow of ethylene to block A be X and to block B be Y, and the HCl recycle be Z.

Then the total moles of DCE produced = $0.98X + 0.95Y$, allowing for the yields, and the moles of HCl produced in block C

$$= (0.98X + 0.95Y)0.995 = Z \tag{a}$$

Consider the flows to and from block B



The yield of DCE based on HCl is 90%, so the moles of DCE produced

$$= 0.5 \times 0.90Z$$

Note: The stoichiometric factor is 0.5 (2 mol HCl per mol DCE).

The yield of DCE based on ethylene is 95%, so

$$0.5 \times 0.9Z = 0.95Y$$
$$Z = 0.95 \times 2Y/0.9$$

Substituting for Z into equation (a) gives

$$Y = (0.98X + 0.95Y)0.995 \times \frac{0.9}{2 \times 0.95} \tag{b}$$
$$Y = 0.837X$$

Turning to block C, total VC produced = 0.99 × total DCE, so

$$0.99(0.98X + 0.95Y) = 200\ \text{kmol/h}$$

Substituting for Y from equation (b) gives $X = \underline{\underline{113.8\ \text{kmol/h}}}$

and $Y = 0.837 \times 113.8 = \underline{\underline{95.3\ \text{kmol/h}}}$

HCl recycle from equation (a)

$$Z = (0.98 \times 113.8 + 0.95 \times 95.3)0.995 = \underline{\underline{201.1\ \text{kmol/h}}}$$

Note: Overall yield on ethylene $= \dfrac{200}{(113.8 + 95.3)} \times 100 = \underline{\underline{96\ \text{percent}}}$

2.15. PURGE

It is usually necessary to bleed off a portion of a recycle stream to prevent the buildup of unwanted material. For example, if a reactor feed contains inert components that are not separated from the recycle stream in the separation units, these inerts would accumulate in the recycle stream until the stream eventually consisted almost entirely of inerts. Some portion of the stream must be purged to keep the inert level within acceptable limits. A continuous purge would normally be used. Under steady-state conditions:

Loss of inert in the purge = Rate of feed of inerts into the system

The concentration of any component in the purge stream is the same as that in the recycle stream at the point where the purge is taken off. So the required purge rate can be determined from the following relationship:

[Feed stream flow rate] × [Feed stream inert concentration]
= [Purge stream flow rate] × [Specified(desired) recycle inert concentration]

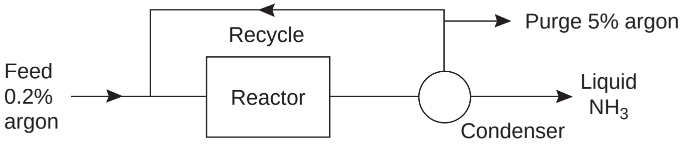
Example 2.14

In the production of ammonia from hydrogen and nitrogen, the conversion, based on either raw material, is limited to 15%. The ammonia produced is condensed from the reactor (converter) product stream, and the unreacted material is recycled. If the feed contains 0.2% argon (from the nitrogen separation process), calculate the purge rate required to hold the argon in the recycle stream below 5.0%. Percentages are by volume.

Solution

Basis: 100 moles feed (purge rate will be expressed as moles per 100 mol feed, as the production rate is not given).

Process diagram:



Volume percentages are taken as equivalent to mol%.

Argon entering system with feed = 100 × 0.2/100 = 0.2 mol.
Let purge rate per 100 mol feed be *F*.
Argon leaving system in purge = $F \times 5/100 = 0.05\,F$.
At the steady state, argon leaving = argon entering

$$0.05F = 0.2$$

$$F = \frac{0.2}{0.05} = 4$$

Purge required: 4 mol per 100 mol feed.

2.16. BYPASS

A flow stream may be divided and some part diverted (bypassed) around some units. This procedure is often used to control stream composition or temperature.

Material balance calculations on processes with bypass streams are similar to those involving recycle, except that the stream is fed forward instead of backward. This usually makes the calculations easier than with recycle.

2.17. UNSTEADY-STATE CALCULATIONS

All the previous material balance examples have been steady-state balances. The accumulation term was taken as zero, and the stream flow rates and compositions did not vary with time. If these conditions are not met, the calculations are more complex. Steady-state calculations are usually sufficient for the calculations of the process flowsheet (Chapter 4). The unsteady-state behavior of a process is important when considering the process startup and shutdown, and the response to process upsets.

Batch processes are also examples of unsteady-state operation; although the total material requirements can be calculated by taking one batch as the basis for the calculation, unsteady-state balances are needed for determination of reaction and separation times.

The procedure for the solution of unsteady-state balances is to set up balances over a small increment of time, which will give a series of differential equations describing the process. For simple problems these equations can be solved analytically. For more complex problems computer methods are used.

The general approach to the solution of unsteady-state problems is illustrated in Example 2.15.

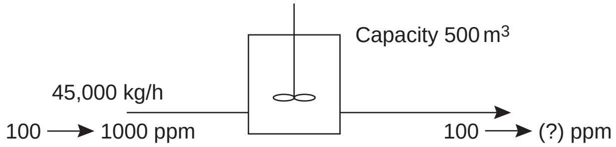
The behavior of processes under non-steady-state conditions is a complex and specialized subject and is beyond the scope of this book. It can be important in process design when assessing the behavior of a process from the point of view of safety and control.

The use of material balances in the modeling of complex unsteady-state processes is discussed in the books by Myers and Seider (1976) and Henley and Rosen (1969).

Example 2.15

A hold tank is installed in an aqueous effluent-treatment process to smooth out fluctuations in concentration of the effluent stream. The effluent feed to the tank normally contains no more than 100 ppm of acetone. The maximum allowable concentration of acetone in the effluent discharge is set at 200 ppm. The surge tank working capacity is 500 m^3 and it can be considered to be perfectly mixed. The effluent flow is 45,000 kg/h. If the acetone concentration in the feed suddenly rises to 1000 ppm, due to a spill in the process plant, and stays at that level for half an hour, will the limit of 200 ppm in the effluent discharge be exceeded?

Solution



Basis: increment of time Δt.

To illustrate the general solution to this type of problem, the balance will be set up in terms of symbols for all the quantities and then actual values for this example substituted.

Let material in the tank = M,
flow rate = F,
initial concentration in the tank = C_0,
concentration at time t after the feed concentration is increased = C,
concentration in the effluent feed = C_1,
change in concentration over time increment $\Delta t = \Delta C$,
average concentration in the tank during the time increment = C_{av}.

Then, as there is no generation in the system, the general material balance (Section 2.3) becomes

$$\text{Input} - \text{Output} = \text{Accumulation}$$

Material balance on acetone.

Note: As the tank is considered to be perfectly mixed, the outlet concentration will be the same as the concentration in the tank.

$$\text{Acetone in} - \text{Acetone out} = \text{Acetone accumulated in the tank}$$

$$FC_1\Delta t - FC_{av}\Delta t = M(C + \Delta C) - MC$$

$$F(C_1 - C_{av}) = M\frac{\Delta C}{\Delta t}$$

Taking the limit, as $\Delta t \to 0$

$$\frac{\Delta C}{\Delta t} = \frac{dC}{dt}, \qquad C_{av} = C$$

$$F(C_1 - C) = M\frac{dC}{dt}$$

Integrating

$$\int_0^t dt = \frac{M}{F}\int_{C_0}^{C} \frac{dC}{(C_1 - C)}$$

$$t = -\frac{M}{F}\ln\left[\frac{C_1 - C}{C_1 - C_0}\right]$$

Substituting the values for the example and noting that the maximum outlet concentration occurs at the end of the half-hour period of high inlet concentration:

$$\begin{aligned}
t &= 0.5\,\text{h} \\
C_1 &= 1000\,\text{ppm} \\
C_0 &= 100\,\text{ppm (normal value)} \\
M &= 500\,\text{m}^3 = 500{,}000\,\text{kg} \\
F &= 45{,}000\,\text{kg/h} \\
0.5 &= -\frac{500{,}000}{45{,}000}\ln\left[\frac{1000 - C}{1000 - 100}\right] \\
0.045 &= -\ln\left[\frac{1000 - C}{900}\right] \\
\text{e}^{-0.045} \times 900 &= 1000 - C \\
C &= \underline{\underline{140\,\text{ppm}}}
\end{aligned}$$

So the maximum allowable concentration is not exceeded.

2.18. GENERAL PROCEDURE FOR MATERIAL-BALANCE PROBLEMS

The best way to tackle a problem will depend on the information given, the information required from the balance, and the constraints that arise from the nature of the problem. No all embracing, best method of solution can be given to cover all possible problems. The following step-by-step procedure is given as an aid to the efficient solution of material balance problems. The same general approach can be usefully employed to organize the solution of energy balances and other design problems.

Procedure

Step 1. Draw a block diagram of the process.

Show each significant step as a block, linked by lines and arrows to show the stream connections and flow direction.

Step 2. List the available data.

Show on the block diagram the known flows (or quantities) and stream compositions.

Step 3. List all the information required from the balance.
Step 4. Decide the system boundaries (see Section 2.6).
Step 5. Write out the chemical reactions involved for the main products and byproducts.
Step 6. Note any other constraints, such as specified stream compositions, azeotropes, phase or reaction equilibrium, tie substances (see Section 2.11).

The use of phase equilibrium relationships and other constraints in determining stream compositions and flows is discussed in more detail in Chapter 4.

Step 7. Note any stream compositions and flows that can be approximated.

Step 8. Check the number of conservation (and other) equations that can be written, and compare with the number of unknowns. Decide which variables are to be design variables; see Section 2.10.

This step would be used only for complex problems.

Step 9. Decide the basis of the calculation; see Section 2.7.

The order in which the steps are taken may be varied to suit the problem.

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2.20. NOMENCLATURE

		Dimensions in **MLT**
C	Concentration after time t, Example 2.15	—
C_{av}	Average concentration, Example 2.15	—
C_0	Initial concentration, Example 2.15	—
C_1	Concentration in feed to tank, Example 2.15	—
ΔC	Incremental change in concentration, Example 2.15	—
F	Flow rate	$\mathbf{MT}^{-1}$

		Dimensions in **MLT**
F_n	Total flow in stream *n*	$\mathbf{MT^{-1}}$
F_1	Water feed to reactor, Example 2.4	$\mathbf{MT^{-1}}$
M	Quantity in hold tank, Example 2.15	**M**
N_c	Number of independent components	—
N_d	Number of variables to be specified	—
N_e	Number of independent balance equations	—
N_s	Number of streams	—
N_v	Number of variables	—
t	Time, Example 2.15	**T**
Δt	Incremental change in time, Example 2.15	**T**
X	Unknown flow, Examples 2.8, 2.10, 2.13	$\mathbf{MT^{-1}}$
$x_{n,m}$	Concentration of component *m* in stream *n*	—
Y	Unknown flow, Examples 2.8, 2.13	$\mathbf{MT^{-1}}$
Z	Unknown flow, Example 2.13	$\mathbf{MT^{-1}}$

2.21. PROBLEMS

2.1. The composition of a gas derived by the gasification of coal is by volume percentage: carbon dioxide 4, carbon monoxide 16, hydrogen 50, methane 15, ethane 3, benzene 2, balance nitrogen. If the gas is burned in a furnace with 20% excess air, calculate

- **i.** The amount of air required per 100 kmol of gas;
- **ii.** The amount of flue gas produced per 100 kmol of gas;
- **iii.** The composition of the flue gases, on a dry basis.

Assume complete combustion.

2.2. Ammonia is removed from a stream of air by absorption in water in a packed column. The air entering the column is at 760 mmHg pressure and 20°C. The air contains 5.0% v/v ammonia. Only ammonia is absorbed in the column. If the flow rate of the ammonia-air mixture to the column is 200 m^3/s and the stream leaving the column contains 0.05% v/v ammonia, calculate

- **i.** The flow rate of gas leaving the column;
- **ii.** The mass of ammonia absorbed;
- **iii.** The flow rate of water to the column, if the exit water contains 1% w/w ammonia.

2.3. The off gases from a gasoline stabilizer are fed to a steam reforming plant to produce hydrogen.

The composition of the off gas, molar%, is CH_4 77.5, C_2H_6 9.5, C_3H_8 8.5, C_4H_{10} 4.5.

The gases entering the reformer are at a pressure of 2 bara and 35 °C and the feed rate is 2000 m^3/h.

The reactions in the reformer are

$$1.\ C_2H_{2n+2} + n(H_2O) \rightarrow n(CO) + (2_n + 1)H_2$$
$$2.\ CO + H_2O \rightarrow CO_2 + H_2$$

The molar conversion of C_2H_{2n+2} in reaction (1) is 96% and of CO in reaction (2) 92%.

Calculate
- **i.** The average molecular mass of the off gas;
- **ii.** The mass of gas fed to the reformer, kg/h;
- **iii.** The mass of hydrogen produced, kg/h.

2.4. Allyl alcohol can be produced by the hydrolysis of allyl chloride. Together with the main product, allyl alcohol, diallyl ether is produced as a byproduct. The conversion of allyl chloride is typically 97% and the selectivity to alcohol is 90%, both on a molar basis. Assuming that there are no other significant side reactions, calculate masses of alcohol and ether produced, per 1000 kg of allyl chloride fed to the reactor.

2.5. Aniline is produced by the hydrogenation of nitrobenzene. A small amount of cyclo-hexylamine is produced as a byproduct. The reactions are

$$1.\ C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$$
$$2.\ C_6H_5NO_2 + 6H_2 \rightarrow C_6H_{11}NH_2 + 2H_2O$$

Nitrobenzene is fed to the reactor as a vapor, with three times the stoichiometric quantity of hydrogen. The conversion of the nitrobenzene, to all products, is 96%, and the selectivity for aniline is 95%.

The unreacted hydrogen is separated from the reactor products and recycled to the reactor. A purge is taken from the recycle stream to maintain the inerts in the recycle stream below 5%. The fresh hydrogen feed is 99.5% pure, the remainder being inerts. All percentages are molar.

For a feed rate of 100 kmol/h of nitrobenzene, calculate
- **i.** The fresh hydrogen feed;
- **ii.** The purge rate required;
- **iii.** The composition of the reactor outlet stream.

2.6. In the manufacture of aniline by the hydrogenation of nitrobenzene, the off gases from the reactor are cooled and the products and unreacted nitrobenzene condensed. The hydrogen and inerts, containing only traces of the condensed materials, are recycled. Using the typical composition of the reactor off gas given below, estimate the stream compositions leaving the condenser.

Composition, kmol/h: aniline 950, cyclo-hexylamine 10, water 1920, hydrogen 5640, nitrobenzene 40, inerts 300.

2.7. In the manufacture of aniline, the condensed reactor products are separated in a decanter. The decanter separates the feed into an organic phase and an aqueous phase. Most of the aniline in the feed is contained in the organic phase and most of the water in the aqueous phase. Using the data given below, calculate the stream compositions.

Data:

Typical feed composition, including impurities and byproducts, weight%: water 23.8, aniline 72.2, nitrobenzene 3.2, cyclo-hexylamine 0.8.

Density of aqueous layer 0.995, density of organic layer 1.006. Therefore, the organic layer will be at the bottom.

Solubility of aniline in water 3.2% w/w, and water in aniline 5.15% w/w.

Partition coefficient of nitrobenzene between the aqueous and organic phases: $C_{organic}/C_{water} = 300$

Solubility of cyclo-hexylamine in the water phase 0.12% w/w and in the organic phase 1.0% w/w.

2.8. In the manufacture of aniline from nitrobenzene, the reactor products are condensed and separated into aqueous and organic phases in a decanter. The organic phase is fed to a striping column to recover the aniline. Aniline and water form an azeotrope, composition 0.96 mole fraction aniline. For the feed composition given below, make a mass balance around the column and determine the stream compositions and flow rates. Take as the basis for the balance 100 kg/h feed and 99.9% recovery of the aniline in the overhead product. Assume that nitrobenzene leaves with the water stream from the base of the column.

Feed composition, weight percentage: water 2.4, aniline 73.0, nitrobenzene 3.2, cyclo-hexylamine trace.

2.9. Guaifenesin (Guaiacol glyceryl ether, 3-(2-Methoxyphenoxy)-1,2-propanediol, $C_{10}H_{14}O_4$) is an expectorant that is found in cough medicines such as Actifed^{TM} and Robitussin^{TM}. U.S. 4,390,732 (to Degussa) describes a preparation of the active pharmaceutical ingredient (API) from guaiacol (2-methoxyphenol, $C_7H_8O_2$) and glycidol (3-hydroxy propylene oxide, $C_3H_6O_2$). When the reaction is catalyzed by NaOH, the reaction yield is 93.8%. The product is purified in a thin-film evaporator giving an overall plant yield of 87%.

i. Estimate the feed flow rates of glycidine and guaiacol that would be needed to produce 100 kg/day of the API.

ii. Estimate how much product is lost in the thin-film evaporator.
iii. How would you recover the product lost in the evaporator?

2.10. 11-[N-ethoxycarbonyl-4-piperidylidene]-8-chloro-6,11-dihydro-5H-benzo-[5,6]-cyclohepta-[1,2-b]-pyridine ($C_{22}H_{23}ClN_2O_2$) is a non-sedative antihistamine, known as Loratadine and marketed as Claritin^{TM}. The preparation of the active pharmaceutical ingredient (API) is described in U.S. 4,282,233 (to Schering). The patent describes reacting 16.2 g of 11-[N-methyl-4-piperidylidene]-8-chloro-6,11-dihydro-5H-benzo-[5,6]-cyclohepta-[1,2-b]-pyridine ($C_{20}H_{21}ClN_2$) in 200 ml of benzene with 10.9 g of ethylchloroformate ($C_3H_5ClO_2$) for 18 hours. The mixture is cooled, poured into ice water, and separated into aqueous and organic phases. The organic layer is washed with water and evaporated to dryness. The residue is triturated (ground to a fine powder) with petroleum ether and recrystallized from isopropyl ether.

i. What is the reaction byproduct?
ii. The reaction appears to be carried out under conditions that maximize both selectivity and conversion (long time at low temperature), as might be expected given the cost of the raw material. If the conversion is 99.9% and the selectivity for the desired ethoxycarbonyl substituted compound is 100%, how much excess ethylchloroformate remains at the end of the reaction?
iii. What fraction of the ethylchloroformate feed is lost to waste products?
iv. Assuming that the volumes of water and isopropyl ether used in the quenching, washing, and recrystallization steps are the same as the initial solvent volume, and that none of these materials are reused in the process, estimate the total mass of waste material produced per kg of the API.
v. If the recovery (plant yield) of the API from the washing and recrystallization steps is 92%, estimate the feed flow rates of 11-[N-methyl-4-piperidylidene]-8-chloro-6,11-dihydro-5H-benzo-[5,6]-cyclohepta-[1,2-b]-pyridine and ethylchloroformate required to produce a batch of 10 kg of the API.
vi. How much API could be produced per batch in a 3.8 m^3 (1000 U.S. gal) reactor?
vii. What would be the advantages and disadvantages of carrying out the other process steps in the same vessel?

Note: Problems 2.5 to 2.8 can be taken together as an exercise in the calculation of a preliminary material balance for the manufacture of aniline by the process described in detail in Appendix F, Problem F.8. Structures for the compounds in problems 2.9 and 2.10 can be found in the Merck Index, but are not required to solve the problems.

3 FUNDAMENTALS OF ENERGY BALANCES AND ENERGY UTILIZATION

Chapter Contents

Key Learning Objectives

- How to use energy balances
- How to calculate the power consumed in compressing a gas
- Methods used for recovering process waste heat
- How to use the pinch design method to optimize process heat recovery

3.1. INTRODUCTION

As with mass, energy can be considered to be separately conserved in all but nuclear processes.

The conservation of energy differs from that of mass in that energy can be generated (or consumed) in a chemical process. Material can change form, new molecular species can be formed by chemical reaction, but the total mass flow into a process unit must be equal to the flow out at the steady state. The same is true of energy, but not of stream enthalpy. The total enthalpy of the outlet streams will not equal that of the inlet streams if energy is generated or consumed in the process; such as that due to heat of reaction. Energy can exist in several forms, including chemical energy, heat, mechanical energy, and electrical energy. The total energy is conserved, but energy can be transformed from one kind of energy to another.

In process design, energy balances are made to determine the energy requirements of the process: the heating, cooling, and power required. In plant operation, an energy balance (energy audit) on the plant will show the pattern of energy use and suggest areas for conservation and savings.

Most energy balances are carried out using process simulation software, but design engineers occasionally have to incorporate energy balances into spreadsheet models or other computer programs. It is therefore important for the design engineer to have a good grasp of the basic principles of energy balances. In this chapter the fundamentals of energy balances are reviewed briefly, and examples are given to illustrate the use of energy balances in process design. The methods used for process energy recovery and conservation are also discussed.

More detailed accounts of the principles and applications of energy balances are given in the texts covering material and energy balance calculations that are cited at the end of Chapter 2.

3.2. CONSERVATION OF ENERGY

As for material (Section 2.3), a general equation can be written for the conservation of energy:

$$\text{Energy out} = \text{Energy in} + \text{generation} - \text{consumption} - \text{accumulation}$$

This is a statement of the first law of thermodynamics.
An energy balance can be written for any process step.
Chemical reaction will evolve energy (exothermic) or consume energy (endothermic).
For steady-state processes the accumulation of both mass and energy will be zero.
Energy can exist in many forms and this, to some extent, makes an energy balance more complex than a material balance.

3.3. FORMS OF ENERGY (PER UNIT MASS OF MATERIAL)

3.3.1. Potential Energy

Energy due to position:

$$\text{Potential energy per unit mass} = gz \tag{3.1}$$

where

z = height above some arbitrary datum, m;
g = gravitational acceleration (9.81 m/s^2).

3.3.2. Kinetic Energy

Energy due to motion:

$$\text{Kinetic energy per unit mass} = \frac{u^2}{2} \tag{3.2}$$

where u = velocity, m/s.

3.3.3. Internal Energy

The energy associated with molecular motion. The temperature T of a material is a measure of its internal energy U:

$$U = \mathrm{f}(T) \tag{3.3}$$

3.3.4. Work

Work is done when a force acts through a distance:

$$W = \int_0^l F \, \mathrm{d}x \tag{3.4}$$

where

F = force, N;
x and l = distance, m.

Work done on a system by its surroundings is conventionally taken as negative; work done by the system on the surroundings, as positive.

Where the work arises from a change in pressure or volume:

$$W = \int_{v_1}^{v_2} P \, \mathrm{d}v \tag{3.5}$$

where

P = pressure, Pa (N/m^2),
v = volume per unit mass, m^3/kg.

To integrate this function, the relationship between pressure and volume must be known. In process design, an estimate of the work done in compressing or expanding a gas is often required. A rough estimate can be made by assuming either reversible adiabatic (isentropic) or isothermal expansion, depending on the nature of the process.

For isothermal expansion (expansion at constant temperature):

$$Pv = \text{constant}$$

For reversible adiabatic expansion (no heat exchange with the surroundings):

$$Pv^{\gamma} = \text{constant}$$

where γ = ratio of the specific heats, C_p/C_v.

The compression and expansion of gases is covered more fully in Section 3.13.

3.3.5. Heat

Energy is transferred either as heat or work. A system does not contain "heat," but the transfer of heat or work to a system changes its internal energy.

Heat taken in by a system from its surroundings is conventionally taken as positive; that given out, as negative.

3.3.6. Electrical Energy

Electrical and the mechanical forms of energy are included in the work term in an energy balance. Electrical energy will be significant only in energy balances on electrochemical processes.

3.4. THE ENERGY BALANCE

Consider a steady-state process represented by Figure 3.1. The conservation equation can be written to include the various forms of energy.

For a unit mass of material:

$$U_1 + P_1v_1 + u_1^2/2 + z_1g + Q = U_2 + P_2v_2 + u_2^2/2 + z_2g + W \tag{3.6}$$

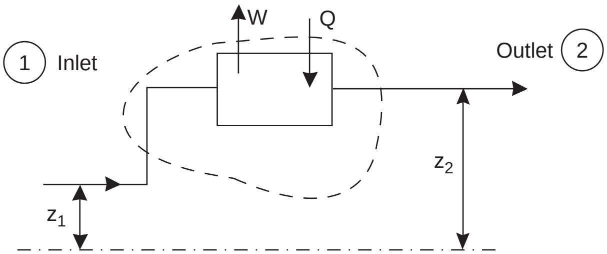


Figure 3.1. General steady-state process.

The suffixes 1 and 2 represent the inlet and outlet points respectively. Q is the heat transferred across the system boundary: positive for heat entering the system, negative for heat leaving the system. W is the work done by the system: positive for work going from the system to the surroundings, and negative for work entering the system from the surroundings.

Equation 3.6 is a general equation for steady-state systems with flow.

In chemical processes, the kinetic and potential energy terms are usually small compared with the heat and work terms, and can normally be neglected.

It is convenient, and useful, to take the terms U and Pv together, defining the stream enthalpy, usually given the symbol H, as

$$H = U + Pv$$

Enthalpy is a function of temperature and pressure. Values for the more common substances have been determined experimentally and are given in the various handbooks (see Chapter 8). Enthalpy can be calculated from specific and latent heat data; see Section 3.5.

If the kinetic and potential energy terms are neglected, equation 3.6 simplifies to

$$H_2 - H_1 = Q - W \tag{3.7}$$

This simplified equation is usually sufficient for estimating the heating and cooling requirements of the various unit operations involved in chemical processes.

As the flow-dependent terms have been dropped, the simplified equation is applicable to both static (nonflow) systems and flow systems. It can be used to estimate the energy requirement for batch processes.

For many processes the work term will be zero, or negligibly small, and equation 3.7 reduces to the simple heat balance equation:

$$Q = H_2 - H_1 \tag{3.8}$$

Where heat is generated in the system; for example, in a chemical reactor:

$$Q = Q_p + Q_s \tag{3.9}$$

Q_s = heat generated in the system. If heat is evolved (exothermic processes), Q_s is taken as *positive,* and if heat is absorbed (endothermic processes), it is taken as *negative*.

Q_p = process heat added to the system to maintain required system temperature.

Hence:

$$Q_p = H_2 - H_1 - Q_s \tag{3.10}$$

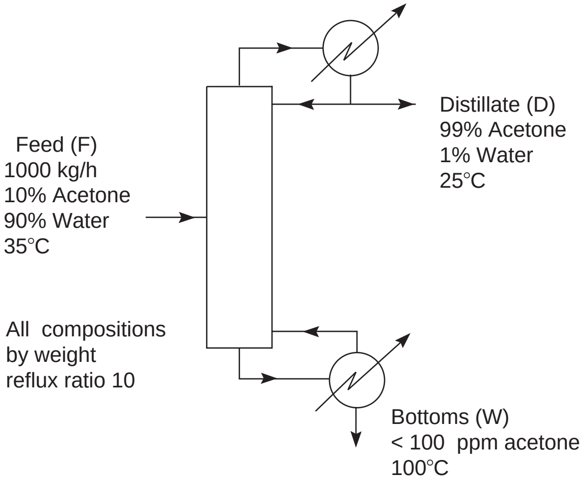
H_1 = enthalpy of the inlet stream;

H_2 = enthalpy of the outlet stream.

Example 3.1

Balance with no chemical reaction. Estimate the steam and the cooling water required for the distillation column shown in the figure.

Steam is available at 25 psig (274 kN/m^2 abs), dry saturated.
The rise in cooling water temperature is limited to 30°C.
Column operates at 1 bar.



Solution

Material Balance

It is necessary to make a material balance to determine the top and bottoms product flow rates.

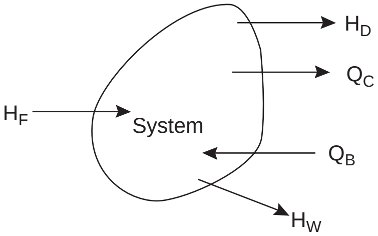
Balance on acetone, acetone loss in bottoms neglected.

$$1000 \times 0.1 = D \times 0.99$$
$$\text{Distillate, } D = 101\,\text{kg/h}$$
$$\text{Bottoms, } B = 1000 - 101 = 899\,\text{kg/h}$$

Energy Balance

The kinetic and potential energy of the process streams will be small and can be neglected.

Take the first system boundary to include the reboiler and condenser.



Inputs: Reboiler heat input Q_B + feed sensible heat H_F.

Outputs: Condenser cooling Q_C + top and bottom product sensible heats $H_D + H_B$.

The heat losses from the system will be small if the column and exchangers are properly lagged (typically less than 5%) and will be neglected.

Basis 25°C, 1 h.

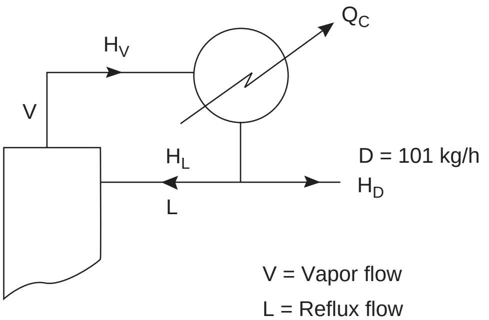
Heat capacity data, average values.

Acetone:	25°C to 35°C	2.2 kJ/kg K
Water:	25°C to 100°C	4.2 kJ/kg K

Heat capacities can be taken as additive.

Feed, 10% acetone $= 0.1 \times 2.2 + 0.9 \times 4.2 = 4.00$ kJ/kg K
Distillate, 99% acetone, taken as acetone, 2.2 kJ/kg K
Bottoms, taken as water, 4.2 kJ/kg K.

Q_C must be determined by taking a balance around the condenser.



V = Vapor flow
L = Reflux flow
H = Enthalpy

Reflux ratio (see Chapter 11):

$$R = \frac{L}{D} = 10$$
$$L = 10 \times 101 = 1010\ \text{kg/h}$$
$$V = L + D = 1111\ \text{kg/h}$$

From vapor – liquid equilibrium data:

Boiling point of 99% acetone/water = 56.5°C

At steady state:

$$\text{input} = \text{output}$$
$$H_V = H_D + H_L + Q_C,$$
$$\text{Hence:}\quad Q_C = H_V - H_D - H_L$$

Assume complete condensation.

Enthalpy of vapor H_V = latent + sensible heat.

There are two ways of calculating the specific enthalpy of the vapor at its boiling point:

1. Latent heat of vaporization at the base temperature + sensible heat to heat the vapor to the boiling point.
2. Latent heat of vaporization at the boiling point + sensible heat to raise liquid to the boiling point.

Values of the latent heat of acetone and water as functions of temperature are given in Coulson et al. (1999), so the second method will be used.

$$\text{Latent heat acetone at } 56.5^\circ\text{C } (330\,\text{K}) = 620\,\text{kJ/kg}$$
$$\text{Water at } 56.5^\circ\text{C } (330\,\text{K}) = 2500\,\text{kJ/kg}$$

Taking latent heats as additive:

$$\begin{aligned} H_V &= 1111[(0.01 \times 2500 + 0.99 \times 620) + (56.5 - 25)2.2] \\ &= 786{,}699\,\text{kJ/h} \end{aligned}$$

The enthalpy of the top product and reflux are zero, as they are both at the base temperature. Both are liquid, and the reflux will be at the same temperature as the product,

$$\text{hence: } Q_C = H_V = \underline{\underline{786{,}699\,\text{kJ/h}}}\ (218.5\,\text{kW})$$

Q_B is determined from a balance over the complete system

$$\begin{aligned} \text{input } &= \text{output} \\ Q_B + H_F &= Q_C + H_D + H_W \\ H_F &= 1000 \times 4.00(35 - 25) = 40{,}000\,\text{kJ/h} \\ H_B &= 899 \times 4.2(100 - 25) = 283{,}185\,\text{kJ/h} \end{aligned}$$

(boiling point of bottom product taken as 100°C).

$$\begin{aligned} \text{Hence: } Q_B &= Q_C + H_B + H_D - H_F \\ &= 786{,}699 + 283,\ 185 + 0 - 40{,}000 \\ &= \underline{\underline{1{,}029{,}884\ \text{kJ/h}}}\ (286.1\,\text{kW}) \end{aligned}$$

Q_B is supplied by condensing steam.

$$\text{Latent heat of steam} = 2174\,\text{kJ/kg at } 274\,\text{kN/m}^2$$
$$\text{Steam required} = \frac{1{,}029{,}884}{2174} = \underline{\underline{473.7\,\text{kg/h}}}$$

Q_C is removed by cooling water with a temperature rise of 30°C

$$Q_C = \text{water flow} \times 30 \times 4.2$$
$$\text{Water flow} = \frac{786,699}{4.2 \times 30} = 6244\,\text{kg/h}$$

3.5. CALCULATION OF SPECIFIC ENTHALPY

Tabulated values of enthalpy are available only for the more common materials. In the absence of published data, the following expressions can be used to estimate the specific enthalpy (enthalpy per unit mass).

For pure materials, with no phase change:

$$H_T = H_{T_d} + \int_{T_d}^{T} C_p \, \mathrm{d}T \tag{3.11}$$

where

H_T = specific enthalpy at temperature T;
C_p = specific heat capacity of the material, constant pressure;
T_d = the datum temperature.

If a phase transition takes place between the specified and datum temperatures, the latent heat of the phase transition is added to the sensible-heat change calculated by equation 3.11. The sensible-heat calculation is then split into two parts:

$$H_T = H_{T_d} + \int_{T_d}^{T_P} C_{p1} \, \mathrm{d}T + \Delta H_P + \int_{T_P}^{T} C_{p2} \, \mathrm{d}T \tag{3.12}$$

where

T_p = phase transition temperature;
C_{p1} = specific heat capacity of first phase, below T_p;
C_{p2} = specific heat capacity of second phase, above T_p;
ΔH_P = the latent heat of the phase change.

The specific heat at constant pressure will vary with temperature, and to use equations 3.11 and 3.12, values of C_p must be available as a function of temperature. For solids and gases, C_p is usually expressed as an empirical power series equation:

$$C_p = a + bT + cT^2 + dT^3 \tag{3.13a}$$

$$\text{or} \quad C_p = a + bT + cT^{-1/2} \tag{3.13b}$$

Absolute (K) or relative (°C) temperature scales may be specified when the relationship is in the form given in equation 3.13a. For equation 3.13b absolute temperatures must be used.

Example 3.2

Estimate the specific enthalpy of ethyl alcohol at 1 bar and 200°C, taking the datum temperature as 0°C.

C_p liquid 0°C 24.65 cal/mol°C
100°C 37.96 cal/mol°C

C_p gas(t°C) $14.66 + 3.758 \times 10^{-2}t - 2.091 \times 10^{-5}t^2 + 4.740 \times 10^{-9}t^3$ cal/mol

Boiling point of ethyl alcohol at 1 bar = 78.4°C.
Latent heat of vaporization = 9.22 kcal/mol.

Solution

Note: As the data taken from the literature are given in cal/mol, the calculation is carried out in these units and the result converted to SI units.

As no data are given on the exact variation of the C_p of the liquid with temperature, use an equation of the form $C_p = a + bt$, calculating a and b from the data given; this will be accurate enough over the range of temperature needed.

$$a = \text{value of } C_p \text{ at } 0^\circ\text{C}, \qquad b = \frac{37.96 - 24.65}{100} = 0.133$$

$$\begin{aligned}
H_{200^\circ\text{C}} &= \int_0^{78.4} (24.65 + 0.133t)\,\mathrm{d}t + 9.22 \times 10^3 + \int_{78.4}^{200} (14.66 + 3.758 \times 10^{-2}t \\
&\quad - 2.091 \times 10^{-5}t^2 + 4.740 \times 10^{-9}t^3)\,\mathrm{d}t \\
&= \left[_0^{78.4} 24.65t + 0.133t^2/2\right] + 9.22 \times 10^3 + \left[_{78.4}^{200} 14.66t + 3.758 \times 10^{-2}t^2/2 - 2.091\right. \\
&\quad \left. \times 10^{-5}t^3/3 + 4.740 \times 10^{-9}t^4/4\right] \\
&= 13.95 \times 10^3 \text{ cal/mol} \\
&= 13.95 \times 10^3 \times 4.18 = \underline{\underline{58.31 \times 10^3 \text{ J/mol}}}
\end{aligned}$$

Specific enthalpy = $\underline{\underline{58.31 \text{ kJ/mol.}}}$

Molecular weight of ethyl alcohol, C_2H_5OH = 46

Specific enthalpy = $58.31 \times 10^3/46 = \underline{\underline{1268 \text{ kJ/kg}}}$

3.6. MEAN HEAT CAPACITIES

The use of mean heat capacities often facilitates the calculation of sensible-heat changes; mean heat capacity over the temperature range t_1 to t_2 is defined by the following equation:

$$C_{pm} \int_{t_1}^{t_2} \mathrm{d}T = \int_{t_1}^{t_2} C_p \, \mathrm{d}T \tag{3.14}$$

Mean specific heat values are tabulated in various handbooks. If the values are for unit mass, calculated from some standard reference temperature, t_r, then the change in enthalpy between temperatures t_1 and t_2 is given by

$$\Delta H = C_{pm,t2}(t_2 - t_r) - C_{pm,t1}(t_1 - t_r) \tag{3.15}$$

where t_r is the reference temperature from which the values of C_{pm} were calculated.

If C_p is expressed as a polynomial of the form $C_p = a + bt + ct^2 + dt^3$, then the integrated form of equation 3.14 will be

$$C_{pm} = \frac{a(t - t_r) + \frac{b}{2}(t^2 - t_r^2) + \frac{c}{3}(t^3 - t_r^3) + \frac{d}{4}(t^4 - t_r^4)}{t - t_r} \tag{3.16}$$

where t is the temperature at which C_{pm} is required.

If the reference temperature is taken at 0°C, equation 3.16 reduces to

$$C_{pm} = a + \frac{bt}{2} + \frac{ct^2}{3} + \frac{dt^3}{4} \tag{3.17}$$

and the enthalpy change from t_1 to t_2 becomes

$$\Delta H = C_{pm,t2}\, t_2 - C_{pm,t1}\, t_1 \tag{3.18}$$

The use of mean heat capacities is illustrated in Example 3.3.

Example 3.3

The gas leaving a combustion chamber has the following composition: CO_2 7.8, CO 0.6, O_2 3.4, H_2O 15.6, N_2 72.6, all volume percentage. Calculate the heat removed if the gas is cooled from 800°C to 200°C.

Solution

Mean heat capacities for the combustion gases are readily available in handbooks and texts on heat and material balances. The following values are taken from K. A. Kobe, *Thermochemistry of Petrochemicals*, reprint No. 44, Pet. Ref. 1958; converted to SI units, J/mol°C, reference temperature 0°C.

T, °C	N_2	O_2	CO_2	CO	H_2O
200	29.24	29.95	40.15	29.52	34.12
800	30.77	32.52	47.94	31.10	37.38

Heat extracted from the gas in cooling from 800°C to 200°C, for each component:

$$= M_c(C_{pm,800} \times 800 - C_{pm,200} \times 200)$$

where M_c = moles of that component.

Basis 100 mol gas (as analysis is by volume), substitution gives

$$\begin{array}{lll}
CO_2 & 7.8(47.94 \times 800 - 40.15 \times 200) = & 236.51 \times 10^3 \\
CO & 0.6(31.10 \times 800 - 29.52 \times 200) = & 11.39 \times 10^3 \\
O_2 & 3.4(32.52 \times 800 - 29.95 \times 200) = & 68.09 \times 10^3 \\
H_2O & 15.6(37.38 \times 800 - 34.12 \times 200) = & 360.05 \times 10^3 \\
N_2 & 72.6(30.77 \times 800 - 29.24 \times 200) = & 1362.56 \times 10^3 \\
\hline
 & = & 2038.60\,\text{kJ/100 mol} \\
 & = & 20.39\,\text{kJ/mol}
\end{array}$$

3.7. THE EFFECT OF PRESSURE ON HEAT CAPACITY

The data on heat capacities given in the handbooks, and in Appendix A, are usually for the ideal gas state. Equation 3.13a should be written as:

$$C_p^\circ = a + bT + cT^2 + dT^3 \tag{3.19}$$

where the superscript ° refers to the ideal gas state.

The ideal gas values can be used for the real gases at low pressures. At high pressures the effect of pressure on the specific heat may be appreciable.

Edmister (1948) published a generalized plot showing the isothermal pressure correction for real gases as a function of the reduced pressure and temperature. His chart, converted to SI units, is shown as Figure 3.2. Edmister's chart was based on hydrocarbons but can be used for other materials to give an indication of the likely error if the ideal gas specific heat values are used without corrections.

The method is illustrated in Example 3.4.

Example 3.4

The ideal state heat capacity of ethylene is given by the equation:

$$C_p^\circ = 3.95 + 15.6 \times 10^{-2}T - 8.3 \times 10^{-5}T^2 + 17.6 \times 10^{-9}T^3 \text{ J/mol K}$$

Estimate the value at 10 bar and 300 K.

Solution

Ethylene:		
	critical pressure	50.5 bar
	critical temperature	283 K

$$\begin{aligned}C_p^\circ &= 3.95 + 15.6 \times 10^{-2} \times 300 - 8.3 \times 10^{-5} \times 300^2 + 17.6 \times 10^{-9} \times 300^3 \\ &= 43.76 \text{ J/mol K}\end{aligned}$$

$$Pr = \frac{10}{50.5} = \underline{\underline{0.20}}$$

$$Tr = \frac{300}{283} = \underline{\underline{1.06}}$$

From Figure 3.2:

$$C_p - C_p^\circ \simeq \underline{\underline{5 \text{ J/mol K}}}$$

$$\text{So} \qquad C_p = 43.76 + 5 = \approx \underline{\underline{49 \text{ J/mol K}}}$$

The error in C_p if the ideal gas value were used uncorrected would be approximately 10%. This would clearly lead to large errors in predicting heat exchanger duties.

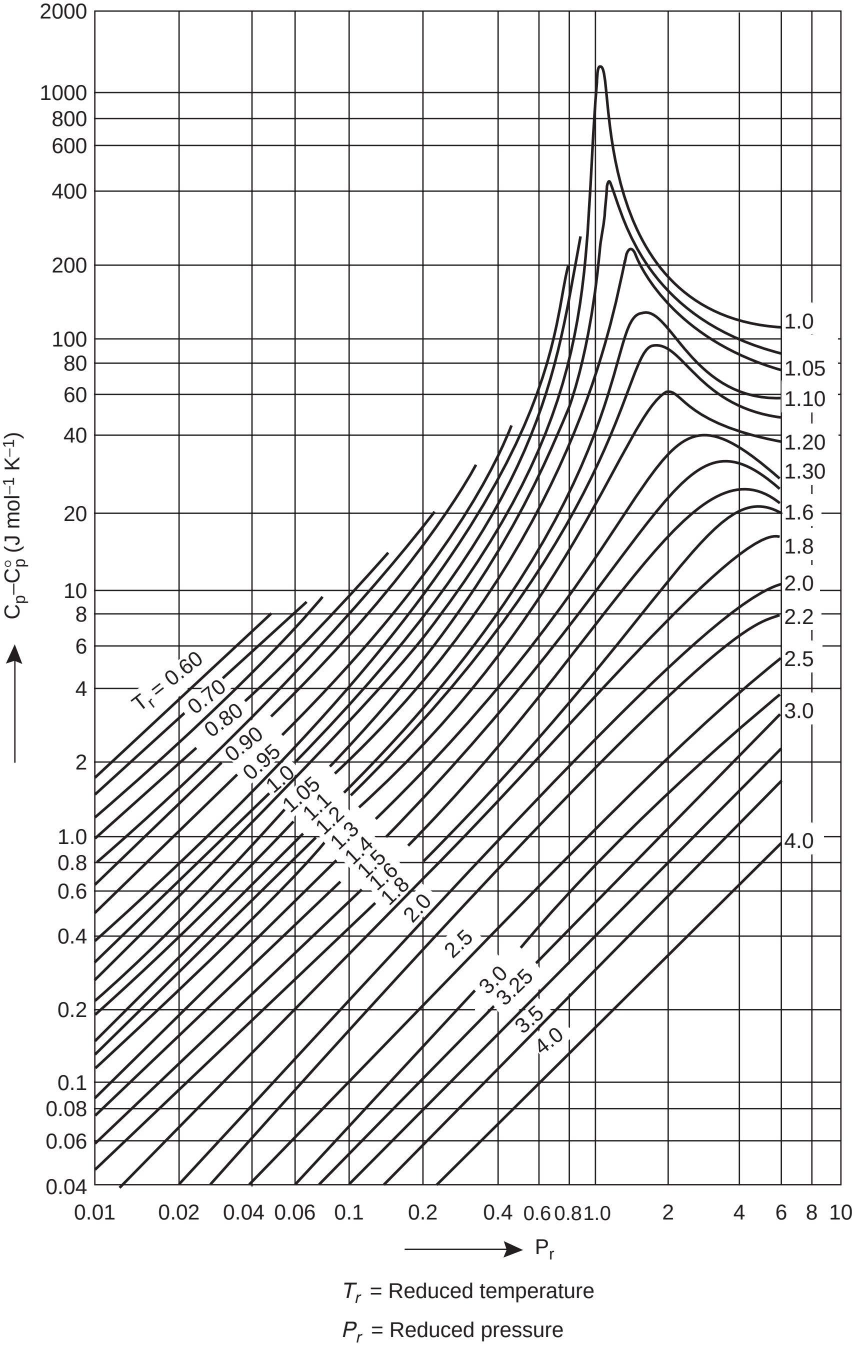


Figure 3.2. Excess heat capacity chart (reproduced from Sterbacek et al. (1979), with permission).

3.8. ENTHALPY OF MIXTURES

For gases, the heats of mixing are usually negligible, and the heat capacities and enthalpies can be taken as additive without introducing any significant error into design calculations, as was done in Example 3.3.

$$C_p(\text{mixture}) = x_a C_{pa} + x_b C_{pb} + x_c C_{pc} + \ldots \tag{3.20}$$

where x_a, x_b, x_c, etc., are the mole fractions of the components a, b, c (or weight fractions if the specific heat per unit mass is used).

For mixtures of liquids and for solutions, the heat of mixing (heat of solution) may be significant, and so must be included when calculating the enthalpy of the mixture.

For binary mixtures, the specific enthalpy of the mixture at temperature t is given by

$$H_{\text{mixture},t} = x_a H_{a,t} + x_b H_{b,t} + \Delta H_{m,t} \tag{3.21}$$

where $H_{a,t}$ and $H_{b,t}$ are the specific enthalpies of the components a and b and $-\Delta H_{m,t}$ is the heat of mixing when 1 mol of solution is formed, at temperature t.

Heats of mixing and heats of solution are determined experimentally and are available in the handbooks for the more commonly used solutions. If no values are available, judgment must be used to decide if the heat of mixing for the system is likely to be significant.

For hydrocarbon mixtures, the heat of mixing is usually small compared with the other heat quantities and can usually be neglected when carrying out a heat balance to determine the process heating or cooling requirements. The heats of solution of organic and inorganic compounds in water can be large, particularly for the strong mineral acids and alkalis.

3.8.1. Integral Heats of Solution

Heats of solution are dependent on concentration. The integral heat of solution at any given concentration is the cumulative heat released, or absorbed, in preparing the solution from pure solvent and solute. The integral heat of solution at infinite dilution is called the *standard integral heat of solution*.

Tables of the integral heat of solution over a range of concentration and plots of the integral heat of solution as a function of concentration are given in the handbooks for many of the materials for which the heat of solution is likely to be significant in process design calculations.

The integral heat of solution can be used to calculate the heating or cooling required in the preparation of solutions, as illustrated in Example 3.5.

Example 3.5

A solution of NaOH in water is prepared by diluting a concentrated solution in an agitated, jacketed vessel. The strength of the concentrated solution is 50% w/w, and

2500 kg of 5% w/w solution is required per batch. Calculate the heat removed by the cooling water if the solution is to be discharged at a temperature of 25°C. The temperature of the solutions fed to the vessel can be taken to be 25°C.

Solution

Integral heat of solution of NaOH – H_2O, at 25°C

mols H_2O/mol NaOH	$-\Delta H^\circ_{soln}$ kJ/mol NaOH
2	22.9
4	34.4
5	37.7
10	42.5
infinite	42.9

Conversion of weight percent to mol/mol:

$$50\%\,\text{w/w} = 50/18 \div 50/40 = 2.22\,\text{mol } H_2O/\text{mol NaOH}$$

$$5\%\,\text{w/w} = 95/18 \div 5/40 = 42.2\,\text{mol } H_2O/\text{mol NaOH}$$

From a plot of the integral heats of solution versus concentration,

$$-\Delta H^\circ_{soln}\ \ 2.22\,\text{mol/mol} = 27.0\,\text{kJ/mol NaOH}$$

$$42.2\,\text{mol/mol} = 42.9\,\text{kJ/mol NaOH}$$

Heat liberated in the dilution per mol NaOH $= 42.9 - 27.0 = \underline{\underline{15.9\,\text{kJ}}}$

$$\text{Heat released per batch} = \text{mol NaOH per batch} \times 15.9$$

$$= \frac{2500 \times 10^3 \times 0.05}{40} \times 15.9$$

$$= \underline{\underline{49.7 \times 10^3\,\text{kJ}}}$$

Heat transferred to cooling water, neglecting heat losses,

49.7 MJ per batch

In Example 3.5 the temperature of the feeds and final solution have been taken as the same as the standard temperature for the heat of solution, 25°C, to simplify the calculation. Heats of solution are analogous to heats of reaction, and examples of heat balances on processes where the temperatures are different from the standard temperature are given in the discussion of heats of reaction, Section 3.10.

3.9. ENTHALPY-CONCENTRATION DIAGRAMS

The variation of enthalpy for binary mixtures is conveniently represented on a diagram. An example is shown in Figure 3.3. The diagram shows the enthalpy of mixtures of ammonia and water versus concentration, with pressure and temperature

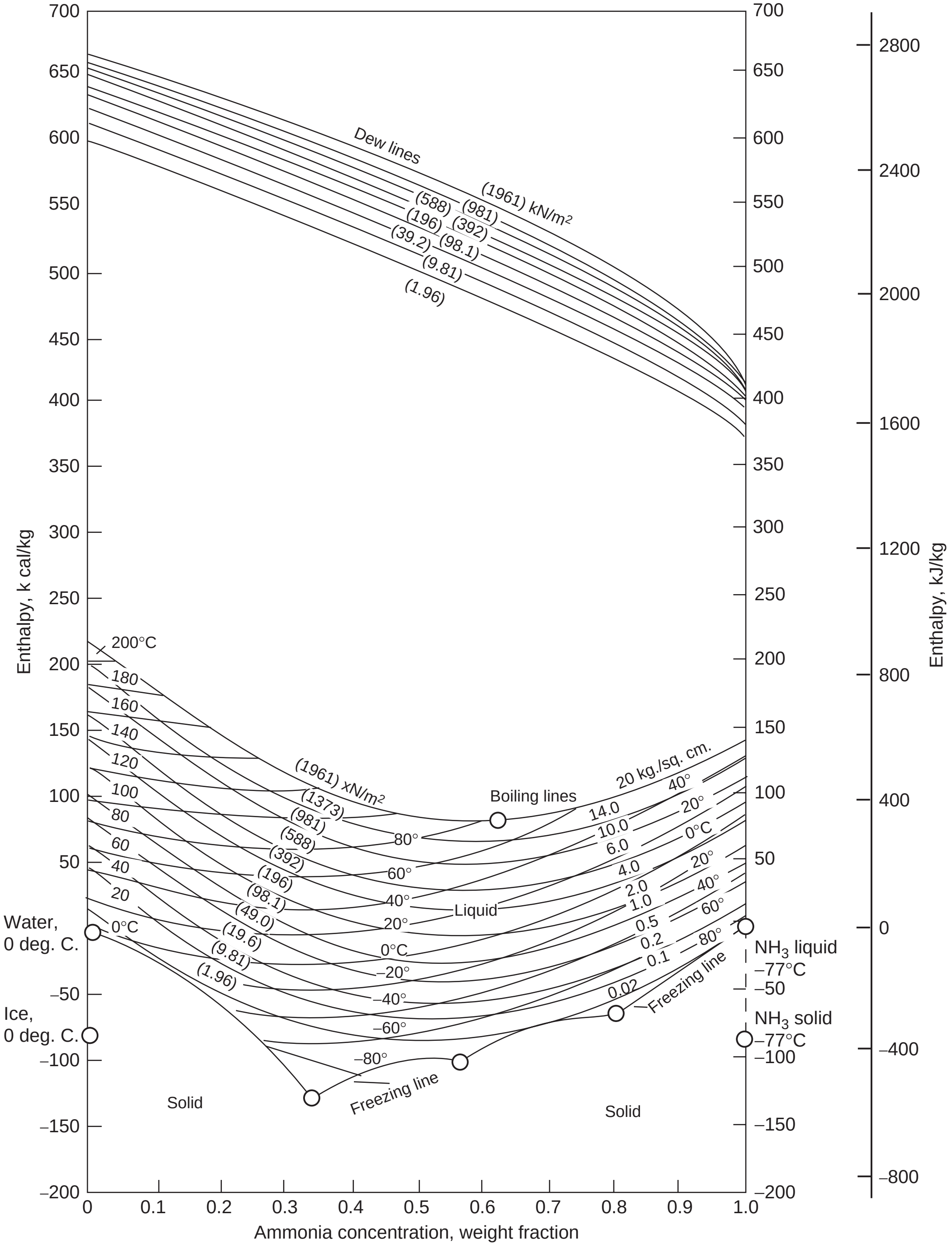


Figure 3.3. Enthalpy-concentration diagram for aqueous ammonia. Reference states: enthalpies of liquid water at 0°C and liquid ammonia at −77°C are zero. (Bosnjakovic, 1935).

as parameters. It covers the phase changes from solid to liquid to vapor, and the enthalpy values given include the latent heats for the phase transitions.

The enthalpy is per kg of the mixture (ammonia + water)

Reference states: enthalpy ammonia at $-77^\circ\mathrm{C} = $ zero
enthalpy water at $0^\circ\mathrm{C} = $ zero

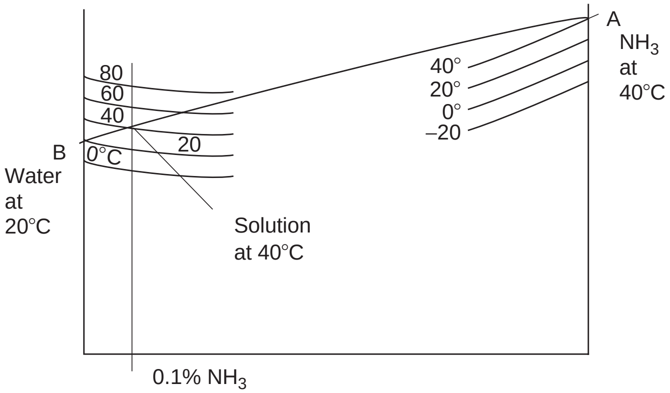
Enthalpy-concentration diagrams greatly facilitate the calculation of energy balances involving concentration and phase changes; this is illustrated in Example 3.6.

Example 3.6

Calculate the maximum temperature reached when liquid ammonia at 40°C is dissolved in water at 20°C to form a 10% solution.

Solution

The maximum temperature will occur if there are no heat losses (adiabatic process). As no heat or material is removed, the problem can be solved graphically in the enthalpy concentration diagram (Figure 3.3). The mixing operation is represented on the diagram by joining the point A representing pure ammonia at 40°C with the point B representing pure water at 20°C. Mixtures of this concentration lie on a vertical line at the required concentration, 0.1. The temperature of the mixture is given by the intersection of this vertical line with the line AB. This method is an application of the "lever rule" for phase diagrams. For a more detailed explanation of the method and further examples, see Himmelblau (1995) or any of the general texts on material and energy balances listed at the end of Chapter 2. The Ponchon-Savarit graphical method used in the design of distillation columns is a further example of the application of the lever rule and the use of enthalpy-concentration diagrams.



Enthalpy-concentration diagrams are convenient for binary mixtures with high heats of mixing. They are used widely in the fertilizer industry and in other industries that are concerned with making inorganic acids and bases.

3.10. HEATS OF REACTION

If a process involves chemical reaction, heat will normally have to be added or removed. The amount of heat given out in a chemical reaction depends on the conditions under which the reaction is carried out. The standard heat of reaction is the heat released when the reaction is carried out under standard conditions: pure components, pressure 1 atm (1.01325 bar) and temperature usually, but not necessarily, 25°C.

Values for the standard heats of reactions are given in the literature or can be calculated by the methods given in Sections 3.11 and 3.12.

When heats of reaction are quoted, the basis should be clearly stated. Either give the chemical equation—for example,

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \quad \Delta H_r^\circ = -56.68\,\text{kJ}$$

(The equation implies that the quantity of reactants and products are moles)

Or state to which quantity the quoted value applies:

$$\Delta H_r^\circ = -56.68\,\text{kJ per mol } NO_2$$

The reaction is exothermic, and the enthalpy change ΔH_r° is therefore *negative*. The heat of reaction $-\Delta H_r^\circ$ is *positive*. The superscript $^\circ$ denotes a value at *standard* conditions, and the subscript r implies that a chemical reaction is involved.

The state of the reactants and products (gas, liquid, or solid) should also be given, if the reaction conditions are such that they may exist in more than one state; for example:

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g), \quad \Delta H_r^\circ = -241.6\,\text{kJ}$$
$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l), \quad \Delta H_r^\circ = -285.6\,\text{kJ}$$

The difference between the two heats of reaction is the latent heat of the water formed.

In process design calculations, it is usually more convenient to express the heat of reaction in terms of the moles of product produced, for the conditions under which the reaction is carried out, kJ/mol product.

Standard heats of reaction can be converted to other reaction temperatures by making a heat balance over a hypothetical process, in which the reactants are brought to the standard temperature, the reaction carried out, and the products then brought to the required reaction temperature, as illustrated in Figure 3.4.

$$\Delta H_{r,t} = \Delta H_r^\circ + \Delta H_{\text{prod.}} - \Delta H_{\text{react.}} \qquad (3.22)$$

where

$-\Delta H_{r,t}$ = heat of reaction at temperature *t;*
$\Delta H_{\text{react.}}$ = enthalpy change to bring reactants to standard temperature;
$\Delta H_{\text{prod.}}$ = enthalpy change to bring products to reaction temperature, t.

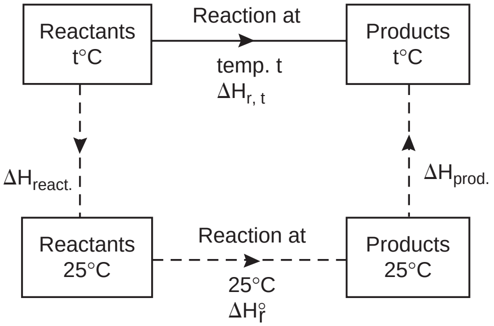


Figure 3.4. ΔH_r at temperature *t*.

For practical reactors, where the reactants and products may well be at temperatures different from the reaction temperature, it is best to carry out the heat balance over the actual reactor using the standard temperature (25°C) as the datum temperature; the standard heat of reaction can then be used without correction.

It must be emphasized that it is unnecessary to correct a heat of reaction to the reaction temperature for use in a reactor heat balance calculation. To do so is to carry out two heat balances, whereas with a suitable choice of datum, only one need be made. For a practical reactor, the heat added (or removed) Q_p to maintain the design reactor temperature will be given by (from equation 3.10):

$$Q_p = H_{\text{products}} - H_{\text{reactants}} - Q_r \tag{3.23}$$

where

H_{products} is the *total* enthalpy of the product streams, including unreacted materials and byproducts, evaluated from a datum temperature of 25°C;

$H_{\text{reactants}}$ is the total enthalpy of the feed streams, including excess reagent and inerts, evaluated from a datum of 25°C;

Q_r is the total heat generated by the reactions taking place, evaluated from the standard heats of reaction at 25°C (298 K).

$$Q_r = \sum -\Delta H_r^\circ \times (\text{mol of product formed}) \tag{3.24}$$

where $-\Delta H_r^\circ$ is the standard heat of reaction per mol of the particular product.

Note: A negative sign is necessary in equation 3.24 as Q_r is positive when heat is evolved by the reaction, whereas the standard enthalpy change will be negative for exothermic reactions. Q_p will be negative when cooling is required (see Section 3.4).

3.10.1. Effect of Pressure on Heats of Reaction

Equation 3.22 can be written in a more general form:

$$\Delta H_{r,P,T} = \Delta H_r^\circ + \int_1^P \left[\left(\frac{\partial H_{\text{prod.}}}{\partial P} \right)_T - \left(\frac{\partial H_{\text{react.}}}{\partial P} \right)_T \right] dP + \int_{298}^T \left[\left(\frac{\partial H_{\text{prod.}}}{\partial T} \right)_P - \left(\frac{\partial H_{\text{react.}}}{\partial T} \right)_P \right] dT \tag{3.25}$$

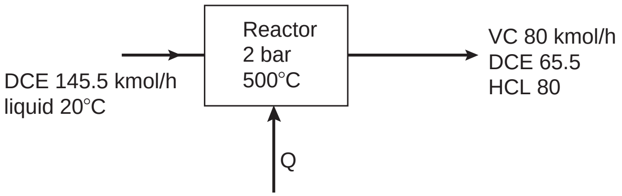
If the effect of pressure is likely to be significant, the change in enthalpy of the products and reactants, from the standard conditions, can be evaluated to include both the effects of temperature and pressure (for example, by using tabulated values of enthalpy) and the correction made in a similar way to that for temperature only.

Example 3.7

Illustrates the manual calculation of a reactor heat balance.

Vinyl chloride (VC) is manufactured by the pyrolysis of 1,2-dichloroethane (DCE). The reaction is endothermic. The flow rates to produce 5000 kg/h at 55% conversion are shown in the diagram (see Example 2.13).

The reactor is a pipe reactor heated with fuel gas, gross calorific value 33.5 MJ/m^3. Estimate the quantity of fuel gas required.



Solution

Reaction: $C_2H_4Cl_2(g) \rightarrow C_2H_3Cl(g) + HCl(g) \quad \Delta H_r^\circ = 70{,}224$ kJ/kmol.

The small quantity of impurities, less than 1%, that would be present in the feed have been neglected for the purposes of this example. Also, the selectivity for VC has been taken as 100%. It would be in the region of 99% at 55% conversion.

Heat capacity data, for vapor phase:

$$C_p^\circ = a + bT + cT^2 + dT^3 \text{kJ/kmolK}$$

	a	$b \times 10^2$	$c \times 10^5$	$d \times 10^9$
VC	5.94	20.16	−15.34	47.65
HCl	30.28	−0.761	1.325	−4.305
DCE	20.45	23.07	−14.36	33.83

for liquid phase: DCE at 20°C, $C_p = 116$ kJ/kmol K, taken as constant over temperature rise from 20 to 25°C.

Latent heat of vaporization of DCE at 25°C = 34.3 MJ/kmol.

At 2 bar pressure the change in C_p with pressure will be small and will be neglected. Take base temperature as 25°C (298 K), the standard state for ΔH_r°.

$$\text{Enthalpy of feed} = 145.5 \times 116(293 - 298) = -84{,}390 \text{ J/h} = \underline{\underline{-84.4 \text{ MJ/h}}}$$

$$\text{Enthalpy of product stream} = \int_{298}^{773} \sum (n_i C_p) \mathrm{d}T$$

Component	n_i (mol/h)	$n_i a$	$n_i b \times 10^2$	$n_i c \times 10^5$	$n_i d \times 10^9$
VC	80	475.2	1612.8	−1227.2	3812.0
HCl	80	2422.4	−60.88	106.0	−344.4
DCE	65.5	1339.5	1511.0	−940.6	2215.9
$\sum n_i C_p$		4237.1	3063.0	−2061.8	5683.5

$$\int_{298}^{773} n_i C_p \mathrm{d}T = \int_{298}^{773} (4237.1 + 3063.0 \times 10^{-2} T - 2061.8 \times 10^{-5} T^2 + 5683.5 \times 10^{-9} T^3)\mathrm{d}T = \underline{\underline{7307.3\,\mathrm{MJ/h}}}$$

Heat consumed in system by the endothermic reaction = ΔH_r° × moles produced

$$= 70{,}224 \times 80 = 5{,}617{,}920\,\mathrm{kJ/h} = 5617.9\,\mathrm{MJ/h}$$

Heat to vaporize feed (gas phase reaction)

$$= 34.3 \times 145.5 = 4990.7\,\mathrm{MJ/h}$$

Heat balance:

$$\text{Output} = \text{Input} + \text{Consumed} + Q$$

$$Q = H_{product} - H_{feed} + \text{Consumed}$$

$$= 7307.3 - (-84.4) + (5617.9 + 4990.7) = \underline{\underline{18{,}002.3\,\mathrm{MJ/h}}}$$

Taking the overall efficiency of the furnace as 70%, the gas rate required

$$= \frac{\text{Heat input}}{(\text{calorific value} \times \text{efficiency})}$$

$$= \frac{18{,}002.3}{33.5 \times 0.7} = 768\,\mathrm{m^3/h}$$

3.11. STANDARD HEATS OF FORMATION

The standard enthalpy of formation ΔH_f° of a compound is defined as the enthalpy change when one mole of the compound is formed from its constituent elements in the standard state. The enthalpy of formation of the elements is taken as zero. The standard heat of any reaction can be calculated from the heats of formation $-\Delta H_f^\circ$ of the products and reactants, if these are available or can be estimated.

Conversely, the heats of formation of a compound can be calculated from the heats of reaction, for use in calculating the standard heat of reaction for other reactions.

The relationship between standard heats of reaction and formation is given by equation 3.26 and illustrated by Examples 3.8 and 3.9:

$$\Delta H_r^\circ = \sum \Delta H_f^\circ,\ \text{products} - \sum \Delta H_f^\circ,\ \text{reactants} \tag{3.26}$$

A comprehensive list of enthalpies of formation is given in Appendix C and is available in MS Excel format in the online material at http://books.elsevier.com/companions.

As with heats of reaction, the state of the materials must be specified when quoting heats of formation.

Example 3.8

Calculate the standard heat of the following reaction, given the enthalpies of formation:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

Standard enthalpies of formation kJ/mol

$NH_3(g)$	-46.2
$NO(g)$	$+90.3$
$H_2O(g)$	-241.6

Solution

Note: The enthalpy of formation of O_2 is zero.

$$\begin{aligned}\Delta H_r^\circ &= \sum \Delta H_f^\circ,\ \text{products} - \sum \Delta H_f^\circ,\ \text{reactants}\\ &= (4 \times 90.3 + 6 \times (-241.6)) - (4 \times (-46.2))\\ &= \underline{\underline{-903.6\ \text{kJ/mol}}}\end{aligned}$$

Heat of reaction $-\Delta H_r^\circ = \underline{\underline{904\ \text{kJ/mol}}}$

3.12. HEATS OF COMBUSTION

The heat of combustion of a compound $-\Delta H_c^\circ$ is the standard heat of reaction for complete combustion of the compound with oxygen. Heats of combustion are relatively easy to determine experimentally. The heats of other reactions can be easily calculated from the heats of combustion of the reactants and products.

The general expression for the calculation of heats of reaction from heats of combustion is

$$\Delta H_r^\circ = \sum \Delta H_c^\circ,\ \text{reactants} - \sum \Delta H_c^\circ,\ \text{products} \tag{3.27}$$

Note: The product and reactant terms are the opposite way round to that in the expression for the calculation from heats of formation (equation 3.26).

For compounds containing nitrogen, the nitrogen will not be oxidized to any significant extent in combustion and is taken to be unchanged in determining the heat of combustion.

Caution: Heats of combustion are large compared with heats of reaction. Do not round off the numbers before subtraction; round off the difference.

Two methods of calculating heats of reaction from heats of combustion are illustrated in Example 3.9.

Example 3.9

Calculate the standard heat of reaction for the following reaction: the hydrogenation of benzene to cyclohexane.

(1) $C_6H_6(g) + 3H_2(g) \rightarrow C_6H_{12}(g)$

(2) $C_6H_6(g) + 7\frac{1}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l) \quad \Delta H_c^\circ = -3287.4\,kJ$

(3) $C_6H_{12}(g) + 9O_2 \rightarrow 6CO_2(g) + 6H_2O(l) \quad \Delta H_c^\circ = -3949.2\,kJ$

(4) $C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_c^\circ = -393.12\,kJ$

(5) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H_c^\circ = -285.58\,kJ$

Note: Unlike heats of formation, the standard state of water for heats of combustion is liquid. Standard pressure and temperature are the same 25°C, 1 atm.

Solution

Method 1

Using the more general equation 3.26

$$\Delta H_r^\circ = \sum \Delta H_f^\circ, \text{ products} - \sum \Delta H_f^\circ, \text{ reactants}$$

the enthalpy of formation of C_6H_6 and C_6H_{12} can be calculated, and from these values the heat of reaction (1).

From reaction (2)

$$\Delta H_c^\circ(C_6H_6) = 6 \times \Delta H_c^\circ(CO_2) + 3 \times \Delta H_c^\circ(H_2O) - \Delta H_f^\circ(C_6H_6)$$

$$3287.4 = 6(-393.12) + 3(-285.58) - \Delta H_f^\circ(C_6H_6)$$

$$\Delta H_f^\circ(C_6H_6) = -3287.4 - 3215.52 = \underline{\underline{71.88\,kJ/mol}}$$

From reaction (3)

$$\Delta H_c^\circ(C_6H_{12}) = -3949.2 = 6(-393.12) + 6(-285.58) - \Delta H_f^\circ(C_6H_{12})$$

$$\Delta H_f^\circ(C_6H_{12}) = 3949.2 - 4072.28 = \underline{\underline{-123.06\,kJ/mol}}$$

$$\Delta H_r^\circ = \Delta H_f^\circ(C_6H_{12}) - \Delta H_f^\circ(C_6H_6)$$

$$\Delta H_r^\circ = (-123.06) - (71.88) = -195\,kJ/mol$$

Note: The enthalpy of formation of H_2 is zero.

Method 2

Using equation 3.27

$$\begin{aligned}\Delta H_r^\circ &= (\Delta H_c^\circ(C_6H_6) + 3 \times \Delta H_c^\circ(H_2)) - \Delta H_c^\circ(C_6H_{12}) \\ &= (-3287.4 + 3(-285.88)) - (-3949.2) = -\underline{\underline{196\,\text{kJ/mol}}}\end{aligned}$$

Heat of reaction $\Delta H_r^\circ = \underline{\underline{196\,\text{kJ/mol}}}$

3.13. COMPRESSION AND EXPANSION OF GASES

The work term in an energy balance is unlikely to be significant unless a gas is expanded or compressed as part of the process. To compute the pressure work term

$$-W = \int_{v_1}^{v_2} P\,dv \tag{3.5a}$$

a relationship between pressure and volume during the expansion is needed.

If the compression or expansion is isothermal (at constant temperature), then for unit mass of an ideal gas

$$Pv = \text{constant} \tag{3.28}$$

and the work done, $$-W = P_1 v_1 \ln\frac{P_2}{P_1} = \frac{RT_1}{M_w}\ln\frac{P_2}{P_1} \tag{3.29}$$

where

P_1 = initial pressure;
P_2 = final pressure;
v_1 = initial volume;
M_w = molecular mass (weight) of gas.

In industrial compressors or expanders the compression or expansion path will be "polytropic," approximated by the expression:

$$Pv^n = \text{constant} \tag{3.30}$$

The work produced (or required) is given by the general expression:

$$-W = P_1 v_1 \frac{n}{n-1}\left[\left(\frac{P_2}{P_1}\right)^{(n-1)/n} - 1\right] = Z\frac{RT_1}{M_w}\frac{n}{n-1}\left[\left(\frac{P_2}{P_1}\right)^{(n-1)/n} - 1\right] \tag{3.31}$$

where

Z = compressibility factor (1 for an ideal gas);
R = universal gas constant, 8.314 $\text{JK}^{-1}\,\text{mol}^{-1}$;
T_1 = inlet temperature, K;
W = work done, J/kg.

The value of n will depend on the design and operation of the machine.

The energy required to compress a gas, or the energy obtained from expansion, can be estimated by calculating the ideal work and applying a suitable efficiency value. For reciprocating compressors, the isentropic work is normally used ($n = \gamma$) (see Figure 3.7); and for centrifugal or axial machines, the polytropic work (see Figure 3.6 and Section 3.13.2).

3.13.1. Mollier Diagrams

If a Mollier diagram (enthalpy-pressure-temperature-entropy chart) is available for the working fluid, the isentropic work can be easily calculated.

$$W = H_1 - H_2 \tag{3.32}$$

where H_1 is the specific enthalpy at the pressure and temperature corresponding to point 1, the initial gas conditions; H_2 is the specific enthalpy corresponding to point 2, the final gas condition.

Point 2 is found from point 1 by tracing a path (line) of constant entropy on the diagram.

The method is illustrated in Example 3.10.

Example 3.10

Methane is compressed from 1 bar and 290 K to 10 bar. If the isentropic efficiency is 0.85, calculate the energy required to compress 10,000 kg/h. Estimate the exit gas temperature.

Solution

From the Mollier diagram, shown diagrammatically in Figure 3.5:

$H_1 = 4500$ cal/mol;
$H_2 = 6200$ cal/mol (isentropic path);
Isentropic work $= 6200 - 4500$
$= 1700$ cal/mol

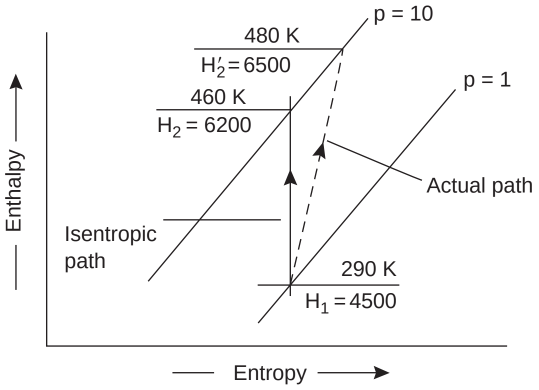


Figure 3.5. Mollier diagram, methane.

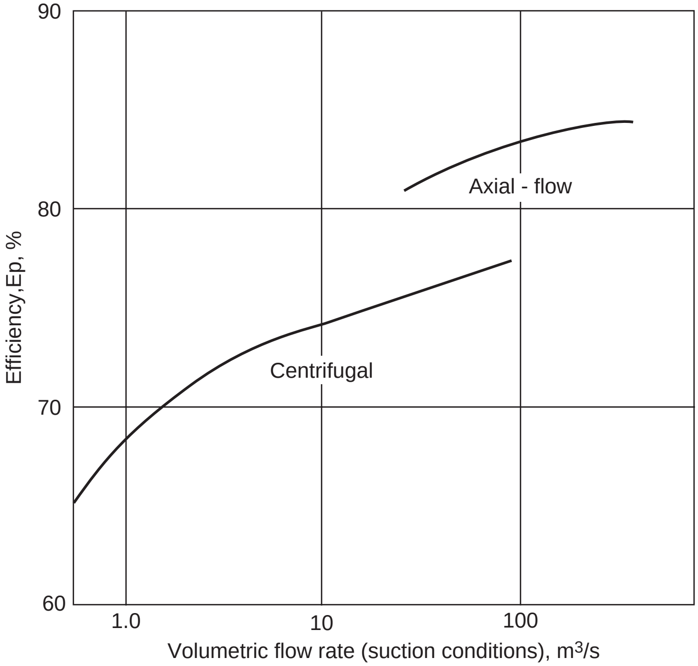


Figure 3.6. Approximate polytropic efficiencies of centrifugal and axial-flow compressors.

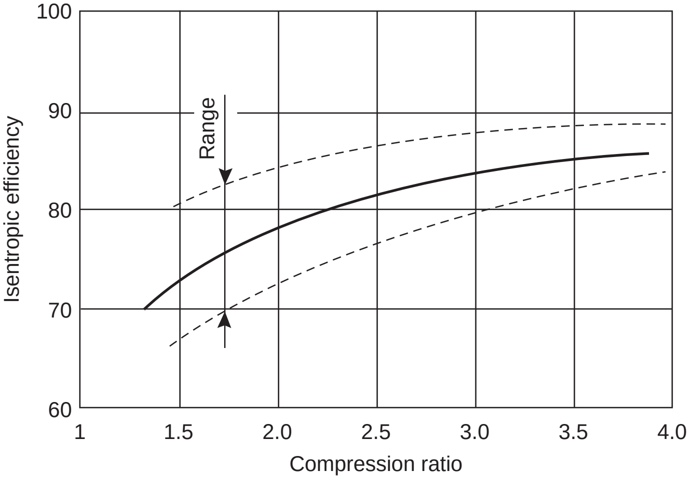


Figure 3.7. Typical efficiencies for reciprocating compressors.

For an isentropic efficiency of 0.85:

$$\text{Actual work done on gas } \frac{1700}{0.85} = 2000\,\text{cal/mol}$$

So, actual final enthalpy

$$H_2^{'} = H_1 + 2000 = \underline{\underline{6500\,\text{cal/mol}}}$$

From the Mollier diagram, if all the extra work is taken as irreversible work done on the gas, the exit gas temperature = $\underline{\underline{480\,\text{K}}}$

Molecular weight of methane = 16

Energy required = (moles per hour) × (specific enthalpy change)

$$\begin{aligned} &= \frac{10,000}{16} \times 2000 \times 10^3 \\ &= 1.25 \times 10^9 \text{ cal/h} \\ &= 1.25 \times 10^9 \times 4.187 \text{ J/h} \\ &= 5.23 \times 10^9 \text{ J/h} \end{aligned}$$

$$\text{Power} = \frac{5.23 \times 10^9}{3600} = \underline{\underline{1.45\,\text{MW}}}$$

3.13.2. Polytropic Compression and Expansion

If no Mollier diagram is available, it is more difficult to estimate the ideal work in compression or expansion processes.

Equation 3.31 can be used if the compressibility Z and polytropic coefficient n are known. Compressibility can be plotted against reduced temperature and pressure, as shown in Figure 3.8.

At conditions away from the critical point

$$n = \frac{1}{1 - m} \tag{3.33}$$

where

$$m = \frac{(\gamma - 1)}{\gamma E_p} \quad \text{for compression} \tag{3.34}$$

$$m = \frac{(\gamma - 1)E_p}{\gamma} \quad \text{for expansion} \tag{3.35}$$

and E_p is the polytropic efficiency, defined by

$$\text{for compression } E_p = \frac{\text{polytropic work}}{\text{actual work required}}$$

$$\text{for expansion } E_p = \frac{\text{actual work obtained}}{\text{polytropic work}}$$

An estimate of E_p can be obtained from Figure 3.6.

The outlet temperature can be estimated from

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^m \tag{3.36}$$

Close to the critical conditions, these equations should not be used. The procedure for calculation of polytropic work of compression or expansion close to the critical point is more complex (Shultz, 1962), and it is easiest to make such calculations using process simulation programs.

Example 3.11

Estimate the power required to compress 5000 kmol/h of HCl at 5 bar, 15°C, to 15 bar.

Solution

For HCl, $P_c = 82$ bar, $T_c = 324.6\,\text{K}$

$$C_p^\circ = 30.30 - 0.72 \times 10^{-2}T + 12.5 \times 10^{-6}T^2 - 3.9 \times 10^{-9}T^3 \ \text{kJ/kmol K}$$

Estimate T_2 from equations 3.34 and 3.35.

For diatomic gases $\gamma \approx 1.4$.

Note: γ could be estimated from the relationship

$$\gamma = \frac{C_p}{C_v}$$

At the inlet conditions, the flow rate in m^3/s

$$= \frac{5000}{3600} \times 22.4 \times \frac{288}{273} \times \frac{1}{5} = 6.56$$

From Figure 3.6 $E_p = 0.73$

From equations 3.34 and 3.35:

$$m = \frac{1.4 - 1}{1.4 \times 0.73} = 0.391$$

$$T_2 = 288\left(\frac{15}{5}\right)^{0.39} = 442\,\text{K}$$

$$T_{r(\text{mean})} = \frac{442 + 288}{2 \times 324.6} = 1.12$$

$$P_{r(\text{mean})} = \frac{5 + 15}{2 \times 82} = 0.12$$

$$\text{at } T_{(\text{mean})},\ C_p^\circ = 29.14\,\text{kJ/kmol K}$$

Correction for pressure from Figure 3.2, 2 kJ/kmol K

$$C_p = 29.14 + 2 \approx 31\,\text{kJ/kmol K}$$

From Figure 3.8, at mean conditions:

$$Z = 0.98$$

From equation 3.33:

$$n = \frac{1}{1 - 0.391} = 1.64$$

From equation 3.31:

$$W \text{ polytropic} = 0.98 \times 288 \times 8.314 \times \frac{1.64}{1.64 - 1}\left(\left(\frac{15}{5}\right)^{(1.64-1)/1.64} - 1\right)$$

$$= 3219\,\text{kJ/kmol}$$

$$\text{Actual work required} = \frac{\text{polytropic work}}{E_p} = \frac{3219}{0.73} = \underline{\underline{4409\,\text{kJ/kmol}}}$$

$$\text{Power} = \frac{4409 \times 5000}{3600} = 6124\,\text{kW, say } \underline{\underline{6.1\,\text{MW}}}$$

3.13.3. Multistage Compressors

Single-stage compressors can be used only for low pressure ratios. At high pressure ratios, the temperature rise is too high for efficient operation.

To cope with the need for high pressure generation, the compression is split into a number of separate stages, with intercoolers between each stage. The interstage pressures are normally selected to give equal work in each stage.

For a two-stage compressor, the interstage pressure is given by

$$P_i = \sqrt{(P_1 \times P_2)} \tag{3.37}$$

where P_i is the intermediate-stage pressure.

Example 3.12

Estimate the power required to compress 1000 m^3/h air from ambient conditions to 700 kN/m^2 gauge, using a two-stage reciprocating compressor with an intercooler.

Solution

Take the inlet pressure, P_1, as 1 atmosphere = 101.33 kN/m^2, absolute.

Outlet pressure, P_2, = 700 + 101.33 = 801.33 kN/m^2, absolute.

For equal work in each stage, the intermediate pressure, P_i,

$$= \sqrt{(1.0133 \times 10^5 \times 8.0133 \times 10^5)} = \underline{\underline{2.8495 \times 10^5\,\text{N/m}^2}}$$

For air, take ratio of the specific heats, γ, to be 1.4.

For equal work in each stage, the total work will be twice that in the first stage.

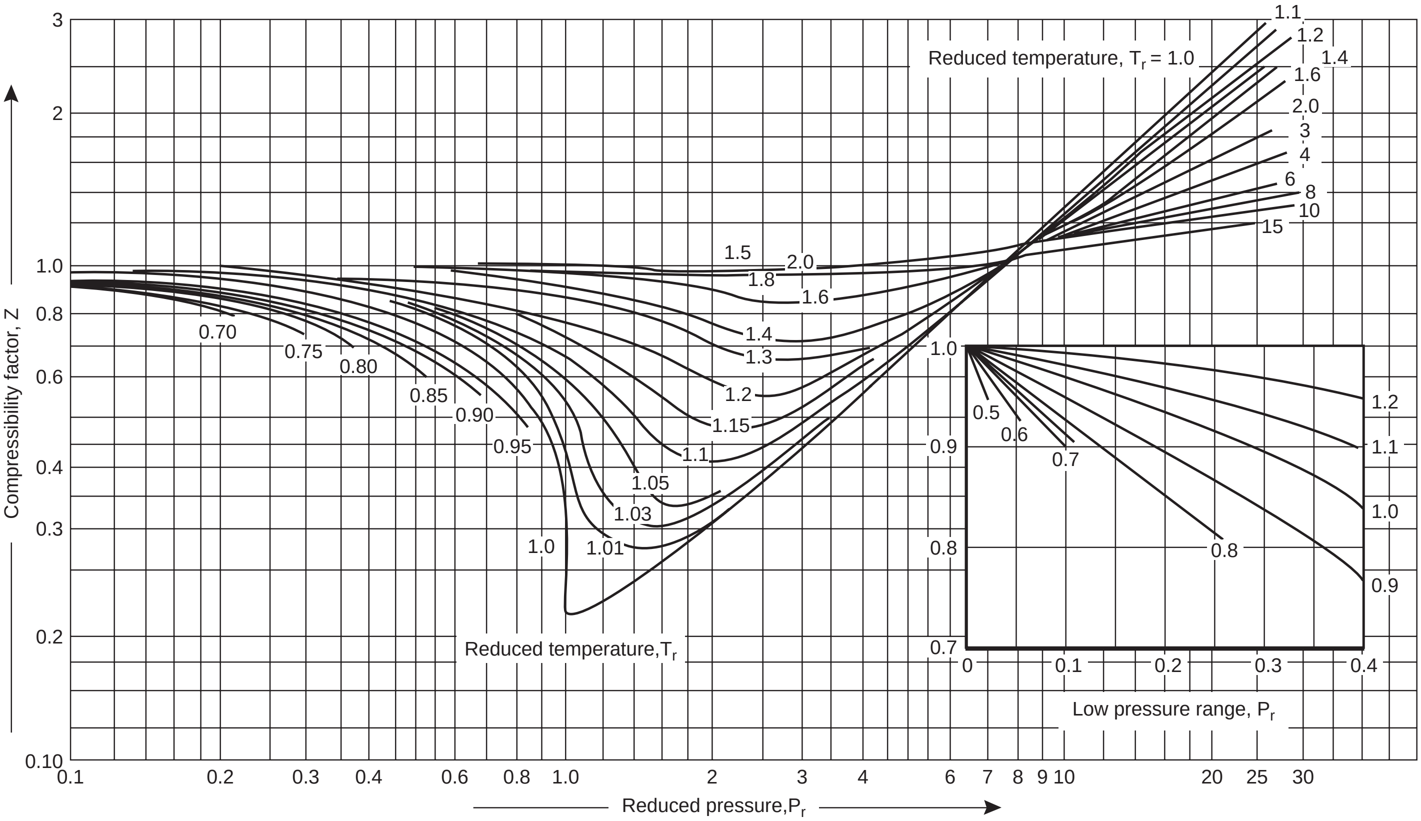


Figure 3.8. Compressibility factors of gases and vapors.

Take the inlet temperature to be 20°C. At that temperature the specific volume is given by

$$v_1 = \frac{29}{22.4} \times \frac{293}{273} = 1.39\,\mathrm{m^3/kg}$$

$$\text{Isentropic work done,} \quad -W = 2 \times 1.0133 \times 10^5 \times 1.39 \times \frac{1.4}{1.4 - 1}\left(\left(\frac{2.8495}{1.0133}\right)^{(1.4-1)/1.4} - 1\right)$$

$$= 338{,}844\,\mathrm{J/kg} = 339\,\mathrm{kJ/kg}$$

From Figure 3.7, for a compression ratio of 2.85, the efficiency is approximately 84%. So work required

$$= 339/0.84 = \underline{\underline{404\,\mathrm{kJ/kg}}}$$

$$\text{Mass flow rate} = \frac{1000}{1.39 \times 3600} = 0.2\,\mathrm{kg/s}$$

$$\text{Power required} = 404 \times 0.2 = \underline{\underline{80\,\mathrm{kW}}}$$

3.13.4. Electrical Drives

The electrical power required to drive a compressor (or pump) can be calculated from a knowledge of the motor efficiency:

$$\text{Power} = \frac{-W \times \text{mass flow-rate}}{E_e} \tag{3.38}$$

where

$-W$ = work of compression per unit mass (equation 3.31);
E_e = electric motor efficiency.

The efficiency of the drive motor will depend on the type, speed, and size. The values given in Table 3.1 can be used to make a rough estimate of the power required.

Table 3.1. Approximate Efficiencies of Electric Motors

Size (kW)	Efficiency (%)
5	80
15	85
75	90
200	92
750	95
>4000	97

3.14. ENERGY BALANCE CALCULATIONS

As with mass balances, energy balances for complex design problems are most easily set up and solved using commercial process simulation software, as described in Chapter 4.

Process simulation software can also be used to help build simple energy balances in spreadsheet models, for example, by entering stream data to calculate mixture heat capacities, to calculate stream enthalpies, or to estimate heats of reaction.

When setting up process simulation models, the design engineer needs to pay careful attention to operations that have an impact on the energy balance and heat use within the process. Some common problems to watch out for include:

1. Avoid mixing streams at very different temperatures. This usually represents a loss of heat (or cooling) that could be better used in the process.
2. Avoid mixing streams at different pressures. The mixed stream will be at the lowest pressure of the feed streams. The higher pressure streams will undergo cooling as a result of adiabatic expansion. This may lead to increased heating or cooling requirements or lost potential to recover shaft work during the expansion.
3. Segment heat exchangers to avoid internal pinches. This is particularly necessary for exchangers where there is a phase change. When a liquid is heated, boiled, and superheated, the variation of stream temperature with enthalpy added looks like Figure 3.9. Liquid is heated to the boiling point (A-B), then the heat of vaporization is added (B-C), and the vapor is superheated (C-D). This is a different temperature-enthalpy profile than a straight line between the initial and final states (A-D). If the stream in Figure 3.9 were matched against a heat source that had a temperature profile like line E-F in Figure 3.10, then the exchanger would appear feasible based on the inlet and outlet temperatures, but would in fact be infeasible because of the crossover of the temperature profiles at B. A simple way to avoid this problem is to break up the preheat, boiling, and superheat into three exchangers in the simulation model, even if they will be carried out in a single piece of equipment in the final design. The same problem also occurs with condensers that incorporate desuperheat and subcooling.
4. Check for heat of mixing. This is important whenever acids or bases are mixed with water. If the heat of mixing is large, then two or more stages of mixing with

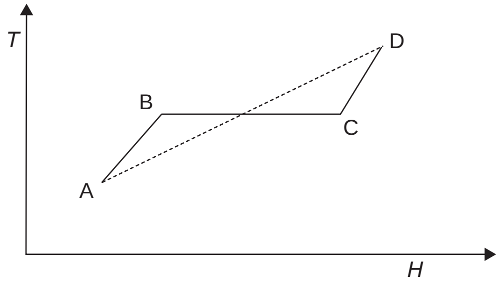


Figure 3.9. Temperature-enthalpy profile for a stream that is vaporized and superheated.

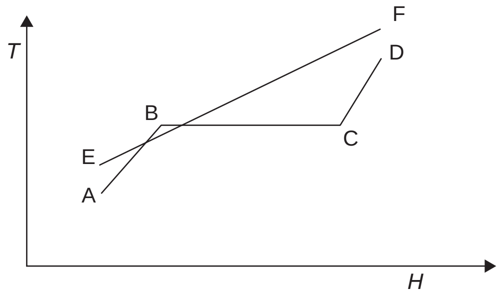


Figure 3.10. Heat transfer to a stream that is vaporized and superheated.

intercoolers may be needed. If a large heat of mixing is expected but is not predicted by the model, then check that the thermodynamic model includes heat of mixing effects.

5. Remember to allow for process inefficiency and design margins. For example, when sizing a fired heater, if process heating is carried out in the radiant section only, then the heating duty calculated in the simulation is only 60% of the total furnace duty (see Section 12.17). The operating duty will then be the process duty divided by 0.6. The design duty must be increased further by a suitable design factor, say 10%. The design duty of the fired heater is then 1.1/0.6 = 1.83 times the process duty calculated in the simulation.

3.15. UNSTEADY STATE ENERGY BALANCES

All the examples of energy balances considered previously have been for steady-state processes, where the rate of energy generation or consumption did not vary with time and the accumulation term in the general energy balance equation was taken as zero.

If a batch process is considered, or if the rate of energy generation or removal varies with time, it is necessary to set up a differential energy balance, similar to the differential material balance considered in Chapter 2. For batch processes the total energy requirements can usually be estimated by taking a single batch as the time basis for the calculation, but the maximum rate of heat generation must also be estimated to size any heat transfer equipment needed.

The application of a differential energy balance is illustrated in Example 3.13.

Example 3.13

Differential Energy Balance

In the batch preparation of an aqueous solution, the water is first heated to 80°C in a jacketed, agitated vessel; 1000 Imp. gal. (4545 kg) is heated from 15°C. If the jacket area is 300 ft^2 (27.9 m^2) and the overall heat transfer coefficient can be taken as 50 Btu $\text{ft}^{-2}\text{h}^{-1}{}^{\circ}\text{F}^{-1}$(285 W $\text{m}^{-2}\text{K}^{-1}$), estimate the heating time. Steam is supplied at 25 psig (2.7 bar).

Solution

The rate of heat transfer from the jacket to the water will be given by the following expression:

$$\frac{dQ}{dt} = U_j A(t_s - t) \tag{a}$$

where

dQ is the increment of heat transferred in the time interval dt; and
U_j = the overall-heat transfer coefficient;
t_s = the steam-saturation temperature;
t = the water temperature.

The incremental increase in the water temperature dt is related to the heat transferred dQ by the energy-balance equation:

$$dQ = MC_p \, dt \tag{b}$$

where MC_p is the heat capacity of the system.

Equating equations (a) and (b)

$$MC_p \frac{dt}{dt} = U_j A(t_s - t)$$

Integrating

$$\int_0^{t_B} dt = \frac{MC_p}{U_j A} \int_{t_1}^{t_2} \frac{dt}{(t_s - t)}$$

Batch heating time:

$$t_B = -\frac{MC_p}{U_j A} \ln \frac{t_s - t_2}{t_s - t_1}$$

For this example

$$MC_p = 4.18 \times 4545 \times 10^3 \, \mathrm{JK^{-1}}$$

$$U_j A = 285 \times 27 \, \mathrm{WK^{-1}}$$

$$t_1 = 15^\circ\mathrm{C}, \; t_2 = 80^\circ\mathrm{C}, \; t_s = 130^\circ\mathrm{C}$$

$$t_B = -\frac{4.18 \times 4545 \times 10^3}{285 \times 27.9} \ln \frac{130 - 80}{130 - 15}$$

$$= 1990\,\mathrm{s} = \underline{\underline{33.2 \, \mathrm{min}}}$$

In this example the heat capacity of the vessel and the heat losses have been neglected for simplicity. They would increase the heating time by 10 to 20%.

3.16. ENERGY RECOVERY

Process streams at high pressure or temperature, and those containing combustible material, contain energy that can be usefully recovered. Whether it is economic to recover the energy content of a particular stream depends on the value of the energy that can be usefully extracted and the cost of recovery. The value of the energy is related to the marginal cost of energy at the site, as discussed in Section 6.4.4. It may be worthwhile recovering energy from a process stream at a site where energy costs are high but not where the primary energy costs are low. The cost of recovery will be the capital and operating cost of any additional equipment required. If the savings exceed the total annualized cost, including capital charges, then the energy recovery will usually be worthwhile. Maintenance costs should be included in the annualized cost (see Chapter 6).

Some processes, such as air separation, depend on efficient energy recovery for economic operation, and in all processes the efficient use of energy recovery techniques will reduce product cost.

Some of the techniques used for energy recovery in chemical process plants are described briefly in the following sections. The references cited give fuller details of each technique. Miller (1968) gives a comprehensive review of process energy systems, including heat exchange and power recovery from high-pressure fluid streams.

Kenney (1984) reviews the application of thermodynamic principles to energy recovery in the process industries.

3.16.1. Heat Exchange

The most common energy-recovery technique is to use the heat in a high-temperature process stream to heat a colder stream. This saves part or all of the cost of heating the cold stream, as well as part or all of the cost of cooling the hot stream. Conventional shell and tube exchangers are normally used. The cost of the heat exchange surface may be increased, due to the reduced temperature driving forces, or decreased, due to needing fewer exchangers. The cost of recovery will be reduced if the streams are located conveniently close.

The amount of energy that can be recovered depends on the temperature, flow, heat capacity, and temperature change possible in each stream. A reasonable temperature driving force must be maintained to keep the exchanger area to a practical size. The most efficient exchanger will be the one in which the shell and tube flows are truly countercurrent. Multiple tube pass exchangers are usually used for practical reasons. With multiple tube passes, the flow is part countercurrent and part cocurrent and temperature crosses can occur, which reduce the efficiency of heat recovery (see Chapter 12).

The hot process streams leaving a reactor or a distillation column are frequently used to preheat the feed streams (“feed-effluent” or “feed-bottoms” exchangers).

In an industrial process there will be many hot and cold streams, and there will be an optimum arrangement of the streams for energy recovery by heat exchange. The problem of synthesizing a network of heat exchangers has been the subject of much research and is covered in more detail in Section 3.17.

3.16.2. Waste-Heat Boilers

If the process streams are at a sufficiently high temperature and there are no attractive options for process-to-process heat transfer, then the heat recovered can be used to generate steam.

Waste-heat boilers are often used to recover heat from furnace flue gases and the process gas streams from high-temperature reactors. The pressure and superheat temperature of the stream generated depend on the temperature of the hot stream and the approach temperature permissible at the boiler exit (see Chapter 12). As with any heat transfer equipment, the area required increases as the mean temperature driving force (log mean ΔT) is reduced. The permissible exit temperature may also be limited by process considerations. If the gas stream contains water vapor and soluble corrosive gases, such as HCl or SO_2, the exit gas temperature must be kept above the dew point.

Hinchley (1975) discusses the design and operation of waste-heat boilers for chemical plants. Both fire tube and water tube boilers are used. A typical arrangement of a water tube boiler on a reformer furnace is shown in Figure 3.11, and a fire tube boiler is shown in Figure 3.12.

The application of a waste-heat boiler to recover energy from the reactor exit streams in a nitric acid plant is shown in Figure 3.13.

The selection and operation of waste-heat boilers for industrial furnaces is discussed in the *Efficient Use of Energy*, Dryden (1975).

3.16.3. High-Temperature Reactors

If a reaction is highly exothermic, cooling will be needed. If the reactor temperature is high enough, the heat removed can be used to generate steam. The lowest steam

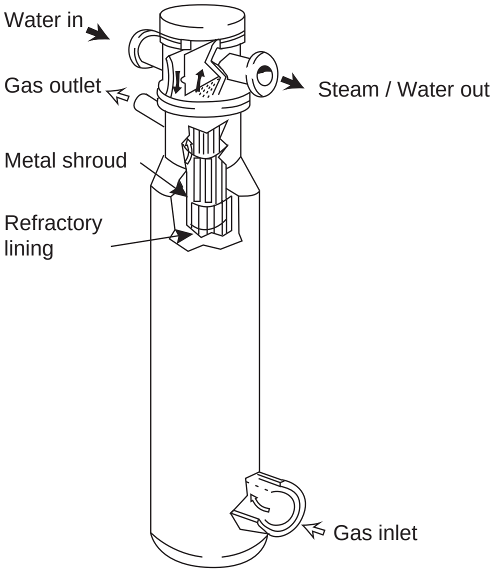


Figure 3.11. Reformed gas waste-heat boiler arrangement of vertical U-tube water-tube boiler. (Reprinted by permission of the Council of the Institution of Mechanical Engineers from the Proceedings of the Conference on Energy Recovery in the Process Industries, London, 1975.)

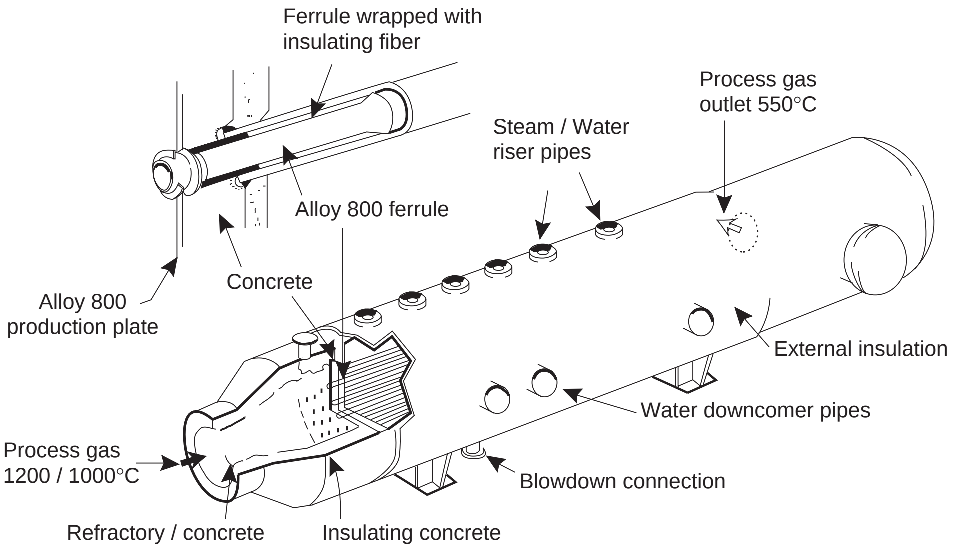
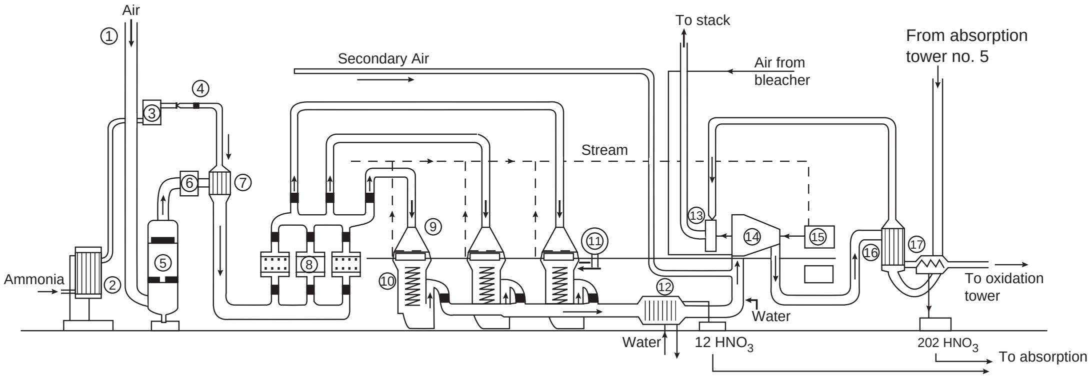


Figure 3.12. Reformed gas waste-heat boiler, principal features of typical natural circulation fire-tube boilers. (Reprinted by permission of the Council of the Institution of Mechanical Engineers from the Proceedings of the Conference on Energy Recovery in the Process Industries, London, 1975.)



1. Air entry
2. Ammonia vaporiser
3. Ammonia filter
4. Control valves
5. Air-scrubbing tower
6. Air preheater
7. Gas mixer
8. Gas filters
9. Converters
10. Lamont boilers
11. Steam drum
12. Gas cooler No. 1
13. Exhaust turbine
14. Compressor
15. Steam turbine
16. Heat exchanger
17. Gas cooler No. 2

(From Nitric Acid Manufacture, Miles (1961), with permission)

Figure 3.13. Connections of a nitric acid plant, intermediate pressure type.

pressure normally used in the process industries is 2.7 bar (25 psig), and steam is normally distributed at a header pressure of around 8 bar (100 psig); so any reactor with a temperature above 200°C is a potential steam generator.

Three systems are used:

1. Figure 3.14a. An arrangement similar to a conventional water-tube boiler. Steam is generated in cooling pipes within the reactor and separated in a steam drum.
2. Figure 3.14b. Similar to the first arrangement but with the water kept at high pressure to prevent vaporization. The high-pressure water is flashed to steam at lower pressure in a flash drum. This system would give more responsive control of the reactor temperature.
3. Figure 3.14c. In this system a heat transfer fluid, such as Dowtherm [see Perry et al. (1997) and Singh (1985) for details of heat transfer fluids], is used to avoid the need for high-pressure tubes. The steam is raised in an external boiler.

3.16.4. Low-Grade Fuels

Process waste products that contain significant quantities of combustible material can be used as low-grade fuels for raising steam or direct process heating. Their use will be economic only if the intrinsic value of the fuel justifies the cost of special burners and other equipment needed to burn the waste. If the combustible content of the waste is too low to support combustion, the waste must be supplemented with higher calorific value primary fuels.

Reactor Off Gases

Reactor off gases (vent gases) and recycle stream purges are often of high enough calorific value to be used as fuels. The calorific value of a gas can be calculated from the heats of combustion of its constituents; the method is illustrated in Example 3.14.

Other factors which, together with the calorific value, determine the economic value of an off gas as a fuel are the quantity available and the continuity of supply. Waste gases are best used for steam raising, rather than for direct process heating, as this decouples the source from the use and gives greater flexibility.

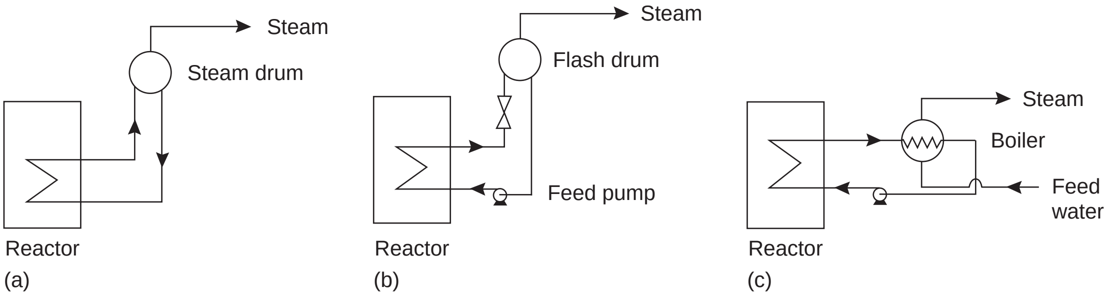


Figure 3.14. (a, b, c) Steam generation.

Example 3.14

Calculation of Waste-Gas Calorific Value

The typical vent-gas analysis from the recycle stream in an oxyhydrochlorination process for the production of dichloroethane (DCE) (British patent BP 1,524,449) is as follows, percentages on volume basis.

$$O_2\ 7.96,\ CO_2 + N_2\ 87.6,\ CO\ 1.79,\ C_2H_4\ 1.99,\ C_2H_6\ 0.1,\ DCE\ 0.54$$

Estimate the vent gas calorific value.

Solution

Component calorific values, from Perry and Chilton (1973):

CO 67.6 kcal/mol = 283 kJ/mol
C_2H_4 372.8 = 1560.9
C_2H_6 337.2 = 1411.9

The value for DCE can be estimated from the heats of formation.
Combustion reaction:

$$C_2H_4Cl_2(g) + 2\frac{1}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(g) + 2HCl(g)$$

ΔH_f° from Appendix D:

$$\begin{aligned} CO_2 &= -393.8\ \text{kJ/mol} \\ H_2O &= -242.0 \\ HCl &= -92.4 \\ DCE &= -130.0 \\ \Delta H_c^\circ &= \sum \Delta H_f^\circ\ \text{products} - \sum \Delta H_f^\circ\ \text{reactants} \\ &= [2(-393.8) - 242.0 + 2(-92.4)] - [-130.0] \\ &= -1084.4\ \text{kJ} \end{aligned}$$

Estimation of vent gas calorific value, basis 100 mol.

Component	mol/100 mol	× Calorific Value (kJ/mol)	= Heating Value
CO	1.79	283.0	506.6
C_2H_4	1.99	1560.9	3106.2
C_2H_6	0.1	1411.9	141.2
DCE	0.54	1084.4	585.7
		Total	4339.7

$$\text{Calorific value of vent gas} = \frac{4339.7}{100} = 43.4\,\text{kJ/mol}$$
$$= \frac{43.4}{22.4} \times 10^3 = \underline{\underline{1938\,\text{kJ/m}^3}}(52\,\text{Btu/ft}^3) \text{ at 1 bar, } 0^\circ\text{C}$$

This calorific value is very low compared to 37 MJ/m^3 (1000 Btu/ft^3) for natural gas. The vent gas is barely worth recovery, but if the gas has to be burnt to avoid pollution, it could be used in an incinerator such as that shown in Figure 3.15, giving a useful steam production to offset the cost of disposal.

Liquid and Solid Wastes

Combustible liquid and solid waste can be disposed of by burning, which is usually preferred to dumping. Incorporating a steam boiler in the incinerator design will enable an otherwise unproductive, but necessary, operation to save energy. If the combustion products are corrosive, corrosion-resistant materials will be needed, and the flue gases must be scrubbed to reduce air pollution. An incinerator designed to handle chlorinated and other liquid and solid wastes is shown in Figure 3.15. This incinerator incorporates a steam boiler and a flue-gas scrubber. The disposal of chlorinated wastes is discussed by Santoleri (1973).

Dunn and Tomkins (1975) discuss the design and operation of incinerators for process wastes. They give particular attention to the need to comply with the current clean-air legislation, and the problem of corrosion and erosion of refractories and heat exchange surfaces.

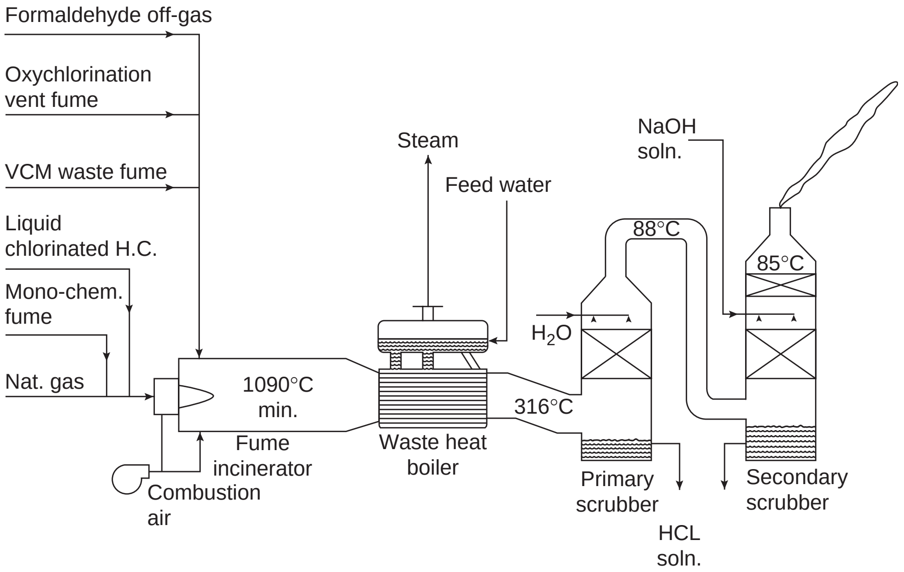


Figure 3.15. Typical incinerator-heat recovery-scrubber system for vinyl-chloride-monomer process waste. (Courtesy of John Thurley Ltd.)

3.16.5. High-Pressure Process Streams

Where high-pressure gas or liquid process streams are throttled to lower pressures, energy can be recovered by carrying out the expansion in a suitable turbine.

Gas Streams

The economic operation of processes that involve the compression and expansion of large quantities of gases, such as ammonia synthesis, nitric acid production and air separation, depends on the efficient recovery of the energy of compression. The energy recovered by expansion is often used to drive the compressors directly, as shown in Figure 3.13. If the gas contains condensable components, it may be advisable to consider heating the gas by heat exchange with a higher temperature process stream before expansion. The gas can then be expanded to a lower pressure without condensation and the power generated increased.

The process gases do not have to be at a particularly high pressure for expansion to be economical if the flow rate is high. For example, Luckenbach (1978) in U.S. patent 4,081,508 describes a process for recovering power from the off gas from a fluid catalytic cracking process by expansion from about 2 to 3 bar (15 to 25 psig) down to just over atmospheric pressure (1.5 to 2 psig).

The energy recoverable from the expansion of a gas can be estimated by assuming polytropic expansion; see Section 3.13.2 and Example 3.15.

The design of turboexpanders for the process industries is discussed by Bloch et al. (1982).

Example 3.15

Consider the extraction of energy from the tail gases from a nitric acid adsorption tower.

Gas composition, kmol/h:

O_2	371.5
N_2	10,014.7
NO	21.9
NO_2	Trace
H_2O	Saturated at 25°C

If the gases leave the tower at 6 atm, 25°C, and are expanded to, say, 1.5 atm, calculate the turbine exit gas temperatures without preheat, and if the gases are preheated to 400°C with the reactor off gas. Also, estimate the power recovered from the preheated gases.

Solution

For the purposes of this calculation, it will be sufficient to consider the tail gas as all nitrogen, flow 10,410 kmol/h.

$$P_c = 33.5\,\text{atm}, \qquad T_c = 126.2\,\text{K}$$

Figure 3.6 can be used to estimate the turbine efficiency.

$$\text{Exit gas volumetric flow rate} = \frac{10{,}410}{3600} \times 22.4 \times \frac{1}{1.5} \approx 43\ \text{m}^3/\text{s}$$

from Figure 3.6 $E_P = 0.75$

$$P_r\ \text{inlet} = \frac{6}{33.5} = 0.18$$

$$T_r\ \text{inlet} = \frac{298}{126.2} = 2.4$$

Using equations 3.33 and 3.35, for $N_2 \gamma = 1.4$

$$m = \frac{1.4 - 1}{1.4} \times 0.75 = 0.21$$

$$n = \frac{1}{1 - m} = \frac{1}{1 - 0.21} = 1.27$$

$$\text{without preheat } T_2 = 298\left(\frac{1.5}{6.0}\right)^{0.21} = 223\ \text{K}$$

$$= \underline{\underline{-50^\circ\text{C}}}$$

This temperature would be problematic. Acidic water would condense out, probably damaging the turbine.

$$\text{With preheat, } T_2 = 673\left(\frac{1.5}{6.0}\right)^{0.21} = 503\ \text{K}$$

$$= 230^\circ\text{C}$$

From equation 3.31, the work done by the gas as a result of polytropic expansion is

$$= -1 \times 673 \times 8.314 \times \frac{1.27}{1.27 - 1}\left\{\left(\frac{1.5}{6.0}\right)^{(1.27-1)/1.27} - 1\right\}$$

$$= 6718\ \text{kJ/kmol}$$

$$\text{Actual work} = \text{polytropic work} \times E_p$$

$$= 6718 \times 0.75 = \underline{\underline{5039\ \text{kJ/kmol}}}$$

$$\text{Power output} = \text{work/kmol} \times \text{kmol/s} = 5039 \times \frac{10{,}410}{3600}$$

$$= 14{,}571\ \text{kJ/s} = \underline{\underline{14.6\ \text{MW}}}$$

This is a significant amount of power and will probably justify the cost of the expansion turbine.

Liquid Streams

As liquids are essentially incompressible, less energy is stored in a compressed liquid than a gas; however, it is often worth considering power recovery from high-pressure liquid streams (>15 bar), as the equipment required is relatively simple and inexpensive. Centrifugal pumps are used as expanders and are often coupled directly to other pumps. The design, operation, and cost of energy recovery from high-pressure liquid streams is discussed by Jenett (1968), Chada (1984), and Buse (1985).

3.16.6. Heat Pumps

A heat pump is a device for raising low-grade heat to a temperature at which the heat can be used. It pumps the heat from a low temperature source to the higher temperature sink, using a small amount of energy relative to the heat energy recovered.

Heat pumps are increasingly finding applications in the process industries. A typical application is the use of the low-grade heat from the condenser of a distillation column to provide heat for the reboiler; see Barnwell and Morris (1982) and Meili (1990). Heat pumps are also used with dryers, heat being abstracted from the exhaust air and used to preheat the incoming air.

Details of the thermodynamic cycles used for heat pumps can be found in most textbooks on engineering thermodynamics, and in Reay and MacMichael (1988). In the process industries, heat pumps operating on the mechanical vapor compression cycle are normally used. A vapor compression heat pump applied to a distillation column is shown in Figure 3.16a. The working fluid, usually a commercial refrigerant, is fed to the reboiler as a vapor at high pressure and condenses, giving up heat to vaporize the process fluid. The liquid refrigerant from the reboiler is then expanded over a throttle valve, and the resulting wet vapor is fed to the column condenser. In the condenser the wet refrigerant is dried, taking heat from the condensing process vapor. The refrigerant vapor is then compressed and recycled to the reboiler, completing the working cycle.

If the conditions are suitable, the process fluid can be used as the working fluid for the heat pump. This arrangement is shown in Figure 3.16b. The hot process liquid at high pressure is expanded over the throttle value and fed to the condenser, to provide cooling to condense the vapor from the column. The vapor from the condenser is compressed and returned to the base of the column. In an alternative arrangement, the process vapor is taken from the top of the column, compressed, and fed to the reboiler to provide heating.

The ‘‘efficiency’’ of a heat pump is measured by the coefficient of performance, *COP*:

$$COP = \frac{\text{energy delivered at higher temperature}}{\text{energy input to the compressor}} \tag{3.39}$$

The *COP* depends principally on the working temperatures. Heat pumps are more efficient (higher *COP*) when operated over a narrow temperature range. They are thus most often encountered on distillation columns that separate close-boiling

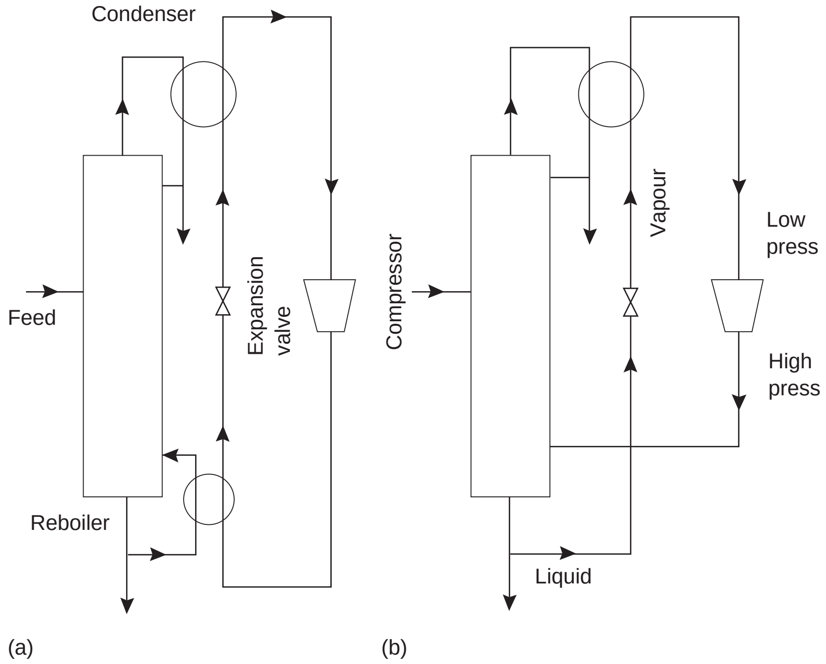


Figure 3.16. Distillation column with heat pump. (a) Separate refrigerant circuit. (b) Using column fluid as the refrigerant.

compounds. Note that the *COP* of a heat pump is not the same as the *COP* of a refrigeration cycle (Section 6.4.4).

The economics of the application of heat pumps in the process industries is discussed by Holland and Devotta (1986). Details of the application of heat pumps in a wide range of industries are given by Moser and Schnitzer (1985).

3.17. HEAT EXCHANGER NETWORKS

The design of a heat exchanger network for a simple process with only one or two streams that need heating and cooling is usually straightforward. When there are multiple hot and cold streams, the design is more complex, and there may be many possible heat exchange networks. The design engineer must determine the optimum extent of heat recovery, while ensuring that the design is flexible to changes in process conditions and can be started up and operated easily and safely.

In the 1980s, there was a great deal of research into design methods for heat exchanger networks; see Gundersen and Naess (1988). One of the most widely applied methods that emerged was a set of techniques termed *pinch technology*, developed by Bodo Linnhoff and his collaborators at ICI, Union Carbide, and the University of Manchester. The term derives from the fact that in a plot of the system temperatures versus the heat transferred, a *pinch* usually occurs between the hot stream and cold stream curves; see Figure 3.22. It has been shown that the pinch represents a distinct thermodynamic break in the system and that, for minimum energy requirements, heat should not be transferred across the pinch (Linnhoff et al., 1982).

In this section the fundamental principles of the pinch technology method for energy integration will be outlined and illustrated with reference to a simple problem. The method and its applications are described fully in a guide published by the Institution of Chemical Engineers, IChemE (1994); see also Douglas (1988) and Smith (2005).

3.17.1. Pinch Technology

The development and application of the method can be illustrated by considering the problem of recovering heat between four process streams: two hot streams that require cooling and two cold streams that must be heated. The process data for the streams is set out in Table 3.2. Each stream starts from a source temperature, T_s, and is to be heated or cooled to a target temperature, T_t. The heat capacity flow rate of each stream is shown as *CP.* For streams where the specific heat capacity can be taken as constant, and there is no phase change, *CP* will be given by

$$CP = mC_p \tag{3.40}$$

where

m = mass flow rate, kg/s;
C_p = average specific heat capacity between T_s and T_t kJ $\text{kg}^{-1\circ}\text{C}^{-1}$.

The heat load shown in the table is the total heat required to heat or cool the stream from the source to the target temperature.

There is clearly scope for energy integration between these four streams. Two require heating and two require cooling; and the stream temperatures are such that heat can be transferred from the hot to the cold streams. The task is to find the best arrangement of heat exchangers to achieve the target temperatures.

Simple Two-Stream Problem

Before we investigate the energy integration of the four streams shown in Table 3.2, we will illustrate the use of a temperature-enthalpy diagram for a simple problem involving only two streams. The general problem of heating and cooling two streams

Table 3.2. Data for Heat Integration Problem

Stream Number	Type	Heat Capacity Flow Rate *CP*, kW/°C	T_s°C	T_t°C	Heat Load, kW
1	hot	3.0	180	60	360
2	hot	1.0	150	30	120
3	cold	2.0	20	135	230
4	cold	4.5	80	140	270

from source to target temperatures is shown in Figure 3.17. Some heat is exchanged between the streams in the heat exchanger. Additional heat, to raise the cold stream to the target temperature, is provided by the hot utility (usually steam) in the heater; and additional cooling to bring the hot stream to its target temperature, by the cold utility (usually cooling water) in the cooler.

In Figure 3.18a the stream temperatures are plotted on the y-axis and the enthalpy change in each stream on the x-axis. This is known as a temperature-enthalpy (*T-H*) diagram. For heat to be exchanged, a minimum temperature difference must be maintained between the two streams. This is shown as $\Delta T_{\min}$ on the diagram. The practical minimum temperature difference in a heat exchanger will usually be between 5 and 30°C; see Chapter 12.

The slope of the lines in the *T-H* plot is proportional to $1/CP$, since $\Delta H = CP \times \Delta T$, so $dT/dH = 1/CP$. Streams with low heat capacity flow rate thus have steep slopes in the *T-H* plot, and streams with high heat capacity flow rate have shallow slopes.

The heat transferred between the streams is given by the range of enthalpy over which the two curves overlap each other, and is shown on the diagram as ΔH_{ex}. The heat transferred from the hot utility, ΔH_{hot}, is given by the part of the

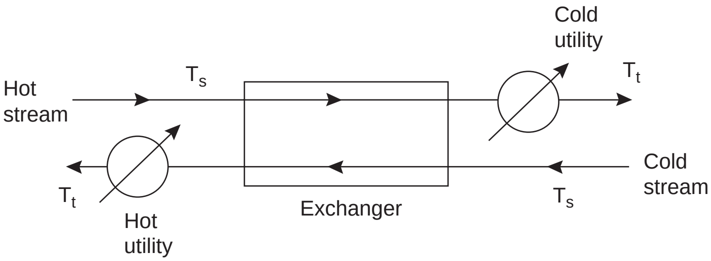


Figure 3.17. Two-stream exchanger problem.

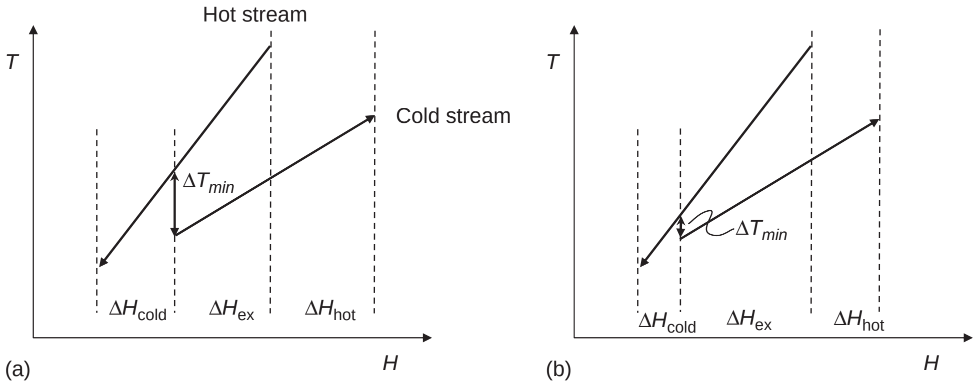


Figure 3.18. (a, b) Temperature-enthalpy (*T-H*) diagram for two-stream example.

cold stream that is not overlapped by the hot stream. The heat transferred to the cold utility, ΔH_{cold}, is similarly given by the part of the hot stream that is not overlapped by the cold stream. The heats can also be calculated as

$$\Delta H = CP \times (\text{temperature change})$$

Since we are concerned only with changes in enthalpy, we can treat the enthalpy axis as a relative scale and slide either the hot stream or the cold stream horizontally. As we do so, we change the minimum temperature difference between the streams, $\Delta T_{\min}$, and also the amount of heat exchanged and the amounts of hot and cold utilities required.

Figure 3.18b shows the same streams plotted with a lower value of $\Delta T_{\min}$. The amount of heat exchanged is increased and the utility requirements have been reduced. The temperature driving force for heat transfer has also been reduced, so the heat exchanger has both a larger duty and a smaller log-mean temperature difference. This leads to an increase in the heat transfer area required and in the capital cost of the exchanger. The capital cost increase is partially offset by capital cost savings in the heater and cooler, which both become smaller, as well as by savings in the costs of hot and cold utilities. In general, there will be an optimum value of $\Delta T_{\min}$, as illustrated in Figure 3.19. This optimum is usually rather flat over the range 10°C to 30°C.

The maximum feasible heat recovery is reached at the point where the hot and cold curves touch each other on the *T-H* plot, as illustrated in Figure 3.20. At this point, the temperature driving force at one end of the heat exchanger is zero and an infinite heat exchange surface is required, so the design is not practical. The exchanger is said to be *pinched* at the end where the hot and cold curves meet. In Figure 3.20, the heat exchanger is pinched at the cold end.

It is not possible for the hot and cold streams to cross each other, as this would be a violation of the second law of thermodynamics.

Four-Stream Problem

In Figure 3.21a the hot streams given in Table 3.2 are shown plotted on a temperature-enthalpy diagram.

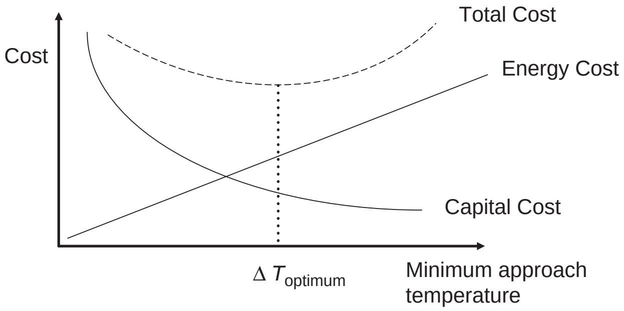


Figure 3.19. The capital-energy trade-off in process heat recovery.

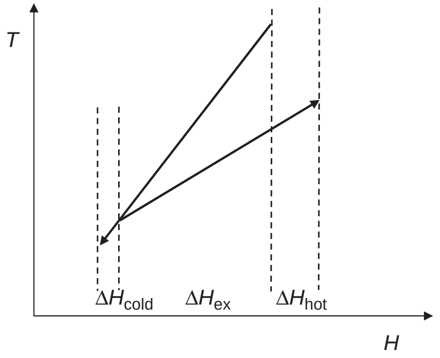


Figure 3.20. Maximum feasible heat recovery for two-stream example.

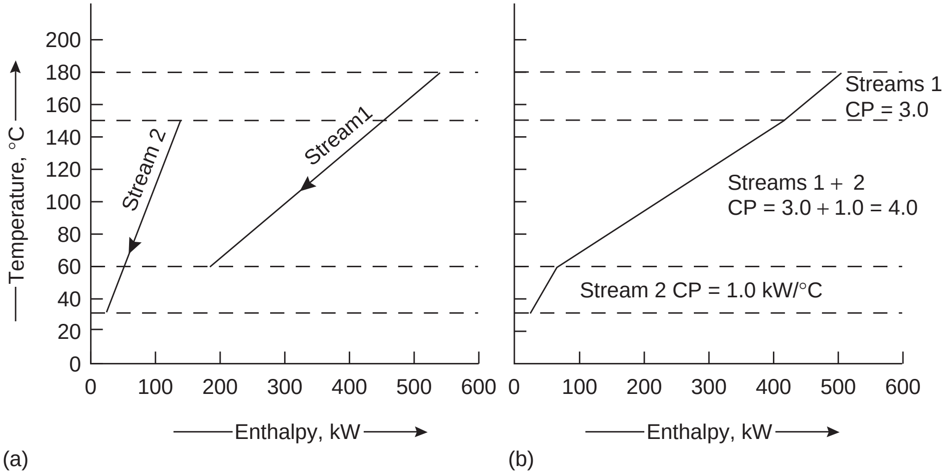


Figure 3.21. Hot stream temperature vs. enthalpy. (a) Separate hot streams. (b) Composite hot streams.

As Figure 3.21a, shows changes in the enthalpy of the streams, it does not matter where a particular curve is plotted on the enthalpy axis, as long as the curve runs between the correct temperatures. This means that where more than one stream appears in a temperature interval, the stream heat capacities can be added to form a composite curve, as shown in Figure 3.21b.

In Figure 3.22, the composite curve for the hot streams and the composite curve for the cold streams are drawn with a minimum temperature difference, the displacement between the curves, of 10°C. This implies that in any of the exchangers to be used in the network, the temperature difference between the streams will not be less than 10°C.

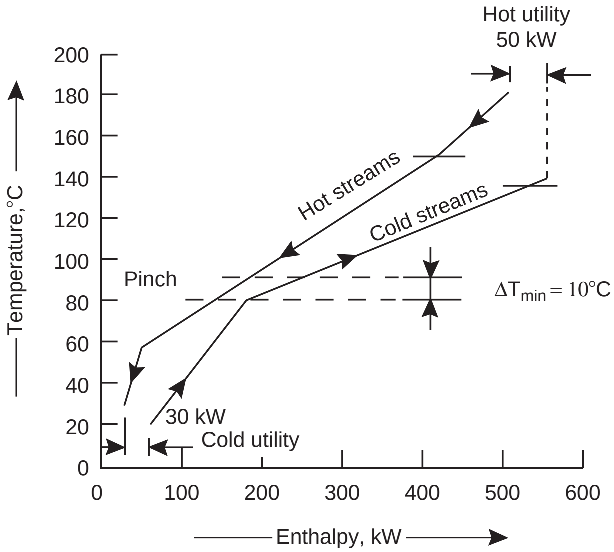


Figure 3.22. Hot and cold stream composite curves.

As for the two-stream problem, the overlap of the composite curves gives a target for heat recovery, and the displacements of the curves at the top and bottom of the diagram give the hot and cold utility requirements. These will be the minimum values needed to satisfy the target temperatures. This is valuable information. It gives the designer target values for the utilities to aim for when designing the exchanger network. Any design can be compared with the minimum utility requirements to check if further improvement is possible.

In most exchanger networks the minimum temperature difference will occur at only one point. This is termed the *pinch*. In the problem being considered, the pinch occurs at between 90°C on the hot stream curve and 80°C on the cold stream curve.

For multistream problems, the pinch will usually occur somewhere in the middle of the composite curves, as illustrated in Figure 3.22. The case when the pinch occurs at the end of one of the composite curves is termed a *threshold problem* and is discussed in Section 3.17.5.

Thermodynamic Significance of the Pinch

The pinch divides the system into two distinct thermodynamic regions. The region above the pinch can be considered a heat sink, with heat flowing into it, from the hot utility, but no heat flowing out of it. Below the pinch the converse is true. Heat flows out of the region to the cold utility. No heat flows across the pinch, as shown in Figure 3.23a.

If a network is designed in which heat is transferred from any hot stream at a temperature above the pinch (including hot utilities) to any cold stream at a temperature below the pinch (including cold utilities), then heat is transferred across the

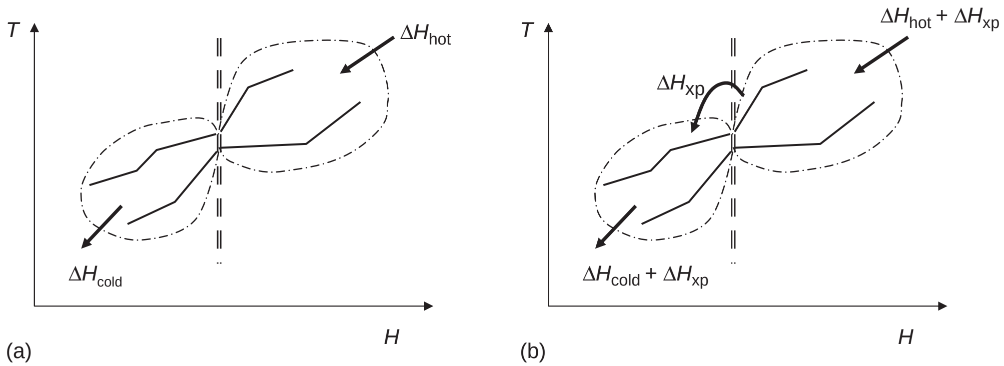


Figure 3.23. (a,b) Pinch decomposition.

pinch. If the amount of heat transferred across the pinch is ΔH_{xp}, then in order to maintain energy balance, the hot utility and cold utility must both be increased by ΔH_{xp}, as shown in Figure 3.23b. Cross-pinch heat transfer thus always leads to consumption of both hot and cold utilities that is greater than the minimum values that could be achieved.

The pinch decomposition is very useful in heat exchanger network design, as it decomposes the problem into two smaller problems. It also indicates the region where heat transfer matches are most constrained, at or near the pinch. When multiple hot or cold utilities are used, there may be other pinches, termed *utility pinches*, that cause further problem decomposition. Problem decomposition can be exploited in algorithms for automatic heat exchanger network synthesis.

3.17.2. The Problem Table Method

The problem table is a numerical method for determining the pinch temperatures and the minimum utility requirements, introduced by Linnhoff and Flower (1978). It eliminates the sketching of composite curves, which can be useful if the problem is being solved manually. It is not widely used in industrial practice any more, due to the wide availability of computer tools for pinch analysis (see Section 3.17.7).

The procedure is as follows:

1. Convert the actual stream temperatures, T_{act}, into interval temperatures, T_{int}, by subtracting half the minimum temperature difference from the hot stream temperatures and by adding half to the cold stream temperatures:

$$\text{hot streams } T_{\mathrm{int}} = T_{\mathrm{act}} - \frac{\Delta T_{\mathrm{min}}}{2}$$

$$\text{cold streams } T_{\mathrm{int}} = T_{\mathrm{act}} + \frac{\Delta T_{\mathrm{min}}}{2}$$

The use of the interval temperature rather than the actual temperatures allows the minimum temperature difference to be taken into account. $\Delta T_{\min} = 10^{\circ}\mathrm{C}$ for the problem being considered; see Table 3.3.

2. Note any duplicated interval temperatures. These are bracketed in Table 3.3.
3. Rank the interval temperatures in order of magnitude, showing the duplicated temperatures only once in the order; see Table 3.4.
4. Carry out a heat balance for the streams falling within each temperature interval.

For the n^{th} interval:

$$\Delta H_n = (\Sigma CP_c - \Sigma CP_h)(\Delta T_n)$$

where

ΔH_n = net heat required in the n^{th} interval;
ΣCP_c = sum of the heat capacities of all the cold streams in the interval;
ΣCP_h = sum of the heat capacities of all the hot streams in the interval;
ΔT_n = interval temperature difference = $(T_{n-1} - T_n)$.

See Table 3.5.

5. "Cascade" the heat surplus from one interval to the next down the column of interval temperatures; see Figure 3.24a.

Cascading the heat from one interval to the next implies that the temperature difference is such that the heat can be transferred between the hot and cold streams. The presence of a negative value in the column indicates that the

Table 3.3. Interval Temperatures for $\Delta T_{min} = 10^{\circ}\mathrm{C}$

Stream	Actual Temperature		Interval Temperature	
1	180	60	175	55
2	150	30	145	25
3	20	135	(25)	140
4	80	140	85	(145)

Table 3.4. Ranked Order of Interval Temperatures

Rank	Interval ΔT_n °C	Streams in Interval
175°C		
145	30	− 1
140	5	4 − (2 + 1)
85	55	(3 + 4) − (1 + 2)
55	30	3 − (1 + 2)
25	30	3 − 2

Note: Duplicated temperatures are omitted. The interval ΔT and streams in the intervals are included, as they are needed for Table 3.5.

Table 3.5. Problem Table

Interval	Interval Temp. °C	ΔT_n °C	$\Sigma CP_c - CP_h$* ←kW°C	ΔH kW	Surplus or Deficit
	175				
1	145	30	−3.0	−90	s
2	140	5	0.5	2.5	d
3	85	55	2.5	137.5	d
4	55	30	−2.0	−60	s
5	25	30	1.0	30	d

**Note:* The streams in each interval are given in Table 3.4.

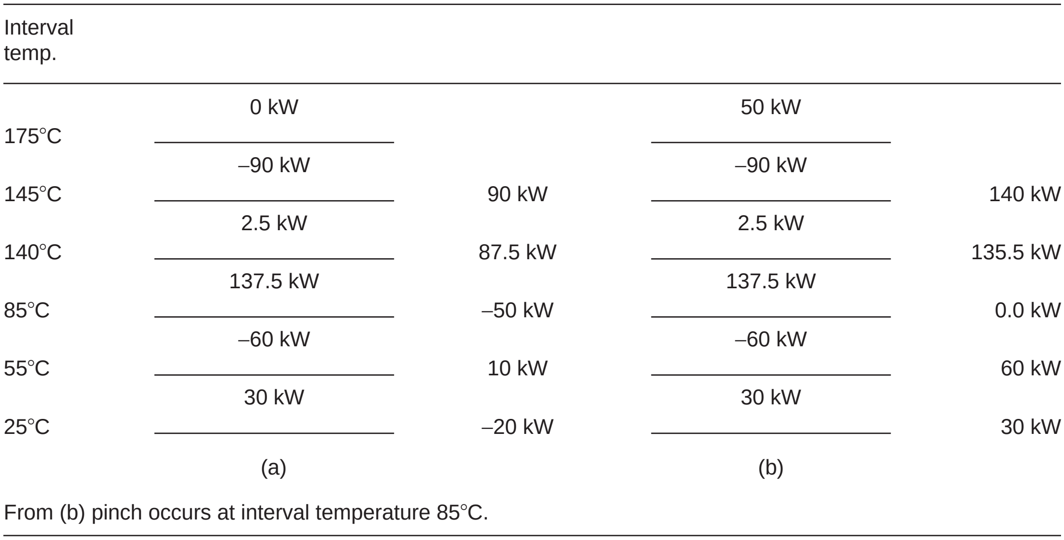


Figure 3.24. (a, b) Heat cascade.

temperature gradient is in the wrong direction and that the exchange is not thermodynamically possible.

This difficulty can be overcome if heat is introduced into the top of the cascade.

6. Introduce just enough heat to the top of the cascade to eliminate all the negative values; see Figure 3.24b.

Comparing the composite curve, Figure 3.22, with Figure 3.24b shows that the heat introduced to the cascade is the minimum hot utility requirement, and the heat removed at the bottom is the minimum cold utility required. The pinch occurs in Figure 3.24b where the heat flow in the cascade is zero. This is as would be expected from the rule that for minimum utility requirements no heat flows across the pinch. In Figure 3.24b the pinch is at an interval temperature of 85°C, corresponding to a cold stream temperature of 80°C and a hot stream temperature of 90°C, as was found using the composite curves.

It is not necessary to draw up a separate cascade diagram. This was done in Figure 3.24 to illustrate the principle. The cascaded values can be added to the problem table as two additional columns; see Example 3.16.

Summary

For maximum heat recovery and minimum use of utilities:

1. Do not transfer heat across the pinch.
2. Do not use hot utilities below the pinch.
3. Do not use cold utilities above the pinch.

3.17.3. Heat Exchanger Network Design

Grid Representation

It is convenient to represent a heat exchanger network as a grid; see Figure 3.25. The process streams are drawn as horizontal lines, with the stream numbers shown in square boxes. Hot streams are drawn at the top of the grid and flow from left to right. The cold streams are drawn at the bottom and flow from right to left. The stream heat capacities *CP* are shown in a column at the end of the stream lines.

Heat exchangers are drawn as two circles connected by a vertical line. The circles connect the two streams between which heat is being exchanged, that is, the streams that would flow through the actual exchanger. Heaters and coolers can be drawn as a single circle, connected to the appropriate utility. If multiple utilities are used, then these can also be shown as streams. Exchanger duties are usually marked under the exchanger, and temperatures are also sometimes indicated on the grid diagram.

Network Design for Maximum Energy Recovery

The analysis carried out in Figure 3.22 and Figure 3.24 has shown that the minimum utility requirements for the problem set out in Table 3.2 are 50 kW of the hot and 30 kW of the cold utility, and that the pinch occurs where the cold streams are at 80°C and the hot streams are at 90°C.

The grid representation of the streams is shown in Figure 3.26. The vertical dotted lines represent the pinch and separate the grid into the regions above and below the pinch. Note that the hot and cold streams are offset at the pinch because of the difference in pinch temperature.

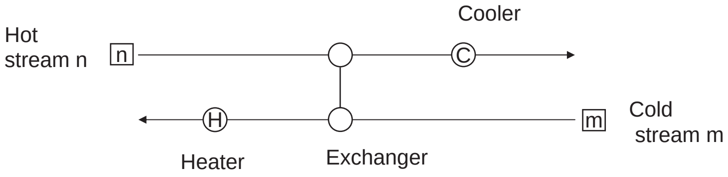


Figure 3.25. Grid representation.

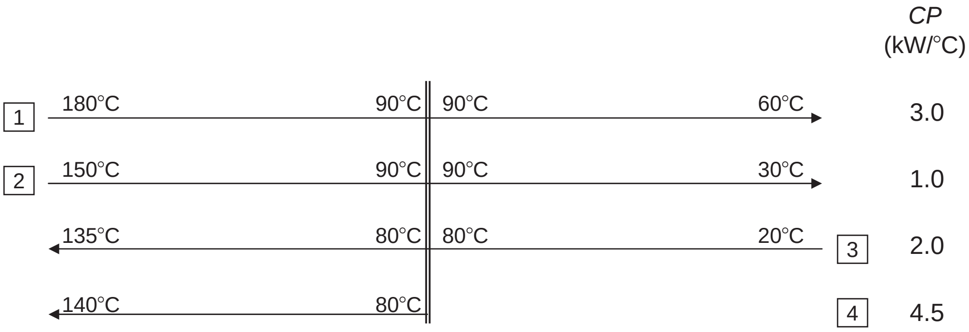


Figure 3.26. Grid for four-stream problem.

For maximum energy recovery (minimum utility consumption), the best performance is obtained if no cooling is used above the pinch. This means that the hot streams above the pinch should be brought to the pinch temperature solely by exchange with the cold streams. The network design is therefore started at the pinch, finding feasible matches between streams to fulfill this aim. In making a match adjacent to the pinch, the heat capacity *CP* of the hot stream must be equal to or less than that of the cold stream. This is to ensure that the minimum temperature difference between the curves is maintained. The slope of a line on the temperature-enthalpy diagram is equal to the reciprocal of the heat capacity. So, above the pinch the lines will converge if CP_{hot} exceeds CP_{cold} and as the streams start with a separation at the pinch equal to $\Delta T_{\min}$, the minimum temperature condition would be violated. Every hot stream must be matched with a cold stream immediately above the pinch; otherwise, it will not be able to reach the pinch temperature.

Below the pinch the procedure is the same, the aim being to bring the cold streams to the pinch temperature by exchange with the hot streams. For streams adjacent to the pinch, the criterion for matching streams is that the heat capacity of the cold stream must be equal to or greater than the hot stream, to avoid breaking the minimum temperature difference condition. Every cold stream must be matched with a hot stream immediately below the pinch.

Network Design Above the Pinch

$$CP_{\text{h}} \leq CP_{\text{c}}$$

1. Applying this condition at the pinch, stream 1 can be matched with stream 4, but not with 3.

   Matching streams 1 and 4 and transferring the full amount of heat required to bring stream 1 to the pinch temperature gives

$$\Delta H_{\text{ex}} = CP(T_s - T_{\text{pinch}})$$
$$\Delta H_{\text{ex}} = 3.0(180 - 90) = 270\,\text{kW}$$

This will also satisfy the heat load required to bring stream 4 to its target temperature:

$$\Delta H_{\text{ex}} = 4.5(140 - 80) = 270\,\text{kW}$$

2. Stream 2 can be matched with stream 3, while satisfying the heat capacity restriction. Transferring the full amount to bring stream 2 to the pinch temperature:

$$\Delta H_{\text{ex}} = 1.0(150 - 90) = 60\,\text{kW}$$

3. The heat required to bring stream 3 to its target temperature, from the pinch temperature, is

$$\Delta H = 2.0(135 - 80) = 110\,\text{kW}$$

So, a heater will have to be included to provide the remaining heat load:

$$\Delta H_{\text{hot}} = 110 - 60 = 50\,\text{kW}$$

This checks with the value given by the problem table, Figure 3.24b.

The proposed network design above the pinch is shown in Figure 3.27.

Network Design Below the Pinch

$$CP_{\text{h}} \geq CP_{\text{c}}$$

1. Stream 4 begins at the pinch temperature, $T_s = 80°\text{C}$, and so is not available for any matches below the pinch.
2. A match between streams 1 and 3 adjacent to the pinch will satisfy the heat capacity restriction but not one between streams 2 and 3. So, 1 is matched with 3, transferring the full amount to bring stream 1 to its target temperature:

$$\Delta H_{\text{ex}} = 3.0(90 - 60) = 90\,\text{kW}$$

3. Stream 3 requires more heat to bring it to the pinch temperature; amount needed:

$$\Delta H = 2.0(80 - 20) - 90 = 30\,\text{kW}$$

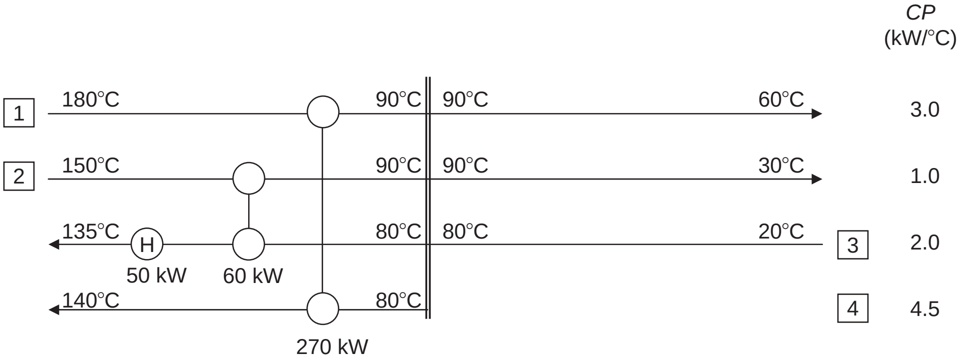


Figure 3.27. Network design above the pinch.

This can be provided from stream 2, as the match is now away from the pinch. The rise in temperature of stream 3 will be given by

$$\Delta T = \Delta H / CP$$

So transferring 30 kW will raise the temperature from the source temperature to

$$20 + 30/2.0 = 35^\circ\mathrm{C}$$

and this gives a stream temperature difference on the outlet side of the exchanger of

$$90 - 35 = 55^\circ\mathrm{C}$$

So, the minimum temperature difference condition, 10°C, will not be violated by this match.

4. Stream 2 needs further cooling to bring it to its target temperature, so a cooler must be included; cooling required:

$$\Delta H_{\mathrm{cold}} = 1.0(90 - 30) - 30 = 30\,\mathrm{kW}$$

This is the amount of the cold utility predicted by the problem table.

The proposed network for maximum energy recovery is shown in Figure 3.28.

Stream Splitting

If the heat capacities of streams are such that it is not possible to make a match at the pinch without violating the minimum temperature difference condition, then the heat capacity can be altered by splitting a stream. Dividing the stream will reduce the mass flow rates in each leg and hence the heat capacities. This is illustrated in Example 3.16.

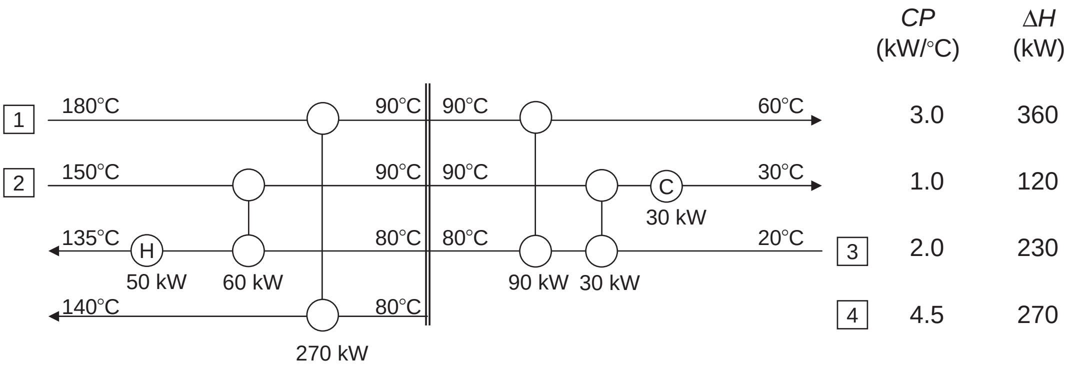


Figure 3.28. Proposed heat exchanger network for $\Delta T_{\min} = 10^\circ\mathrm{C}$.

Similarly, if not enough streams are available to make all of the required matches at the pinch, then streams with large *CP* can be split to increase the number of streams.

Guide rules for stream matching and splitting are given in the Institution of Chemical Engineers Guide, IChemE (1994) and by Smith (2005).

Summary

The guide rules for devising a network for maximum heat recovery are given below:

1. Divide the problem at the pinch.
2. Design away from the pinch.
3. Above the pinch match streams adjacent to the pinch, meeting the restriction:

$$CP_h \leq CP_c$$

4. Below the pinch match streams adjacent to the pinch, meeting the restriction:

$$CP_h \geq CP_c$$

5. If the stream matching criteria cannot be satisfied, split a stream.
6. Maximize the exchanger heat loads.
7. Supply external heating only above the pinch and external cooling only below the pinch.

3.17.4. Minimum Number of Exchangers

The network shown in Figure 3.28 was designed to give the maximum heat recovery and will therefore give the minimum consumption, and cost, of the hot and cold utilities.

This will not necessarily be the optimum design for the network. The optimum design will be that which gives the lowest total annualized cost, taking into account the capital cost of the system, in addition to the utility and other operating costs. The number of exchangers in the network and their size will determine the capital cost.

In Figure 3.28 it is clear that there is scope for reducing the number of exchangers. The 30 kW exchanger between streams 2 and 3 can be deleted and the heat loads of the cooler and heater increased to bring streams 2 and 3 to their target temperatures. Heat would cross the pinch, and the consumption of the utilities would be increased. Whether the revised network would be better, or more economic, depends on the relative cost of capital and utilities and the operability of each design. For any network, there will be an optimum design that gives the least annual cost: capital charges plus utility and other operating costs. The estimation of capital and operating costs is covered in Chapter 6.

To find the optimum design, it is necessary to cost a number of alternative designs, seeking a compromise between the capital costs, determined by the number and size of the exchangers, and the utility costs, determined by the heat recovery achieved.

For simple networks Holmann (1971) has shown that the minimum number of exchangers is given by

$$Z_{min} = N' - 1 \tag{3.41}$$

where

Z_{min} = minimum number of exchangers needed, including heaters and coolers;
N' = the number of streams, including the utilities.

For complex networks a more general expression is needed to determine the minimum number of exchangers:

$$Z_{\text{min}} = N' + L' - S \tag{3.42}$$

where

L' = the number of internal loops present in the network;
S = the number of independent branches (subsets) that exist in the network.

A loop exists where a closed path can be traced through the network. There is a loop in the network shown in Figure 3.28. The loop is shown by itself in Figure 3.29. The presence of a loop indicates that there is scope for reducing the number of exchangers.

For a full discussion of equation 3.42 and its applications, see Linnhoff et al. (1979), IChemE (1994), and Smith (2005).

In summary, to seek the optimum design for a network

1. Start with the design for maximum heat recovery. The number of exchangers needed will be equal to or less than the number for maximum energy recovery.
2. Identify loops that cross the pinch. The design for maximum heat recovery will usually contain loops.
3. Starting with the loop with the least heat load, break the loops by adding or subtracting heat.
4. Check that the specified minimum temperature difference ΔT_{min} has not been violated. If the violation is significant, revise the design as necessary to restore ΔT_{min}. If the violation is small, then it may not have much impact on the total annualized cost and can be ignored.
5. Estimate the capital and operating costs and the total annual cost.
6. Repeat the loop breaking and network revision to find the lowest cost design.
7. Consider the safety, operability, and maintenance aspects of the proposed design.

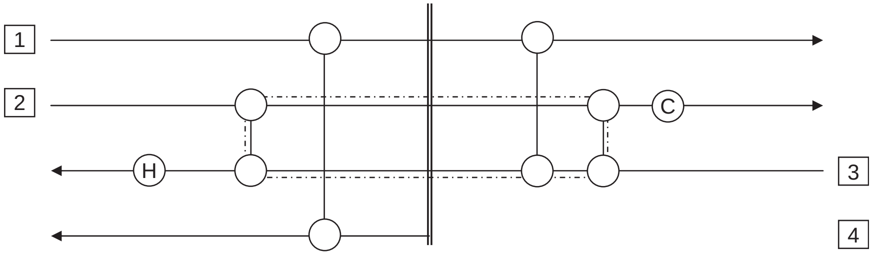


Figure 3.29. Loop in network.

3.17.5. Threshold Problems

Problems that show the characteristic of requiring only either a hot utility or a cold utility (but not both) over a range of minimum temperature differences, from zero up to a threshold value, are known as threshold problems. A threshold problem is illustrated in Figure 3.30.

To design the heat exchanger network for a threshold problem, it is normal to start at the most constrained point. The problem can often be treated as one half of a problem exhibiting a pinch.

Threshold problems are often encountered in the process industries. A pinch can be introduced in such problems if multiple utilities are used, as in the recovery of heat to generate steam, or if the chosen value of $\Delta T_{\min}$ is greater than the threshold value.

The procedures to follow in the design of threshold problems are discussed by Smith (2005) and IChemE (1994).

3.17.6. Process Integration: Integration of Other Process Operations

The pinch technology method can give many other insights into process synthesis, beyond the design of heat exchanger networks. The method can also be applied to the integration of other process units, such as separation columns, reactors, compressors and expanders, boilers, and heat pumps. The wider applications of pinch technology are discussed in the Institution of Chemical Engineers Guide, IChemE (1994) and by Smith (2005).

The techniques of process integration have been expanded for use in optimizing mass transfer operations and have been applied in waste reduction, water conservation, and pollution control; see Dunn and El-Halwagi (2003).

3.17.7. Computer Tools for Heat Exchanger Network Design

Most pinch analysis in industry is carried out using commercial pinch analysis software. Programs such as Aspen HX-Net$^{\text{TM}}$ (Aspen Technology Inc.), SUPERTARGET$^{\text{TM}}$

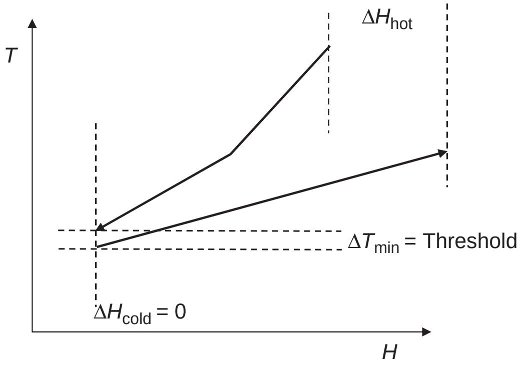


Figure 3.30. Threshold problem.

(Linnhoff March Ltd.), and UniSim ExchangerNet^{TM} (Honeywell Inc.) allow the design engineer to plot composite curves, optimize $\Delta T_{\min}$, set targets for multiple utilities, and design the heat exchanger network.

Most of these programs are able to automatically extract stream data from process simulation programs, although great care should be taken to check the extracted data. There are many possible pitfalls in data extraction; for example, not recognizing changes in the *CP* of a stream or partial vaporization or condensation of a stream, any of which could lead to a kink in the stream *T-H* profile. See Smith (2005) for more information on data extraction.

The commercial pinch technology tools also usually include automatic heat exchanger network synthesis features. The automatic synthesis methods are based on MINLP optimization of superstructures of possible exchanger options (see Chapter 1 for discussion of MINLP methods). These tools can be used to arrive at a candidate network, but the optimization must be properly constrained so that it does not introduce a large number of stream splits and add a lot of small exchangers. Experienced designers seldom use automatic heat exchanger network synthesis methods, as it usually requires more effort to turn the resulting network into something practical than it would take to design a practical network manually. The NLP optimization capability of the software is widely used though, for fine-tuning the network temperatures by exploitation of loops and stream split ratios.

Example 3.16

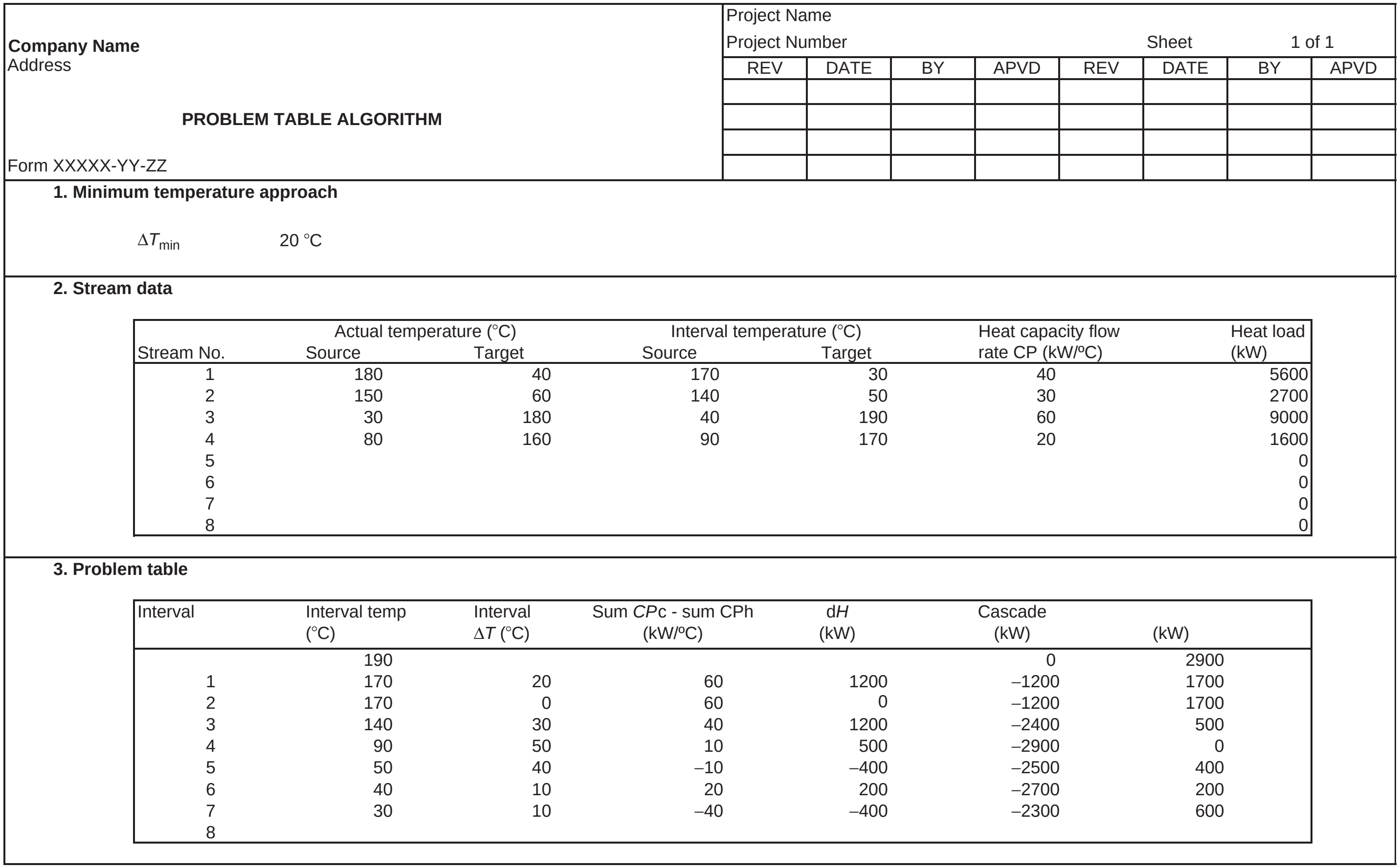
Determine the pinch temperatures and the minimum utility requirements for the streams set out in the following table, for a minimum temperature difference between the streams of 20°C. Devise a heat exchanger network to achieve the maximum energy recovery.

Stream Number	Type	Heat Capacity Flow Rate kW/°C	Source Temp. °C	Target Temp. °C	Heat Load kW
1	hot	40.0	180	40	5600
2	hot	30.0	150	60	1800
3	cold	60.0	30	180	9000
4	cold	20.0	80	160	1600

Solution

The problem table to find the minimum utility requirements and the pinch temperature can be built in a spreadsheet. The calculations in each cell are repetitive, and the formula can be copied from cell to cell using the cell copy commands. A spreadsheet template for the problem table algorithm is available in MS Excel format in the online material at http://books.elsevier.com/companions. The use of the spreadsheet is illustrated in Figure 3.31 and described here.

First, calculate the interval temperatures, for $\Delta T_{\min} = 20°\text{C}$
hot streams $T_{\text{int}} = T_{\text{act}} - 10°\text{C}$
cold streams $T_{\text{int}} = T_{\text{act}} + 10°\text{C}$



Company Name
Address

PROBLEM TABLE ALGORITHM

Form XXXXX-YY-ZZ

Project Name
Project Number Sheet 1 of 1

REV	DATE	BY	APVD	REV	DATE	BY	APVD

1. Minimum temperature approach

$\Delta T_{\min}$ 20 °C

2. Stream data

Stream No.	Actual temperature (°C) Source	Target	Interval temperature (°C) Source	Target	Heat capacity flow rate CP (kW/ºC)	Heat load (kW)
1	180	40	170	30	40	5600
2	150	60	140	50	30	2700
3	30	180	40	190	60	9000
4	80	160	90	170	20	1600
5						0
6						0
7						0
8						0

3. Problem table

Interval	Interval temp (°C)	Interval ΔT (°C)	Sum CPc - sum CPh (kW/ºC)	dH (kW)	Cascade (kW)	(kW)
	190				0	2900
1	170	20	60	1200	–1200	1700
2	170	0	60	0	–1200	1700
3	140	30	40	1200	–2400	500
4	90	50	10	500	–2900	0
5	50	40	–10	–400	–2500	400
6	40	10	20	200	–2700	200
7	30	10	–40	–400	–2300	600
8						

Figure 3.31. Problem table algorithm spreadsheet.

	Actual Temp. °C		Interval Temp. °C	
Stream	Source	Target	Source	Target
1	180	40	170	30
2	150	60	140	50
3	30	180	40	190
4	80	160	90	170

In the spreadsheet this can be done by using an IF function to determine whether the source temperature is larger than the target temperature, in which case the stream is a cold stream and should have $\Delta T_{\mathrm{min}}/2$ added.

Next, rank the interval temperatures, ignoring any duplicated values. In the spreadsheet this is done using the LARGE function. Determine which streams occur in each interval. For a stream to be present in a given interval, the largest stream interval temperature must be greater than the lower end of the interval range, and the lowest stream interval temperature must also be greater than or equal to the lower end of the interval range. This can be calculated in the spreadsheet using IF, AND, and OR functions. Once the streams in each interval have been determined, it is possible to calculate the combined stream heat capacities. These calculations are not strictly part of the problem table, so they have been hidden in the spreadsheet (in columns to the right of the table).

The sum of CP values for the cold streams minus that for the hot streams can then be multiplied by the interval ΔT to give the interval ΔH, and the interval ΔH values can be cascaded to give the overall heat flow. The amount of heat that must be put in to prevent the heat flow from becoming negative is the lowest value in the column, which can be found using the SMALL function. The final column then gives a cascade showing only positive values, with zero energy cascading at the pinch temperature.

In the last column 2900 kW of heat have been added to eliminate the negative values in the previous column; so the hot utility requirement is 2900 kW, and the cold utility requirement, the bottom value in the column, is 600 kW.

The pinch occurs where the heat transferred is zero, that is, at interval number 4, interval temperature 90°C.

So at the pinch hot streams will be at

$$90 + 10 = 100^{\circ}\mathrm{C}$$

and the cold streams will be at

$$90 - 10 = 80^{\circ}\mathrm{C}$$

Note that in the table both stream 1 and stream 4 had an interval temperature of 170°C, which led to a duplicate line in the list of ranked interval temperatures. Strictly, this line could have been eliminated, but since it gave a zero value for the ΔT, it did not affect the calculation. The programming of the spreadsheet is a lot easier if duplicate temperatures are handled in this manner.

To design the network for maximum energy recovery, start at the pinch and match streams, following the rules on stream heat capacities for matches adjacent to the pinch. Where a match is made, transfer the maximum amount of heat.

The proposed network is shown in Figure 3.32.

The methodology followed in devising this network was as follows:

Above Pinch

1. $CP_h \leq CP_c$
2. Can match stream 1 or 2 with stream 3, but neither stream can match with stream 4. This creates a problem, since if we match stream 1 with 3, then stream 2 will not be able to make a match at the pinch. Likewise, if we match stream 2 with 3, then stream 1 will not be able to make a match at the pinch.
3. Check the heat available in bringing the hot streams to the pinch temperature:

$$\begin{aligned} &\text{stream 1} \quad \Delta H = 40.0(180 - 100) = 3200\,\text{kW} \\ &\text{stream 2} \quad \Delta H = 30.0(150 - 100) = 1500\,\text{kW} \end{aligned}$$

4. Check the heat required to bring the cold streams from the pinch temperature to their target temperatures:

$$\begin{aligned} &\text{stream 3} \quad \Delta H = 60.0(180 - 80) = 6000\,\text{kW} \\ &\text{stream 4} \quad \Delta H = 20.0(160 - 80) = 1600\,\text{kW} \end{aligned}$$

5. If we split stream 3 into two branches with *CP* of 40.0 and 20.0, then we can match the larger branch with stream 1 and transfer 3200 kW, which satisfies (ticks off) stream 1.
6. We now have two cold streams, both with *CP* of 20.0 and one hot stream (2) with *CP* of 30.0. We need to split stream 2 into two branches. As an initial guess, these can both have *CP* of 15.0. We can then match one branch of stream 2 with the smaller branch of 4 and transfer 750 kW, and the other branch with stream 3, also for 750 kW, which then ticks off stream 2.

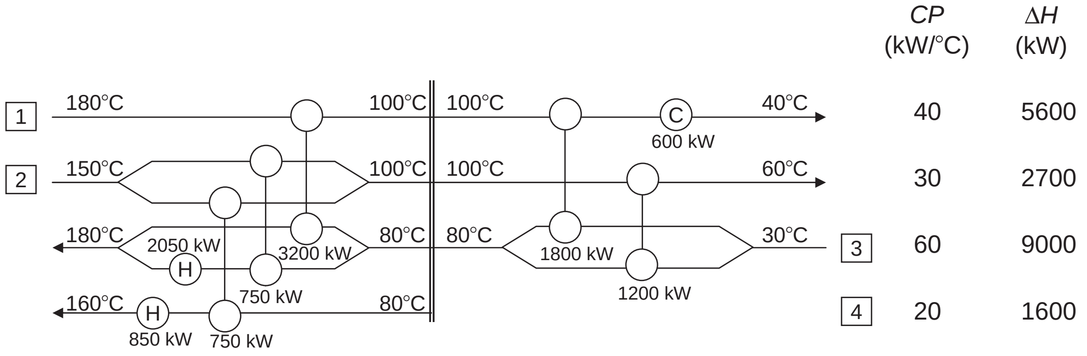


Figure 3.32. Proposed heat exchanger network for Example 3.17.

7. Include a heater on the smaller branch of stream 3 to provide the balance of the heat required:

$$\Delta H_{\text{hot}} = 6000 - 3200 - 750 = 2050\,\text{kW}$$

8. Include a heater on stream 4 to provide the balance of the heat required:

$$\Delta H_{\text{hot}} = 1600 - 750 = 850\,\text{kW}$$

Check sum of heater duties = 2050 + 850 = 2900 kW = hot utility target.

Below Pinch

9. $CP_{\text{h}} \geq CP_{\text{c}}$
10. Note that stream 4 starts at the pinch temperature so cannot provide any cooling below the pinch.
11. Cannot match stream 1 or 2 with stream 3 at the pinch.
12. Split stream 3 to reduce *CP.*
13. Check the heat available from bringing the hot streams from the pinch temperature to their target temperatures:

$$\text{stream 1} \quad \Delta H = 40.0(100 - 40) = 2400\,\text{kW}$$
$$\text{stream 2} \quad \Delta H = 30.0(100 - 60) = 1200\,\text{kW}$$

14. Check the heat required to bring the cold streams from their source temperatures to the pinch temperature:

$$\text{stream 3} \quad \Delta H = 60.0(80 - 30) = 3000\,\text{kW}$$

stream 4 is at the pinch temperature.

15. Note that stream 1 cannot be brought to its target temperature of 40°C by full interchange with stream 3, as the source temperature of stream 3 is 30°C, so ΔT_{min} would be violated. So transfer 1800 kW to one leg of the split stream 3.
16. Check temperature at exit of this exchanger:

$$\text{Temp out} = 100 - \frac{1800}{40} = 55^{\circ}\text{C, satisfactory}$$

17. Provide cooler on stream 1 to bring it to its target temperature, cooling needed:

$$\Delta H_{\text{cold}} = 2400 - 1800 = 600\,\text{kW}$$

18. Transfer the full heat load from stream 2 to second leg of stream 3; this satisfies both streams.

Note that the heating and cooling loads, 2900 kW and 600 kW, respectively, match those predicted from the problem table.

Note also that in order to satisfy the pinch decomposition and the stream matching rules, we ended up introducing a large number of stream splits. This is quite common in heat exchanger network design. None of the three split fractions were optimized, so substantial savings as well as simplification of the network could be possible. For example, loops exist between the branches of stream 3 and stream 1 and between the branches of stream 3 and stream 2. With the current split ratios, these loops cannot be eliminated, but with other ratios, it might be possible to eliminate one or two exchangers.

The introduction of multiple stream splits is often cited as a drawback of the pinch method. Stream splits can be problematic in process operation. For example, when an oil or other multicomponent stream is heated and partially vaporized, then the stream is a two-phase mixture. It is difficult to control the splitting of such streams to give the required flow rate in each branch. Experienced designers usually constrain the network to avoid multiple stream splits whenever possible, even if this leads to designs that have higher than minimum utility consumption.

3.18. REFERENCES

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3.19. NOMENCLATURE

		Dimensions in **MLTθ**
A	Area	$\mathbf{L}^2$
a	Constant in specific heat equation (equation 3.13)	$\mathbf{L}^2\mathbf{T}^{-2}\boldsymbol{\theta}^{-1}$
B	Bottoms flow rate	$\mathbf{M}\mathbf{T}^{-1}$
b	Constant in specific heat equation (equation 3.13)	$\mathbf{L}^2\mathbf{T}^{-2}\boldsymbol{\theta}^{-2}$
CP	Stream heat capacity flow rate	$\mathbf{M}\mathbf{L}^2\mathbf{T}^{-2}\boldsymbol{\theta}^{-1}$
CP_c	Stream heat capacity flow rate, cold stream	$\mathbf{M}\mathbf{L}^2\mathbf{T}^{-2}\boldsymbol{\theta}^{-1}$
CP_h	Stream heat capacity flow rate, hot stream	$\mathbf{M}\mathbf{L}^2\mathbf{T}^{-2}\boldsymbol{\theta}^{-1}$
C_p	Specific heat at constant pressure	$\mathbf{L}^2\mathbf{T}^{-2}\boldsymbol{\theta}^{-1}$

		Dimensions in $\mathbf{MLT\theta}$
C_{pa}	Specific heat component *a*	$L^{2}T^{-2}\theta^{-1}$
C_{pb}	Specific heat component *b*	$L^{2}T^{-2}\theta^{-1}$
C_{pc}	Specific heat component *c*	$L^{2}T^{-2}\theta^{-1}$
C_{pm}	Mean specific heat	$L^{2}T^{-2}\theta^{-1}$
C_{p1}	Specific heat first phase	$L^{2}T^{-2}\theta^{-1}$
C_{p2}	Specific heat second phase	$L^{2}T^{-2}\theta^{-1}$
C_{v}	Specific heat at constant volume	$L^{2}T^{-2}\theta^{-1}$
C_{p}°	Ideal gas state specific heat	$L^{2}T^{-2}\theta^{-1}$
c	Constant in specific heat equation (equation 3.13)	$L^{2}T^{-2}\theta^{-3}$ or $L^{2}T^{-2}\theta^{-1/2}$
ΣCP_{c}	Sum of heat capacity flow rates of cold streams	$ML^{2}T^{-2}\theta^{-1}$
ΣCP_{h}	Sum of heat capacity flow rates of hot streams	$ML^{2}T^{-2}\theta^{-1}$
D	Distillate flow rate	MT^{-1}
E_{e}	Efficiency, electric motors	—
E_{p}	Polytropic efficiency, compressors and turbines	—
F	Force	MLT^{-2}
g	Gravitational acceleration	LT^{-2}
H	Enthalpy	$ML^{2}T^{-2}$
H_{a}	Specific enthalpy of component *a*	$L^{2}T^{-2}$
H_{B}	Enthalpy of bottom product stream (Example 3.1)	$ML^{2}T^{-3}$
H_{b}	Specific enthalpy of component *b*	$L^{2}T^{-2}$
H_{D}	Enthalpy of distillate stream (Example 3.1)	$ML^{2}T^{-3}$
H_{F}	Enthalpy feed stream (Example 3.1)	$ML^{2}T^{-3}$
H_{products}	Total enthalpy of products	$ML^{2}T^{-3}$
$H_{\mathrm{reactants}}$	Total enthalpy of reactants	$ML^{2}T^{-3}$
H_{T}	Specific enthalpy at temperature *T*	$L^{2}T^{-2}$
H_{V}	Enthalpy of vapor stream (Example 3.1)	$ML^{2}T^{-3}$
ΔH	Change in enthalpy	$ML^{2}T^{-2}$
ΔH_{cold}	Heat transfer from cold utility	$ML^{2}T^{-3}$
ΔH_{ex}	Heat transfer in exchanger	$ML^{2}T^{-3}$
ΔH_{hot}	Heat transfer from hot utility	$ML^{2}T^{-3}$
ΔH_{n}	Net heat required in nth interval	$ML^{2}T^{-3}$
$\Delta H_{\mathrm{react.}}$	Enthalpy change to bring reactants to standard temperature	$ML^{2}T^{-3}$
ΔH_{p}	Latent heat of phase change	$L^{2}T^{-2}$

		Dimensions in $\mathbf{MLT\theta}$
$\Delta H_{\text{prod.}}$	Enthalpy change to bring products to standard temperature	$\mathbf{ML^{2}T^{-3}}$
ΔH_{xp}	Cross-pinch heat transfer	$\mathbf{ML^{2}T^{-3}}$
$-\Delta H_{m,t}$	Heat of mixing at temperature t	$\mathbf{L^{2}T^{-2}}$
$-\Delta H_{r,t}$	Heat of reaction at temperature t	$\mathbf{L^{2}T^{-2}}$
$-\Delta H_{c}^{\circ}$	Standard heat of combustion	$\mathbf{L^{2}T^{-2}}$
ΔH_{f}°	Standard enthalpy of formation	$\mathbf{L^{2}T^{-2}}$
$-\Delta H_{r}^{\circ}$	Standard heat of reaction	$\mathbf{L^{2}T^{-2}}$
$-\Delta H_{soln}^{\circ}$	Integral heat of solution	$\mathbf{L^{2}T^{-2}}$
L	Liquid flow rate	$\mathbf{MT^{-1}}$
L'	Number of internal loops in network	—
l	Distance	$\mathbf{L}$
M	Mass	$\mathbf{M}$
M_c	Moles of component c	$\mathbf{M}$
M_w	Molecular mass (weight)	—
m	Polytropic temperature exponent	—
m	Mass flow rate	$\mathbf{MT^{-1}}$
N	Number of cold streams, heat exchanger networks	—
N'	Number of streams	—
n	Expansion or compression index (equation 3.30)	—
n_i	Molar flow of component i	$\mathbf{MT^{-1}}$
P	Pressure	$\mathbf{ML^{-1}T^{-2}}$
P_c	Critical pressure	$\mathbf{ML^{-1}T^{-2}}$
P_i	Inter-stage pressure	$\mathbf{ML^{-1}T^{-2}}$
P_r	Reduced pressure	—
P_1	Initial pressure	$\mathbf{ML^{-1}T^{-2}}$
P_2	Final pressure	$\mathbf{ML^{-1}T^{-2}}$
Q	Heat transferred across system boundary	$\mathbf{ML^{2}T^{-2}}$ or $\mathbf{ML^{2}T^{-3}}$
Q_B	Reboiler heat load (Example 3.1)	$\mathbf{ML^{2}T^{-3}}$
Q_C	Condenser heat load (Example 3.1)	$\mathbf{ML^{2}T^{-3}}$
Q_p	Heat added (or subtracted) from a system	$\mathbf{ML^{2}T^{-2}}$ or $\mathbf{ML^{2}T^{-3}}$
Q_r	Heat from reaction	$\mathbf{ML^{2}T^{-2}}$ or $\mathbf{ML^{2}T^{-3}}$
Q_s	Heat generated in the system	$\mathbf{ML^{2}T^{-2}}$ or $\mathbf{ML^{2}T^{-3}}$
R	Reflux ratio (Example 3.1)	—

		Dimensions in **MLT$\boldsymbol{\theta}$**
R	Universal gas constant	$\mathbf{L^2T^{-2}\boldsymbol{\theta}^{-1}}$
S	Number of independent branches	—
T	Temperature, absolute	$\boldsymbol{\theta}$
T_1	Initial temperature	$\boldsymbol{\theta}$
T_2	Final temperature	$\boldsymbol{\theta}$
T_{act}	Actual stream temperature	$\boldsymbol{\theta}$
T_c	Critical temperature	$\boldsymbol{\theta}$
T_d	Datum temperature for enthalpy calculations	$\boldsymbol{\theta}$
T_{int}	Interval temperature	$\boldsymbol{\theta}$
T_n	Temperature in *n*th interval	$\boldsymbol{\theta}$
T_p	Phase-transition temperature	$\boldsymbol{\theta}$
T_{pinch}	Pinch temperature	$\boldsymbol{\theta}$
T_r	Reduced temperature	—
T_s	Source temperature	$\boldsymbol{\theta}$
T_t	Target temperature	$\boldsymbol{\theta}$
ΔT	Change in temperature	$\boldsymbol{\theta}$
ΔT_{min}	Minimum temperature difference (minimum approach) in heat exchanger	$\boldsymbol{\theta}$
ΔT_n	Internal temperature difference	$\boldsymbol{\theta}$
t	Temperature, relative scale	$\boldsymbol{\theta}$
$\mathbf{t}$	Time	$\mathbf{T}$
t_r	Reference temperature, mean specific heat	$\boldsymbol{\theta}$
t_s	Steam saturation temperature	$\boldsymbol{\theta}$
U	Internal energy per unit mass	$\mathbf{L^2T^{-2}}$
U_j	Jacket heat transfer coefficient	$\mathbf{MT^{-3}\boldsymbol{\theta}^{-1}}$
u	Velocity	$\mathbf{LT^{-1}}$
V	Vapor flow rate	$\mathbf{MT^{-1}}$
v	Volume per unit mass	$\mathbf{M^{-1}L^3}$
x	Distance	$\mathbf{L}$
x_a	Mole fraction component *a* in a mixture	—
x_b	Mole fraction component *b* in a mixture	—
x_c	Mole fraction component *c* in a mixture	—
W	Work per unit mass	$\mathbf{L^2T^{-2}}$
Z	Compressibility factor	—
z	Height above datum	$\mathbf{L}$
Z_{min}	Minimum number of heat exchangers in network	—
γ	Ratio of specific heats	—

3.20. PROBLEMS

3.1. A liquid stream leaves a reactor at a pressure of 100 bar. If the pressure is reduced to 3 bar in a turbine, estimate the maximum theoretical power that could be obtained from a flow rate of 1000 kg/h. The density of the liquid is 850 kg/m^3.

3.2. Calculate the specific enthalpy of water at a pressure of 1 bar and temperature of 200°C. Check your value using steam tables. The specific heat capacity of water can be calculated from the equation:

$$C_p = 4.2 - 2 \times 10^{-3} t; \text{ where } t \text{ is in } {}^\circ\text{C and } C_p \text{ in kJ/kg.}$$

Take the other data required from Appendix C.

3.3. A gas produced as a byproduct from the carbonization of coal has the following composition, mole percent: carbon dioxide 4, carbon monoxide 15, hydrogen 50, methane 12, ethane 2, ethylene 4, benzene 2, balance nitrogen. Using the data given in Appendix C, calculate the gross and net calorific values of the gas. Give your answer in MJ/m^3, at standard temperature and pressure.

3.4. In the manufacture of aniline, liquid nitrobenzene at 20°C is fed to a vaporizer where it is vaporized in a stream of hydrogen. The hydrogen stream is at 30°C, and the vaporizer operates at 20 bar. For feed rates of 2500 kg/h nitrobenzene and 366 kg/h hydrogen, estimate the heat input required. The nitrobenzene vapor is not superheated.

3.5. Aniline is produced by the hydrogenation of nitrobenzene. The reaction takes place in a fluidized bed reactor operating at 270°C and 20 bar. The excess heat of reaction is removed by a heat transfer fluid passing through tubes in the fluidized bed. Nitrobenzene vapor and hydrogen enter the reactor at a temperature of 260°C. A typical reactor off gas composition, mole percent, is aniline 10.73, cyclo-hexylamine 0.11, water 21.68, nitrobenzene 0.45, hydrogen 63.67, inerts (take as nitrogen) 3.66. Estimate the heat removed by the heat transfer fluid, for a feed rate of nitrobenzene to the reactor of 2500 kg/h.

The specific heat capacity of nitrobenzene can be estimated using the methods given in Chapter 8. Take the other data required from Appendix C.

3.6. Hydrogen chloride is produced by burning chlorine with an excess of hydrogen. The reaction is highly exothermic and reaches equilibrium very rapidly. The equilibrium mixture contains approximately 4% free chlorine, but this is rapidly combined with the excess hydrogen as the mixture is cooled. Below 200°C the conversion of chlorine is essentially complete.

The burner is fitted with a cooling jacket, which cools the exit gases to 200°C. The gases are further cooled, to 50°C, in an external heat exchanger.

For a production rate of 10,000 metric tons (tonnes) per year of hydrogen chloride, calculate the heat removed by the burner jacket and the heat removed in the external cooler. Take the excess hydrogen as 1% over stoichiometric. The hydrogen supply contains 5% inerts (take as nitrogen) and is fed to the burner at 25°C. The chlorine is essentially pure and is fed to the burner as a saturated vapor. The burner operates at 1.5 bar.

3.7. A supply of nitrogen is required as an inert gas for blanketing and purging vessels. After generation, the nitrogen is compressed and stored in a bank of cylinders, at a pressure of 5 barg. The inlet pressure to the compressor is 0.5 barg, and the temperature is 20°C. Calculate the maximum power required to compress 100 m^3/h. A single-stage reciprocating compressor will be used.

3.8. Hydrogen chloride gas, produced by burning chlorine with hydrogen, is required at a supply pressure of 600 kN/m^2, gauge. The pressure can be achieved by either operating the burner under pressure or by compressing the hydrogen chloride gas. For a production rate of hydrogen chloride of 10,000 kg/h, compare the power requirement of compressing the hydrogen supply to the burner with that to compress the product hydrogen chloride. The chlorine feed is supplied at the required pressure from a vaporizer. Both the hydrogen and chlorine feeds are essentially pure. Hydrogen is supplied to the burner one percent excess of the stoichiometric requirement.

A two-stage centrifugal compressor will be used for both duties. Take the polytropic efficiency for both compressors as 70%. The hydrogen supply pressure is 120 kN/m^2 and the temperature 25°C. The hydrogen chloride is cooled to 50°C after leaving the burner. Assume that the compressor intercooler cools the gas to 50°C, for both duties.

Which process would you select and why?

3.9. Estimate the work required to compress ethylene from 32 MPa to 250 MPa in a two-stage reciprocating compressor where the gas is initially at 30°C and leaves the intercooler at 30°C.

3.10. Determine the pinch temperature and the minimum utility requirements for the process set out here. Take the minimum approach temperature as 15°C. Devise a heat exchanger network to achieve maximum energy recovery.

Stream Number	Type	Heat Capacity kW/°C	Source Temp. °C	Target Temp. °C
1	hot	13.5	180	80
2	hot	27.0	135	45
3	cold	53.5	60	100
4	cold	23.5	35	120

3.11. Determine the pinch temperature and the minimum utility requirements for the process set out here. Take the minimum approach temperature as 15°C. Devise a heat exchanger network to achieve maximum energy recovery.

Stream Number	Type	Heat capacity kW/°C	Source Temp. °C	Target Temp.°C
1	hot	10.0	200	80
2	hot	20.0	155	50
3	hot	40.0	90	35
4	cold	30.0	60	100
5	cold	8.0	35	90

3.12. To produce a high purity product, two distillation columns are operated in series. The overhead stream from the first column is the feed to the second column. The overhead from the second column is the purified product. Both columns are conventional distillation columns fitted with reboilers and total condensers. The bottom products are passed to other processing units, which do not form part of this problem. The feed to the first column passes through a preheater. The condensate from the second column is passed through a product cooler. The duty for each stream is summarized as follows:

No.	Stream	Type	Source Temp. °C.	Target Temp. °C	Duty, kW
1	Feed preheater	cold	20	50	900
2	First condenser	hot	70	60	1350
3	Second condenser	hot	65	55	1100
4	First reboiler	cold	85	87	1400
5	Second reboiler	cold	75	77	900
6	Product cooler	hot	55	25	30

Find the minimum utility requirements for this process, for a minimum approach temperature of 10 °C.

Note: The stream heat capacity is given by dividing the exchanger duty by the temperature change.

3.13. At what value of the minimum approach temperature does the problem in Example 3.16 become a threshold problem? Design a heat exchanger network for the resulting threshold problem. What insights does this give into the design proposed in Example 3.16?

4 FLOWSHEETING

Chapter Contents

Key Learning Objectives

- How to prepare and present a process flow diagram
- How to use commercial process simulation software to build a process heat and material balance model
- How to use user-specified models and components when the simulator does not have what you need
- How to converge flowsheets that include recycles

4.1. INTRODUCTION

This chapter covers the preparation and presentation of the process flowsheet, also known as the *process flow diagram* (PFD). The flowsheet is the key document in process design. It shows the arrangement of the equipment selected to carry out the process, the stream connections, stream flow rates and compositions, and the operating conditions. It is a diagrammatic model of the process.

The flowsheet is used by specialist design groups as the basis for their designs. These include piping, instrumentation, and equipment design and plant layout. It is also used by operating personnel for the preparation of operating manuals and operator training. During plant startup and subsequent operation, the flowsheet forms a basis for comparison of operating performance with design.

The flowsheet is drawn up from material balances made over the complete process and each individual unit operation. Energy balances are also made to determine the energy flows and the utility requirements.

Most flowsheet calculations are carried out using commercial process simulation programs. The process simulation programs contain models for most unit operations as well as thermodynamic and physical property models. All the commercial programs feature some level of custom modeling capability that allows the designer to add models for nonstandard operations.

Many companies developed proprietary flowsheeting programs between 1960 and 1980. The cost of maintaining and updating proprietary software is high; consequently, very few of the proprietary flowsheeting programs are still in use, and most companies now rely entirely on commercially available software. Each of the commercial process simulation programs has its own unique idiosyncrasies, but they share many common features. The discussion in this chapter addresses general problems of process simulation and flowsheeting rather than software-specific issues. The latter are usually thoroughly documented in the user manuals and online help that come with the software. Examples have been provided in this chapter using both Aspen Plus® (Aspen Technology Inc.) and UniSim Design™ (Honeywell Inc.). UniSim Design is based on the Hysys™ software that was originally developed by Hyprotech Ltd. and is now owned and licensed by Honeywell.

Because flowsheeting is usually carried out using computer programs, it is necessary for the design engineer to have a good understanding of how to set up and solve computer models. The flowsheet model that is solved on the computer to generate a mass and energy balance is often not an exact representation of the process flow diagram. The designer may need to use combinations of simulation library models and user models to capture the performance of process equipment. Spreadsheet or hand calculations are also often helpful in setting up process simulation models and providing good initial estimates, so as to accelerate convergence.

The next step in process design after the flowsheet is the preparation of *Piping and Instrument diagrams* (abbreviated to *P & I diagrams* or *PIDs*), often also called the *engineering flowsheet* or *mechanical flowsheet*. The P & I diagrams, as the name implies, show the engineering details of the process, and are based on the process flowsheet. The preparation and presentation of P & I diagrams is discussed in Chapter 5.

4.2. FLOWSHEET PRESENTATION

As the process flowsheet is the definitive document on the process, the presentation must be clear, comprehensive, accurate, and complete. The various types of flowsheets are discussed in the following sections.

4.2.1. Block Diagrams

A *block diagram* is the simplest form of presentation. Each block can represent a single piece of equipment or a complete stage in the process. Block diagrams were used to illustrate the examples in Chapters 2 and 3. They are useful for showing simple processes. With complex processes, their use is limited to showing the overall process, broken down into its principal stages, as in Example 2.13 (vinyl chloride). In that example, each block represented the equipment for a complete reaction stage: the reactor, separators, and distillation columns.

Block diagrams are useful for representing a process in a simplified form in reports, textbooks, and presentations, but have only limited use as engineering documents.

The stream flow rates and compositions can be shown on the diagram adjacent to the stream lines, when only a small amount of information is to be shown, or tabulated separately.

Block diagrams are often drawn using simple graphics programs such as Visio^{TM} or Microsoft PowerPoint^{TM}.

4.2.2. Pictorial Representation

On the detailed flowsheets used for design and operation, the equipment is normally drawn in a stylized pictorial form. For tender documents or company brochures, actual scale drawings of the equipment are sometimes used, but it is more usual to use a simplified representation. There are several international standards for PFD symbols, but most companies use their own standard symbols, as the cost of converting all of their existing drawings would be excessive. ISO 10628 is the international standard for PFD drawing symbols. Very few North American companies apply this standard. The symbols given in British Standard, BS 1553 (1977) “Graphical Symbols for General Engineering” Part 1, “Piping Systems and Plant,” are more typical of those in common use, and a selection of symbols from BS 1553 is given in Appendix A. The symbols in BS 1553 are used in the UK and commonwealth countries. Most European countries have adopted ISO 10628 as their standard.

4.2.3. Presentation of Stream Flow Rates

The data on the flow rate of each individual component, on the total stream flow rate, and the percentage composition can be shown on the flowsheet in various ways. The simplest method, suitable for simple processes with few pieces of equipment, is to tabulate the data in blocks alongside the process stream lines, as shown in Figure 4.1.

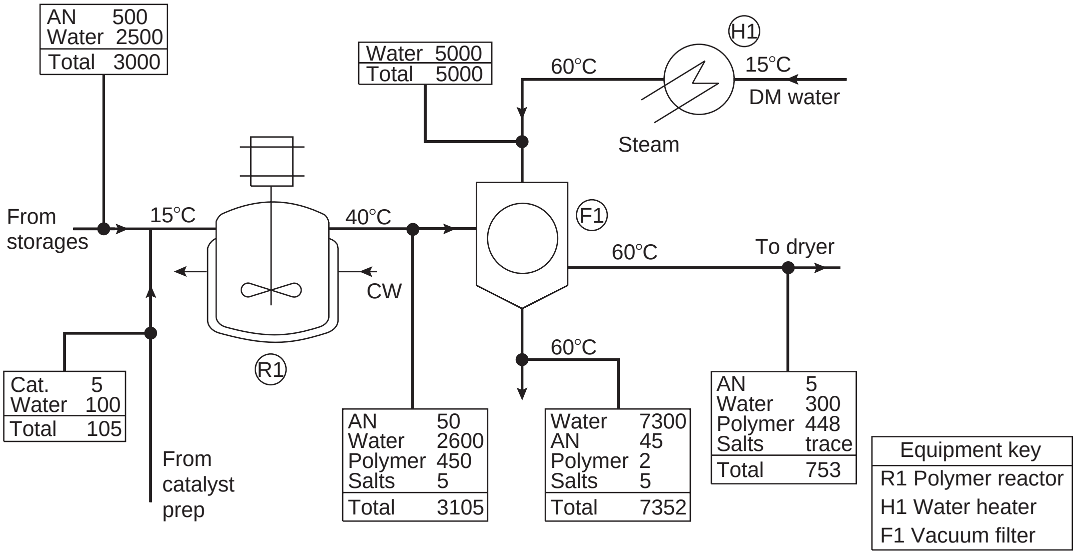


Figure 4.1. Flowsheet: polymer production.

Only a limited amount of information can be shown this way, and it is difficult to make neat alterations or to add additional data.

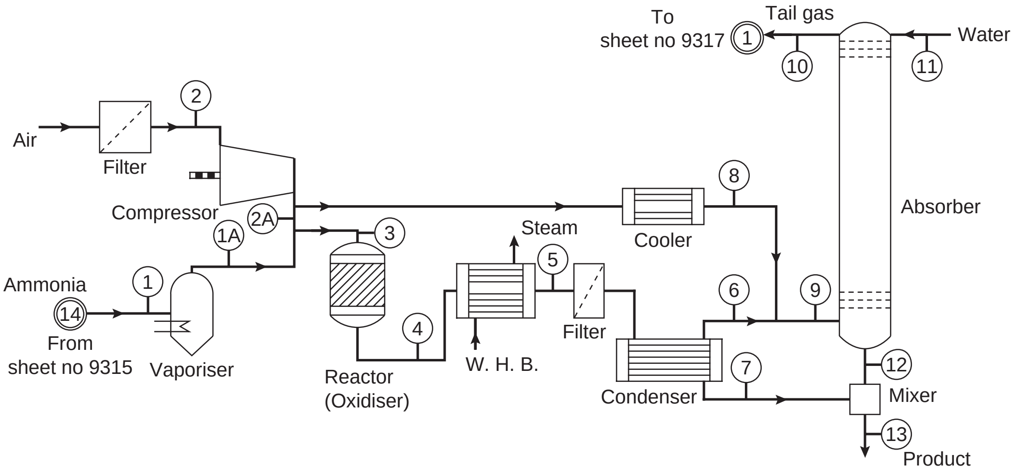
A better method for the presentation of data on flowsheets is shown in Figure 4.2. In this method each stream line is numbered and the data are tabulated at the bottom of the sheet. Alterations and additions can be easily made. This is the method generally used by professional design offices. A typical commercial flowsheet is shown in Figure 4.3. Guide rules for the layout of this type of flowsheet presentation are given in Section 4.2.5.

4.2.4. Information to Be Included

The amount of information shown on a flowsheet will depend on the custom and practice of the particular design office. The following list has therefore been divided into essential items and optional items. The essential items must always be shown; the optional items add to the usefulness of the flowsheet but are not always included.

Essential Information

1. Stream composition, either
   - **i.** the flow rate of each individual component, kg/h, which is preferred; or
   - **ii.** the stream composition as a weight fraction.
2. Total stream flow rate, kg/h;
3. Stream temperature, degrees Celsius preferred;
4. Nominal operating pressure (the required operating pressure);
5. Stream enthalpy, kJ/h.



Flows kg/h Pressures nominal

Line no. Stream Component	1 Ammonia feed	1A Ammonia vapour	2 Filtered air	2A Oxidiser air	3 Oxidiser feed	4 Oxidiser outlet	5 W.H.B. outlet	6 Condenser gas	7 Condenser acid	8 Secondary air	9 Absorber feed	10 Tail(2) gas	11 Water feed	12 Absorber acid	13 Product acid	
NH_3	731.0	731.0	—	—	731.0	Nil	—	—	—	—	—	—	—	—	—	
O_2	—	—	3036.9	2628.2	2628.2	935.7	(935.7)(1)	275.2	Trace	408.7	683.9	371.5	—	Trace	Trace	
N_2	—	—	9990.8	8644.7	8644.7	8668.8	8668.8	8668.8	Trace	1346.1	10,014.7	10,014.7	—	Trace	Trace	
NO	—	—	—	—	—	1238.4	(1238.4)(1)	202.5	—	—	202.5	21.9	—	Trace	Trace	
NO_2		—	—	—	—	—	Trace	(?)(1)	967.2	—	—	967.2	(Trace)(1)	—	Trace	Trace
HNO_3		—	—	—	—	—	Nil	Nil	—	850.6	—	—	—	—	1704.0	2554.6
H_2O		—	—	Trace	—	—	1161.0	1161.0	29.4	1010.1	—	29.4	26.3	1376.9	1136.0	2146.0
Total	731.0	731.0	13,027.7	11,272.9	12,003.9	12,003.9	12,003.9	10,143.1	1860.7	1754.8	11,897.7	10,434.4	1376.9	2840.0	4700.6	
Press bar	8	8	1	8	8	8	8	8	1	8	8	1	8	1	1	
Temp. °C	15	20	15	230	204	907	234	40	40	40	40	25	25	40	43	

C & R Construction Inc

Nitric acid 60 percent
100,000 t/y
Client BOP Chemicals
SLIGO

Sheet no. 9316

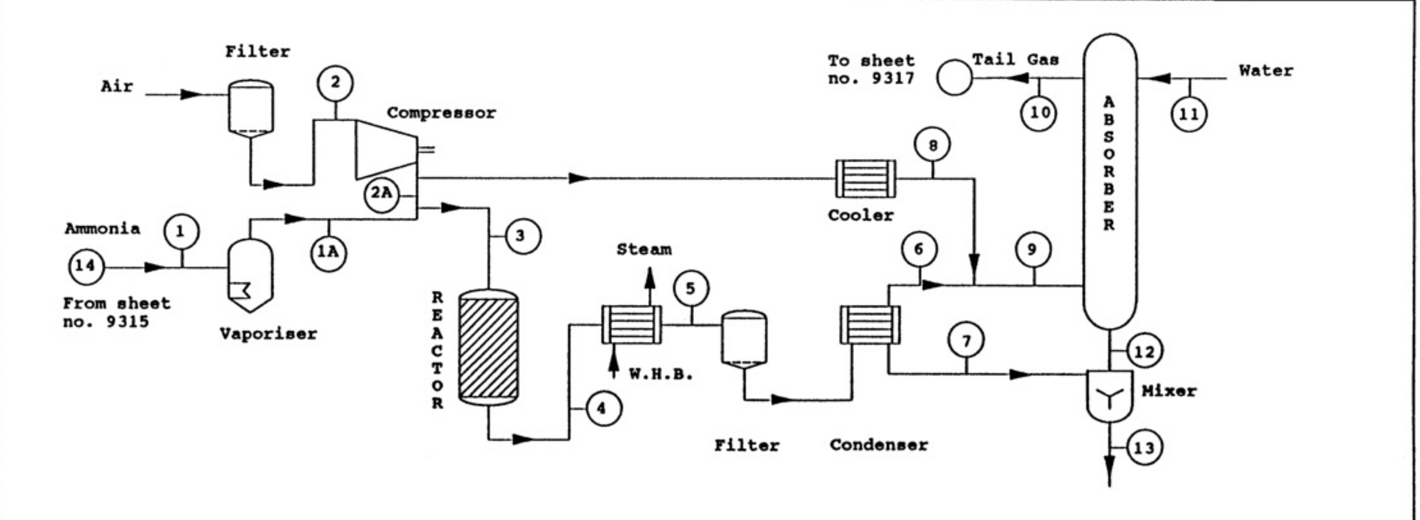
Dwg by
Checked

Date
25/7/1980

Figure 4.2. Flowsheet: simplified nitric acid process.

(Continued)

C & R Construction Inc.	Title : Nitric Acid 60 per cent Client : BOP Chemicals SILGO	Dwg by : GRM Chk by : RKS	DATE : 14/12/1992



Flows (kg/h)   Pressures nominal

Line No.	1	1A	2	2A	3	4	5	6	7	8	9	10	11	12	13
Stream	Ammonia	Ammonia	Filtered	Oxidiser	Oxidiser	Oxidiser	W.H.B.	Condenser	Condenser	Condenser	Absorber	Tail (2)	Water	Absorber	Product
Component	Feed	Vapour	Air	Air	Feed	Outlet	Outlet	Gas	Acid	Air	Feed	Gas	Feed	Acid	Acid
NH3	731.0	731.0	--	--	731.0	NIL	--	--	--	--	--	--	--	--	--
O2	--	--	3036.9	2628.2	2628.2	935.7	935.7	275.2	TRACE	408.7	683.9	371.5	--	TRACE	TRACE
N2	--	--	9990.8	8644.7	8644.7	8668.8	8668.8	8668.8	TRACE	1346.1	10014.7	10014.7	--	TRACE	TRACE
NO	--	--	--	--	--	1238.4	1238.4	202.5	--	--	202.5	21.9	--	TRACE	TRACE
NO2	--	--	--	--	--	TRACE	(?)	967.2	--	--	967.2	TRACE	--	TRACE	TRACE
HNO3	--	--	--	--	--	NIL	NIL	--	850.6	--	--	--	--	1704.0	2554.6
H20	--	--	TRACE	TRACE	--	1161.0	1161.0	29.4	1010.1	--	29.4	26.3	1376.9	1136.0	2146.0
Total	731.0	731.0	13027.7	11272.9	12003.9	12003.9	12003.9	10143.1	1860.7	1754.8	11897.7	10434.4	1376.9	2840.0	4700.6
Press (Bar)	8	8	1	8	8	8	8	8	1	8	8	1	8	1	1
Temp (°C)	15	20	15	230	204	907	234	40	40	40	40	25	25	40	43

Figure 4.2a. Alternative presentation.

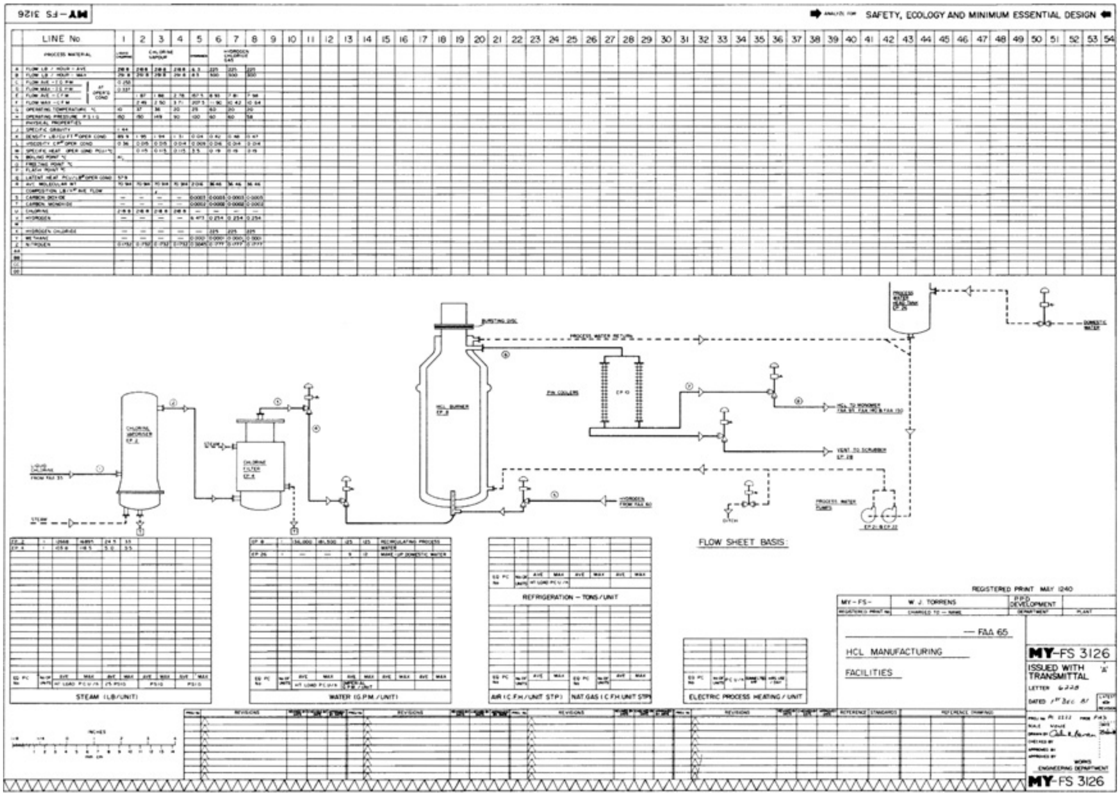


Figure 4.3. A typical flowsheet.

Optional Information

1. Molar percentage composition and/or molar flow rates;
2. Physical property data, mean values for the stream, such as
   - i. density, kg/m^3
   - ii. viscosity, mN s/m^2.
3. Stream name, a brief, one- or two-word description of the nature of the stream, for example, "ACETONE COLUMN BOTTOMS."

4.2.5. Layout

The sequence of the main equipment items shown symbolically on the flowsheet follows that of the proposed plant layout. Some license must be exercised in the placing of ancillary items, such as heat exchangers and pumps, or the layout will be too congested. The aim should be to show the flow of material from stage to stage as it will occur, and to give a general impression of the layout of the actual process plant.

The equipment should be drawn approximately to scale. Again, some license is allowed for the sake of clarity, but the principal equipment items should be drawn roughly in the correct proportion. Ancillary items can be drawn out of proportion. For a complex process, with many process units, several sheets may be needed, and the continuation of the process streams from one sheet to another must be clearly shown. One method of indicating a line continuation is shown in Figure 4.2; those lines that are continued over to another drawing are indicated by a double concentric circle around the line number, and the continuation sheet number is written below. An alternative method is to extend lines to the side of the page and then indicate the drawing sheet on which the line is continued.

The table of stream flows and other data can be placed above or below the equipment layout. Normal practice is to place it below. The components should be listed down the left side of the table, as in Figure 4.2. For a long table, it is good practice to repeat the list at the right side, so the components can be traced across from either side.

The stream line numbers should follow consecutively from left to right of the layout, as far as is practicable, so that when reading the flowsheet, it is easy to locate a particular line and the associated column containing the data.

All the process stream lines shown on the flowsheet should be numbered and the data for the stream given. There is always a temptation to leave out the data on a process stream if it is clearly just formed by the addition of two other streams, as at a junction, or if the composition is unchanged when flowing through a process unit, such as a heat exchanger; this should be avoided. What may be clear to the process designer is not necessarily clear to the others who will use the flowsheet. Complete, unambiguous information on all streams should be given, even if this involves some repetition. The purpose of the flowsheet is to show the function of each process unit, even when the function has no discernible impact on the mass and energy balance.

4.2.6. Precision of Data

The total stream and individual component flows do not normally need to be shown to a high precision on the process flowsheet; three or four significant figures are all that is usually justified by the accuracy of the flowsheet calculations and will typically be sufficient. The flows should, however, balance to within the precision shown. If a stream or component flow is so small that it is less than the precision used for the larger flows, it can be shown to a greater number of places, if its accuracy justifies this and the information is required. Imprecise small flows are best shown as "TRACE." If the composition of a trace component is specified as a process constraint, as, say, for an effluent stream or product quality specification, it can be shown in parts per million (ppm).

A trace quantity should not be shown as zero, or the space in the tabulation left blank, unless the process designer *is sure* that it has no significance. Trace quantities can be important. Only a trace of an impurity is needed to poison a catalyst, and trace quantities can determine the selection of the materials of construction; see Chapter 7. If the space in the data table is left blank opposite a particular component, the quantity may be assumed to be zero by the specialist design groups who take their information from the flowsheet.

4.2.7. Basis of the Calculation

It is good practice to show on the flowsheet the basis used for the flowsheet calculations. This includes the operating hours per year, the reaction and physical yields, and the datum temperature used for energy balances. It is also helpful to include a list of the principal assumptions used in the calculations. This alerts the user to any limitations that may have to be placed on the flowsheet information.

If the amount of information that needs to be presented is excessive, then it can be summarized in a separate document that is referenced on the flowsheet.

In some cases, mass and energy balances are prepared for multiple scenarios. These might include winter and summer operating conditions, start of catalyst life and end of catalyst life, manufacture of different products or product grades, etc. Usually these different scenarios are shown as several tables on the same flowsheet, but occasionally different flowsheets are drawn for each case.

4.2.8. Batch Processes

Flowsheets drawn up for batch processes normally show the quantities required to produce one batch. If a batch process forms part of an otherwise continuous process, it can be shown on the same flowsheet, providing a clear break is made when tabulating the data between the continuous and batch sections, i.e., the change from kg/h to kg/batch.

A continuous process may include batch make-up of minor reagents, such as the catalyst for a polymerization process. Batch flows into a continuous process are usually labeled "Normally no flow" and show the flow rates that will be obtained when the stream is flowing. It is these instantaneous flow rates that govern the equipment design, rather than the much lower time-averaged flow rates.

4.2.9. Utilities

To avoid cluttering up the flowsheet, it is not normal practice to show the utility (service) headers and lines on the process flowsheet. The utility connections required on each piece of equipment should be shown and labeled, for example, "CTW" for cooling tower water. The utility requirements for each piece of equipment should be tabulated on the flowsheet.

4.2.10. Equipment Identification

Each piece of equipment shown on the flowsheet must be identified with a code number and name. The identification number (usually a letter and some digits) is normally that assigned to a particular piece of equipment as part of the general project control procedures and is used to identify it in all the project documents.

If the flowsheet is not part of the documentation for a project, then a simple, but consistent, identification code should be devised. The easiest code is to use an initial letter to identify the type of equipment, followed by digits to identify the particular piece; for example, H—heat exchangers, C—columns, R—reactors. Most companies have a standard convention that should be followed, but if there is no agreed standard, then the key to the code should be shown on the flowsheet.

4.2.11. Computer-Aided Drafting

Most design offices use drafting software for the preparation of flowsheets and other process drawings. With drafting software, standard symbols representing the process equipment, instruments, and control systems are held in files, and these symbols are called up as required when drawing flowsheets and piping and instrumentation diagrams (see Chapter 5). Final flowsheet drawings are usually produced by professional drafters, who are experienced with the drafting software and conventions, rather than by the design engineer. The design engineer has to provide the required numbers, sketch the flowsheet, and review the final result.

To illustrate the use of a commercial computer-aided design program, Figure 4.2 has been redrawn using the program FLOSHEET and is shown as Figure 4.2a. FLOSHEET is part of a suite of programs called PROCEDE, described by Preece et al. (1991).

Although most process simulation programs feature a graphical user interface (GUI) that creates a drawing that resembles a PFD, printouts of these drawings are very seldom used as actual process flow diagrams. The unit operations shown in the process simulation usually do not exactly match the unit operations of the process. The simulation may include dummy items that do not physically exist and may omit some equipment that is needed in the plant but is not part of the simulation.

4.3. PROCESS SIMULATION PROGRAMS

The most commonly used commercial process simulation programs are listed in Table 4.1. Most of these programs can be licensed by universities for educational purposes at nominal cost.

Note: Contact the website to check the full features of the most recent versions of the programs.

Detailed discussion of the features of each of these programs is beyond the scope of this book. For a general review of the requirements, methodology, and application of process simulation programs, refer to the books by Husain (1986), Wells and Rose (1986), Leesley (1982), Benedek (1980), and Westerberg et al. (1979). The features of the individual programs are described in their user manuals and online help. Two of these simulators have been used to generate the examples in this chapter: Aspen Plus® (v.11.1) and UniSim Design™ (R360.1).

Process simulation programs can be divided into two basic types:

Sequential-modular programs: in which the equations describing each process unit operation (module) are solved module-by-module in a stepwise manner. Iterative techniques are then used to solve the problems arising from the recycle of information.

Simultaneous (also known as *equation-oriented*) programs: in which the entire process is described by a set of equations, and the equations are solved simultaneously, not stepwise as in the sequential approach. Simultaneous programs

Table 4.1. Simulation Packages

Name	Type	Source	Internet Address http//www.—
Aspen Plus	steady-state	Aspen Technology Inc. Ten Canal Park Cambridge, MA 02141-2201, USA	Aspentech.com
CHEMCAD	steady-state	Chemstations Inc. 2901 Wilcrest, Suite 305 Houston, TX 77042 USA	Chemstations.net
DESIGN II	steady-state	WinSim Inc. P.O. Box 1885 Houston, TX 77251-1885, USA	Winsim.com
HYSYS	steady-state and dynamic	Aspen Technology Inc. Ten Canal Park Cambridge, MA 02141-2201, USA	Aspentech.com
PRO/II and DYNSIM	steady-state and dynamic	SimSci-Esscor 5760 Fleet Street Suite 100 Carlsbad, CA 92009, USA	Simsci.com
UniSim Design	steady-state and dynamic	Honeywell 300-250 York Street London, Ontario N6A 6K2, Canada	Honeywell.com

can simulate the unsteady-state operation of processes and equipment, and can give faster convergence when multiple recycles are present.

In the past, most simulation programs available to designers were of the sequential-modular type. They were simpler to develop than the equation-oriented programs and required only moderate computing power. The modules are processed sequentially, so essentially only the equations for a particular unit are in the computer memory at one time. Also, the process conditions, temperature, pressure, flow rate, etc., are fixed in time. With the sequential modular approach, computational difficulties can arise due to the iterative methods used to solve recycle problems and obtain convergence. A major limitation of sequential modular simulators is the inability to simulate the dynamic, time-dependent behavior of a process.

Simultaneous, dynamic simulators require appreciably more computing power than steady-state simulators to solve the thousands of differential equations needed to describe a process, or even a single item of equipment. With the development of fast, powerful computers, this is no longer a restriction. By their nature, simultaneous programs do not experience the problems of recycle convergence inherent in sequential simulators; however, as temperature, pressure, and flow rate are not fixed and the input of one unit is not determined by the calculated output from the previous unit in the sequence, simultaneous programs demand more computer time. This has led to the development of hybrid programs in which the steady-state simulator is used to generate the initial conditions for the equation-oriented or dynamic simulation.

The principal advantage of simultaneous, dynamic simulators is their ability to model the unsteady-state conditions that occur at startup and during fault conditions. Dynamic simulators are being increasingly used for safety studies and in the design of control systems, as discussed in Section 4.9.

The structure of a typical simulation program is shown in Figure 4.4.

The program consists of

1. A main executive program that controls and keeps track of the flowsheet calculations and the flow of information to and from the subroutines.
2. A library of equipment performance subroutines (modules) that simulate the equipment and enable the output streams to be calculated from information on the inlet streams.
3. A data bank of physical properties. To a large extent, the utility of a sophisticated flowsheeting program depends on the comprehensiveness of the physical property data bank. The collection of the physical property data required for the design of a particular process and its transformation into a form suitable for a particular flowsheeting program can be very time-consuming.
4. Subroutines for thermodynamics, such as the calculation of vapor-liquid equilibrium and stream enthalpies.
5. Subprograms and data banks for equipment sizing and costing. Process simulation programs enable the designer to consider alternative processing schemes,

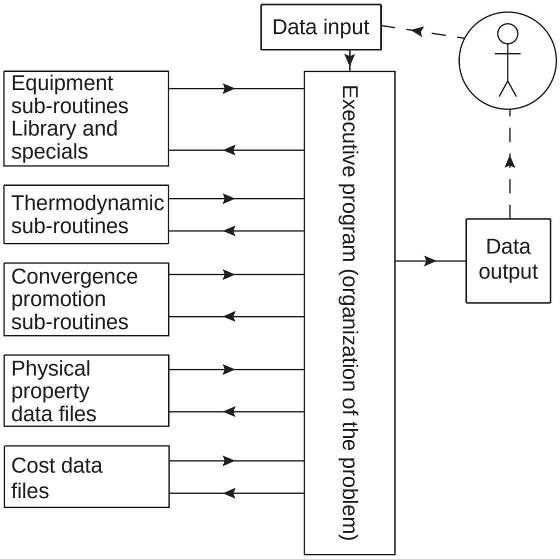


Figure 4.4. A typical simulation program.

and the cost routines allow quick economic comparisons to be made. Some programs include optimization routines. To make use of a costing routine, the program must be capable of producing at least approximate equipment designs.

In a sequential-modular program, the executive program sets up the flowsheet sequence, identifies the recycle loops, and controls the unit operation calculations, while interacting with the unit operations library, physical property data bank, and the other subroutines. The executive program also contains procedures for the optimum ordering of the calculations and routines to promote convergence.

In an equation-oriented simulator, the executive program sets up the flowsheet and the set of equations that describe the unit operations and then solves the equations using data from the unit operations library and the physical property data bank and calling on the file of thermodynamics subroutines.

All process simulators use graphical user interfaces to display the flowsheet and facilitate the input of information to the package. The entry of data is usually intuitive to anyone familiar with the MS Windows^{TM} operating systems.

4.4. SPECIFICATION OF COMPONENTS AND PHYSICAL PROPERTY MODELS

The first step in building a process simulation is usually establishing the chemical basis for the model. This consists of choosing the components that will be included in the mass balance and deciding which models to use for the prediction of physical properties and phase equilibrium. The correlation of physical properties and prediction of phase equilibrium are described in detail in Chapter 8. This section thus focuses on the selection of suitable components.

4.4.1. Pure Components

Each of the commercial process simulation programs contains a large data bank of pure component compounds. Most of the pure components are organic compounds, but inorganic compounds and electrolytes are also included.

The fact that a pure component is listed in a simulator data bank does not guarantee that any of the properties given for that component are based on measured data. If the properties of a compound are critical to process performance, then the scientific literature should be consulted to confirm that the values used in the simulation are realistic.

The most important decision when building a pure component model is choosing the right number of components. The design engineer needs to consider carefully which components will have a significant impact on process design, operation and economics. If too few components are used, then the model will be inadequate for process design, as it will not correctly predict the performance of reactors and separation equipment. Conversely, if too many components are used, then the model can become difficult to converge, particularly if there are multiple recycles in the design.

Some guidelines to keep in mind when building a component list include

1. Always include any component that has a specified limit in any of the products if that component is present in any of the feeds or could be formed in the process. This is critical to determining whether the separations are meeting product specifications.
2. Always include any component that has a specified limit in any of the feeds. These components can be a source of byproducts or can act as catalyst or enzyme inhibitors. They must be tracked to ensure that they do not accumulate in the process or make it difficult to meet product specifications. In some cases, an additional separation may be needed to remove a feed contaminant.
3. Always include components that are expected to be formed in side reactions or consecutive reactions. It is important to understand where these components will accumulate or leave the process, even if their yield is not yet known.
4. Always include any compounds that are expected to be present and are known to have significant health, safety, or environmental concerns, such as compounds with high toxicity or explosivity, known carcinogens, or listed hazardous air pollutants (see Chapter 14). These compounds must be tracked to make sure that they do not reach unsafe levels in any stream and to understand where they might be released to the environment.
5. Usually include any compound that might be present at a mass or mole fraction greater than 2% in any stream in the process.
6. Do not include isomers unless the process specifically requires distinction between isomers (for example, if the process is selective for one isomer, gives different products for different isomers, or is designed to separate isomers). Considering all of the possible isomers of organic compounds becomes combinatorially explosive at high carbon numbers. For fuels and bulk petrochemical processes that are carried out at relatively high temperatures, it is often reasonable to assume an equilibrium distribution of isomers. For fine chemical and pharmaceutical processes, it is usually important to track isomers separately, particularly enantiomers, as the desired product is often only one of the isomers.

In general, pure component models solve more efficiently with fewer than about 40 components. If the number of components becomes too large and there are many recycles, then it may be necessary to build two models. The first is a high-level model that contains only the main bulk components. This model is then used to initialize a second, more detailed model that has the full component list.

4.4.2. Pseudocomponents

Pseudocomponents (hypocomponents) are components created by the simulator to match the boiling curves of petroleum mixtures.

Crude oil; fuels such as gasoline, kerosene and diesel; and most intermediate streams in oil refinery consist of many different hydrocarbon compounds. The number of possible hydrocarbon isomers present depends on the carbon number, and both increase with boiling range. For diesel, crude oil, and heavy fuel oils, the number of possible compounds can be from 10^4 to $>10^6$. At the time of writing, there is no characterization method that can identify all of these compounds, so it would be impossible to include them all in a model even if the resulting model could be solved. Instead, a large number of possible compounds with boiling points in a given range are "lumped" together and represented by a single pseudocomponent with a boiling point in the middle of that range. A set of 10 to 30 pseudocomponents can then be fitted to any petroleum assay and used to model that oil.

Pseudocomponent models are very useful for oil fractionation and blending problems. They can also be used to characterize heavy products in some chemical processes such as ethane cracking. Pseudocomponents are treated as inert in most of the reactor models, but they can be converted or produced in yield-shift reactors (see Section 4.5.1).

Some of the commercial simulation programs use a standard default set of pseudocomponents and fit the composition of each to match a boiling curve of the oil that is entered by the user. This can sometimes lead to errors when predicting ASTM D86 or D2887 curves for products from a feed that has been defined based on a true boiling point (TBP) curve, or when making many subcuts or cuts with tight distillation specifications. It is often better to work back from the product distillation curves and add extra pseudocomponents around the cut points to make sure that the recoveries and 5% and 95% points on the product distillation curves are predicted properly. All of the simulators have the option to add pseudocomponents to the default set or use a user-generated curve.

4.4.3. Solids and Salts

Most chemical and pharmaceutical processes involve some degree of solids handling. Examples of solids that must be modeled include

- Components that are crystallized for separation, recovery, or purification;
- Pharmaceutical products that are manufactured as powders or tablets;
- Insoluble salts formed by the reaction of acids and bases or other electrolytes;
- Hydrates, ice, and solid carbon dioxide that can form in cryogenic processes;
- Cells, bacteria, and immobilized enzymes in biological processes;
- Pellets or crystals of polymer formed in polymerization processes;
- Coal and ash particles in power generation;
- Catalyst pellets in processes in which the catalyst is fluidized or transported as a slurry;
- Mineral salts and ores that are used as process feeds;
- Fertilizer products;
- Fibers in paper processing.

Some solid phase components can be characterized as pure components and can interact with other components in the model through phase and reaction equilibrium. Others, such as cells and catalysts, are unlikely to equilibrate with other components, although they can play a vital role in the process.

In Aspen Plus, solid components are identified as different types. Pure materials with measurable properties such as molecular weight, vapor pressure, and critical temperature and pressure are known as *conventional solids* and are present in the MIXED substream with other pure components. They can participate in any of the phase or reaction equilibria specified in any unit operation. If the solid phase participates only in reaction equilibrium but not in phase equilibrium (for example, when the solubility in the fluid phase is known to be very low), then it is called a *conventional inert solid* and is listed in a substream CISOLID. If a solid is not involved in either phase or reaction equilibrium, then it is a *nonconventional solid* and is assigned to substream NC. Nonconventional solids are defined by attributes rather than molecular properties and can be used for coal, cells, catalysts, bacteria, wood pulp, and other multicomponent solid materials.

In UniSim Design, nonconventional solids can be defined as hypothetical components (see Section 4.4.4). The solid phases of pure components are predicted in the phase and reaction equilibrium calculations and do not need to be identified separately.

Many solids-handling operations have an effect on the particle size distribution (PSD) of the solid phase. The particle size distribution can also be an important product property. Aspen Plus allows the user to enter a particle size distribution as an attribute of a solid substream. In UniSim Design, the particle size distribution is entered on the "PSD Property" tab, which appears under "worksheet" on the stream editor window for any stream that contains a pure or hypothetical solid component. Unit operations such as yield-shift reactor, crusher, screen, cyclone, electrostatic precipitator, and crystallizer can then be set up to modify the particle size distribution, typically by using a conversion function or a particle capture efficiency in each size range.

When inorganic solids and water are present, an electrolyte phase equilibrium model must be selected for the aqueous phase, to properly account for the dissolution of the solid and formation of ions in solution.

4.4.4. User Components

The process simulators were originally developed for petrochemical and fuels applications; consequently, many molecules that are made in specialty chemical and pharmaceutical processes are not listed in the component data banks. All of the simulators allow the designer to overcome this drawback by adding new molecules to customize the data bank.

In UniSim Design, new molecules are added as hypothetical components. The minimum information needed to create a new hypothetical pure component is the normal boiling point, although the user is encouraged to provide as much information as is available. If the boiling point is unknown, then the molecular weight and density are used instead. The input information is used to tune the UNIFAC correlation to predict the physical and phase equilibrium properties of the molecule, as described in Chapter 8.

User-defined components are created in Aspen Plus using a "user-defined component wizard." The minimum required information is the molecular weight and normal boiling point. The program also allows the designer to enter molecular structure, specific gravity, enthalpy, and Gibbs energy of formation, ideal gas heat capacity, and Antoine vapor pressure coefficients, but for complex molecules usually only the molecular structure is known.

It is often necessary to add user components to complete a simulation model. The design engineer should always be cautious when interpreting simulation results for models that include user components. Phase equilibrium predictions for flashes, decanters, extraction, distillation, and crystallization operations should be carefully checked against laboratory data to ensure that the model is correctly predicting the component distribution between the phases. If the fit is poor, the binary interaction parameters in the phase equilibrium model can be tuned to improve the prediction.

4.5. SIMULATION OF UNIT OPERATIONS

A process simulation is built up from a set of unit operation models connected by mass and energy streams. The commercial simulators include many unit operation subroutines, sometimes referred to as *library models*. These operations can be selected from a palette or menu and then connected together using the simulator graphical user interface. Table 4.2 gives a list of the main unit operation models available in Aspen Plus and UniSim Design. Details of how to specify unit operations are given in the simulator manuals. This section provides general advice on unit operations modeling and modeling of nonstandard unit operations.

4.5.1. Reactors

The modeling of real industrial reactors is usually the most difficult step in process simulation. It is usually easy to construct a model that gives a reasonable prediction of the yield of main product, but the simulator library models are not sophisticated enough to fully capture all the details of hydraulics, mixing, mass transfer, catalyst and enzyme inhibition, cell metabolism, and other effects that often play a critical role in determining the reactor outlet composition, energy consumption, rate of catalyst deactivation, and other important design parameters.

In the early stages of process design, the simulator library models are usually used with simplistic reaction models that give the design engineer a good enough idea of yields and enthalpy changes to allow design of the rest of the process. If the design seems economically attractive, then more detailed models can be built and substituted into the flowsheet. These detailed models are usually built as user models, as described in Section 4.6.

Most of the commercial simulation programs have variants on the reactor models described in the following sections.

Table 4.2. Unit Operation Models in Aspen Plus® and UniSim Design™

Unit Operation	Aspen Plus Models	UniSim Design Models
Stream mixing	Mixer	Mixer
Component splitter	Sep, Sep2	Component Splitter
Decanter	Decanter	3-Phase Separator
Flash	Flash2, Flash3	Separator, 3-Phase Separator
Piping components		
Piping	Pipe, Pipeline	Pipe Segment, Compressible Gas Pipe
Valves & fittings	Valve	Valve, Tee, Relief Valve
Hydrocyclone	HyCyc	Hydrocyclone
Reactors		
Conversion reactor	RStoic	Conversion Reactor
Equilibrium reactor	REquil	Equilibrium Reactor
Gibbs reactor	RGibbs	Gibbs Reactor
Yield reactor	RYield	Yield-shift Reactor
CSTR	RCSTR	Continuous Stirred Tank Reactor
Plug-flow reactor	RPlug	Plug-flow Reactor
Columns		
Shortcut distillation	DSTWU, Distl, SCFrac	Shortcut column
Rigorous distillation	RadFrac, MultiFrac	Distillation, 3-Phase Distillation
Liquid-liquid extraction	Extract	Liquid-Liquid Extractor
Absorption and stripping	RadFrac	Absorber, Refluxed Absorber, Reboiled Absorber
Fractionation	PetroFrac	3 Stripper Crude, 4 Stripper Crude, Vacuum Resid Column, FCCU Main Fractionator
Rate-based distillation	RATEFRAC™	
Batch distillation	BatchFrac	
Heat transfer equipment		
Heater or cooler	Heater	Heater, Cooler
Heat exchanger	HeatX, HxFlux, Hetran, HTRI-Xist	Heat Exchanger
Air cooler	Aerotran	Air Cooler
Fired heater	Heater	Fired Heater
Multi-stream exchanger	MheatX	LNG Exchanger
Rotating equipment		
Compressor	Compr, MCompr	Compressor
Turbine	Compr, MCompr	Expander
Pump, hydraulic turbine	Pump	Pump
Solids handling		
Size reduction	Crusher	
Size selection	Screen	Screen
Crystallizer	Crystallizer	Crystallizer, Precipitation
Neutralization		Neutralizer
Solids washing	SWash	
Filter	Fabfl, CFuge, Filter	Rotary Vacuum Filter
Cyclone	HyCyc, Cyclone	Hydrocyclone, Cyclone
Solids decanting	CCD	Simple Solid Separator
Solids transport		Conveyor
Secondary recovery	ESP, Fabfl, VScrub	Baghouse Filter
User models	User, User2, User3	User Unit Op

Conversion Reactor (Stoichiometric Reactor)

A conversion reactor requires a reaction stoichiometry and an extent of reaction, which is usually specified as an extent of conversion of a limiting reagent. No reaction kinetics information is needed, so it can be used when the kinetics are unknown (which is often the case in the early stages of design) or when the reaction is known to proceed to full conversion. Conversion reactors can handle multiple reactions, but care is needed in specifying the order in which they are solved if they use the same limiting reagent.

Equilibrium Reactor

An equilibrium reactor finds the equilibrium product distribution for a specified set of stoichiometric reactions. Phase equilibrium is also solved. The engineer can enter the outlet temperature and pressure and let the reactor model calculate the duty needed to reach that condition, or else enter a heat duty and let the model predict the outlet conditions from an energy balance.

An equilibrium reactor solves only the equations specified, so it is useful in situations in which one or more reactions equilibrate rapidly, while other reactions proceed much more slowly. An example is the steam reforming of methane to hydrogen. In this process, the water-gas-shift reaction between water and carbon monoxide equilibrates rapidly at temperatures above 450°C, while methane conversion requires catalysis even at temperatures above 800°C. This process chemistry is explored in Example 4.2.

In some simulation programs, the equilibrium reactor model requires the designer to specify both liquid and vapor phase products, even though one of the streams may be calculated to have zero flow. If the real reactor has a single outlet, then the two product streams in the model should be mixed back together.

Gibbs Reactor

The Gibbs reactor solves the full reaction (and optionally phase) equilibrium of all species in the component list by minimization of the Gibbs free energy, subject to the constraint of the feed mass balance. A Gibbs reactor can be specified with restrictions such as a temperature approach to equilibrium or a fixed conversion of one species.

The Gibbs reactor is very useful when modeling a system that is known to come to equilibrium, in particular high-temperature processes involving simple molecules. It is less useful when complex molecules are present, as these usually have high Gibbs energy of formation; consequently, very low concentrations of these species are predicted unless the number of components in the model is very restricted.

The designer must specify the components carefully when using a Gibbs reactor in the model, as the Gibbs reactor can solve only for specified components. If a component that is actually formed is not listed in the component set, then the Gibbs reactor results will be meaningless. Furthermore, if some of the species have high Gibbs free energy, their concentrations may not be properly predicted by the model. An example is aromatic hydrocarbon compounds such as benzene, toluene, and xylenes, which have Gibbs free energy of formation greater than zero. If these species are in a model component set that also contains hydrogen and carbon, then a Gibbs reactor will predict that only carbon and hydrogen are formed. Although hydrogen and coke are indeed the final equilibrium products, the aromatic hydrocarbons are kinetically stable and there are many processes that convert aromatic hydrocarbon compounds without significant coke yields. In this situation, the designer must either omit carbon from the component list or else use an equilibrium reactor in the model.

Continuous Stirred Tank Reactor (CSTR)

The CSTR is a model of the conventional well-mixed reactor. It can be used when a model of the reaction kinetics is available and the reactor is believed to be well mixed; i.e., the conditions everywhere in the reactor are the same as the outlet conditions. By specifying forward and reverse reactions, the CSTR model can model equilibrium and rate-based reactions simultaneously. The main drawback of using the CSTR model is that a detailed understanding of kinetics is necessary if byproducts are to be predicted properly.

Plug-Flow Reactor (PFR)

A plug-flow reactor models the conventional plug-flow behavior, assuming radial mixing but no axial dispersion. The reaction kinetics must be specified, and the model has the same limitations as the CSTR model.

Most of the simulators allow heat input or removal from a plug-flow reactor. Heat transfer can be with a constant wall temperature (as encountered in a fired tube, steam-jacketed pipe, or immersed coil) or with counter-current flow of a utility stream (as in a heat exchanger tube or jacketed pipe with cooling water).

Yield-Shift Reactor

The yield-shift reactor overcomes some of the drawbacks of the other reactor models by allowing the designer to specify a yield pattern. Yield-shift reactors can be used when there is no model of the kinetics, but some laboratory or pilot plant data are available, from which a yield correlation can be established.

Yield-shift reactors are particularly useful when modeling streams that contain pseudocomponents, solids with a particle size distribution, or processes that form small amounts of many byproducts. These can all be described easily in yield correlations but can be difficult to model with the other reactor types.

The main difficulty in using the yield-shift reactor is in establishing the yield correlation. If a single point—for example, from a patent—is all that is available, then entering the yield distribution is straightforward. If, on the other hand, the purpose is to optimize the reactor conditions, then a substantial set of data must be collected to build a model that accurately predicts yields over a wide enough range of conditions. If different catalysts can be used, the underlying reaction mechanism may be different for each, and each will require its own yield model. The development of yield models can be an expensive process and is often not undertaken until corporate management has been satisfied that the process is likely to be economically attractive.

Modeling Real Reactors

Industrial reactors are usually more complex than the simple simulator library models. Real reactors usually involve multiple phases and have strong mass transfer, heat transfer, and mixing effects. The residence time distributions of real reactors can be determined by tracer studies and seldom exactly match the simple CSTR or PFR models.

Sometimes a combination of library models can be used to model the reaction system. For example, a conversion reactor can be used to establish the conversion of main feeds, followed by an equilibrium reactor that establishes an equilibrium distribution among specified products. Similarly, reactors with complex mixing patterns can be modeled as networks of CSTR and PFR models, as described in Section 1.9.10 and illustrated in Figure 1.19.

When a combination of library models is used to simulate a reactor, it is a good idea to group these models in a subflowsheet. The subflowsheet can be given a suitable label such as "reactor" that indicates that all the unit operations it contains are modeling a single piece of real equipment. This makes it less likely that someone else using the model will misinterpret it as containing additional distinct operations.

Detailed models of commercial reactors are usually written as user models. These are described in Section 4.6.

Example 4.1

When heavy oils are cracked in a catalytic or thermal cracking process, lighter hydrocarbon compounds are formed. Most cracking processes on heavy oil feeds form products with carbon numbers ranging from 2 to greater than 20. How does the equilibrium distribution of hydrocarbon compounds with five carbons (C_5 compounds) change as the temperature of the cracking process is increased at 200 kPa?

Solution

This problem was solved using UniSim Design.

The problem asks for an equilibrium distribution, so the model should contain either a Gibbs reactor or an equilibrium reactor.

A quick glance at the component list in UniSim Design shows that there are 22 hydrocarbon species with five carbons. To model the equilibrium among these species, we also need to include hydrogen to allow for the formation of alkenes, dienes, and alkynes. Although it would be possible to enter 21 reactions and use an equilibrium reactor, it is clearly easier to use a Gibbs reactor for this analysis. Figure 4.5 shows the Gibbs reactor model.

To specify the feed, we must enter the temperature, pressure, flow rate, and composition. The temperature, pressure, and flow rate are entered in the stream editor window, as illustrated in Figure 4.6. The feed composition can be entered as 100% of any of the C_5 paraffin species, for example, normal pentane. The results from a Gibbs reactor would be the same if 100% isopentane were entered. It should be noted, however, that if a mixture of a pentane and a pentene were specified, then the overall ratio of hydrogen to carbon would be different and different results would be obtained.

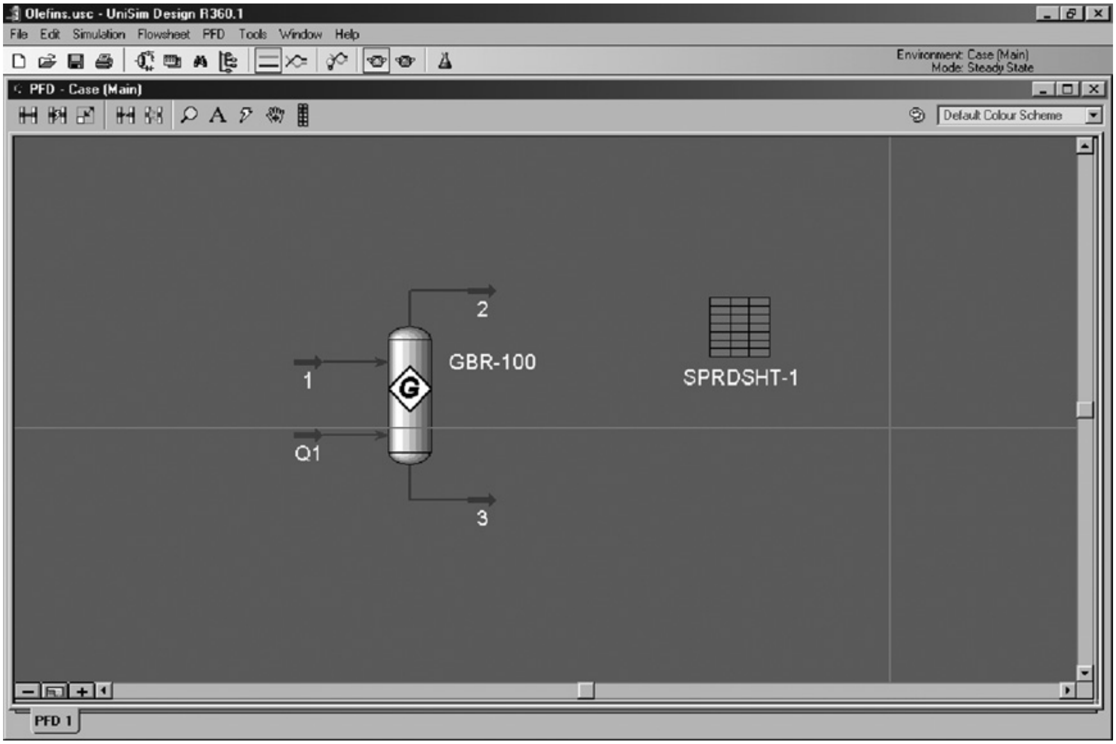


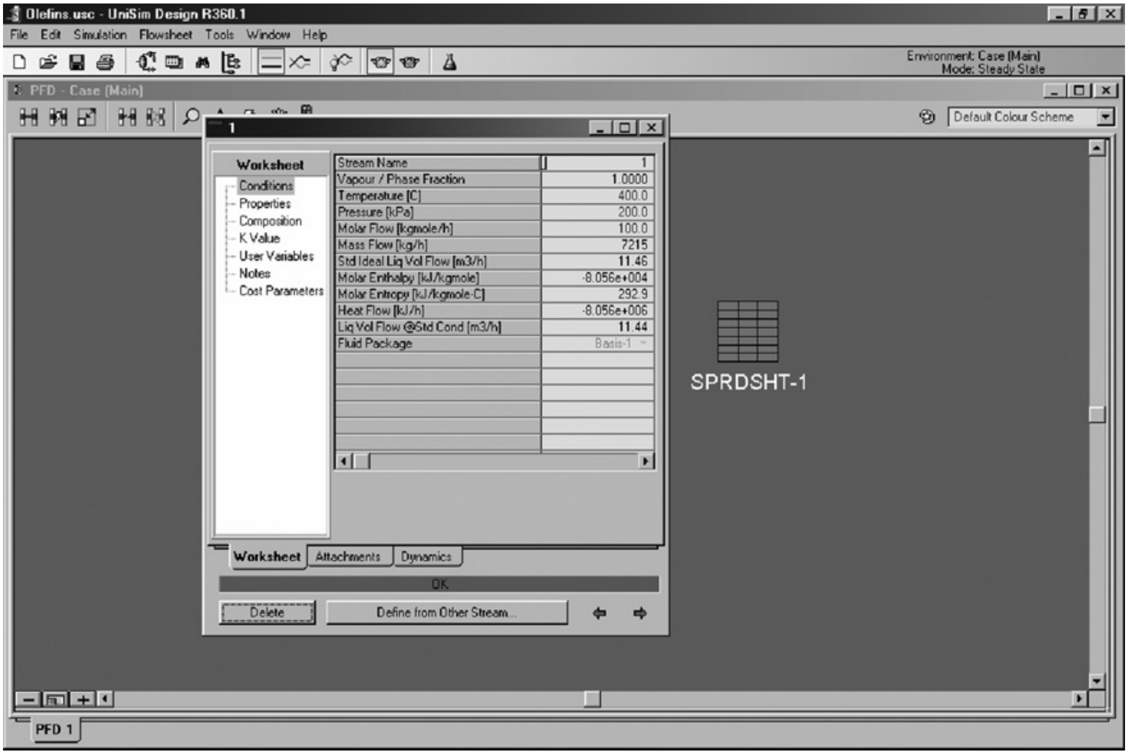
Figure 4.5. Gibbs reactor model.

A spreadsheet was also added to the model, as illustrated in Figure 4.5, to make it easier to capture and download the results. The spreadsheet was set up to import component mole fractions from the simulation, as shown in Figure 4.7. The simulation was then run for a range of temperatures, and after each run a new column was entered in the spreadsheet, as shown in Figure 4.8.

When the results are examined, many of the individual species are present at relatively low concentrations. It thus makes sense to group some compounds together by molecular type, for example, adding all the dienes together and adding all the alkynes (acetylenes) together.

The spreadsheet results were corrected to give the distribution of C_5 compounds by dividing by one minus the mole fraction of hydrogen, and then plotted to give the graph in Figure 4.9.

It can be seen from the graph that the equilibrium products at temperatures below 500°C are mainly alkanes (also known as *paraffins* or *saturated hydrocarbons*), with the equilibrium giving roughly a 2:1 ratio of isopentane to normal pentane. As the temperature is increased from 500°C to 600°C, there is increased formation of alkene compounds (also known as *olefins*). At 700°C, we see increased formation of cyclopentene and of dienes, and above 800°C dienes are the favored product.



Stream Name	1
Vapour / Phase Fraction	1.0000
Temperature [C]	400.0
Pressure [kPa]	200.0
Molar Flow [kgmole/h]	100.0
Mass Flow [kg/h]	7215
Std Ideal Liq Vol Flow [m3/h]	11.46
Molar Enthalpy [kJ/kgmole]	-8.056e+004
Molar Entropy [kJ/kgmole-C]	292.9
Heat Flow [kJ/h]	-8.056e+006
Liq Vol Flow @Std Cond [m3/h]	11.44
Fluid Package	Basis-1

Figure 4.6. Stream entry.

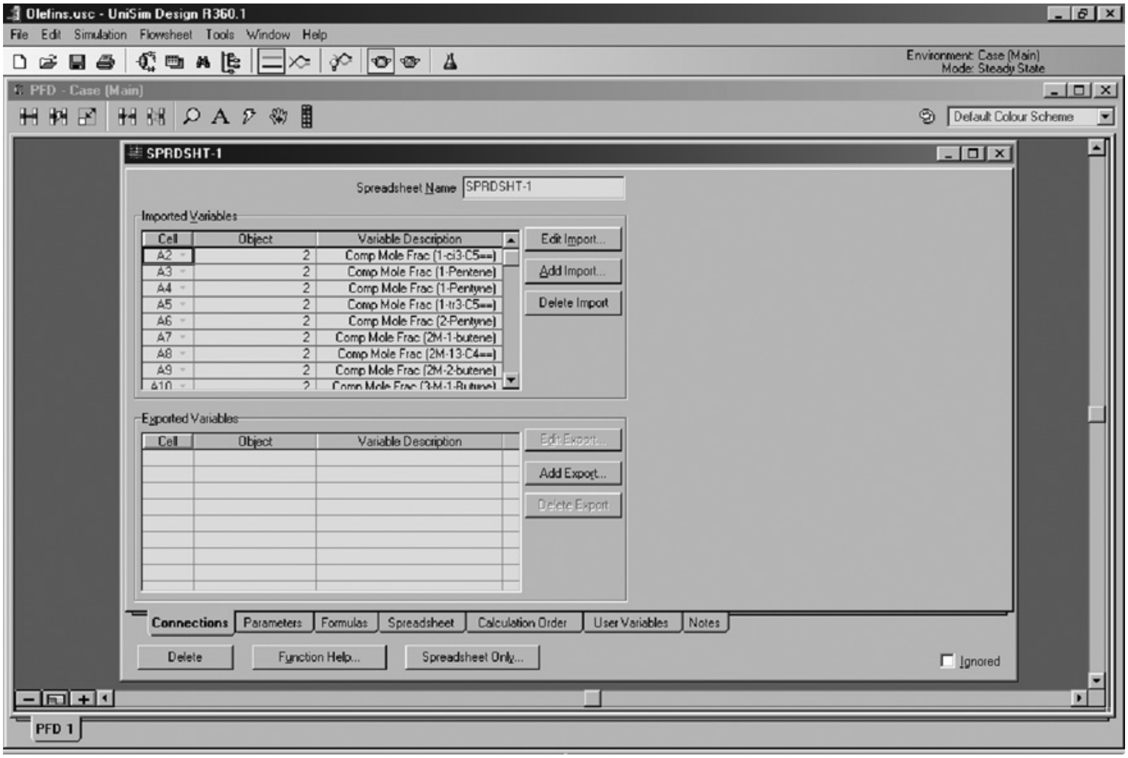
Of course, this is an incomplete picture, as the relative fraction of C_5 compounds would be expected to decrease as the temperature is raised and C_5 species are cracked to lighter compounds in the C_2 and C_3 range. The model also did not contain carbon (coke), and so could not predict the temperature at which coke would become the preferred product. A more rigorous equilibrium model of a cracking process might include all of the possible hydrocarbon compounds up to C_7 or higher.

A real reactor might give a very different distribution of C_5 compounds from that calculated using the Gibbs reactor model. Dienes formed at high temperatures might recombine with hydrogen during cooling, giving a mixture that looked more like the equilibrium product at a lower temperature. There might also be formation of C_5 compounds by condensation reactions of C_2 and C_3 species during cooling, or loss of dienes and cyclopentene due to coke formation.

Example 4.2

Hydrogen can be made by steam reforming of methane, which is a highly endothermic process:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H^{\circ}_{rxn} = 2.1 \times 10^5 \text{ kJ/kgmol}$$



Spreadsheet Name SPRDSHT-1

Cell	Object	Variable Description
A2	2	Comp Mole Frac (1-ci3-C5==)
A3	2	Comp Mole Frac (1-Pentene)
A4	2	Comp Mole Frac (1-Pentyne)
A5	2	Comp Mole Frac (1-tr3-C5==)
A6	2	Comp Mole Frac (2-Pentyne)
A7	2	Comp Mole Frac (2M-1-butene)
A8	2	Comp Mole Frac (2M-13-C4==)
A9	2	Comp Mole Frac (2M-2-butene)
A10	2	Comp Mole Frac (3-M-1-Butyne)

☐ Ignored

Figure 4.7. Product composition spreadsheet.

Steam reforming is usually carried out in fired tubular reactors, with catalyst packed inside the tubes and fuel fired on the outside of the tubes to provide the heat of reaction. The product gas mixture contains carbon dioxide and water vapor as well as carbon monoxide and hydrogen and is conventionally known as *synthesis gas* or *syngas*.

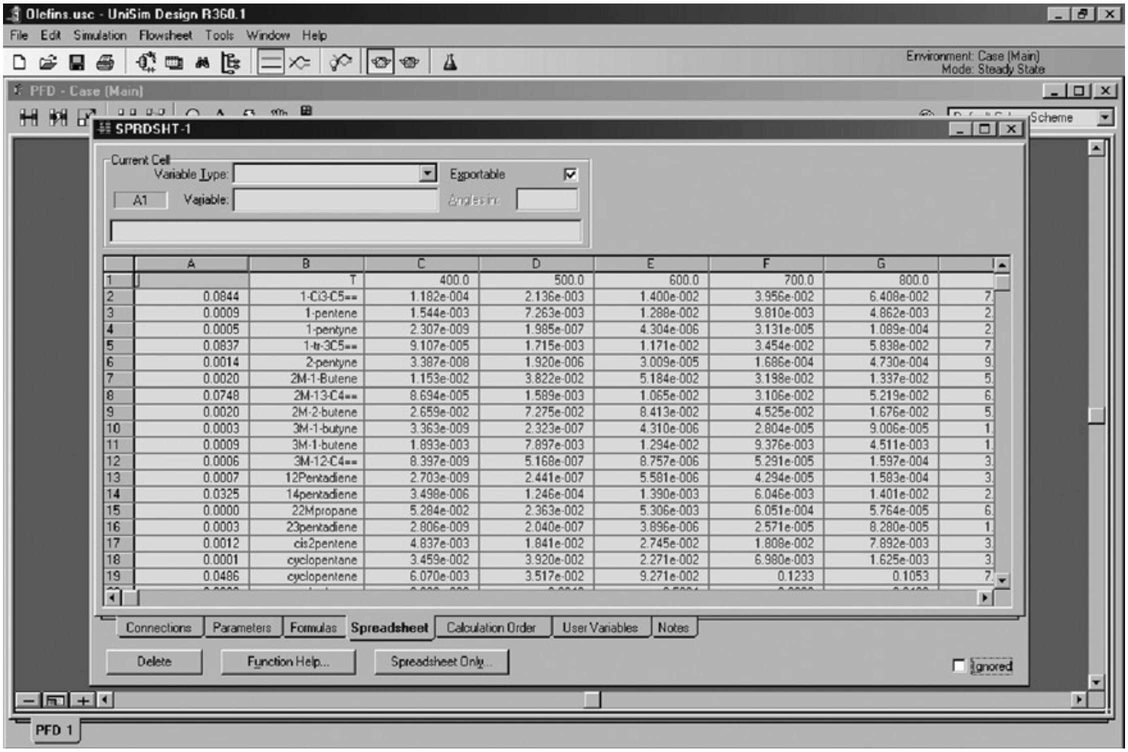
Hydrogen can also be made by partial oxidation of methane, which is an exothermic process, but yields less product per mole of methane feed:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \quad \Delta H^\circ_{rxn} = -7.1 \times 10^4\ \text{kJ/kgmol}$$

When steam, oxygen, and methane are combined, heat from the partial oxidation reaction can be used to provide the heat for steam reforming. The combined process is known as *autothermal reforming*. Autothermal reforming has the attraction of requiring less capital investment than steam reforming (because it does not need a fired-heater reactor), but giving higher yields than partial oxidation.

The yield of hydrogen can be further increased by carrying out the water gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^\circ_{rxn} = -4.2 \times 10^4\ \text{kJ/kgmol}$$



	A	B	C	D	E	F	G	
1		T	400.0	500.0	600.0	700.0	800.0	
2	0.0844	1-Ci3-C5==	1.182e-004	2.136e-003	1.400e-002	3.956e-002	6.408e-002	7.
3	0.0009	1-pentene	1.544e-003	7.263e-003	1.288e-002	9.810e-003	4.862e-003	2.
4	0.0005	1-pentyne	2.307e-009	1.985e-007	4.304e-006	3.131e-005	1.089e-004	2.
5	0.0837	1-tr-3C5==	9.107e-005	1.715e-003	1.171e-002	3.454e-002	5.838e-002	7.
6	0.0014	2-pentyne	3.387e-008	1.920e-006	3.009e-005	1.686e-004	4.730e-004	9.
7	0.0020	2M-1-Butene	1.153e-002	3.822e-002	5.184e-002	3.198e-002	1.337e-002	5.
8	0.0748	2M-13-C4==	8.694e-005	1.589e-003	1.065e-002	3.106e-002	5.219e-002	6.
9	0.0020	2M-2-butene	2.659e-002	7.275e-002	8.413e-002	4.525e-002	1.676e-002	5.
10	0.0003	3M-1-butyne	3.363e-009	2.323e-007	4.310e-006	2.804e-005	9.006e-005	1.
11	0.0009	3M-1-butene	1.893e-003	7.897e-003	1.294e-002	9.376e-003	4.511e-003	1.
12	0.0006	3M-12-C4==	8.397e-009	5.168e-007	8.757e-006	5.291e-005	1.597e-004	3.
13	0.0007	12Pentadiene	2.703e-009	2.441e-007	5.581e-006	4.294e-005	1.583e-004	3.
14	0.0325	14pentadiene	3.498e-006	1.246e-004	1.390e-003	6.046e-003	1.401e-002	2.
15	0.0000	22Mpropane	5.284e-002	2.363e-002	5.306e-003	6.051e-004	5.764e-005	6.
16	0.0003	23pentadiene	2.806e-009	2.040e-007	3.896e-006	2.571e-005	8.280e-005	1.
17	0.0012	cis2pentene	4.837e-003	1.841e-002	2.745e-002	1.808e-002	7.892e-003	3.
18	0.0001	cyclopentane	3.459e-002	3.920e-002	2.271e-002	6.980e-003	1.625e-003	3.
19	0.0486	cyclopentene	6.070e-003	3.517e-002	9.271e-002	0.1233	0.1053	7.

Figure 4.8. Spreadsheet results.

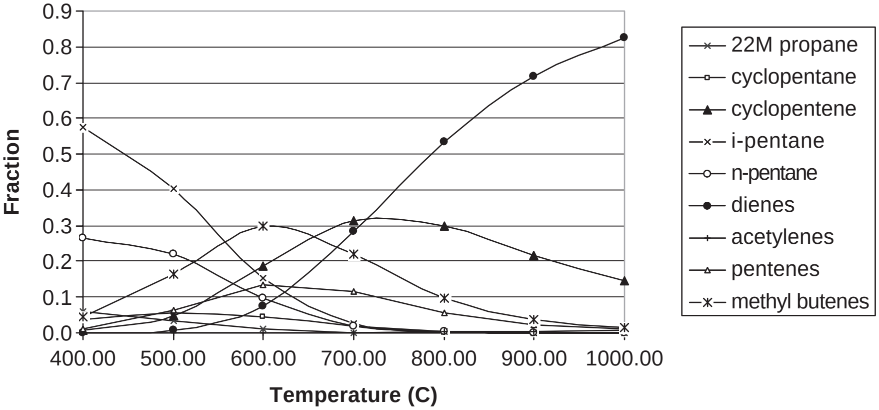


Figure 4.9. Product distribution.

The water gas shift reaction equilibrates rapidly at temperatures above about 450°C. At high temperatures this reaction favors the formation of carbon monoxide, while at low temperatures more hydrogen is formed. When hydrogen is the desired product, the shift reaction is promoted at lower temperatures by using an excess of steam and providing a medium- or low-temperature shift catalyst.

In an autothermal reforming process, 1000 kmol/h of methane at 20°C is compressed to 10 bar, mixed with 2500 kmol/h of saturated steam and reacted with pure oxygen to give 98% conversion of the methane. The resulting products are cooled and passed over a medium-temperature shift catalyst that gives an outlet composition corresponding to equilibrium at 350°C.

i. How much heat is required to vaporize the steam?
ii. How much oxygen is needed?
iii. What is the temperature at the exit of the autothermal reforming reactor?
iv. What is the final molar flow rate of each component of the synthesis gas?

Solution

This problem was solved using Aspen Plus. The model must simulate the high temperature reforming reaction and also the re-equilibration of the water gas shift reaction as the product gas is cooled. A Gibbs reactor can be used for the high temperature reaction, but an equilibrium reactor must be specified for the shift reactor, as only the water gas shift reaction will re-equilibrate at 350°C. Because the methane compressor supplies some heat to the feed, it should be included in the model. Since the question asks how much heat is needed to vaporize the steam, a steam boiler should also be included. The oxygen supply system can also be included, giving the model shown in Figure 4.10.

The heat duty to the reforming reactor is specified as zero. The oxygen flow rate can then be adjusted until the desired methane conversion is achieved. For 98% conversion, the flow rate of methane in the autothermal reactor product (stream 502) is 2% of the flow rate in the reactor feed (stream 501), i.e., 20 kmol/h. For the purpose of this example, the oxygen flow rate was adjusted manually, although a controller could have been used, as described in Section 4.8. The results are shown in Figure 4.11.

When the simulation model was run, the following values were calculated:

i. The steam heater requires 36 MW of heat input.
ii. 674 kmol/h of oxygen is needed.
iii. The temperature at the exit of the reforming reactor is 893°C.
iv. The molar flow rates at the outlet of the shift reactor (stream 504) are

H_2	2504
H_2O	1956
CO	68
CO_2	912
CH_4	20

It should be immediately apparent from the model output that the process as simulated is far from optimal. The oxygen consumption is larger than the 500 kmol/h that would have been needed for partial oxidation. The excess oxygen is needed

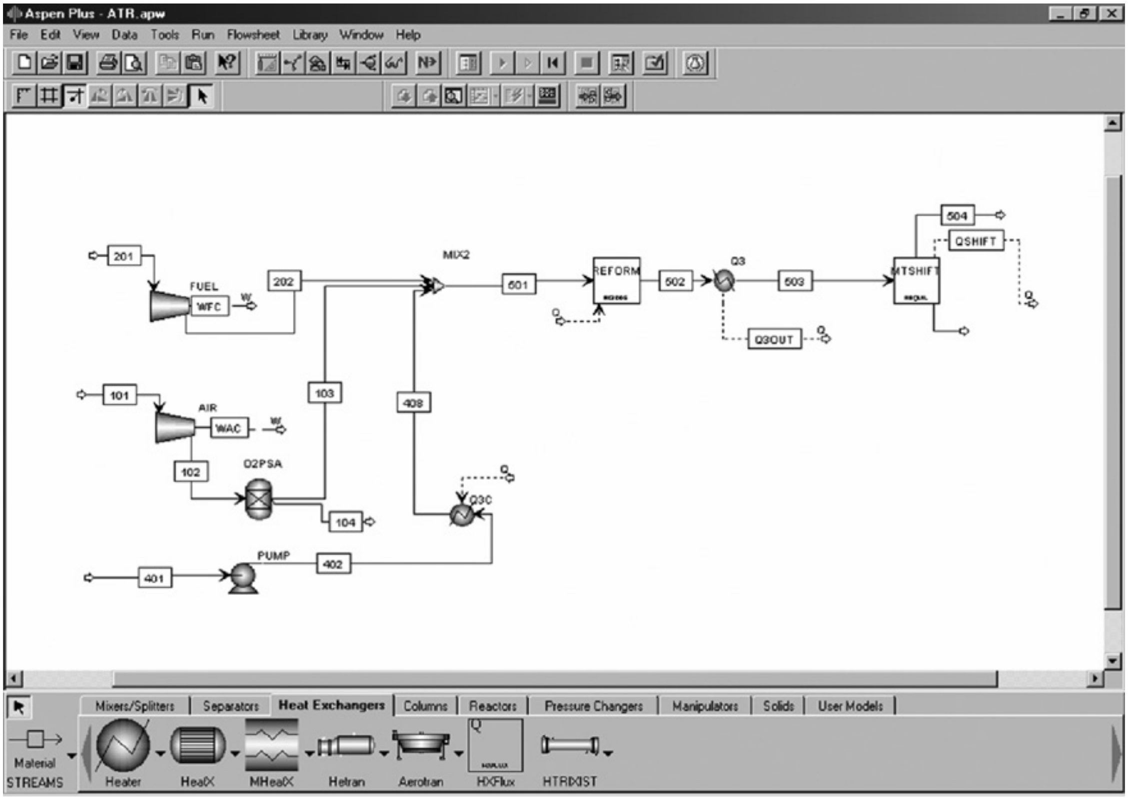


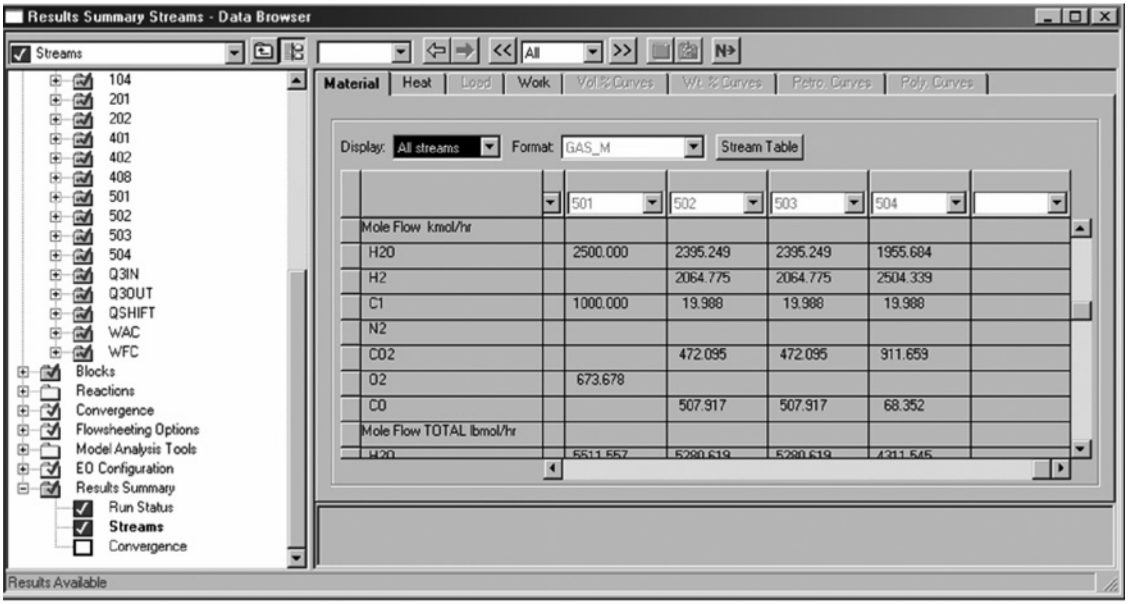
Figure 4.10. Autothermal reforming model.

because the additional steam that is being fed must also be heated to the reactor outlet temperature, which requires more of the feed methane to be burned. The corollary of this result is that the hydrogen yield, at roughly 2.5 moles per mole methane, is not much better than could have been obtained with partial oxidation followed by shift, despite the large excess of steam used.

The designer has several options that could be examined to improve this process:

1. Increase heat recovery from the product gas to the feed streams to preheat the reactor feed and reduce the amount of oxygen that is needed.
2. Reduce the amount of steam fed with the methane.
3. Bypass a part of the steam from the reformer feed to the shift reactor feed, so as to obtain the benefit of driving the equilibrium in the shift reactor without the cost of providing extra heat to the reformer.
4. Reduce the conversion of methane so that a lower reactor conversion and lower outlet temperature are required.

In practice, all of these options are implemented to some extent to arrive at the optimal autothermal reforming conditions. This optimization is explored further in problem 4.13.



Display: All streams Format: GAS_M

	501	502	503	504	
Mole Flow kmol/hr					
H20	2500.000	2395.249	2395.249	1955.684	
H2		2064.775	2064.775	2504.339	
C1	1000.000	19.988	19.988	19.988	
N2					
C02		472.095	472.095	911.659	
02	673.678				
C0		507.917	507.917	68.352	
Mole Flow TOTAL lbmol/hr					
H20	5511.557	5280.619	5280.619	4311.545	

Figure 4.11. Autothermal reactor model results.

4.5.2. Distillation

The commercial process simulators contain a range of distillation models with different degrees of sophistication. The design engineer must choose a model that is suitable for the purpose, depending on the problem type, the extent of design information available, and the level of detail required in the solution. In some cases, it may make sense to build different versions of the flowsheet, using different levels of detail in the distillation models so that the simpler model can be used to initialize a more detailed model.

Shortcut Models

The simplest distillation models to set up are the shortcut models. These models use the Fenske-Underwood-Gilliland or Winn-Underwood-Gilliland method to determine the minimum reflux and number of stages or to determine the required reflux given a number of trays or the required number of trays for a given reflux ratio. These methods are described in Chapter 11. The shortcut models can also estimate the condenser and reboiler duties and determine the optimum feed tray.

The minimum information needed to specify a shortcut distillation model is

- The component recoveries of the light and heavy key components;
- The condenser and reboiler pressures;
- Whether the column has a total or partial condenser.

In some cases, the designer can specify the purities of the light and heavy key components in the bottoms and distillate respectively. Care is needed when using purity as a specification, as it is easy to specify purities or combinations of purity and recovery that are infeasible.

The easiest way to use a shortcut distillation model is to start by estimating the minimum reflux and number of stages. The optimum reflux ratio is usually between 1.05 and 1.25 times the minimum reflux ratio, R_{min}, so $1.15 \times R_{min}$ is often used as an initial estimate. Once the reflux ratio is specified, the number of stages and optimum feed stage can be determined. The shortcut model results can then be used to set up and initialize a rigorous distillation simulation.

Shortcut models can also be used to initialize fractionation columns (complex distillation columns with multiple products), as described later.

Shortcut distillation models are robust and are solved quickly. They do not give an accurate prediction of the distribution of non-key components, and they do not perform well when there is significant liquid-phase nonideality, but they are an efficient way of generating a good initial design for a rigorous distillation model. In processes that have a large number of recycle streams, it is often worthwhile to build one model with shortcut columns and a second model with rigorous columns. The simple model will converge more easily and can be used to provide good initial estimates of column conditions and recycle streams for the detailed model.

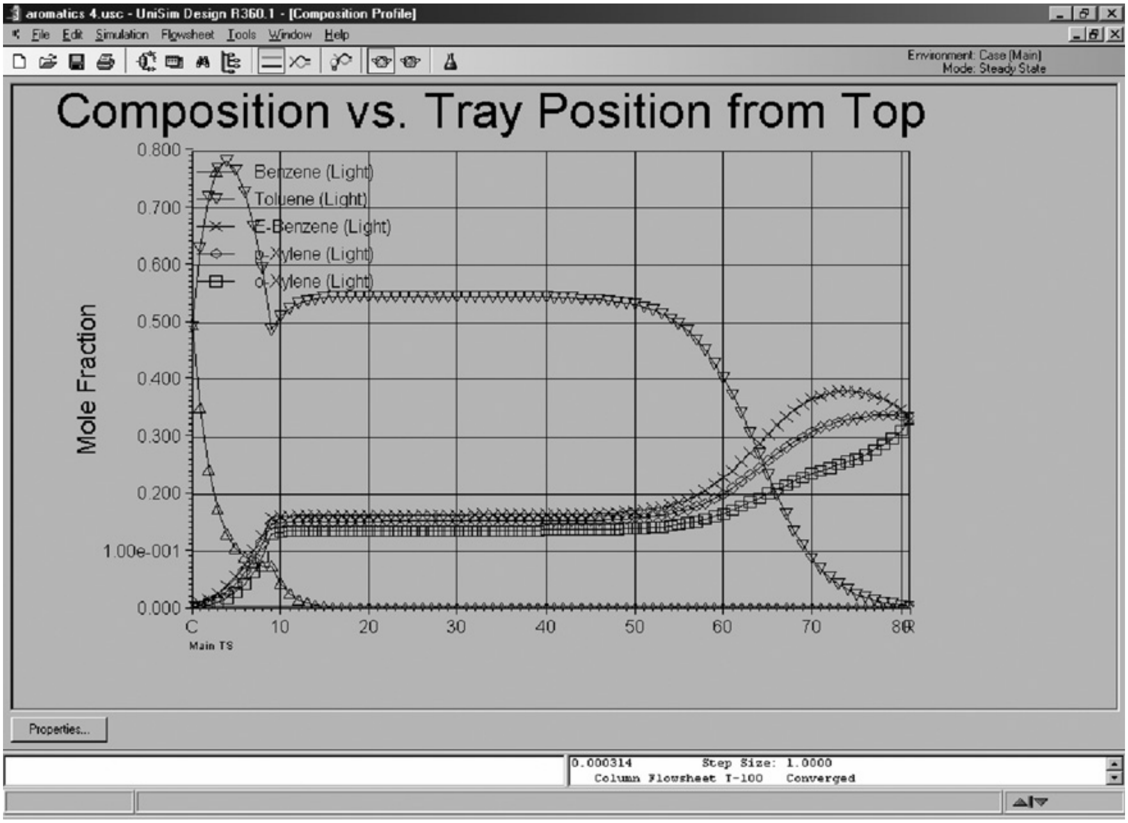
The main drawback of shortcut models is that they assume constant relative volatility, usually calculated at the feed condition. If there is significant liquid- or vapor-phase nonideality, then constant relative volatility is a very poor assumption and shortcut models should not be used.

Rigorous Models

Rigorous models carry out full stage-by-stage mass and energy balances. They give better predictions of the distribution of components than shortcut models, particularly when the liquid phase behaves nonideally, as the flash calculation is made on each stage. Rigorous models allow many more column configurations, including use of side streams, intermediate condensers and reboilers, multiple feeds, and side strippers and rectifiers. Rigorous models can be much harder to converge, particularly if poor initial estimates are used or if the column is improperly specified.

The two main types of rigorous distillation models are equilibrium-stage models and rate-based models. Equilibrium-stage models assume either full vapor-liquid equilibrium on each stage or else an approach to equilibrium based on a stage efficiency entered by the designer. When an equilibrium-stage model is used for column sizing, the stage efficiencies must be entered. Stage efficiency is typically less than 0.8, and is discussed in more detail in Chapter 11. Rate-based models do not assume phase equilibrium, except at the vapor-liquid interface, and instead solve the inter-phase mass transfer and heat transfer equations. Rate-based models are more realistic than the idealized equilibrium-stage models, but because it can be difficult to predict the interfacial area and mass transfer coefficients, rate-based models are less widely used in practice.

Rigorous distillation models can be used to model absorber columns, stripper columns, refluxed absorbers, three-phase systems such as extractive distillation columns, many possible complex column configurations, and columns that include



```
0.000314          Step Size:  1.0000
   Column Flowsheet T-100   Converged
```

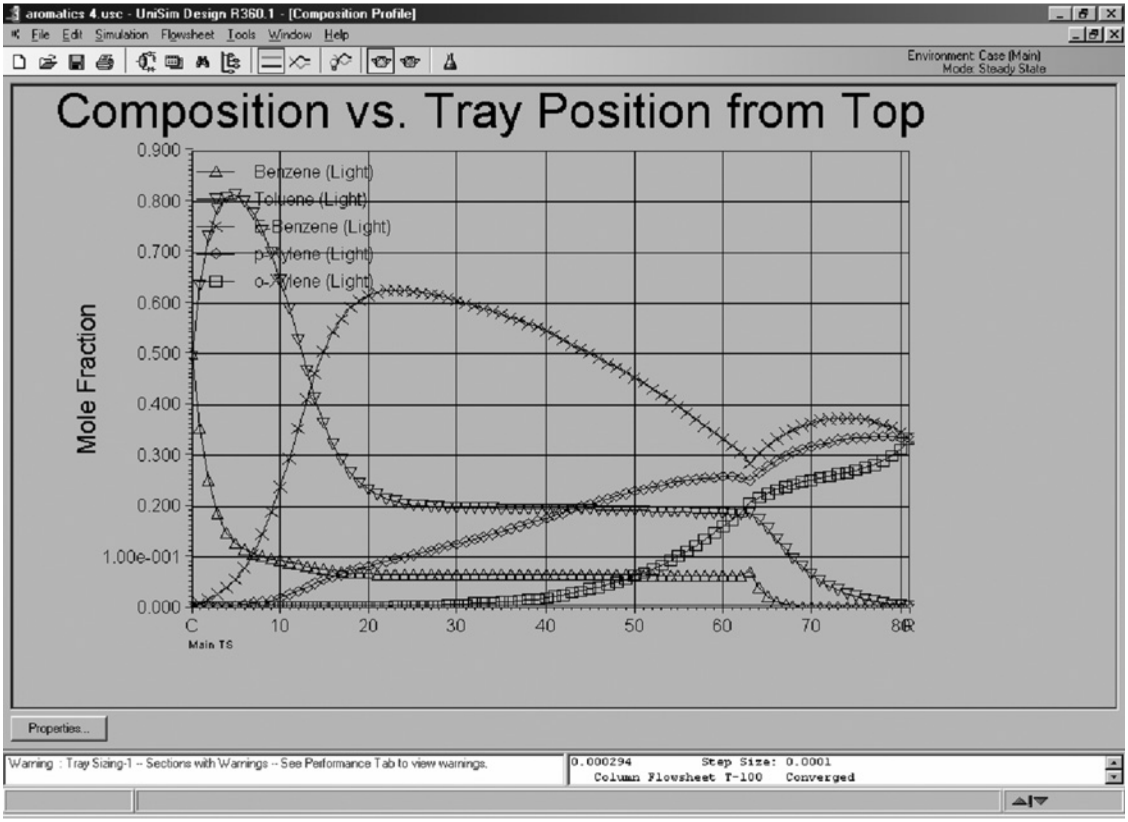
Figure 4.12. Feed tray too high.

reactions such as reactive distillation and reactive absorption columns. The formation of a second liquid phase (usually a water phase) in the column can be predicted if the designer has selected a liquid phase activity model that allows for the prediction of two liquid phases.

One of the most useful features of the rigorous distillation models in the commercial simulation programs is that most include a tool for plotting column profiles. The design engineer can generate plots showing the molar composition of each species in either phase versus tray number. These plots can be helpful in troubleshooting column designs.

For example, Figures 4.12 to 4.17 show column profiles for the distillation problem introduced in Example 1.1, which is described in more detail in Examples 4.3 and 4.4. The column was simulated in UniSim Design.

- In Figure 4.12, the feed stage was moved up to tray 10, which is too high. The column profiles show a broad flat region between trays 20 and 45, indicating that nothing much is going on over this part of the column. There are too many trays in the stripping section and the feed tray should be moved lower. Sections



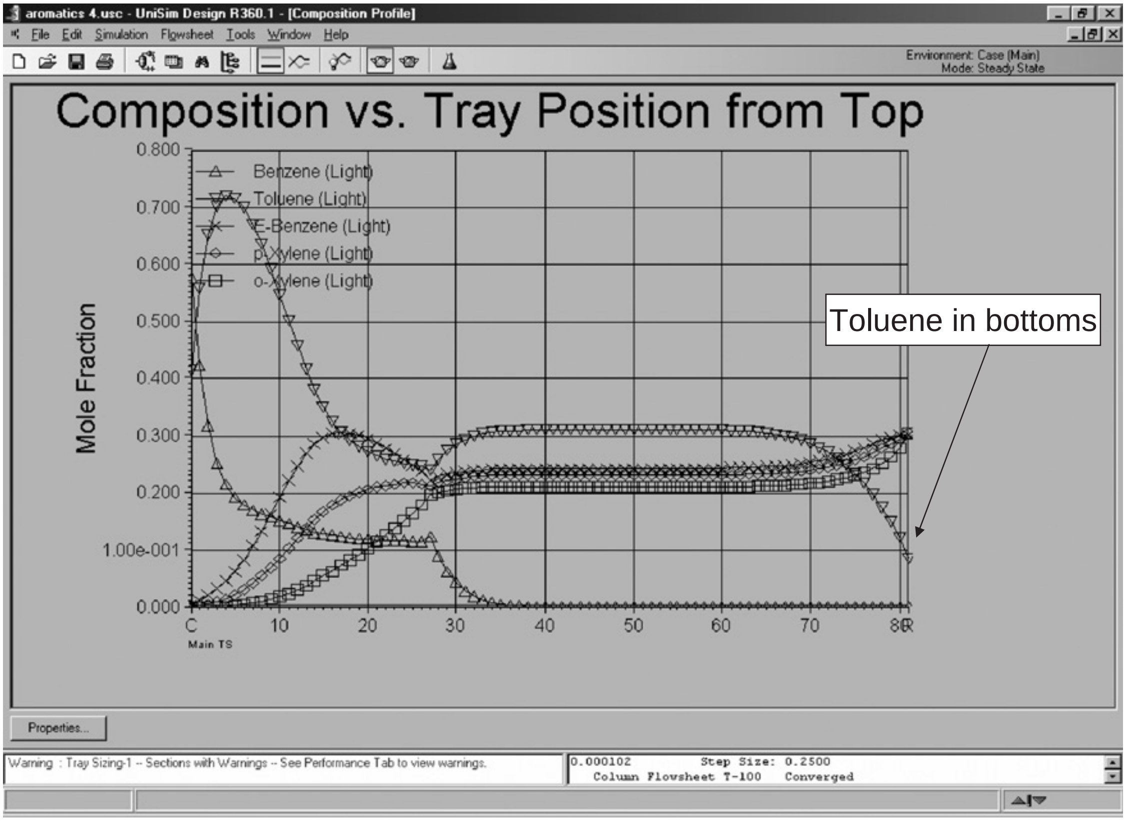
Warning : Tray Sizing-1 -- Sections with Warnings -- See Performance Tab to view warnings.

```
0.000294          Step Size: 0.0001
  Column Flowsheet T-100    Converged
```

Figure 4.13. Feed tray too low.

with very small change in composition can also be indicative of pinched regions where an azeotropic mixture is being formed.

- In Figure 4.13, the feed tray has been moved down to tray 63, which is too low. The column profiles for benzene and toluene, the light components, are flat between trays 30 and 60 in the rectifying section, indicating that the feed tray should be moved higher.
- In Figure 4.14, the column specification was changed from toluene recovery to reflux ratio, and a low value of reflux ratio (2.2) was entered. This is less than the minimum reflux required for the specified separation; consequently, the desired recovery of toluene cannot be achieved. The recovery of toluene is reduced to 72%.
- In Figure 4.15, the reflux ratio was increased to 4.0. The recovery of toluene is now 100%, which is greater than the 99% required. This represents a suboptimal use of energy and capital.
- Figure 4.16 shows the column profiles when the number of trays was reduced to 25, with the feed on tray 8. The column profile for toluene shows that there are



Warning : Tray Sizing-1 -- Sections with Warnings -- See Performance Tab to view warnings.

```
0.000102          Step Size: 0.2500
  Column Flowsheet T-100   Converged
```

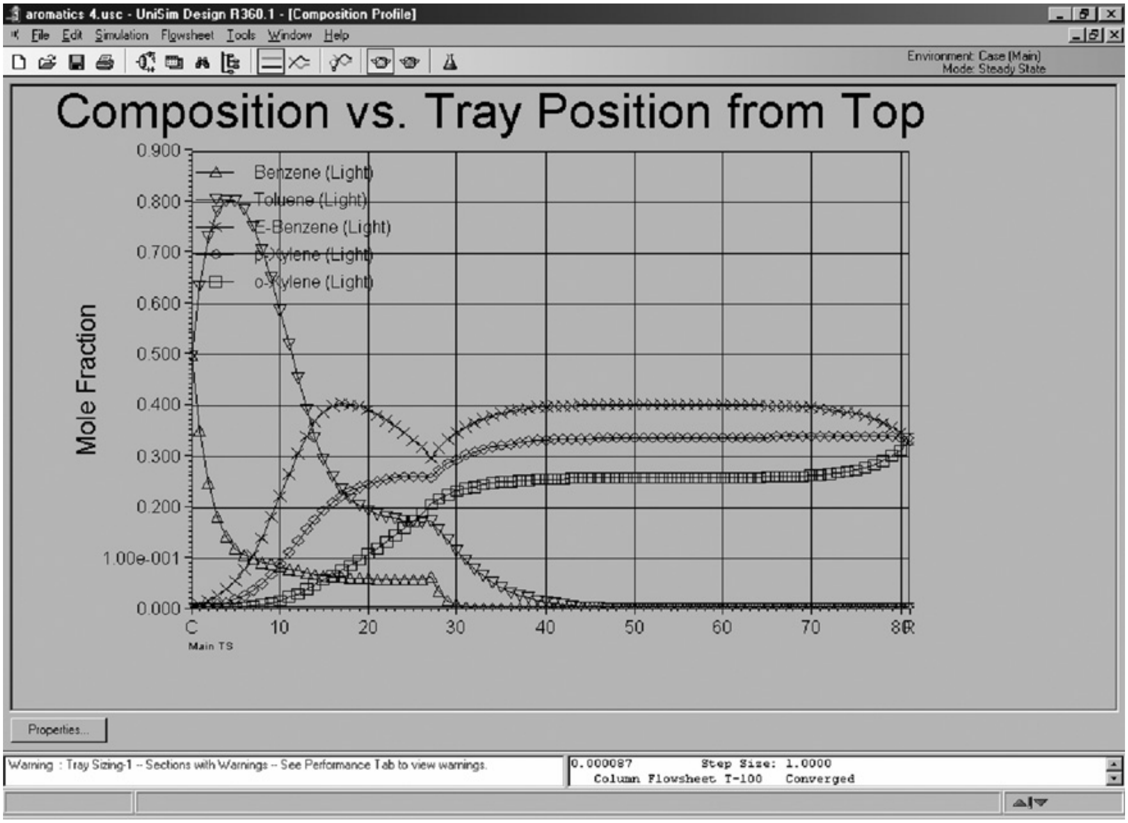
Figure 4.14. Reflux ratio too low: toluene recovery 72%.

insufficient stages (and/or reflux). Although the profile is changing smoothly, the recovery in the distillate is only 24.5%.

- The column profiles with the optimum conditions determined in Example 1.1 are shown in Figure 4.17. The poor features shown in the other profiles are absent.

Complex Columns for Fractionation

Several of the commercial simulation programs offer preconfigured complex column rigorous models for petroleum fractionation. These models include charge heaters, several side strippers, and one or two pump-around loops. These fractionation column models can be used to model refinery distillation operations such as crude oil distillation, vacuum distillation of atmospheric residue oil, fluidized catalytic cracking (FCC) process main columns, and hydrocracker or coker main columns. Aspen Plus also has a shortcut fractionation model, SCFrac, which can be used to configure fractionation columns in the same way that shortcut distillation models are used to initialize multicomponent rigorous distillation models.



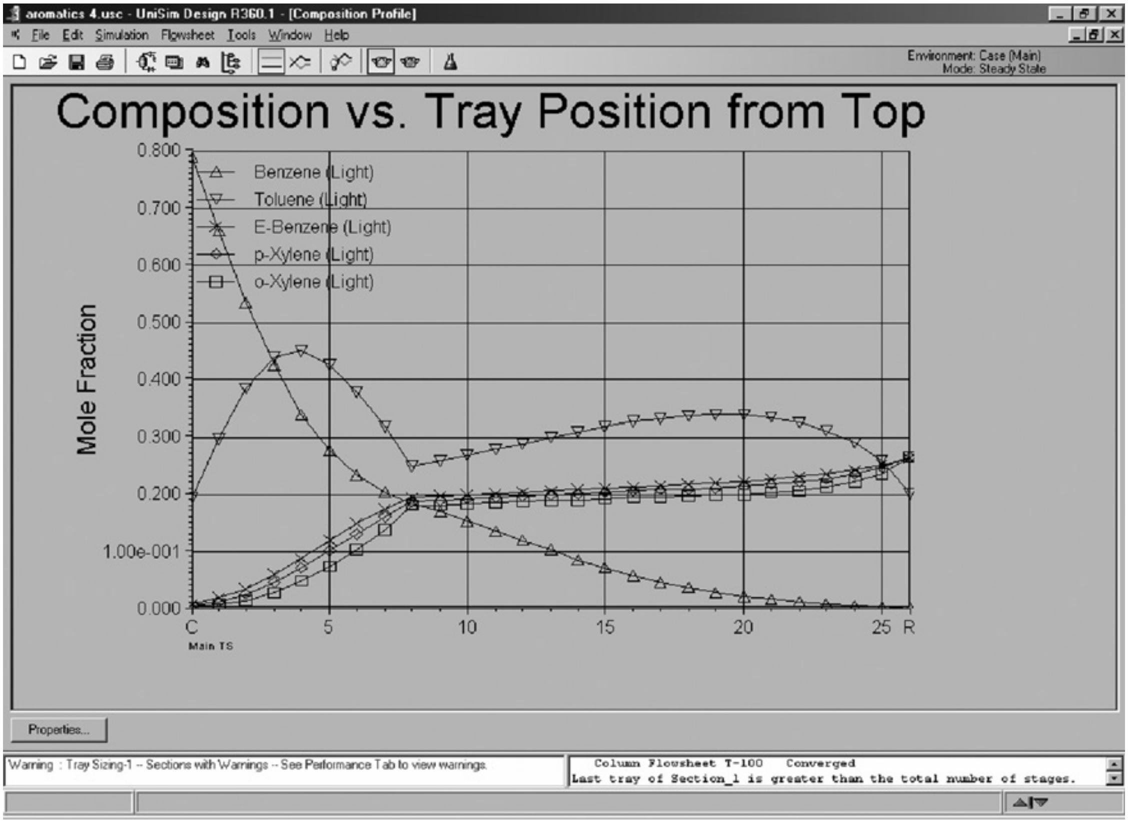
Warning : Tray Sizing-1 -- Sections with Warnings -- See Performance Tab to view warnings.

```
0.000087         Step Size: 1.0000
   Column Flowsheet T-100   Converged
```

Figure 4.15. Reflux ratio too high: toluene recovery 100%.

A typical crude oil distillation column is illustrated in Figure 4.18, which shows a simulation using an Aspen Plus PetroFrac model. The crude oil is preheated in a heat exchange network and charge heater and is then fed to the flash zone at the bottom of the column. Stripping steam is also added at the bottom of the column to provide additional vapor flow. Products with different boiling ranges are withdrawn from the column. The intermediate products are withdrawn from the bottom of side-stripper columns, so as to minimize loss of lighter products in the side stream. Although the exact distillation ranges can vary depending on the local fuels specifications and the sophistication of the refinery, the typical products taken in a crude oil distillation unit are (from the bottom up)

1. Atmospheric residue oil (Residue), containing compounds that boil above about 340°C (650°F). This is normally sent to a vacuum distillation unit to recover more light products, but parts of it may be blended into high sulfur fuels such as heating oil or bunker fuel (marine fuel).
2. Atmospheric gas oil (AGO), containing compounds that boil in the range 275°C to 340°C (530°F to 650°F). This material is too high-boiling for use as a



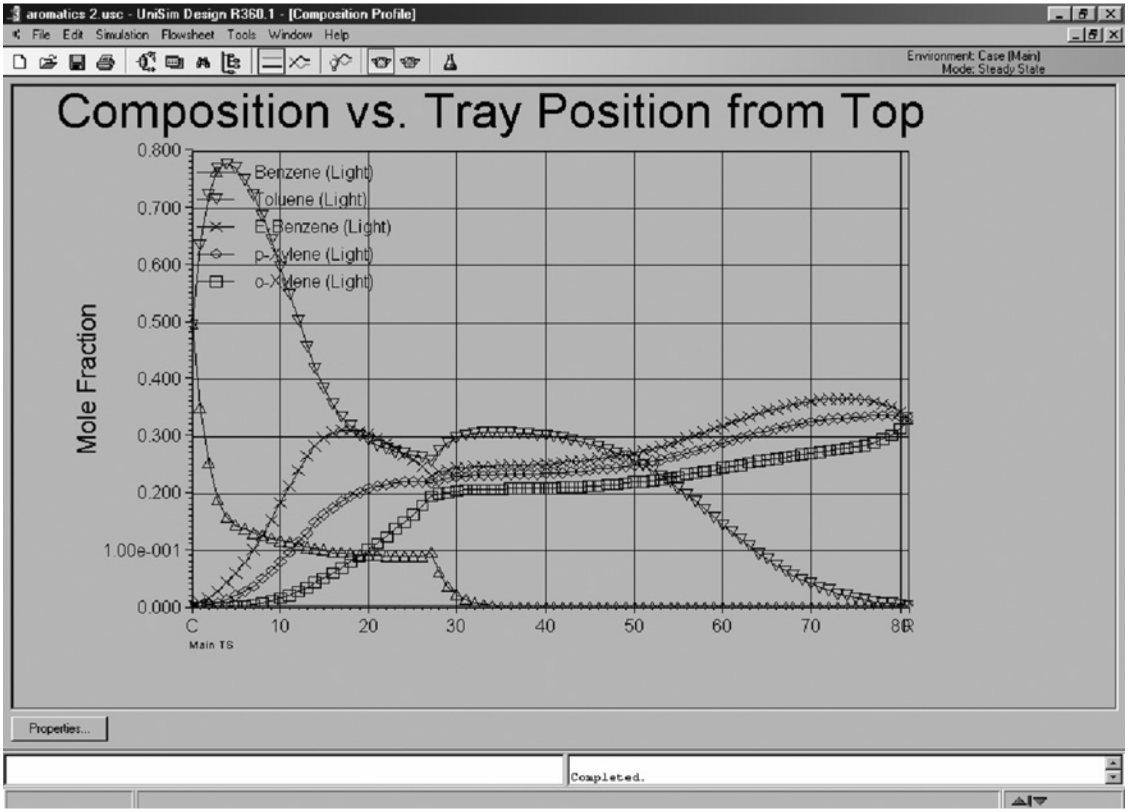
Warning : Tray Sizing-1 -- Sections with Warnings -- See Performance Tab to view warnings.

```
Column Flowsheet T-100   Converged
Last tray of Section_1 is greater than the total number of stages.
```

Figure 4.16. Too few trays: toluene recovery 24.5%.

transportation fuel and is usually sent to a hydrocracker or FCC unit for conversion to lighter products.

3. Heavy distillate (straight-run distillate or SRD), containing compounds that boil in the range 205°C to 275°C (400°F to 530°F). This material is hydrotreated to remove sulfur compounds and can then be blended into heating oils and diesel fuels for trucks, railroad engines, and off-road applications such as tractors and mining equipment.
4. Light distillate (straight-run kerosene or SRK), containing compounds that boil in the range 175°C to 230°C (350°F to 450°F). Light distillate is hydro treated to remove sulfur and can then be blended into jet fuel or sold as kerosene (sometimes called paraffin) for lamp and cooking fuel.
5. Naphtha, boiling in the range 25°C to 205°C (80°F to 400°F). Naphtha is usually sent to an additional column for separation into a light naphtha boiling below 80°C (180°F) and a heavy naphtha. Heavy naphtha has the right boiling range for gasoline, but usually has a very low octane number. It is typically upgraded by catalytic reforming using noble metal catalysts, to increase the concentration of



Completed.

Figure 4.17. Optimized column profiles.

aromatic hydrocarbons in the naphtha and raise the octane number. Catalytic reforming is also the first step in the production of aromatic hydrocarbons for petrochemicals manufacture. Light naphtha also boils in a suitable range for blending into gasoline and often has an acceptable octane number. It is usually treated to oxidize odiferous mercaptan sulfur compounds. Light naphtha is also widely used as a petrochemical feedstock for steam cracking to produce olefin compounds such as ethylene and propylene.

6. The overhead product of the crude unit contains hydrogen, methane, carbon dioxide, hydrogen sulfide, and hydrocarbons up to butanes and some pentanes. It is usually sent to a set of distillation columns known as a "saturate gas plant" for recovery of propane and butane for sale. The lighter gases are then used as refinery fuel.

The design of refinery fractionation columns can be complex. The pump-around streams function as intermediate condensers and remove surplus heat from the column. This heat is usually recovered by heat exchange with the cold crude oil feed. Oil refineries are often designed to handle many different crude oils with

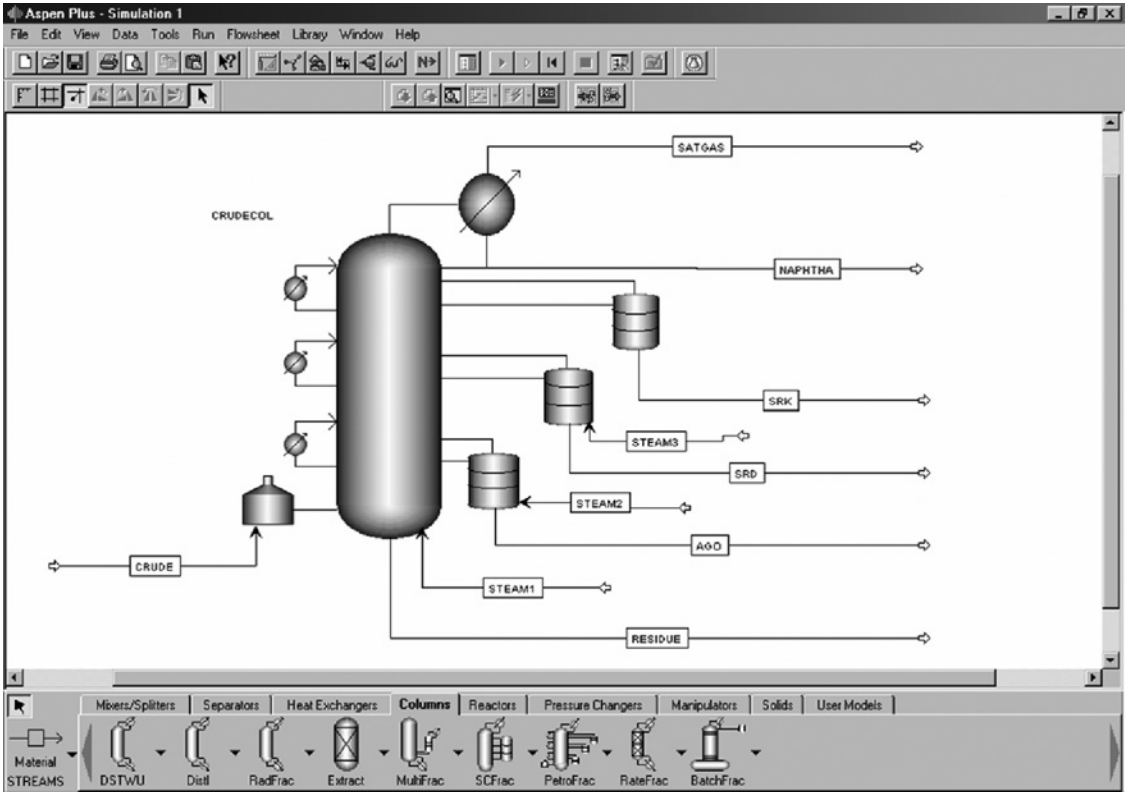


Figure 4.18. Crude oil fractionation.

different boiling assays. The refinery may make different product slates at different times of the year, or in response to market conditions. The crude oil distillation and associated heat exchange network must be flexible enough to handle all of these variations, while still achieving tight specifications on the boiling point curves of every product.

Column Sizing

The rigorous column models allow the design engineer to carry out tray sizing and hydraulics calculations for the basic types of distillation trays and for some types of random and structured packing. Different commercial simulators use different tray sizing correlations, but they all follow a method similar to that described in Chapter 11.

The tray sizing tools are not always enabled when running the distillation models. In some of the simulation programs, the design engineer must enable a tray sizing program and/or enter default values for tray type and tray spacing before the sizing algorithm will work properly. If the column diameter does not change when the reflux rate is significantly changed (or if all the columns in the simulation appear to have the same diameter), then the designer should check to make sure that the tray sizing part of the program is properly configured.

The tray sizing options in the simulators are restricted to standard internals such as sieve trays, valve trays, bubble-cap trays, random packings, and structured packings. They do not include high-capacity trays, high-efficiency trays, or the latest packing designs. When a column is designed that has many stages or a large diameter, it is always worth contacting the column internals vendors for estimates, as use of high-capacity, high-efficiency internals can lead to substantial savings. Advanced internals are also usually used when revamping an existing column to a higher throughput or tighter product specifications.

The design engineer should always allow for tray inefficiency when using column sizing tools in conjunction with an equilibrium-stage model. Failure to do so would underpredict number of stages and hence have an impact on the column pressure drop and hydraulics. Estimation of stage efficiency is discussed in Chapter 11. For initial design purposes, a stage efficiency of 0.7 to 0.8 is usually used. For detailed design, stage efficiencies depend on the type of tray used and are often provided by the column internals vendor.

The design engineer must remember to allow a suitable design factor or design margin when sizing columns. Design factors are discussed in Section 1.7. It may be necessary to create two versions of the flowsheet. One version will have the design basis flow rates for producing the mass and energy balances, while the second will have flow rates that are 10% larger for purposes of sizing equipment.

The simulation of distillation processes is discussed in more detail by Luyben (2006).

Example 4.3

This example provides more detail on the solution of the problem that was introduced as Example 1.1. The original problem statement was to optimize the design of a distillation column to separate 225 metric tons per hour of an equimolar mixture of benzene, toluene, ethylbenzene, paraxylene, and orthoxylene with minimum total annualized cost. The feed is a saturated liquid at 330 kPa. The recovery of toluene in the distillate should be greater than 99%, and the recovery of ethylbenzene in the bottoms should be greater than 99%.

In this example, a column simulation should be set up using a shortcut model. The shortcut model results will be used to initialize a rigorous model in the example that follows. Determine

- **i.** The minimum reflux ratio;
- **ii.** The minimum number of trays;
- **iii.** The actual number of trays when the reflux is 1.15 $R_{\min}$;
- **iv.** The optimum feed tray.

Solution

This problem was solved using UniSim Design. The problem was set up as a shortcut column, as shown in Figure 4.19.

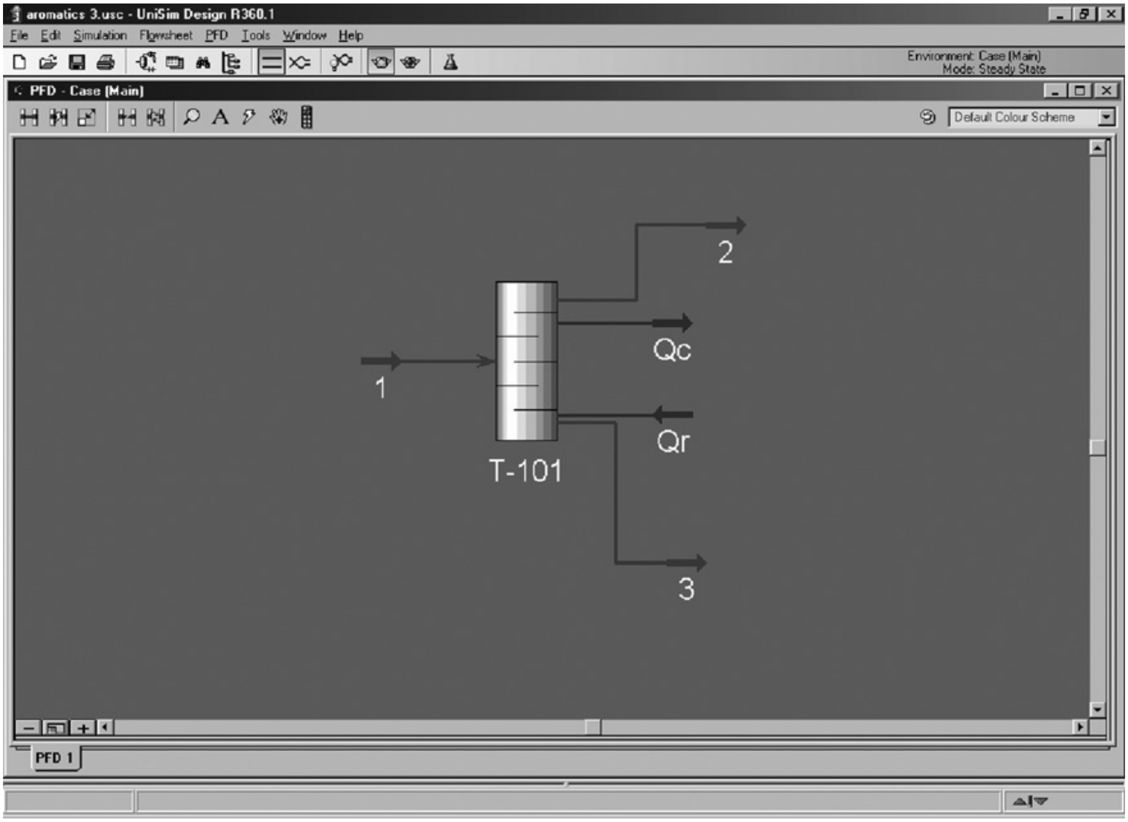


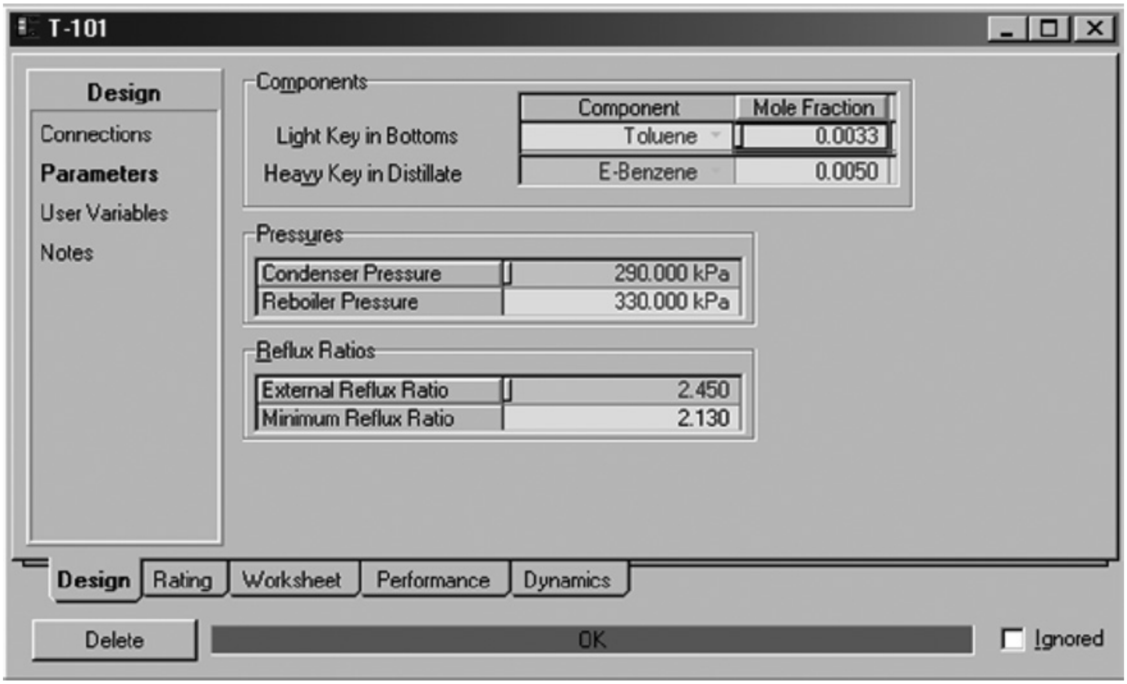
Figure 4.19. Shortcut distillation.

UniSim Design requires the designer to specify the mole fraction of the light key component in the bottoms and the heavy key component in the distillate. We have an equimolar feed, so if we take a basis of 100 mol/h of feed, then the molar flow rate of each component is 20 mol/h. A 99% recovery of each key component corresponds to allowing 0.2 mol/h of that component into the other stream. The mole fractions are then

$$\text{Ethylbenzene in distillate} = 0.2/40 = 0.005$$
$$\text{Toluene in bottoms} = 0.2/60 = 0.00333$$

When these are entered into the shortcut column as specifications, the minimum reflux is calculated to be $R_{\min} = 2.130$. The actual reflux ratio can then be specified as $2.13 \times 1.15 = 2.45$, as shown in Figure 4.20.

The shortcut column results are shown in Figure 4.21. The minimum number of stages is calculated as 16.4, which should be rounded up to 17. The actual number of trays required is 39, with feed at stage 18.



Components

	Component	Mole Fraction
Light Key in Bottoms	Toluene	0.0033
Heavy Key in Distillate	E-Benzene	0.0050

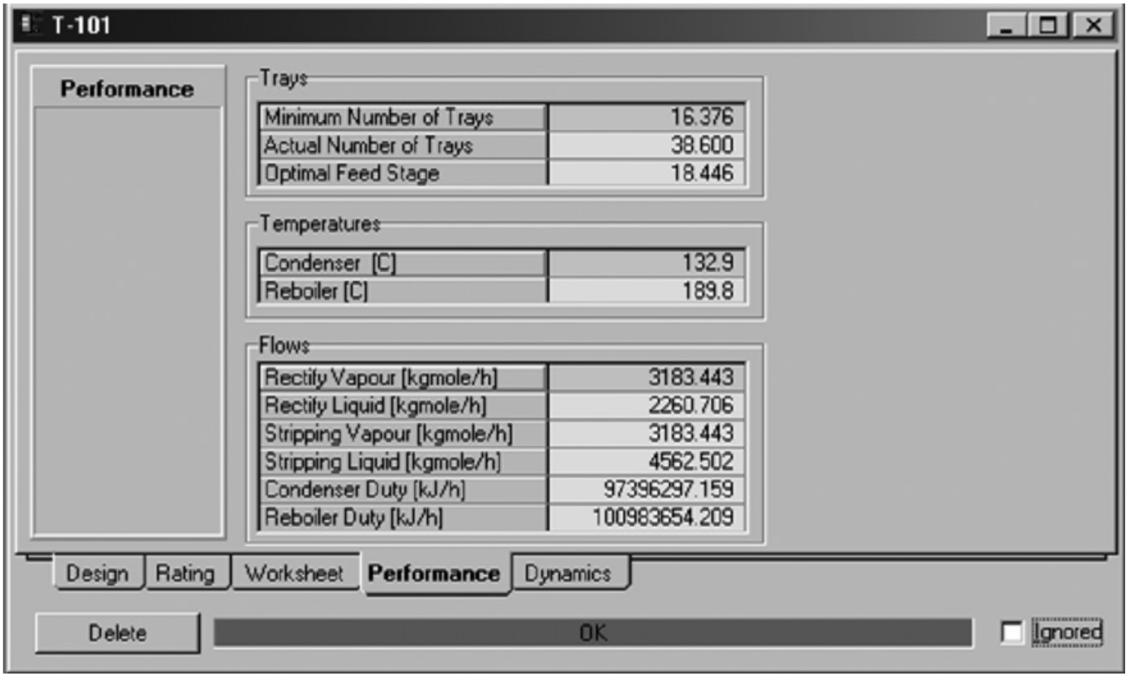
Pressures

Condenser Pressure	290.000 kPa
Reboiler Pressure	330.000 kPa

Reflux Ratios

External Reflux Ratio	2.450
Minimum Reflux Ratio	2.130

Figure 4.20. Shortcut column specifications.



Trays

Minimum Number of Trays	16.376
Actual Number of Trays	38.600
Optimal Feed Stage	18.446

Temperatures

Condenser [C]	132.9
Reboiler [C]	189.8

Flows

Rectify Vapour [kgmole/h]	3183.443
Rectify Liquid [kgmole/h]	2260.706
Stripping Vapour [kgmole/h]	3183.443
Stripping Liquid [kgmole/h]	4562.502
Condenser Duty [kJ/h]	97396297.159
Reboiler Duty [kJ/h]	100983654.209

Figure 4.21. Shortcut column results.

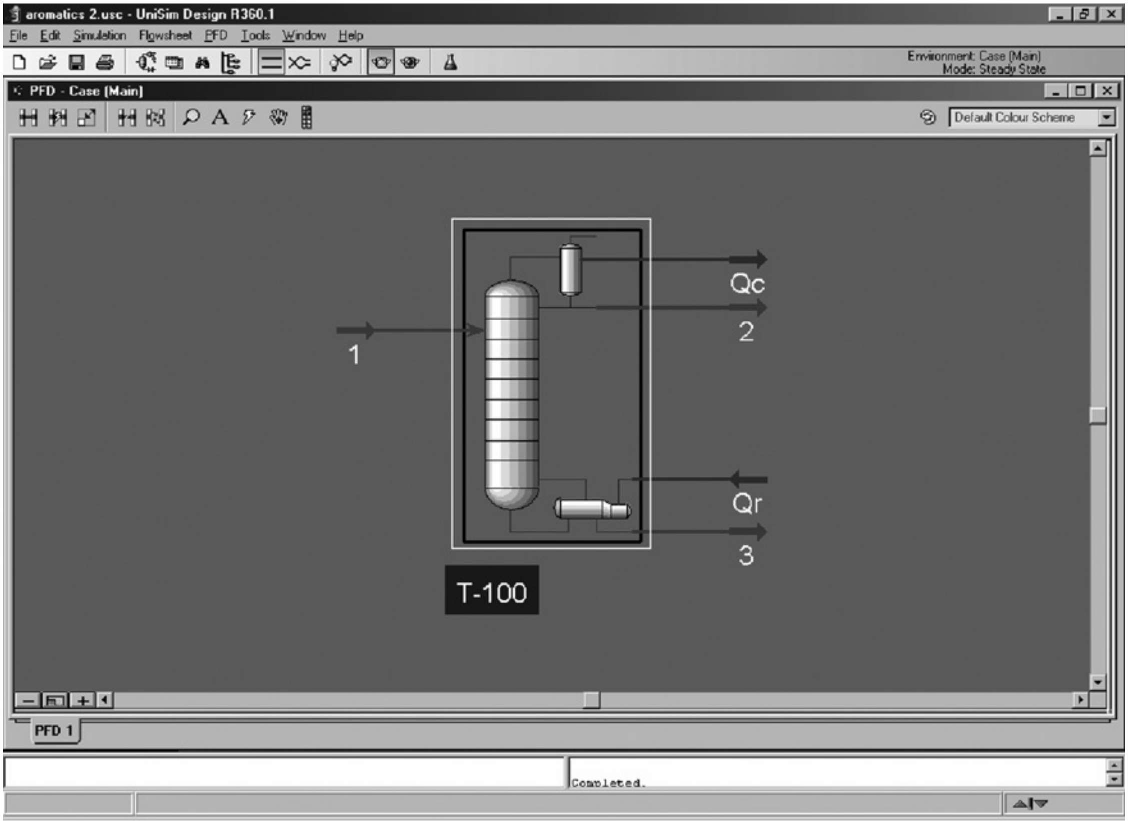
Example 4.4

Continuing the problem defined in Example 4.3, use a rigorous simulation to carry out tray sizing and estimate the required column diameter.

Solution

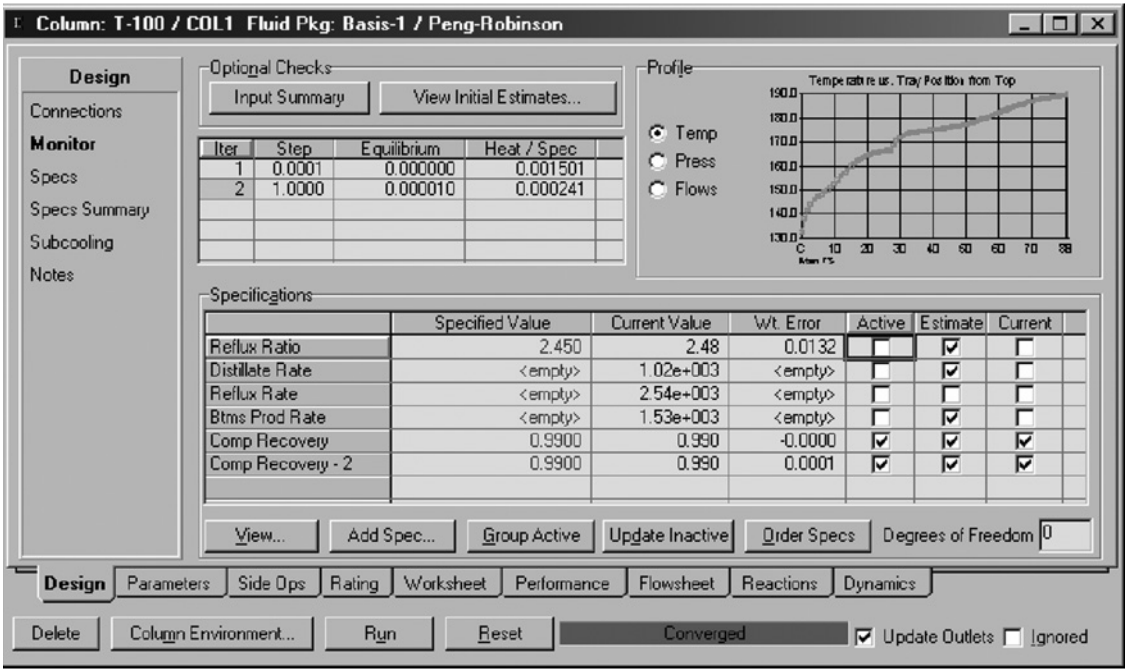
Since we are now sizing the column, the first step is to increase the flow rate to allow for a design factor. The process design basis is 225 metric tons per hour of feed. The equipment design should include at least a 10% safety factor, so the equipment design basis was set at 250 metric tons per hour of feed (rounding up from 247.5 for convenience).

Figure 4.22 shows the rigorous column simulation. UniSim Design allows the designer to enter any two specifications for the column, so instead of entering the reflux ratio as a specification, we can enter the required recoveries and provide the value of reflux ratio found in the shortcut model as an initial estimate, as shown in Figure 4.23.



Completed.

Figure 4.22. Rigorous distillation.



Column: T-100 / COL1 Fluid Pkg: Basis-1 / Peng-Robinson

Iter	Step	Equilibrium	Heat / Spec
1	0.0001	0.000000	0.001501
2	1.0000	0.000010	0.000241

● Temp ○ Press ○ Flows

	Specified Value	Current Value	Wt. Error	Active	Estimate	Current
Reflux Ratio	2.450	2.48	0.0132	☐	☑	☐
Distillate Rate	<empty>	1.02e+003	<empty>	☐	☑	☐
Reflux Rate	<empty>	2.54e+003	<empty>	☐	☐	☐
Btms Prod Rate	<empty>	1.53e+003	<empty>	☐	☑	☐
Comp Recovery	0.9900	0.990	-0.0000	☑	☑	☑
Comp Recovery - 2	0.9900	0.990	0.0001	☑	☑	☑

Degrees of Freedom 0

Converged ☑ Update Outlets ☐ Ignored

Figure 4.23. Rigorous column specifications.

The column converges quickly with the good estimate provided from the shortcut model. The column profiles can be checked by selecting the "Performance" tab in the column environment and then selecting "Plots" from the menu on the left and "Composition" from the list of possible plots, as shown in Figure 4.24. This generates composition profiles like those presented in Figures 4.12 to 4.17.

To size the trays in UniSim Design, we must activate the tray sizing utility (from the Tools menu via Tools/Utilities/Tray Sizing). When sieve trays are selected with the default spacing of 609.6 mm (2 ft) and the other default parameters shown in Figure 4.25, then the results in Figure 4.26 are obtained. The column diameter is found to be 4.42 m.

The data on column size, number of trays, reboiler, and condenser duty can then be extracted from the simulation and put into a cost model or spreadsheet to carry out optimization of the total annual cost of production. The results of the optimization are described in Example 1.1.

4.5.3. Other Separations

Other multistage vapor-liquid separations such as absorption and stripping can be modeled using variations of the rigorous distillation models, as can multistage liquid-liquid extraction.

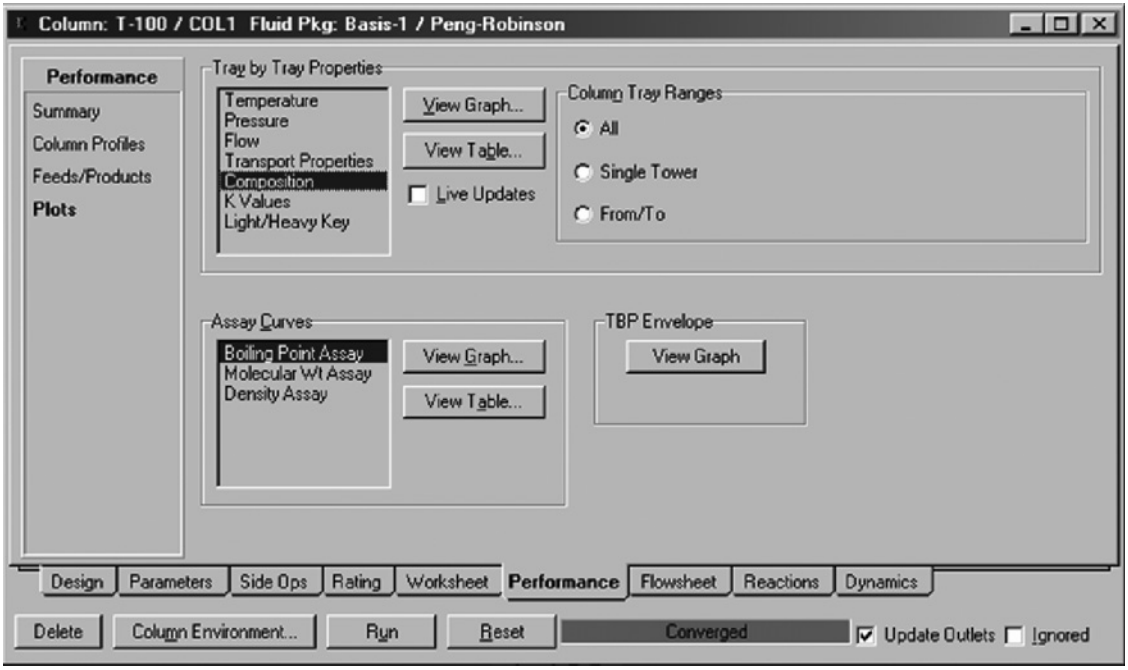
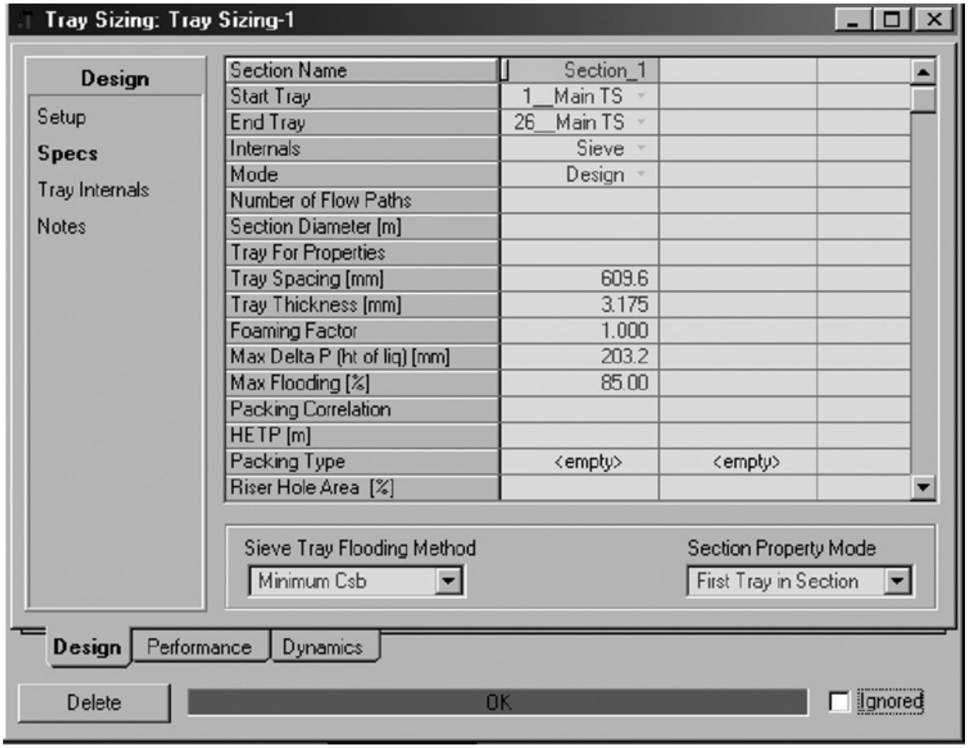


Figure 4.24. Generating column profiles.

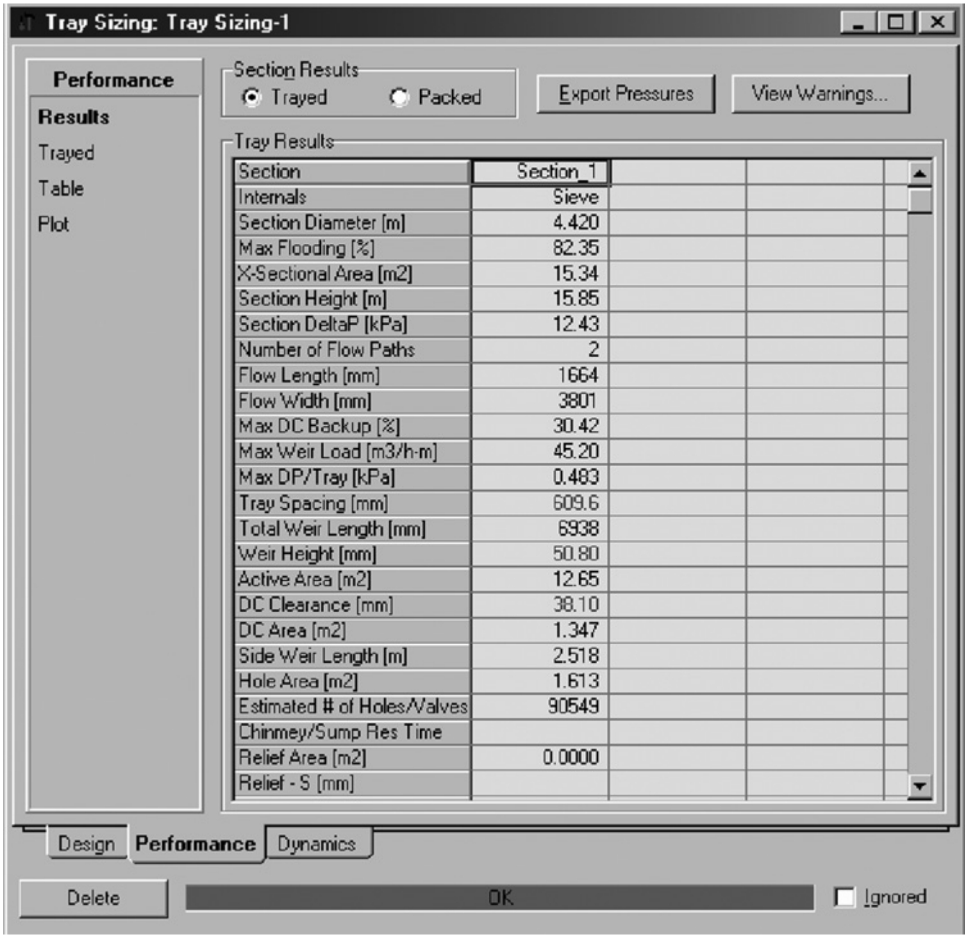


Section Name	Section_1	
Start Tray	1__Main TS	
End Tray	26__Main TS	
Internals	Sieve	
Mode	Design	
Number of Flow Paths		
Section Diameter [m]		
Tray For Properties		
Tray Spacing [mm]	609.6	
Tray Thickness [mm]	3.175	
Foaming Factor	1.000	
Max Delta P (ht of liq) [mm]	203.2	
Max Flooding [%]	85.00	
Packing Correlation		
HETP [m]		
Packing Type	<empty>	<empty>
Riser Hole Area [%]		

Sieve Tray Flooding Method: Minimum Csb

Section Property Mode: First Tray in Section

Figure 4.25. Default tray sizing options.



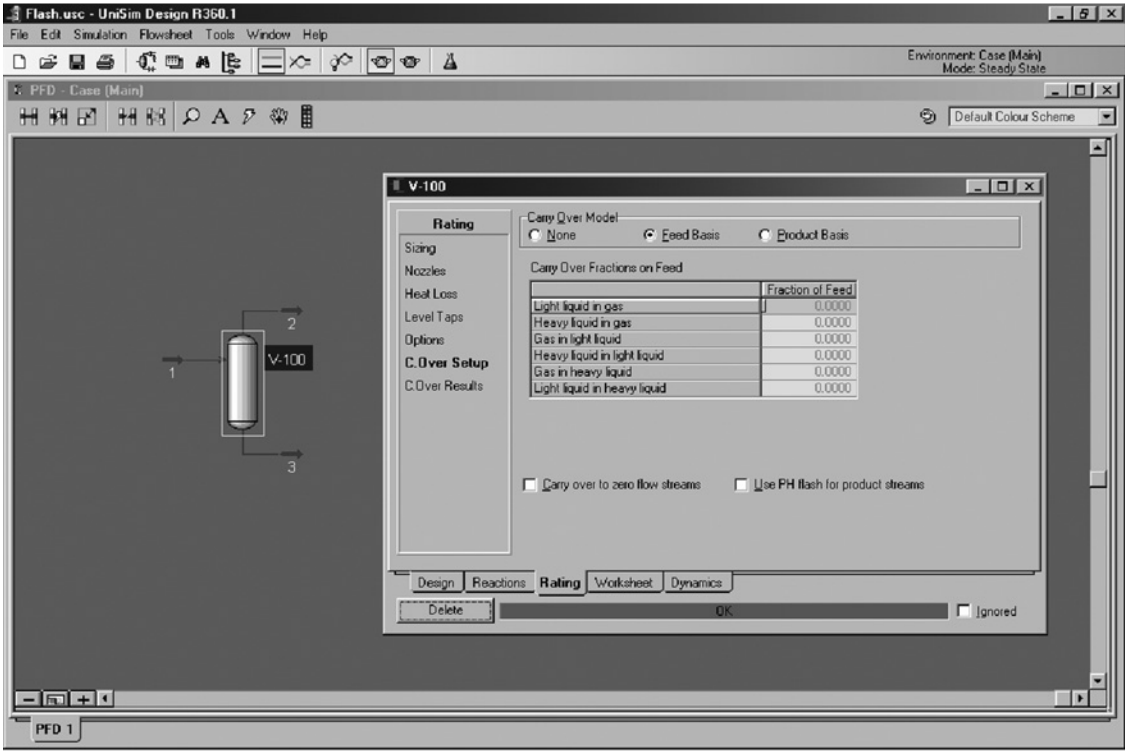
Section Results: ● Trayed ○ Packed

Tray Results

Section	Section_1
Internals	Sieve
Section Diameter [m]	4.420
Max Flooding [%]	82.35
X-Sectional Area [m2]	15.34
Section Height [m]	15.85
Section DeltaP [kPa]	12.43
Number of Flow Paths	2
Flow Length [mm]	1664
Flow Width [mm]	3801
Max DC Backup [%]	30.42
Max Weir Load [m3/h-m]	45.20
Max DP/Tray [kPa]	0.483
Tray Spacing [mm]	609.6
Total Weir Length [mm]	6938
Weir Height [mm]	50.80
Active Area [m2]	12.65
DC Clearance [mm]	38.10
DC Area [m2]	1.347
Side Weir Length [m]	2.518
Hole Area [m2]	1.613
Estimated # of Holes/Valves	90549
Chinmey/Sump Res Time	
Relief Area [m2]	0.0000
Relief - S [mm]	

Figure 4.26. Tray sizing results.

Single-stage liquid-liquid or vapor-liquid separation can be modeled as a flash vessel, but some caution is needed. The simulation programs assume perfect separation in a flash unless the designer specifies otherwise. If there is entrainment of droplets or bubbles, then the outlet compositions of a real flash vessel will be different from those predicted by the simulation. If the flash is critical to process performance, then the designer should make an allowance for entrainment. Most of the simulation programs allow the designer to specify a fraction of each phase that is entrained with the other phases. This is illustrated in Figure 4.27, which shows the data entry sheet for entrained flows for UniSim Design. In UniSim Design, the entrained fractions are entered on the "Rating" tab of the flash model window. Users can also use built-in correlation models with their specified information such as vessel dimensions and nozzle locations. More sophisticated real separator modeling can be found in the



Carry Over Model
○ None ● Feed Basis ○ Product Basis

Carry Over Fractions on Feed

	Fraction of Feed
Light liquid in gas	0.0000
Heavy liquid in gas	0.0000
Gas in light liquid	0.0000
Heavy liquid in light liquid	0.0000
Gas in heavy liquid	0.0000
Light liquid in heavy liquid	0.0000

☐ Carry over to zero flow streams ☐ Use PH flash for product streams

☐ Ignored

Figure 4.27. Flash model with entrainment.

three-phase separator model in UniSim Design. The fraction that is entrained depends on the design of the vessel, as described in Chapter 10.

Most of the simulators contain several models for fluid-solid separation. These models can be used to manipulate the particle size distribution when solids are present.

None of the commercial process simulators contains a good library model for adsorptive separations or membrane separations at the time of writing. These separation methods are important for gas-gas separations, chromatographic separations, and size-exclusion or permeation-based separations. All of these processes must be modeled using component splitters, as described next.

Component Splitter Models

A component splitter is a subroutine in the simulation that allows a set of components from a stream to be transferred into another stream with a specified recovery. Component splitters are convenient for modeling any separation process that cannot be described using one of the library models. Examples of real operations that are usually modeled as component splitters include

- Pressure-swing adsorption
- Temperature-swing adsorption

- Chromatography
- Simulated-moving-bed adsorption
- Membrane separation
- Ion exchange
- Guard beds (irreversible adsorption)

When a component splitter is used in a model, it is a good practice to give the splitter a label that identifies the real equipment that is being modeled.

Component splitters are sometimes used in place of distillation columns when building simple models to provide initial estimates for processes with multiple recycles. There is little advantage to this approach compared with using shortcut distillation models, as the component splitter will not calculate the distribution of non-key components unless a recovery is entered for each. Estimating and entering the recoveries for every component is difficult and tedious, and poor estimates of recoveries can lead to poor estimates of recycle flows, so the use of component splitters in this context effectively adds another layer of iteration to the model.

4.5.4. Heat Exchange

All of the commercial simulators include models for heaters, coolers, heat exchangers, fired heaters, and air coolers. The models are easy to configure, and the only inputs that are usually required on the process side are the estimated pressure drop and either the outlet temperature or the duty. A good initial estimate of pressure drop is 0.3 to 0.7 bar (5 to 10 psi).

The heater, cooler, and heat exchanger models allow the design engineer to enter estimates of film transfer coefficients, and hence calculate the exchanger area. As with distillation columns, the designer must remember to add a design factor to the sizes predicted by the model. Design factors are discussed in Section 1.7.

Problems often arise when using heat exchanger models to simulate processes that have a high degree of process-to-process heat exchange. Whenever a process-to-process heat exchanger is included in a simulation, it sets up an additional recycle of information; consequently, an additional loop must be converged. A common situation is one in which the effluent from a reactor or the bottoms from a distillation column is used to preheat the reactor or column feed, as illustrated in Figure 4.28. If these process flow schemes are simulated using heat exchangers, a recycle of energy is set up between the product and the feed. This recycle must be converged every time the flowsheet is calculated (i.e., at every iteration of any other recycle loop in the process). If more than a few of these exchangers are present, then the overall flowsheet convergence can become difficult.

Instead, it is usually a good practice to model the process using only heaters and coolers and then set up subproblems to model the heat exchangers. This facilitates data extraction for pinch analysis, makes it easier for the designer to recognize when exchangers might be internally pinched or have low F factors (see Chapter 12), and improves convergence.

Another problem that is often encountered when simulating heat exchangers and heat exchange networks is *temperature cross*. A temperature cross occurs when the

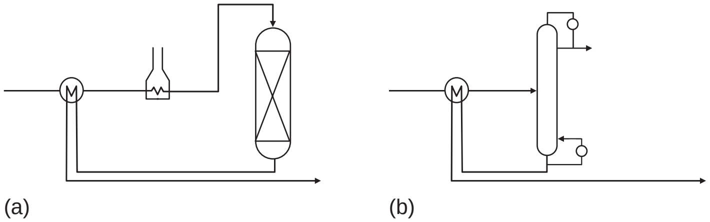


Figure 4.28. Common feed heating schemes (a) Feed-effluent exchange, (b) Feed-bottoms exchange.

cold stream outlet temperature is hotter than the hot stream outlet temperature (Section 12.6). When temperature cross occurs, many types of shell and tube heat exchangers give a very poor approximation of counter-current flow, and consequently have low *F* factors and require large surface areas. In some of the commercial simulation programs, the heat exchanger models will indicate if the *F* factor is low. If this is the case, then the designer should split the exchanger into several shells in series so that temperature cross is avoided. Some of the simulation programs allow the designer to plot profiles of temperature versus heat flow in the exchanger. These plots can be useful in identifying temperature crosses and internal pinches.

Example 4.5

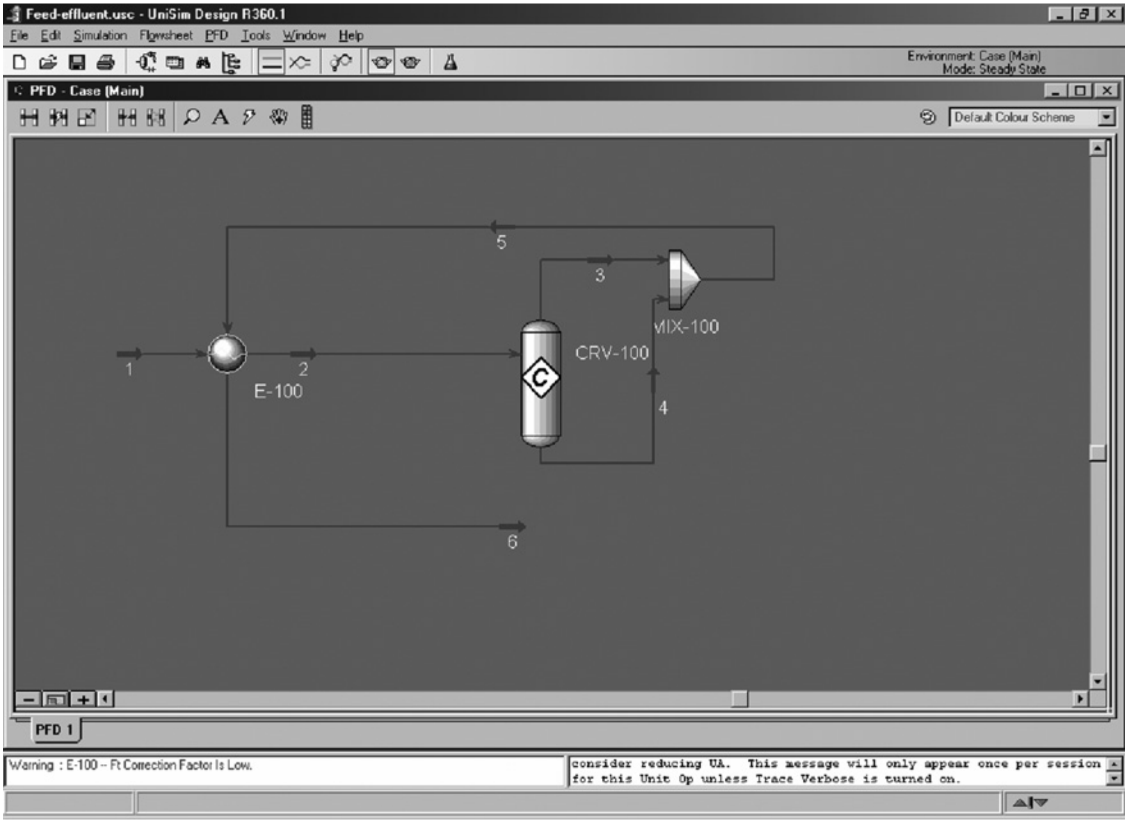
A mixture of 100 kgmol/h of 80 mol% benzene and 20 mol% ethylene at 40°C and 100 kPa is fed to a feed-effluent exchanger, where it is heated to 300°C and fed to a reactor. The reaction proceeds to 100% conversion of ethylene, and the reactor products are withdrawn, cooled by heat exchange with the feed, and sent to further processing. Estimate the outlet temperature of the product after heat exchange and the total surface area required if the average heat transfer coefficient is 200 $\mathrm{Wm^{-2}K^{-1}}$.

Solution

This problem was solved using UniSim Design. The reaction goes to full conversion, so a conversion reactor can be used. The simulation model is shown in Figure 4.29.

When the temperature at the outlet of the exchanger on the feed side is specified, the duty of the exchanger is defined and there is no recycle of information. The model thus solves very quickly, but it is necessary to check the results to see that the exchanger design makes sense.

The outlet temperature of the product (stream 6) is found to be 96.9°C, so there is enough heat in the product mixture to give an approach temperature of nearly 60°C, which seems perfectly adequate. If we open the exchanger worksheet though, there is a warning that the *F* factor is too low. Figure 4.30 shows the exchanger worksheet, and the *F* factor is only 0.2, which is not acceptable. When we examine the temperature-heat duty plot shown in Figure 4.31 (generated from the Performance tab of the exchanger worksheet), it is clear that there is a substantial temperature cross. This temperature cross causes the exchanger to have such a low *F* factor and gives a *UA*



Warning : E-100 -- Ft Correction Factor Is Low.

consider reducing UA. This message will only appear once per session for this Unit Op unless Trace Verbose is turned on.

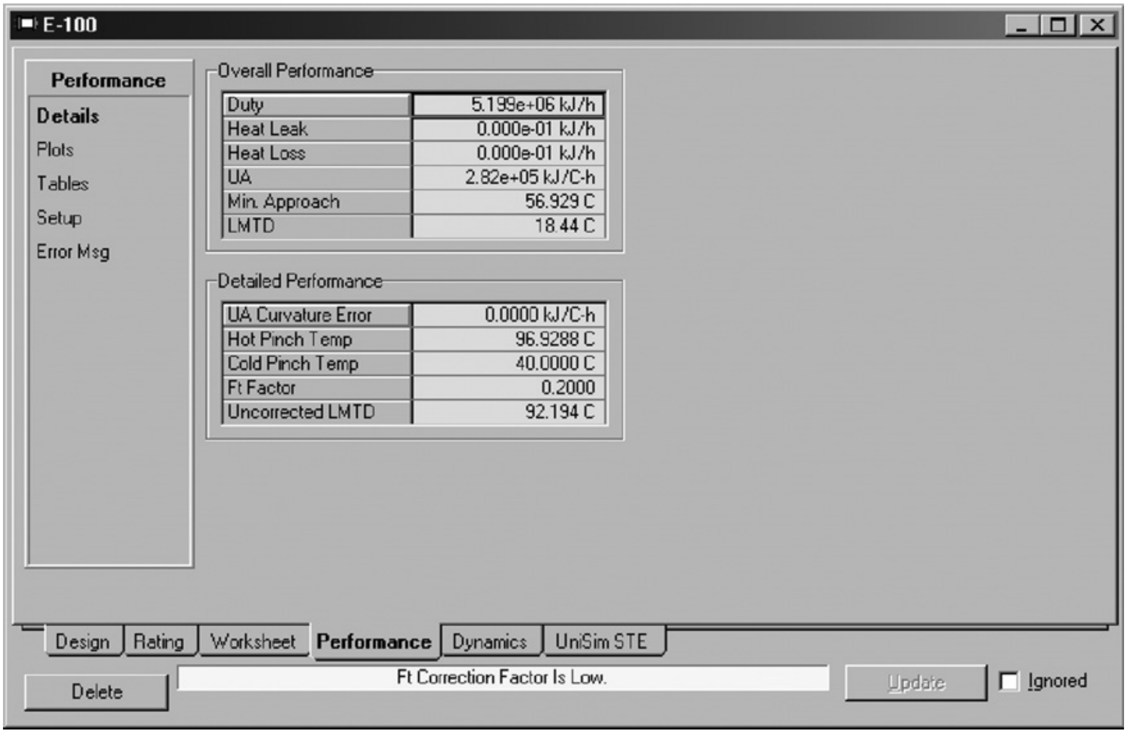
Figure 4.29. Feed-effluent heat exchange model for Example 4.5.

value of 78.3×10^3 WK^{-1}, where U is the overall heat transfer coefficient in $\text{Wm}^{-2}\text{K}^{-1}$ and A is the area in m^2.

If $UA = 78.3 \times 10^3$ WK^{-1} and $U = 200\,\text{Wm}^{-2}\text{K}^{-1}$, then the exchanger area is $A = 392\,\text{m}^2$. This would be a feasible size of exchanger, but is large for the duty and is not acceptable because of the low F factor. We should add more shells in series.

By examining the temperature-heat duty plot in Figure 4.31, we can see that if we break the exchanger into two shells, with the first shell heating the feed up to the dew point (the kink in the lower curve), then the first shell will not have a temperature cross. This design corresponds to an outlet temperature of about 70°C for the first exchanger. The second exchanger would still have a temperature cross though. If we break this second exchanger into two more exchangers, then the temperature cross is eliminated. We thus need at least three heat exchangers in series to avoid the temperature cross. This result could have been obtained by "stepping off" between the temperature-duty plots, as illustrated in Figure 4.32.

Figure 4.33 shows a modified flowsheet with two additional heat exchangers added in series. The outlet temperature of the second exchanger was specified as 200°C, to divide the duty of the second and third exchangers roughly equally. The results are



Overall Performance

Duty	5.199e+06 kJ/h
Heat Leak	0.000e-01 kJ/h
Heat Loss	0.000e-01 kJ/h
UA	2.82e+05 kJ/C-h
Min. Approach	56.929 C
LMTD	18.44 C

Detailed Performance

UA Curvature Error	0.0000 kJ/C-h
Hot Pinch Temp	96.9288 C
Cold Pinch Temp	40.0000 C
Ft Factor	0.2000
Uncorrected LMTD	92.194 C

Ft Correction Factor Is Low.

Figure 4.30. Exchanger worksheet for a single-shell design.

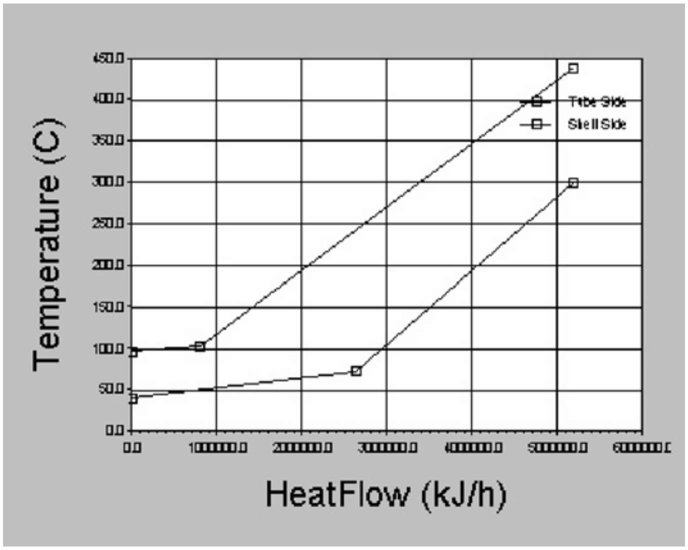


Figure 4.31. Temperature-heat flow plot for a single-shell design.

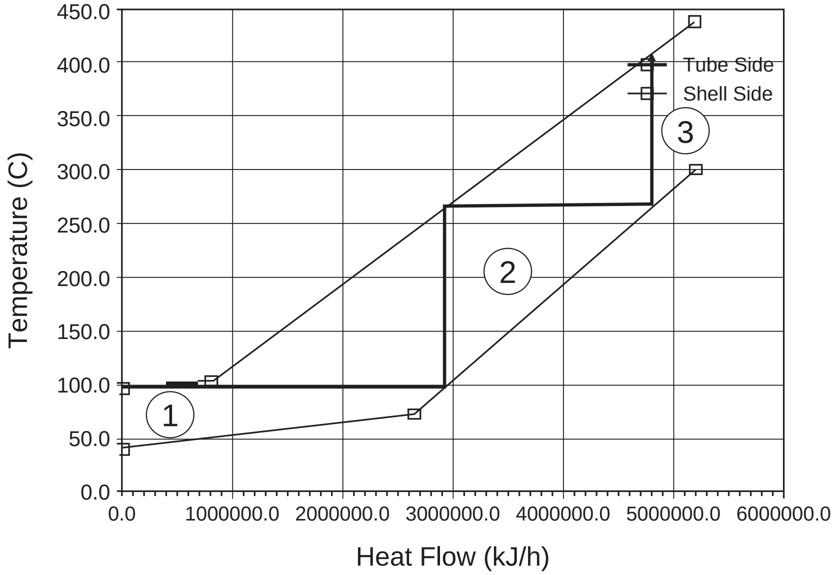
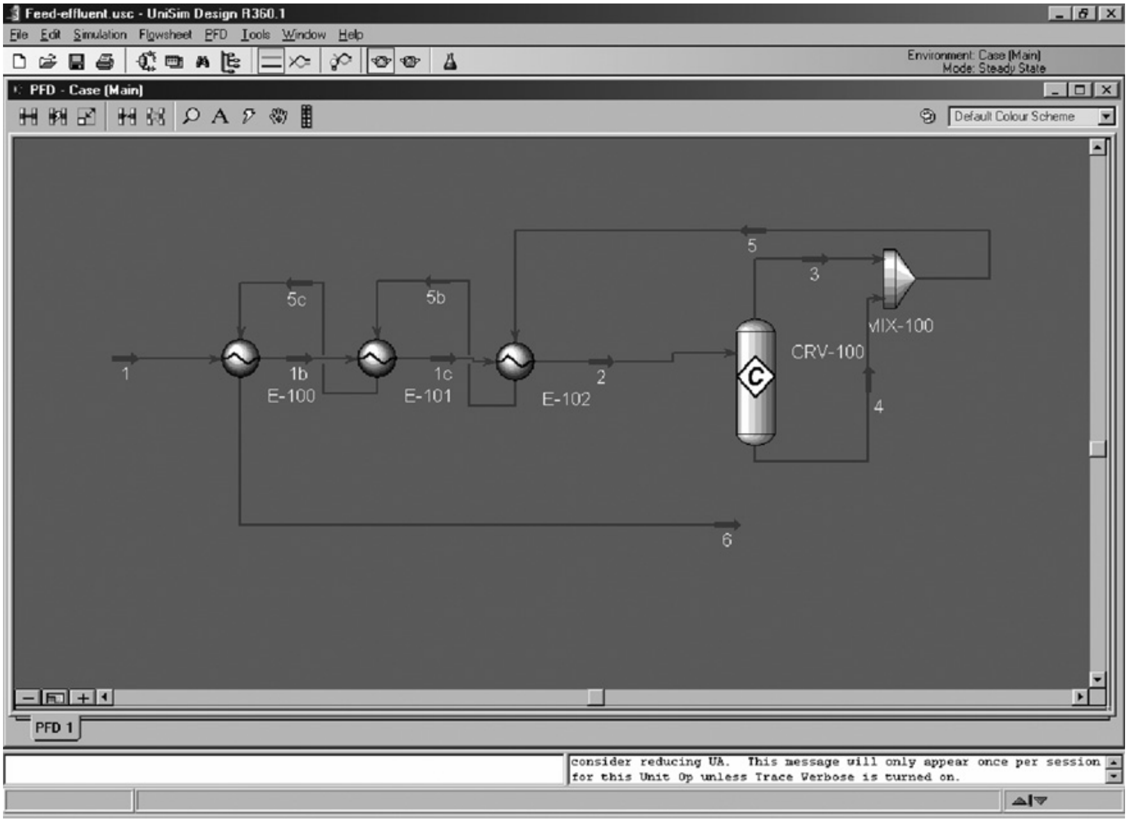


Figure 4.32. Stepping between heat profiles to avoid temperature cross.



consider reducing UA. This message will only appear once per session for this Unit Op unless Trace Verbose is turned on.

Figure 4.33. Feed-effluent heat exchange with three shells in series.

Table 4.3. Heat Exchanger Results

Design Case	Original (Single Shell)	Modified (Multiple Shell)		
Exchanger	E100	E100	E101	E102
Duty (MW)	1.44	0.53	0.57	0.35
UA (W/K)	78,300	6,310	4,780	2,540
F	0.2	0.93	0.82	0.93
$\Delta T_{\min}$	56.9	56.9	134.3	139.7
ΔT_{lmtd}	18.4	83.6	118.7	138.4
$A(\text{m}^2)$	392	32	24	13
Total area (m^2)	392		68	

given in Table 4.3. Temperature-heat flow plots for the three exchangers are given in Figure 4.34.

The modified design achieved a reduction in surface area from 392 m^2 to 68 m^2 at the price of having three shells instead of the original one. More importantly, the modified design is more practical than the original design and is less likely to suffer from internal pinch points. The modified design is not yet optimized. Optimization of this problem is explored in problem 4.11.

4.5.5. Hydraulics

Most of the commercial simulation programs contain models for valves, pipe segments, tees, and elbows. These models can be used to make an initial estimate of system pressure drop for the purposes of sizing pumps and compressors.

If a process hydraulic model is built, then care must be taken to specify pressure drop properly in the unit operation models. Rules of thumb are adequate for initial estimates, but in a hydraulic model these should be replaced with rigorous pressure drop calculations.

A hydraulic model will not be accurate unless some consideration has been given to plant layout and piping layout. Ideally, the hydraulic model should be built after the piping isometric drawings have been produced, when the designer has a good idea of pipe lengths and bends. The designer should also refer to the piping and instrumentation diagram for isolation valves, flow meters, and other obstructions that cause increased pressure drop. These subjects are discussed in Chapter 5 and Chapter 14.

Care is needed when modeling compressible gas flows, flows of vapor-liquid mixtures, slurry flows, and flows of non-Newtonian liquids. Some simulators use different pipe models for compressible flow. The prediction of pressure drop in multiphase flow is inexact at best and can be subject to very large errors if the extent of vaporization is unknown. In most of these cases, the simulation model should be replaced by a computational fluid dynamics (CFD) model of the important parts of the plant.

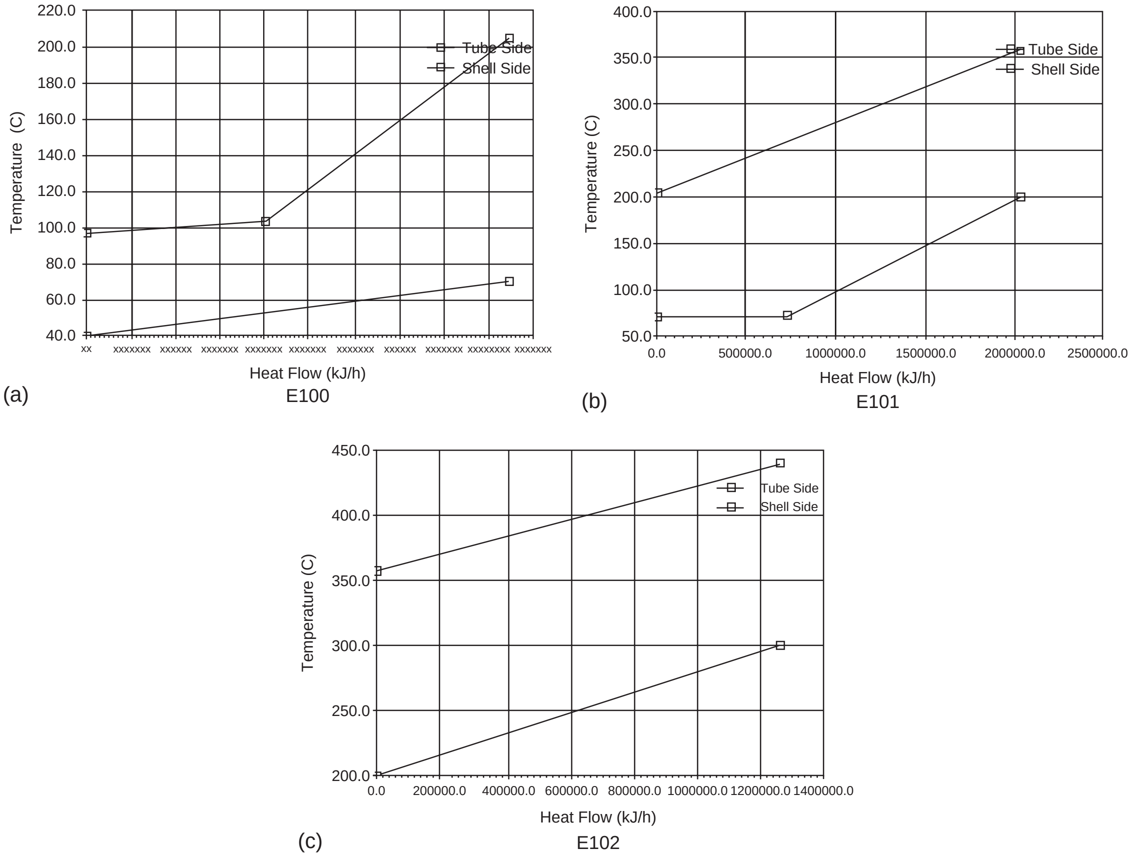


Figure 4.34. Temperature-heat flow profiles for the three exchangers in series (a) E100, (b) E101, and (c) E102.

4.5.6. Solids Handling

The commercial simulation programs were originally developed mainly for petrochemical applications, and none of them has a complete set of solids-handling operations. Although models for filters, crystallizers, decanters, and cyclones are present in most of the simulators, the designer may have to add user models for operations such as

- Hoppers
- Belt conveyors
- Elevators
- Pipe conveyors
- Screw conveyors
- Kneaders
- Washers
- Flocculators
- Spray driers
- Prill towers
- Rotary driers
- Rotary kilns
- Crushers and pulverizers
- Jet mills
- Ball mills
- Agglomerators
- Granulators
- Tableting presses

- Extruders
- Slurry pumps
- Fluidized bed heaters
- Fluidized bed reactors
- Belt driers
- Centrifuges
- Falling film evaporators
- Moving bed reactors
- Paper machines
- Classifiers
- Electrostatic precipitators

Because solids are handled in many commodity chemical processes as well as pharmaceuticals, polymers, and biological processes, the simulation software vendors are under pressure from their customers to enhance the capability of the programs for modeling solids operations. This continues to be an area of evolution of the commercial software.

4.6. USER MODELS

When the design engineer needs to specify a unit operation that is not represented by a library model and cannot be approximated by a simple model such as a component splitter or a combination of library models, then it is necessary to construct a user model. All of the commercial simulators allow the user to build add-in models of varying sophistication.

4.6.1. Spreadsheet Models

Models that require no internal iteration are easily coded as spreadsheets. Most of the simulators offer some degree of spreadsheet capability, ranging from simple calculation blocks to full Microsoft Excel^{TM} functionality.

In UniSim Design, spreadsheets can be created by selecting the spreadsheet option on the unit operations palette. The spreadsheet is easy to configure and allows data to be imported from streams and unit operations. The functionality of the UniSim Design spreadsheet is rather basic at the time of writing, but is usually adequate for simple input-output models. Values calculated by the spreadsheet can be exported back to the simulation model. The spreadsheet can thus be set up to act as a unit operation. The use of a spreadsheet as a unit operation is illustrated in Example 4.6. Aspen Plus has a similar simple spreadsheet capability using Microsoft Excel, which can be specified as a calculator block (via Data/Flowsheet Options/Calculator). The Excel calculator block in Aspen Plus requires a little more time to configure than the UniSim Design spreadsheet, but at the time of writing it can perform all of the functions available in MS Excel 97.

For more sophisticated spreadsheet models, Aspen Plus allows the user to link a spreadsheet to a simulation via a user model known as a USER2 block. The designer can create a new spreadsheet or customize an existing spreadsheet to interact with an Aspen Plus simulation. The USER2 block is much easier to manipulate when handling large amounts of input and output data, such as streams with many components or unit operations that involve multiple streams. The procedure for setting up a USER2 MS Excel model is more complex than using a calculator block but avoids having to identify every number required from the flowsheet individually. Instructions on how to build USER2 spreadsheet models are given in the Aspen Plus manuals and online help (Aspen Technology, 2001).

4.6.2. User Subroutines

Models that require internal convergence are best written as subroutines rather than spreadsheets, as more efficient solution algorithms can be used. Most user subroutines are written in FORTRAN or Visual Basic, though some of the simulators allow other programming languages to be used.

It is generally a good practice to compile and test a user model in a simplified flowsheet or as a standalone program before adding it to a complex flowsheet with recycles. It is also a good practice to check the model carefully over a wide range of input values, or else constrain the inputs to ranges where the model is valid.

Detailed instructions on how to write user models to interface with commercial simulation programs can be found in the simulator manuals. The manuals also contain specific requirements for how the models should be compiled and registered as extensions or shared libraries (.dll files in Microsoft Windows). In Aspen Plus, user models can be added as USER or USER2 blocks, following the instructions in the Aspen Plus manuals. In UniSim Design, it is very easy to add user models using the User Unit Operation, which can be found on the object palette or under the Flowsheet/Add Operation menu. The UniSim Design User Unit Operation can be linked to any program without requiring an extension file to be registered. The User Unit Operation is not documented in the UniSim Design manual, but instructions on setting it up and adding code are given in the online help.

Example 4.6

A gas turbine engine is fueled with 3000 kg/h of methane at 15°C and 1000 kPa, and supplied with ambient air at 15°C. The air and fuel are compressed to 2900 kPa and fed to a combustor. The air flow rate is designed to give a temperature of 1400°C at the outlet of the combustor. The hot gas leaving the combustor is expanded in the turbine. Shaft work produced by the turbine is used to power the two compressors and run a dynamo for generating electricity.

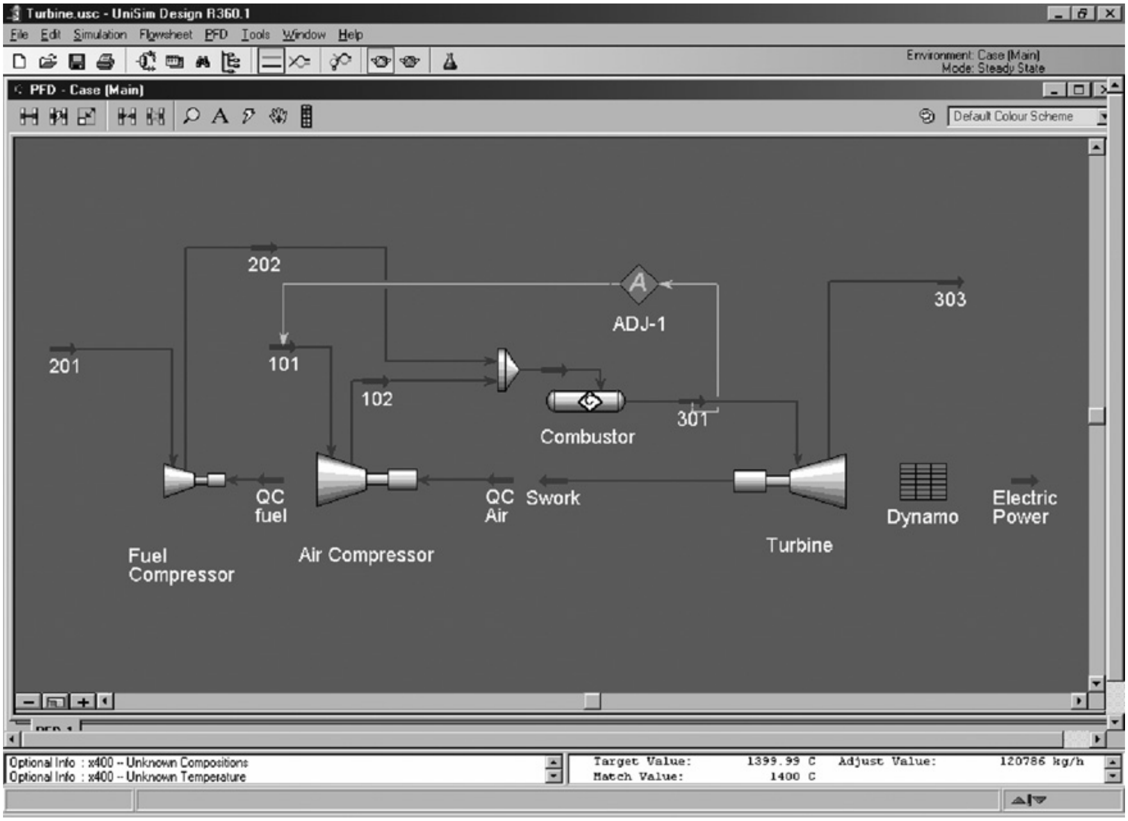
If the efficiency of the compressors is 98% and that of the turbine is 88%, and 1% of the shaft work is lost due to friction and losses in the dynamo, estimate the rate of power production and the overall cycle efficiency.

Solution

This problem was solved using UniSim Design.

A gas turbine engine should run with a large excess of air to provide full combustion of the fuel, so the combustor can be modeled as a conversion reactor. There is no model for a dynamo in UniSim Design, so the dynamo and shaft losses can be modeled using a spreadsheet operation, as shown in Figure 4.35.

Figure 4.35 also illustrates the use of an “Adjust” controller to set the air flow rate so as to give the desired reactor outlet temperature. The specifications for the Adjust



```
Optional Info : x400 -- Unknown Compositions
Optional Info : x400 -- Unknown Temperature
```

```
Target Value:     1399.99 C   Adjust Value:     120786 kg/h
Match Value:         1400 C
```

Figure 4.35. Gas turbine model.

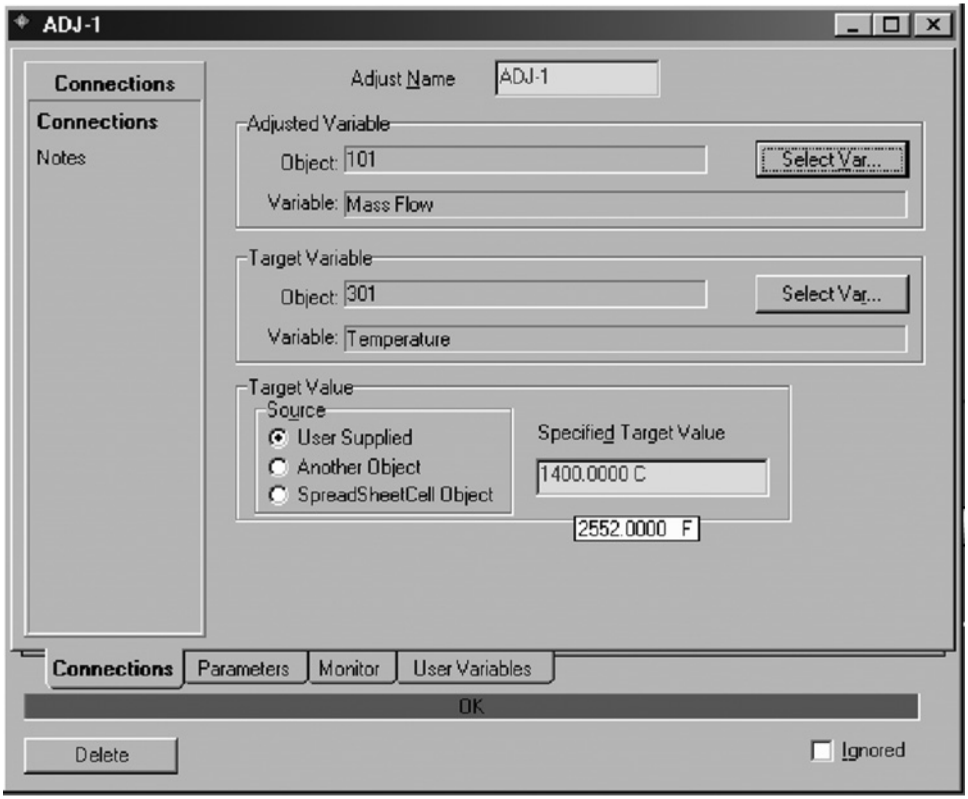
are shown in Figures 4.36 and 4.37. The Adjust was specified with a minimum air flow rate of 60,000 kg/h to ensure that the solver did not converge to a solution in which the air flow did not give full conversion of methane. The stoichiometric requirement is $3000 \times 2 \times (32/16)/0.21 = 57{,}000$ kg/h of air.

The spreadsheet model of the dynamo is relatively simple, as illustrated in Figure 4.38. The model takes the turbine shaft work and compressor duties as inputs. The friction losses are estimated as 1% of the turbine shaft work. The friction losses and compressor duties are then subtracted from the shaft work to give the net power from the dynamo, which is calculated to be 17.7 MW.

The cycle efficiency is the net power produced divided by the heating rate of the fuel. The heating rate is the molar flow of fuel multiplied by the standard molar heat of combustion:

$$\text{Heating rate (kW)} = \text{molar flow (mol/h)} \times \Delta H_c^\circ(\text{kJ/mol})/3600 \qquad (4.1)$$

The cycle efficiency is calculated to be 42.7%.



Adjust Name: ADJ-1

Adjusted Variable
Object: 101
Variable: Mass Flow

Target Variable
Object: 301
Variable: Temperature

Target Value
Source
● User Supplied
○ Another Object
○ SpreadSheetCell Object
Specified Target Value: 1400.0000 C
2552.0000 F

☐ Ignored

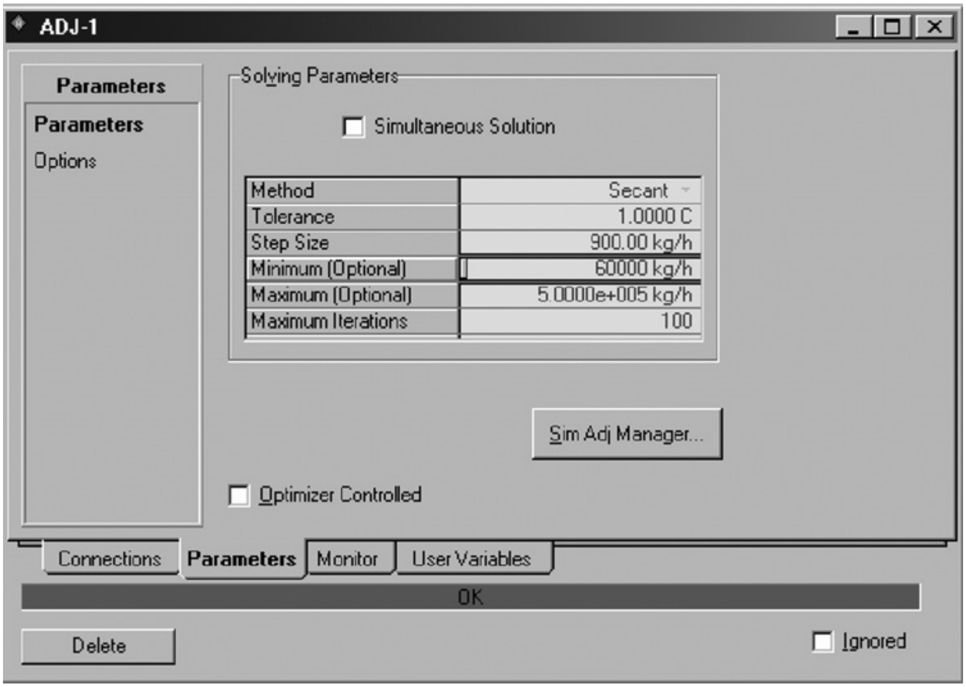
Figure 4.36. Adjust specifications.

4.7. FLOWSHEETS WITH RECYCLE

Recycles of solvents, catalysts, unconverted feed materials, and byproducts are found in many processes. Most processes contain at least one material recycle, and some may have six or more. Furthermore, when energy is recovered by process-to-process heat transfer, then energy recycles are created, as discussed in Section 4.5.4.

4.7.1. Tearing the Flowsheet

For a sequential-modular simulation program to be able to solve a flowsheet with a recycle, the design engineer needs to provide an initial estimate of a stream somewhere in the recycle loop. This is known as a "tear" stream, as the loop is "torn" at that point. The program can then solve and update the tear stream values with a new estimate. The procedure is repeated until the difference between values at each iteration becomes less than a specified tolerance, at which point the flowsheet is said to be converged to a solution.



☐ Simultaneous Solution

Method	Secant
Tolerance	1.0000 C
Step Size	900.00 kg/h
Minimum (Optional)	60000 kg/h
Maximum (Optional)	5.0000e+005 kg/h
Maximum Iterations	100

☐ Optimizer Controlled

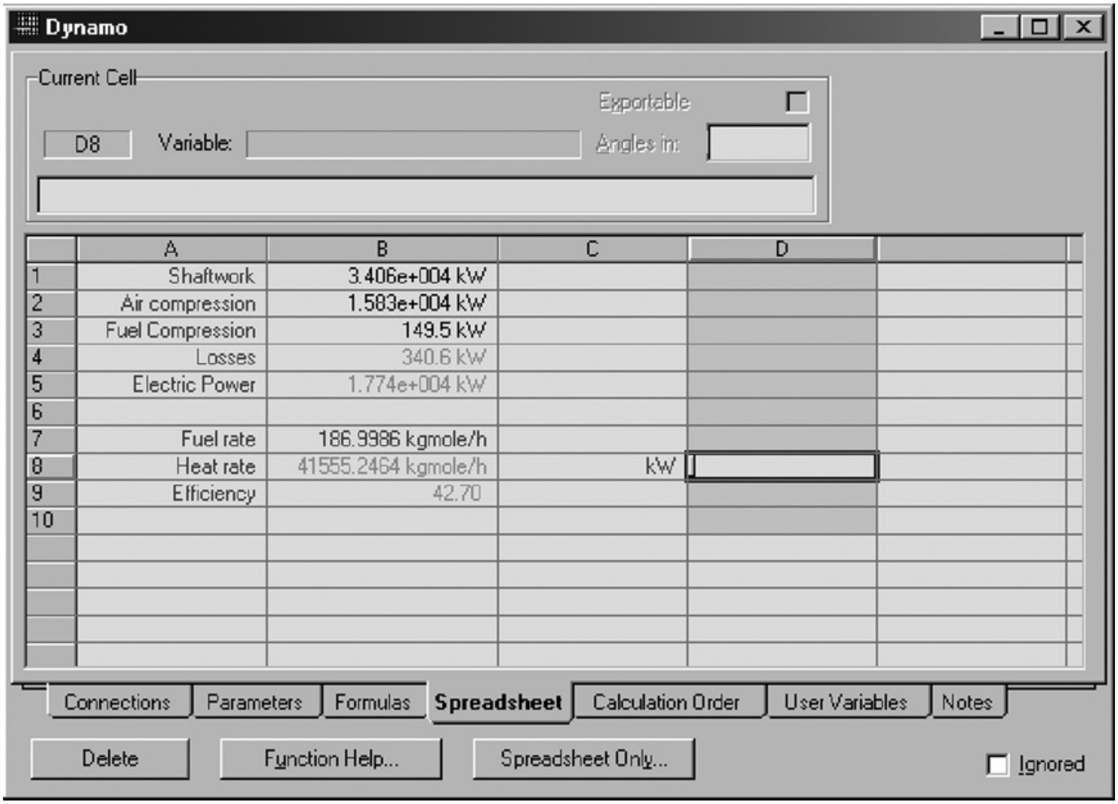
☐ Ignored

Figure 4.37. Adjust solving parameters.

The procedure for tearing and solving a simulation can be illustrated by a simple example. Figure 4.39 shows a process in which two feeds, A and B, are combined and fed to a fixed bed reactor. The reactor product is sent to a stripping column to remove light ends and is then sent to a column that separates heavy product from unreacted feed B. The unreacted feed B is recycled to the reactor.

To solve the reactor model, we need to specify the reactor feeds, streams 2 and 4. Stream 4 is made by adding fresh feed stream 1 to recycle stream 3, so a logical first approach might be to make an estimate of the recycle stream, in which case stream 3 is the tear stream. Figure 4.40 shows the flowsheet torn at stream 3. The designer provides an initial estimate of stream 3a. The flowsheet then solves and calculates stream 3b. The design engineer specifies a recycle operation connecting streams 3a and 3b, and the simulator then updates stream 3a with the values from stream 3b (or with other values if an accelerated convergence method is used, as discussed below). The calculation is then repeated until the convergence criteria are met.

The choice of tear stream can have a significant impact on the rate of convergence. For example, if the process of Figure 4.39 were modeled with a yield-shift reactor, then tearing the flowsheet at stream 5 would probably give faster convergence. Some of the simulation programs automatically identify the best tear stream.



Current Cell: D8

Variable:

	A	B	C	D
1	Shaftwork	3.406e+004 kW		
2	Air compression	1.583e+004 kW		
3	Fuel Compression	149.5 kW		
4	Losses	340.6 kW		
5	Electric Power	1.774e+004 kW		
6				
7	Fuel rate	186.9986 kgmole/h		
8	Heat rate	41555.2464 kgmole/h	kW	
9	Efficiency	42.70		
10				

Figure 4.38. Spreadsheet model of dynamo.

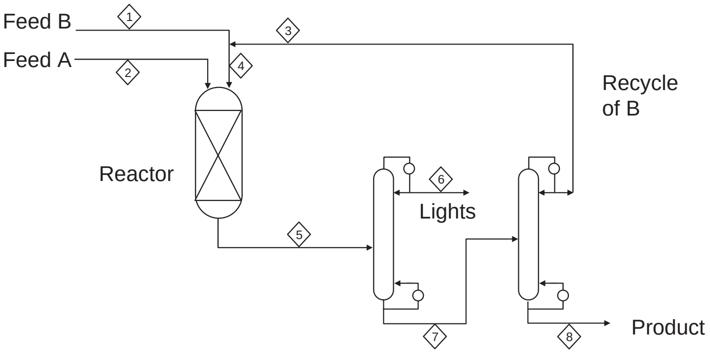


Figure 4.39. Sample process with recycle.

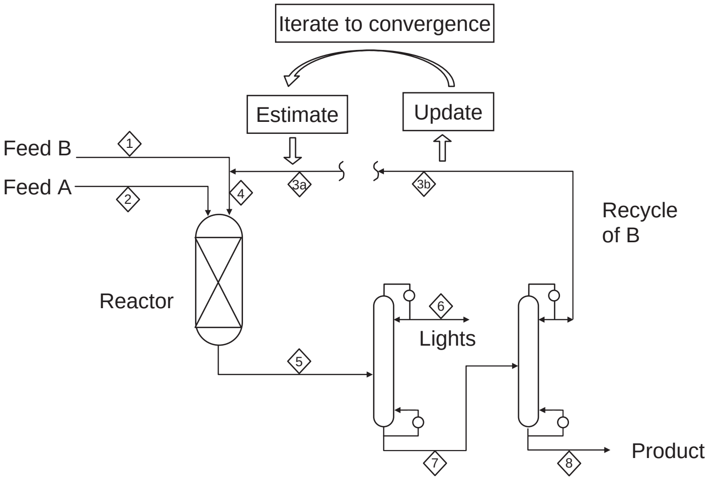


Figure 4.40. Tearing the recycle loop.

4.7.2. Convergence Methods

The methods used to converge recycle loops in the commercial process simulation programs are similar to the methods described in Section 1.9. Most of the commercial simulation programs include the methods described below.

Successive Substitution (Direct Substitution)

In this method, an initial estimate, x_k, is used to calculate a new value of the parameter, $f(x_k)$. The estimate is then updated using the calculated value:

$$\begin{aligned} x_{k+1} &= f(x_k) \qquad (4.2)\\ x_{k+2} &= f(x_{k+1}), \text{ etc.} \end{aligned}$$

This method is simple to code but is computationally inefficient, and convergence is not guaranteed.

Bounded Wegstein

The bounded Wegstein method is the default method in most of the simulation programs. It is a linear extrapolation of successive substitution.

The Wegstein method initially starts out with a direct substitution step:

$$x_1 = f(x_0) \qquad (4.3)$$

An acceleration parameter, q, can then be calculated:

$$q = \frac{s}{s-1} \qquad (4.4)$$

$$\text{where } s = \frac{f(x_k) - f(x_{k-1})}{x_k - x_{k-1}} \tag{4.5}$$

and the next iteration is then:

$$x_{k+1} = q\, x_k + (1 - q)\, f(x_k) \tag{4.6}$$

If $q = 0$, the method is the same as successive substitution. If $0 < q < 1$, then convergence is damped, and the closer q is to 1.0, the slower convergence becomes. If q is less than 0, then the convergence is accelerated. The bounded Wegstein method sets bounds on q, usually keeping it in the range $-5 < q < 0$, so as to guarantee acceleration without overshooting the solution too widely.

The bounded Wegstein method is usually fast and robust. If convergence is slow, then the designer should consider reducing the bounds on q. If convergence oscillates, then consider damping the convergence by setting bounds such that $0 < q < 1$.

Newton and Quasi-Newton Methods

The Newton method uses an estimate of the gradient at each step to calculate the next iteration, as described in Section 1.9.6. Quasi-Newton methods such as Broyden's method use linearized secants rather than gradients. This approach reduces the number of calculations per iteration, although the number of iterations may be increased.

Newton and quasi-Newton methods are used for more difficult convergence problems, for example, when there are many recycle streams, or many recycles that include operations that must be converged at each iteration, such as distillation columns. The Newton and quasi-Newton methods are also often used when there are many recycles and control blocks (see Section 4.8.1). The Newton method should not normally be used unless the other methods have failed, as it is more computationally intensive and can be slower to converge for simple problems.

4.7.3. Manual Calculations

The convergence of recycle calculations is almost always better if a good initial estimate of the tear stream is provided.

If the tear stream is chosen carefully, then it may be easy for the design engineer to generate a good initial estimate. This can be illustrated by returning to the problem of Figure 4.39. We can tear the recycle loop at the reactor effluent, as shown in Figure 4.41. We can then state the following about the reactor effluent:

1. The reactor effluent must contain the net production rate of product (which is known), plus any product that is in the recycle. Recycling product to the reactor is not a good idea, as it is likely to lead to byproduct formation. A reasonable estimate of product recovery in the separation section is probably 99% or greater, so a good initial estimate of the amount of product in stream 5b is the net production rate divided by the separation recovery, or roughly 101% of the net production rate.

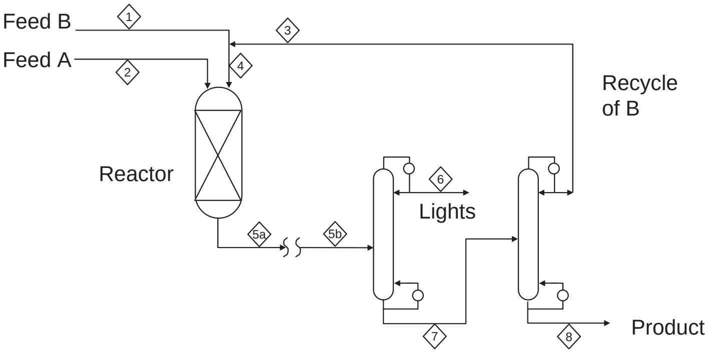


Figure 4.41. Tearing at the reactor outlet.

2. Since feed B is recycled and feed A is not, it looks like we are using an excess of B to drive full conversion of A. A good initial estimate of the flow rate of component A in stream 5b is therefore zero. If we have conversion data in terms of A, then we could produce a better estimate.
3. Feed B is supplied to the reactor in excess. The amount of B consumed in the reactor must be equal to the amount required by stoichiometry to produce the product. The amount of B remaining in the reactor effluent is given by

$$\begin{aligned}\frac{\text{moles B remaining}}{\text{per mole product}} &= \frac{\text{moles B fed}}{\text{stoichiometric moles B per mole product}} - 1 \\ &= \frac{1}{\text{conversion of B}} - 1 \qquad (4.7)\end{aligned}$$

So, knowing the flow rate of product, we can get a good initial estimate of the flow rate of B if we know either the conversion of B or the ratio in excess of the stoichiometric feed rate of B that we want to supply.

We can thus make good estimates of the three major components that are present in stream 5b. If light or heavy byproducts are formed in the reactor but not recycled, then a single successive substitution step will provide good estimates for these components, as well as a better estimate of the conversion of B and the amount of A that is required in excess of stoichiometric requirements.

Manual calculations are also very useful when solving flowsheets that use recycle and purge. Purge streams are often withdrawn from recycles to prevent the accumulation of species that are difficult to separate, as described in Section 2.15. A typical recycle and purge flow scheme is illustrated in Figure 4.42. A liquid feed and a gas are mixed, heated, reacted, cooled and separated to give a liquid product. Unreacted gas from the separator is recycled to the feed. A make-up stream is added to the gas recycle to make up for consumption of gas in the process. If the make-up gas contains any inert gases, then over time these would accumulate in the recycle and eventually the reaction would be slowed down when the partial pressure of reactant

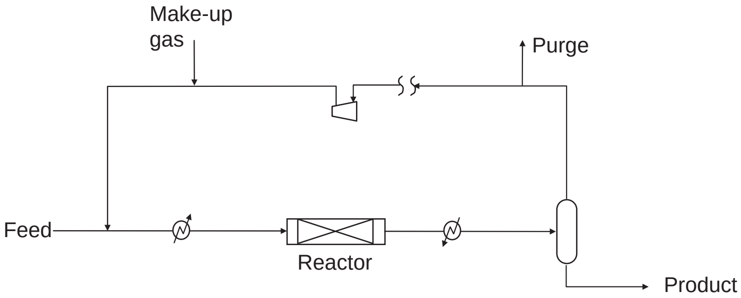


Figure 4.42. Process with gas recycle and purge.

gas fell. To prevent this situation from occurring, we withdraw a purge stream to maintain the inerts at an acceptable level. We can provide a good initial estimate of the recycle stream by noting

1. The flow rate of inerts in the purge is equal to the flow rate of inerts in the make-up gas.
2. The required partial pressure of reactant gas at the reactor outlet sets the concentration of reactant gas and inerts in the recycle and the unconverted gas flow rate if the reactor pressure is specified.

We can then write a mass balance on inerts:

$$My_M = Py_R \tag{4.8}$$

and on reactant gas:

$$M(1 - y_M) = G + P(1 - y_R) \tag{4.9}$$

hence

$$M(1 - y_M) = G + M\frac{y_M}{y_R}(1 - y_R)$$

where

M = make-up molar flow rate;
P = purge molar flow rate;
y_M = mole fraction of inerts in make-up;
y_R = mole fraction of inerts in recycle and purge;
G = molar rate of consumption of gas in reactor.

Hence we can solve for M and P if G is known.

The temperature of the recycle gas at the outlet of the compressor is not easily estimated, so the logical place to tear the recycle is between the purge and the compressor, as indicated in Figure 4.42.

4.7.4. Convergence Problems

If a flowsheet is not converged, or if the process simulation software runs and gives a statement "converged with errors," then the results *cannot be used* for design. The designer must take steps to improve the simulation so that a converged solution can be found.

The first steps that an experienced designer would usually take would be

1. Make sure that the specifications are feasible.
2. Try increasing the number of iterations.
3. Try a different convergence algorithm.
4. Try to find a better initial estimate.
5. Try a different tear stream.

If one or more unit operations have been given infeasible specifications, then the flowsheet will never converge. This problem also occurs with multicomponent distillation columns, particularly when purity specifications or flow rate specifications are used, or when nonadjacent key components are chosen. A quick manual mass balance around the column can usually determine whether the specifications are feasible. Remember that all the components in the feed must exit the column somewhere. The use of recovery specifications is usually more robust, but care is still needed to make sure that the reflux ratio and number of trays are greater than the minimum required. A similar problem is encountered in recycle loops if a component accumulates because of the separation specifications that have been set. Adding a purge stream usually solves this problem.

For large problems with multiple recycles, it may be necessary to increase the number of iterations to allow the flow sheet time to converge. This strategy can be effective but is obviously inefficient if underlying problems in the model are causing the poor convergence.

In some cases, it may be worthwhile to develop a simplified simulation model to arrive at a first estimate of tear stream composition, flow rate, and conditions (temperature and pressure). Models can be simplified by using faster and more robust unit operation models, for example, substituting shortcut column models for rigorous distillation models. Models can also be simplified by reducing the number of components in the model. Reducing the number of components often leads to a good estimate of the bulk flows and stream enthalpies, which can be useful if there are interactions between the mass and energy balances. Another simplification strategy that is often used is to model heat exchangers using a dummy stream on one side (usually the side that is downstream in the process). The recycle of energy from downstream to upstream is then not converged until after the rest of the flow sheet has been converged. Alternatively, heaters and coolers can be used in a simplified model, or even in the rigorous model, as long as the stream data is then extracted and used to design the real exchangers.

Another approach that is widely used is to "creep up on" the converged solution. This entails building up the model starting from a simplified version and successively adding detail while reconverging at each step. As more complexity is added, the values from the previous run are used to initialize the next version. This is a slow but effective method. The design engineer must remember to save the intermediate versions every so often, in case later problems are encountered. A similar strategy is often used when running sensitivity analyses or case studies that require perturbations of a converged model. The designer changes the relevant parameters in small steps to reach the new conditions, while reconverging at each step. The results of each step then provide a good initial estimate for the next step, and convergence problems are avoided.

When there are multiple recycles present, it is sometimes more effective to solve the model in a simultaneous (equation-oriented) mode rather than in a sequential modular mode. If the simulation problem allows simultaneous solution of the equation set, this can be attempted. If the process is known to contain many recycles, then the designer should anticipate convergence problems and should select a process simulation program that can be run in a simultaneous mode.

Example 4.7

Light naphtha is a mixture produced by distillation of crude oil. Light naphtha primarily contains alkane compounds (paraffins), and it can be blended into gasoline. The octane value of methyl-substituted alkanes (iso-paraffins) is higher than that of straight-chain compounds (normal paraffins), so it is often advantageous to isomerize the light naphtha to increase the proportion of branched compounds.

A simple naphtha isomerization process has a feed of 10,000 barrels per day (bpd) of a 50 wt% mixture of n-hexane and methyl pentane. The feed is heated and sent to a reactor, where it is brought to equilibrium at 1300 kPa and 250°C. The reactor products are cooled to the dew point and fed to a distillation column operated at 300 kPa. The bottoms product of the distillation is rich in n-hexane and is recycled to the reactor feed. An overall conversion of n-hexane of 95% is achieved.

Simulate the process to determine the recycle flow rate and composition.

Solution

This problem was solved using UniSim Design. The first step is to convert the volumetric flow rate into a mass flow rate in metric units. We can set up a stream that has a 50:50 mixture by weight of n-hexane and methyl pentane. This stream has a density of 641 kg/m^3 at 40°C, so the required flow rate is

$$10{,}000\,\text{bpd} = 10{,}000 \times 641\ (\text{kg/m}^3) \times 0.1596(\text{m}^3/\text{bbl})/24 = 42.627\ \text{metric tons/h}$$

In a real isomerization process, a part of the feed will be lost due to cracking reactions; however, in our simplified model the only reactions that occur are isomerization reactions. Because we consider only isomerization reactions, all of the product and feed components have the same molecular weight (C_6H_{14}, $M_w = 86$). The feed flow rate of n-hexane is thus $42.627 \times 0.5 = 21.31$ metric tons/h. So for 95% conversion of n-hexane, the amount of n-hexane in the product is $0.05 \times 21.31 = 1.0655$ metric tons/h, or $1065.5/86 = 12.39$ kgmol/h. The mole fraction of n-hexane in the product is 5% of 50%, or 2.5 mol%.

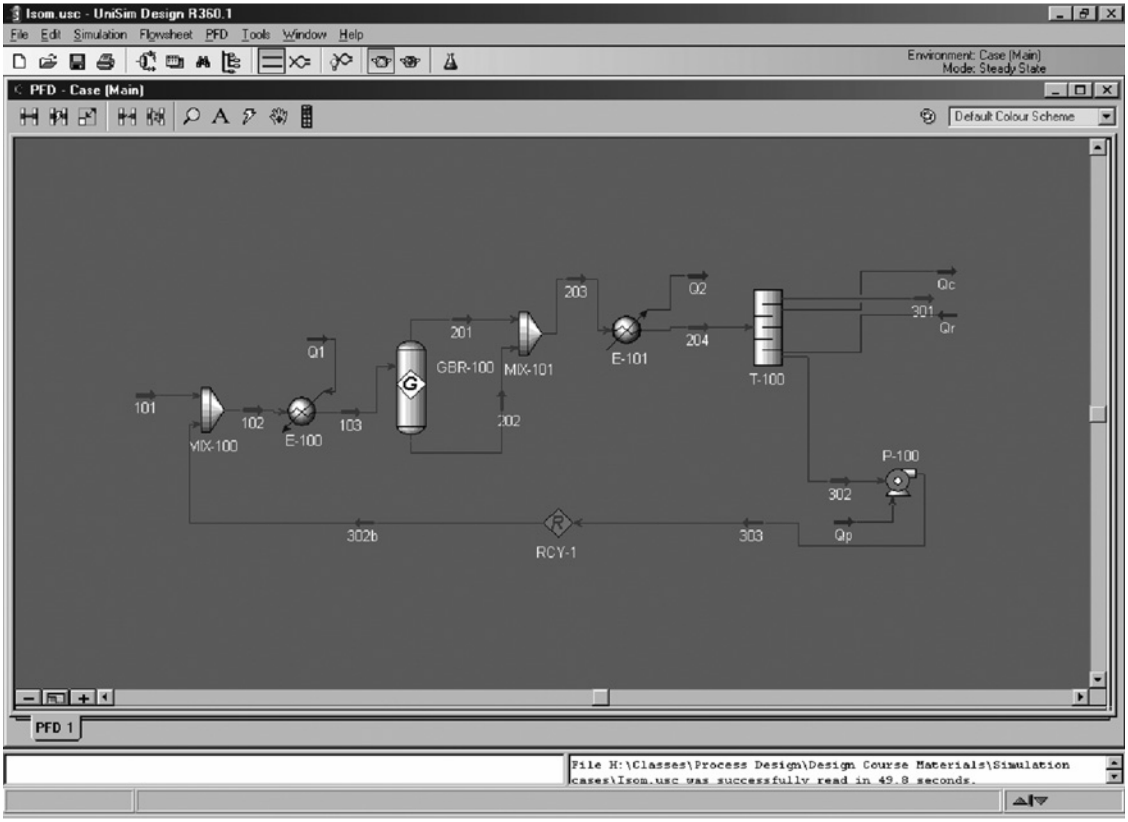


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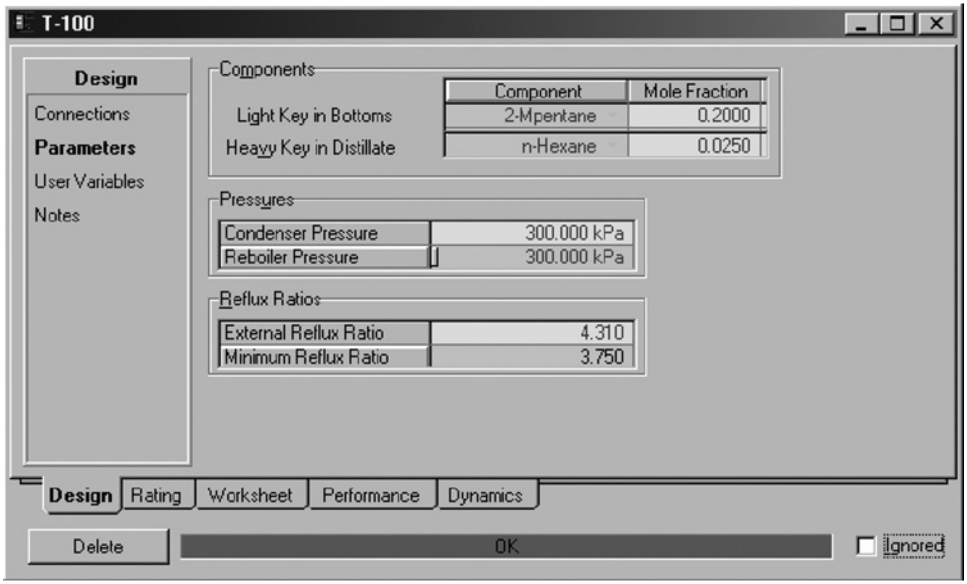
Figure 4.43. Isomerization process model using shortcut distillation.

To get an initial estimate of the distillation column conditions, the process was first simulated using a shortcut column model, as shown in Figure 4.43. If we assume that no cyclic compounds are formed in the process, then the component list includes all of the available C_6 paraffin compounds, i.e., n-hexane, 2-methyl pentane, 3-methyl pentane, 2,3-methyl butane, and 2,2-methyl butane. The reactor achieves complete equilibrium between these species and so can be modeled using a Gibbs reactor.

The shortcut column model requires a second specification, given in terms of the heavy key component. We can define either of the methyl pentane species as the heavy key. In the simplified model that we have built, the level of methyl pentane in the recycle is not important to the process performance. Increasing the recycle of methyl pentane species increases the process yield of dimethyl butane species, which would lead to an improvement in the product octane number. In reality, the presence of side reactions that caused cracking to less valuable light hydrocarbons would establish a trade-off that would set the optimum level of methyl pentane recycle. For now, we will assume that the mole fraction of 2-methyl pentane in the bottoms is 0.2.

With these conditions, and with the recycle not closed, the shortcut column model predicts a minimum reflux of 3.75. The reflux ratio is then set at $1.15 \times R_{min} = 4.31$,



Components

	Component	Mole Fraction
Light Key in Bottoms	2-Mpentane	0.2000
Heavy Key in Distillate	n-Hexane	0.0250

Pressures

Condenser Pressure	300.000 kPa
Reboiler Pressure	300.000 kPa

Reflux Ratios

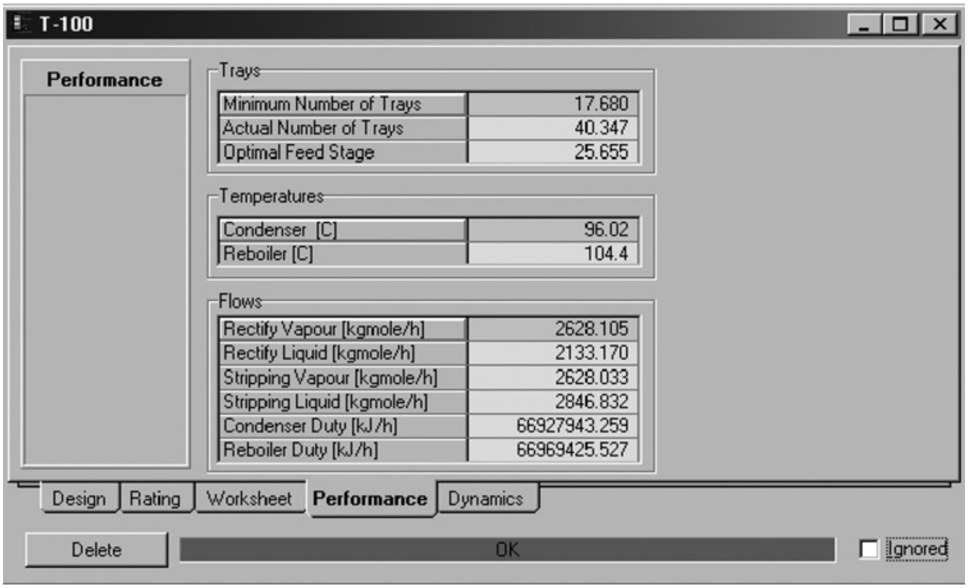
External Reflux Ratio	4.310
Minimum Reflux Ratio	3.750

Figure 4.44. Shortcut column specifications.

as shown in Figure 4.44. The shortcut model then calculates that we need 41 theoretical trays, with optimal feed tray 26, as shown in Figure 4.45. The column bottoms flow rate is 18,900 kg/h, which can be used as an initial estimate for the recycle flow. The recycle loop can now be closed and run. The converged solution still has $R_{min} = 3.75$, so the reflux ratio does not need to be adjusted. The converged recycle flow rate is 18.85 metric tons/h or 218.7 kgmol/h, as shown in Figure 4.46. The shortcut column design of the converged flowsheet still has 41 trays with the feed on tray 26.

The results from the shortcut model can now be used to provide a good initial estimate for a rigorous model. The shortcut column is replaced with a rigorous column, as shown in Figure 4.47. The rigorous column model can be set up with the number of stages and feed stage predicted by the shortcut model, as shown in Figure 4.48. If we specify the reflux ratio and bottoms product rate as column specifications, as in Figure 4.49, then the flowsheet converges quickly.

The results from the rigorous model with the inputs specified as above show a flow rate of 1084.5 kg/h of n-hexane in the distillate product. This exceeds the requirements calculated from the problem statement (1065.5 kg/h). The simplest way to get back to the required specification is to use it directly as a specification for the column. From the "Design" tab on the column window, we can select "Monitor" and then "Add spec" to add a specification on the distillate flow rate of n-hexane, as shown in Figure 4.50. This specification can then be made active, and the bottoms flow rate specification can be relaxed. When the simulation is reconverged, the bottoms flow rate increases to 19,350 kg/h, and the n-hexane in the distillate meets the specification flow rate of 1065.5 kg/h.



Trays

Minimum Number of Trays	17.680
Actual Number of Trays	40.347
Optimal Feed Stage	25.655

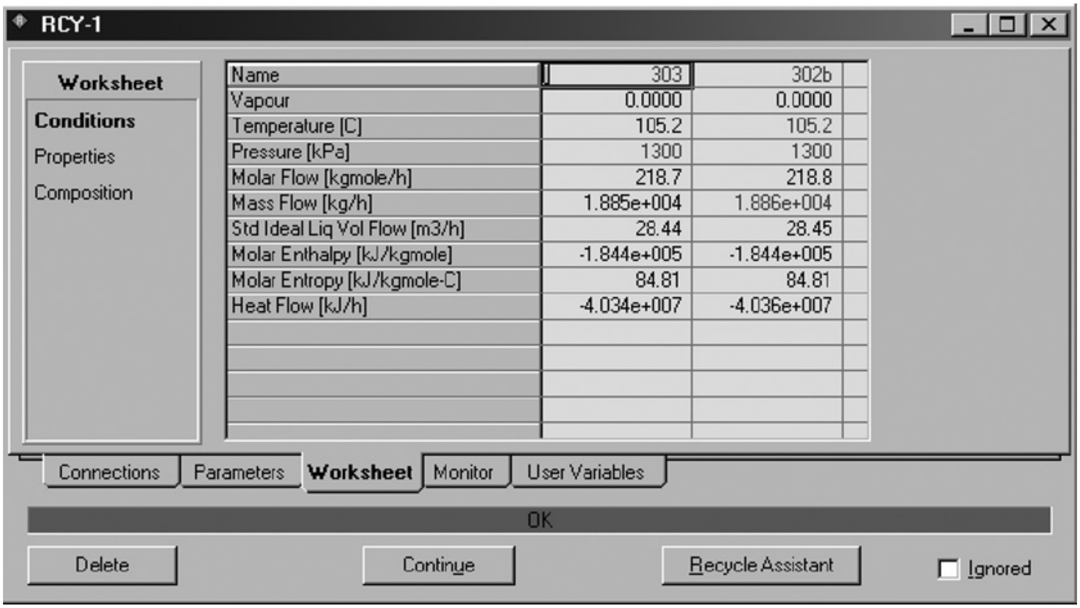
Temperatures

Condenser [C]	96.02
Reboiler [C]	104.4

Flows

Rectify Vapour [kgmole/h]	2628.105
Rectify Liquid [kgmole/h]	2133.170
Stripping Vapour [kgmole/h]	2628.033
Stripping Liquid [kgmole/h]	2846.832
Condenser Duty [kJ/h]	66927943.259
Reboiler Duty [kJ/h]	66969425.527

Figure 4.45. Shortcut column results.



Name	303	302b
Vapour	0.0000	0.0000
Temperature [C]	105.2	105.2
Pressure [kPa]	1300	1300
Molar Flow [kgmole/h]	218.7	218.8
Mass Flow [kg/h]	1.885e+004	1.886e+004
Std Ideal Liq Vol Flow [m3/h]	28.44	28.45
Molar Enthalpy [kJ/kgmole]	-1.844e+005	-1.844e+005
Molar Entropy [kJ/kgmole-C]	84.81	84.81
Heat Flow [kJ/h]	-4.034e+007	-4.036e+007

Figure 4.46. Converged recycle results for the shortcut column model.

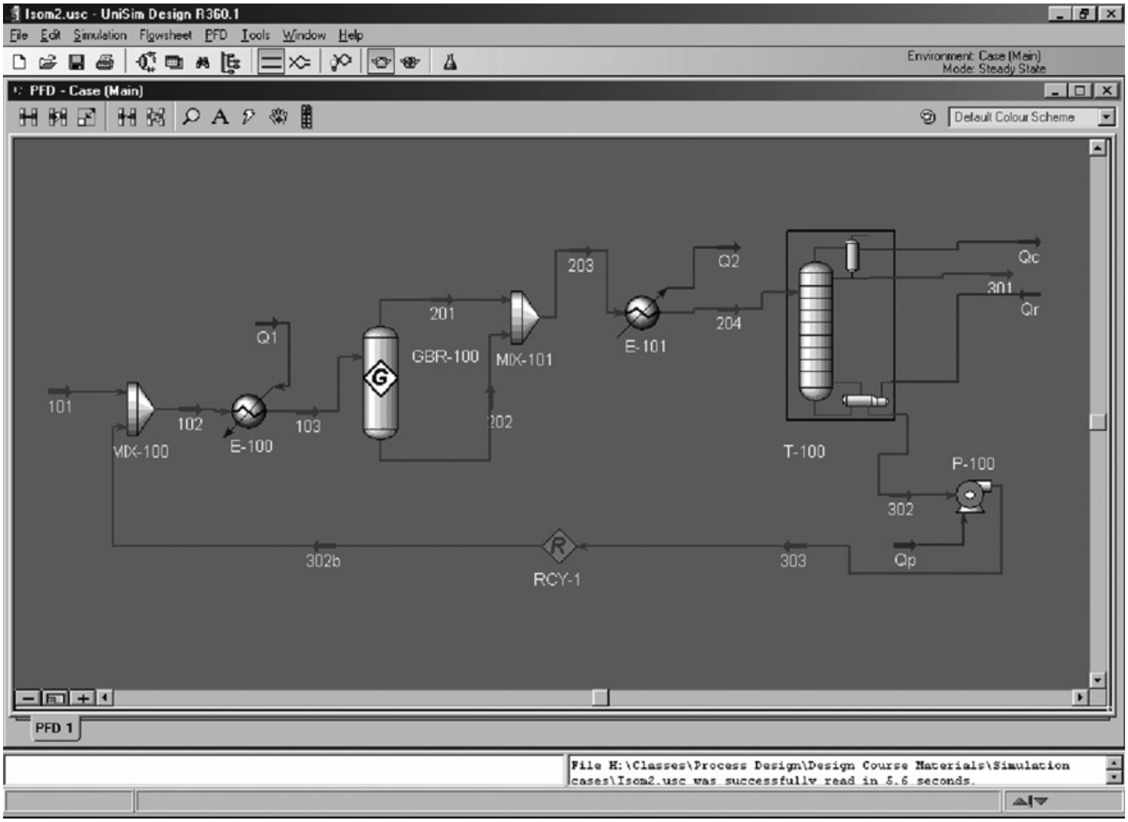


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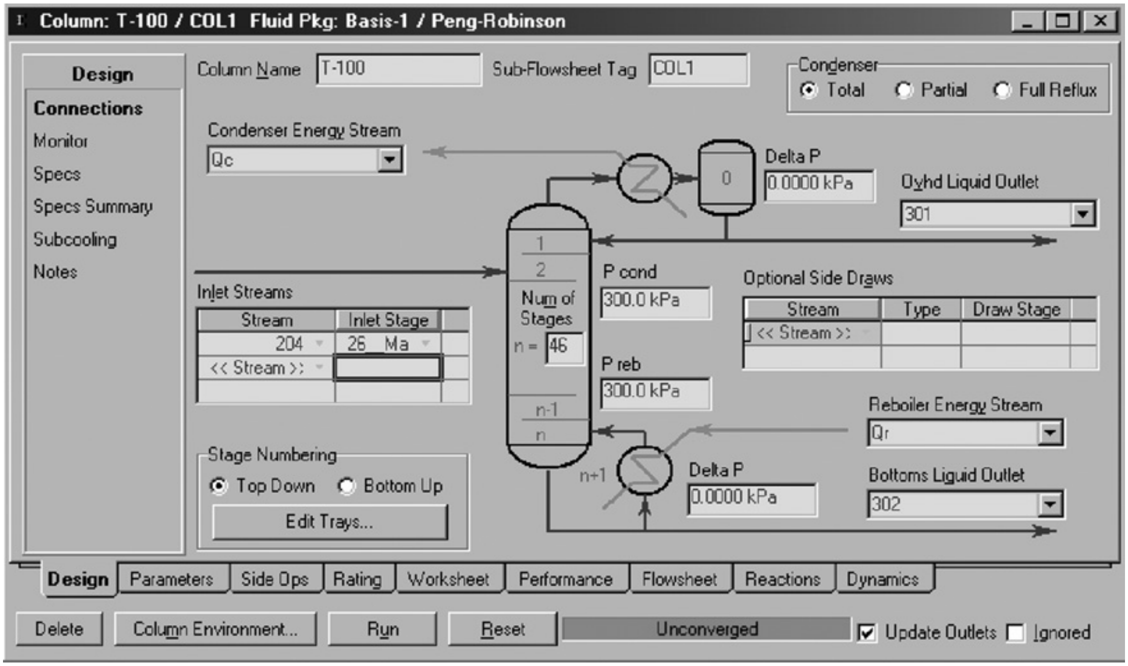
Figure 4.47. Isomerization process model using rigorous distillation.

The column profiles for the rigorous distillation model are shown in Figure 4.51. The profiles do not show any obvious poor design of the column, although the design is not yet optimized.

The simulation was converged to achieve the target conversion of n-hexane with a recycle of 19.35 metric tons/h. The recycle composition is 50.0 mol% n-hexane, 21.1 mol% 2-methyl pentane, 25.1 mol% 3-methyl pentane, 3.6 mol% 2,3-methyl butane, and 0.2 mol% 2,2-methyl butane. This is a converged solution, but it is only one of many possible converged solutions. No attempt has yet been made to optimize the design. The optimization of this process is examined in problem 4.14. For more realistic information on isomerization process conditions, consult Meyers (2003).

4.8. FLOWSHEET OPTIMIZATION

After achieving a converged simulation of the process, the designer will usually want to carry out some degree of optimization. The commercial simulation programs have a limited optimization capability that can be used with suitable caution.



Column: T-100 / COL1 Fluid Pkg: Basis-1 / Peng-Robinson

Column Name: T-100

Sub-Flowsheet Tag: COL1

Condenser: ● Total ○ Partial ○ Full Reflux

Condenser Energy Stream: Qc

Delta P: 0.0000 kPa

Ovhd Liquid Outlet: 301

P cond: 300.0 kPa

Num of Stages: n = 46

P reb: 300.0 kPa

Inlet Streams

Stream	Inlet Stage
204	26__Ma
<< Stream >>	

Optional Side Draws

Stream	Type	Draw Stage
<< Stream >>		

Reboiler Energy Stream: Qr

Delta P: 0.0000 kPa

Bottoms Liquid Outlet: 302

Stage Numbering: ● Top Down ○ Bottom Up

Unconverged

☑ Update Outlets ☐ Ignored

Figure 4.48. Design parameters for the rigorous distillation column.

4.8.1. Use of Controllers

The simplest form of optimization is to impose additional constraints on the simulation so that it meets requirements specified by the designer. For example, if the designer made estimates of the feed rates, then the production rate of product that is predicted by the model may be less (or more) than the desired rate. The designer could correct this by calculating the appropriate ratio, multiplying all the feed streams by this ratio, and then reconverging the model, but this approach would soon become tedious.

Instead, the simulation programs allow the designer to impose constraints on the model. In the preceding example, this would be a constraint that the product flow rate is equal to a target value. Constraints are imposed using controller functions, known as a "Design Spec" in Aspen Plus or a "Set" or "Adjust" in UniSim Design. Controllers are specified either as

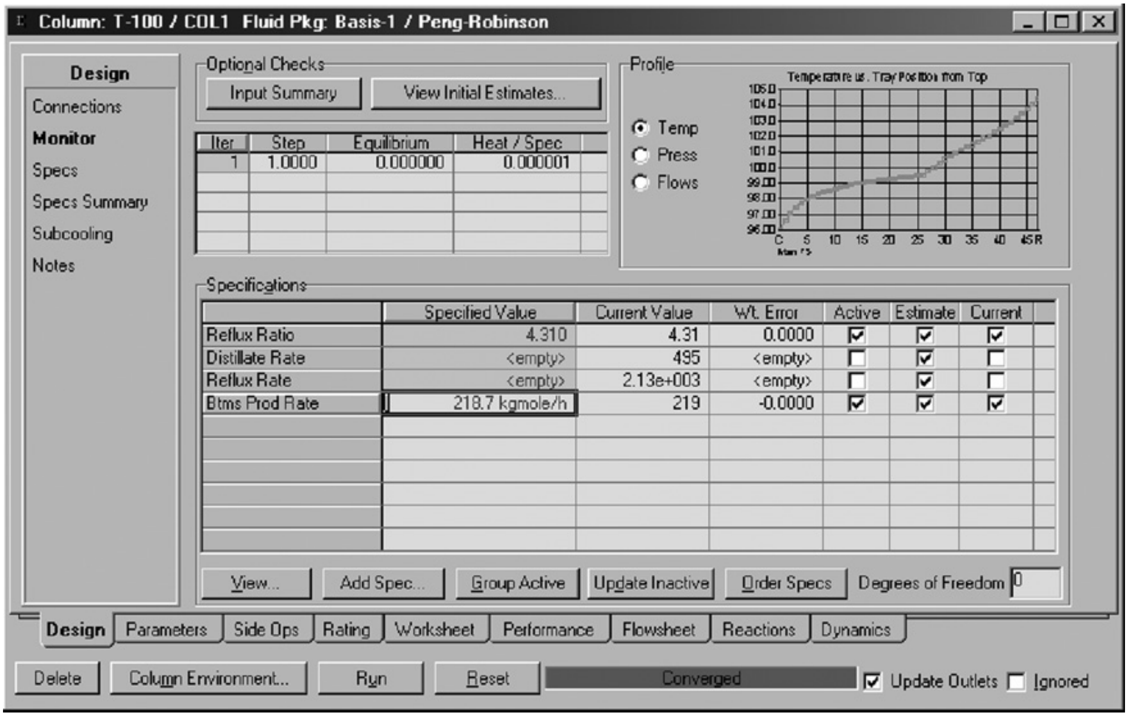
Set variable x to value z

or

Adjust variable x to value y by manipulating variable z

where z is an unknown variable or set of variables that will be calculated by the simulation and x is the variable that the designer wants to specify.

Controllers can be used to capture all kinds of design constraints and specifications. They are particularly useful for setting feed ratios and controlling purge rates and recycle ratios to achieve target compositions. Some care is needed to ensure that they



Iter	Step	Equilibrium	Heat / Spec
1	1.0000	0.000000	0.000001

	Specified Value	Current Value	Wt. Error	Active	Estimate	Current
Reflux Ratio	4.310	4.31	0.0000	☑	☑	☑
Distillate Rate	<empty>	495	<empty>	☐	☑	☐
Reflux Rate	<empty>	2.13e+003	<empty>	☐	☑	☐
Btms Prod Rate	218.7 kgmole/h	219	-0.0000	☑	☑	☑

Degrees of Freedom 0

Converged ☑ Update Outlets ☐ Ignored

Figure 4.49. Specifications for the rigorous distillation column.

are used sparingly; otherwise, too many recycles of information can be introduced and convergence becomes difficult.

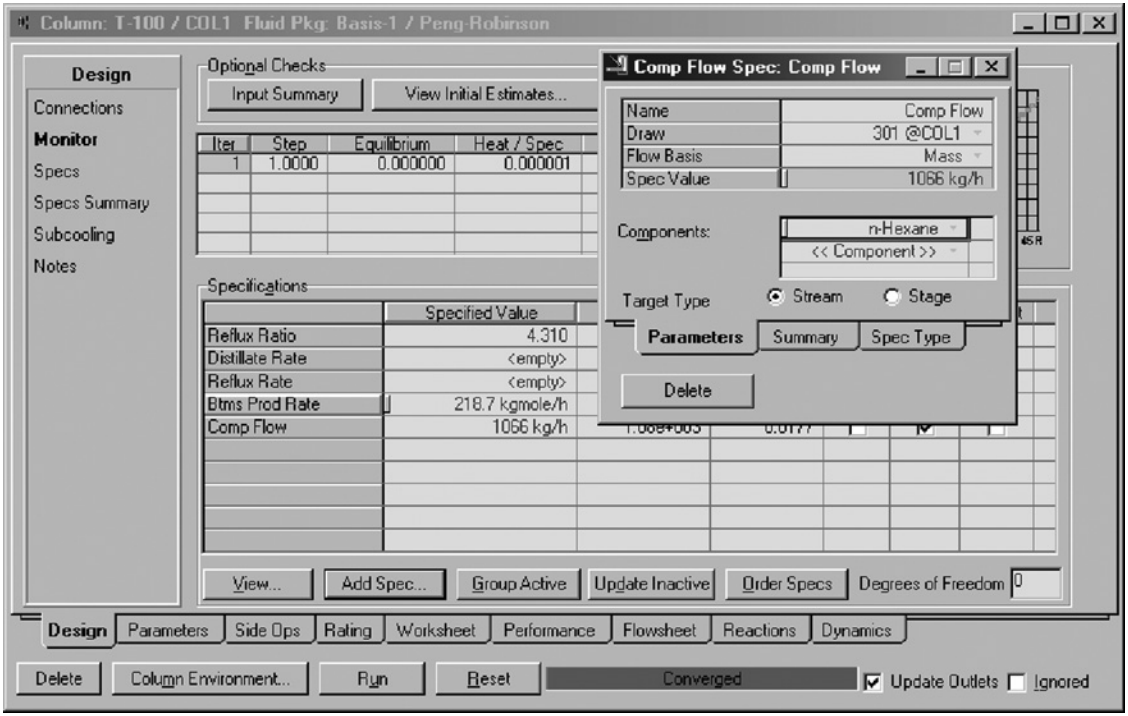
Controllers behave much like recycles, and it is usually a good idea to generate a converged simulation to act as a good initial estimate before adding controllers. This does not apply to simple controller functions such as feed ratio controllers.

In a dynamic simulation, controllers are used to model the real control valves of the process. When converting a steady-state simulation to a dynamic simulation, some care is needed to ensure that the controller functions correspond to physically achievable control structures.

4.8.2. Optimization Using Process Simulation Software

The commercial process simulation programs all have the ability to solve optimization problems that can be posed as nonlinear programming (NLP) problems. At the time of writing, they do not allow the designer to carry out discrete optimization using integer variables. It is, therefore, not possible to optimize integer parameters such as number of trays or feed tray, while simultaneously optimizing continuous variables. It is also not possible to carry out superstructure optimization using the commercial simulation programs.

Optimization of a large process simulation model is intrinsically difficult, particularly if there are multiple recycles. As noted in Section 1.9.9, the solution algorithms



Column: T-100 / COL1 Fluid Pkg: Basis-1 / Peng-Robinson

Iter	Step	Equilibrium	Heat / Spec
1	1.0000	0.000000	0.000001

	Specified Value					
Reflux Ratio	4.310					
Distillate Rate	<empty>					
Reflux Rate	<empty>					
Btms Prod Rate	218.7 kgmole/h					
Comp Flow	1066 kg/h	1.069e+003	0.0177	☐	☑	☐

Comp Flow Spec: Comp Flow

Name	Comp Flow
Draw	301 @COL1
Flow Basis	Mass
Spec Value	1066 kg/h

Components: n-Hexane
<< Component >>

Target Type ● Stream ○ Stage

Degrees of Freedom 0

Converged ☑ Update Outlets ☐ Ignored

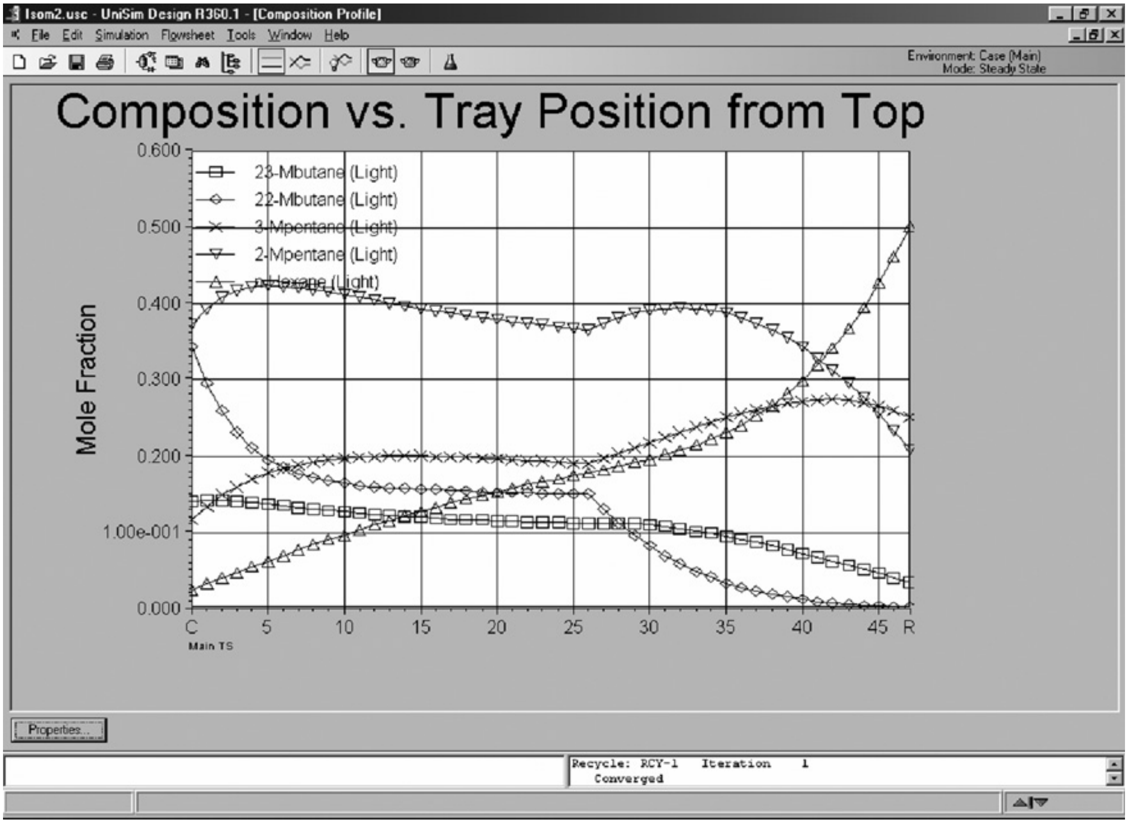
Figure 4.50. Adding a specification on n-hexane mass flow.

for NLP problems require multiple solutions of the model, which must be converged at each solution.

An additional complication of flowsheet optimization is the formulation of the objective function. The objective function for industrial design is always a measure of economic performance. The design parameters calculated by the simulation program can be used to give relatively good estimates of equipment cost, but this typically requires exporting the parameters into a specialized cost-estimating program, such as Aspen ICARUS, as described in Section 6.3.8. Furthermore, the equipment must usually be oversized by a suitable design factor compared to the design flow rates, as discussed in Section 1.7. The simplest way to address this problem is to generate two or three simulation runs with variations of the key design parameters. These designs can then be costed to develop approximate cost curves, which can then be used in the optimization tool of the simulation program.

The Aspen Plus manual provides several useful recommendations for specifying optimization problems (Aspen Technology, 2001):

1. Start by converging a simulation of the flowsheet. This helps the designer detect errors, ensures that specifications are feasible, and provides good estimates for tear streams.



```
Recycle: RCY-1   Iteration    1
   Converged
```

Figure 4.51. Column profiles for the rigorous distillation model.

2. Carry out a sensitivity analysis to determine which variables have the most impact on the objective function. These are the variables that should be used as decision variables. It is also important to determine reasonable ranges for these variables and set upper and lower bound constraints. If the ranges set are too narrow, then the optimum may not be found. If they are too wide, then convergence may be difficult.
3. While carrying out the sensitivity analysis, see if the optimum is broad or sharp. If there are only small changes in the objective function, then further optimization may not be justified.

Another approach that is often used is to carry out optimization using simplified models to fix the process structure and determine the approximate values of key decision variables. A final NLP optimization can then be carried out using a rigorous model.

4.9. DYNAMIC SIMULATION

Most continuous processes are simulated only in steady-state mode. Some of the simulation programs allow a steady-state simulation to be converted to run in a dynamic mode. Dynamic simulation is useful for

1. Simulating batch and semicontinuous processes to determine rate-controlling steps and investigate batch-to-batch recycles and heat recovery;
2. Simulating process startup and shutdown;
3. Simulating cyclic processes;
4. Simulating process disturbances to evaluate control system performance and tune controllers;
5. Simulating emergency conditions to evaluate alarm system and relief system responses and ensure that they are adequate.

For a good dynamic simulation, the designer must specify the actual control system from the piping and instrumentation diagram (see Chapter 5) and also all of the vessel designs so that holdups can be calculated. Mass transfer rates and reaction rates must also be known or assumed.

Dynamic simulation is more computationally intensive than steady-state simulation. Dynamic simulation is usually applied to parts of a process (or even single unit operations) rather than an entire process. Different simulation strategies are needed to give a robust dynamic model. Good introductions to dynamic simulation are given in the books by Luyben (2006), Ingham et al. (2007), Seborg et al. (2003), and Asprey and Machietto (2003) and the paper by Pantelides (1988).

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4.11. NOMENCLATURE

		Dimensions in **MLT**
A	Heat exchanger area	$\mathbf{L}^2$
F	Shell and tube exchanger factor (for noncountercurrent flow)	—
G	Molar rate of consumption of gas in reactor	$\mathbf{MT}^{-1}$
M	Make-up gas molar flow rate	$\mathbf{MT}^{-1}$
P	Purge gas molar flow rate	$\mathbf{MT}^{-1}$
q	Wegstein method acceleration parameter	—
s	Wegstein method estimate of gradient	—
U	Overall heat transfer coefficient	$\mathbf{MT}^{-3}\theta^{-1}$
x_k	Estimate of parameter x at k^{th} iteration	—
x	Controlled parameter	—
y	Target value	—
y_M	Mole fraction of inerts in make-up	—
y_R	Mole fraction of inerts in recycle and purge	—
z	Target value or unknown variable calculated by simulation program	—

4.12. PROBLEMS

4.1. Monochlorobenzene is produced by the reaction of benzene with chlorine. A mixture of monochlorobenzene and dichlorobenzene is produced, with a small amount of trichlorobenzene. Hydrogen chloride is produced as a byproduct. Benzene is fed to the reactor in excess to promote the production of monochlorobenzene.

The reactor products are fed to a condenser where the chlorobenzenes and unreacted benzene are condensed. The condensate is separated from the noncondensable gases in a separator. The noncondensables, hydrogen chloride and unreacted chlorine, pass to an absorption column where the hydrogen chloride is absorbed in water. The chlorine leaving the absorber is recycled to the reactor.

The liquid phase from the separator, containing chlorobenzenes and unreacted benzene, is fed to a distillation column, where the chlorobenzenes are separated from the unreacted benzene. The benzene is recycled to the reactor.

Using the following data, calculate the stream flows and draw up a preliminary flowsheet for the production of 1.0 metric ton (tonne) of monochlorobenzene per day.

Data:

Reactor

$$\text{Reactions:}\quad \begin{array}{l} C_6H_6 + Cl_2 \rightarrow C_6H_5 + HCl \\ C_6H_6 + 2Cl_2 \rightarrow C_6H_4\ Cl_2 + 2HCl \end{array}$$

Mol ratio $Cl_2 : C_6H_6$ at inlet to reactor = 0.9
Overall conversion of benzene = 55.3%
Yield of monochlorobenzene = 73.6%
Yield of dichlorobenzene = 27.3%
Production of other chlorinated compounds can be neglected.

Separator

Assume 0.5% of the liquid stream is entrained with the vapor.

Absorber

Assume 99.99% absorption of hydrogen chloride and that 98% of the chlorine is recycled, the remainder being dissolved in the water. The water supply to the absorber is set to produce a 30% w/w strength hydrochloric acid.

Distillation column

Take the recovery of benzene to be 95%, and 99.99% recovery of the chlorobenzenes.

Note: This problem can be solved without using process simulation software. Start the mass balance at the reactor inlet (after the recycle streams have been added) and assume 100 kgmol/h of benzene at this point.

4.2. Methyl tertiary butyl ether (MTBE) is used as an antiknock additive in gasoline.

It is manufactured by the reaction of isobutene with methanol. The reaction is highly selective and practically any C_4 stream containing isobutene can be used as a feedstock:

$$CH_2 = C(CH_3)_2 + CH_3OH \rightarrow (CH_3)_3\text{–}C\text{–}O\text{–}CH_3$$

A 10% excess of methanol is used to suppress side reactions.

In a typical process, the conversion of isobutene in the reactor stage is 97%.

The product is separated from the unreacted methanol and any C_4 compounds by distillation.

The essentially pure, liquid, MTBE leaves the base of the distillation column and is sent to storage. The methanol and C_4 compounds leave the top of the column as vapor and pass to a column where the methanol is separated by absorption in water. The C_4 compounds leave the top of the absorption column, saturated with water, and are used as a fuel gas. The methanol is separated from the water solvent by distillation and recycled to the reactor stage. The water, which leaves the base of the column, is recycled to the absorption column. A purge is taken from the water recycle stream to prevent the buildup of impurities.

1. Draw up a block flow diagram for this process.
2. Estimate the feeds for each stage.
3. Draw a flowsheet for the process.

Treat the C_4 compounds, other than isobutene, as one component.

Data:

1. Feedstock composition, mol%: n-butane = 2, butene-1 = 31, butene-2 = 18, isobutene = 49.
2. Required production rate of MTBE, 7000 kg/h.
3. Reactor conversion of isobutene, 97%.
4. Recovery of MTBE from the distillation column, 99.5%.
5. Recovery of methanol in the absorption column, 99%.
6. Concentration of methanol in the solution leaving the absorption column, 15%.
7. Purge from the water recycle stream, to waste treatment, 10% of the flow leaving the methanol recovery column.
8. The gases leave the top of the absorption column saturated with water at 30°C.
9. Both columns operate at essentially atmospheric pressure.

4.3. Ethanol can be produced by fermentation of sugars and is used as a gasoline blending component. Because the sugars can be derived from biomass, ethanol is potentially a renewable fuel. In the fermentation of cane sugar to ethanol, sucrose ($C_{11}H_{22}O_{11}$) is converted by yeast (*Saccharomyces cerevisae*) to yield ethanol and CO_2. Some sucrose is also consumed in maintaining the cell culture in the fermentation reactor. The fermentation reaction can be carried out in a continuous reactor as long as the ethanol concentration does not exceed about 8 wt%, at which point the productivity of the yeast declines significantly. The sucrose is fed as a 12.5 wt% solution in water, which must be sterilized before it can be fed to the reactor. The sterilization is usually accomplished by heating with steam. Carbon dioxide is vented from the fermentation reactor. The liquid product of the fermentation reactor is sent to a hydrocyclone to concentrate the yeast for recycle to the reactor.

The remaining liquid is sent to a distillation column known as a "beer column," which concentrates the alcohol to about 40 mol% ethanol and 60 mol% water in the distillate. The recovery of ethanol in the beer column is 99.9%. The bottoms stream from the beer column contains the remaining components of the fermentation broth and can be processed for use as animal feed.

1. Draw a flowsheet for this process.
2. Estimate the stream flow rates and compositions for a production rate of 200,000 U.S. gal/d of dry (100%) ethanol.
3. Estimate the ethanol lost in the CO_2 vent gas.
4. Estimate the reboiler duty of the beer column.

Data:

1. Yield per kg sucrose: ethanol 443.3 g, CO_2 484 g, nonsugar solids 5.3 g, yeast 21 g, fermentation byproducts 43.7 g, higher alcohols (fusel oil) 2.6 g.
2. Conversion of sucrose, 98.5%.
3. Yeast concentration in fermentation reactor at steady state, 3 wt%.
4. Fermenter temperature, 38°C.

4.4. In an ethanol plant, the mixture of water and ethanol from the beer column distillate contains about 40% ethanol (molar basis) in water, together with the fusel oils described in the previous problem. This mixture is distilled to give an azeotropic mixture of ethanol and water (89% ethanol) overhead, with 99.9% recovery of ethanol. The fusel oil can cause blending problems if it is allowed to accumulate in the distillate. Fusel oil is a mixture of higher alcohols and ethers that can be approximated as a mixture of n-butanol and diethyl ether. This mixture is usually removed as a side stream from the column. When the side stream is contacted with additional water, a two-phase mixture can be formed and the oil phase can be decanted to leave an ethanol-water phase that is returned to the column.

1. Draw a flowsheet for this process.
2. Estimate the stream flow rates and compositions for a production rate of 200,000 U.S. gal/d of dry (100%) ethanol.
3. Optimize the distillation column using the cost correlations given in Section 6.3 and assuming that reboiler heat costs $5/MMBtu. Minimize the total annualized cost of the column.

4.5. Water and ethanol form a low boiling point azeotrope; hence, water cannot be completely separated from ethanol by conventional distillation. To produce absolute (100%) ethanol, it is necessary to add an entraining agent to break the azeotrope. Benzene is an effective entrainer and is used where the product is not required for food products. Three columns are used in the benzene process.

Column 1. This column separates the ethanol from the water. The bottom product is essentially pure ethanol. The water in the feed is carried overhead as the ternary azeotrope of ethanol, benzene, and water (roughly 24% ethanol, 54% benzene, 22% water). The overhead vapor is condensed and the condensate separated in a decanter into a benzene-rich phase (22% ethanol, 74% benzene, 4% water) and a water-rich phase (35% ethanol, 4% benzene, 61% water). The benzene-rich phase is recycled to the column as reflux. A benzene make-up stream is added to the reflux to make up any loss of benzene from the process. The water-rich phase is fed to the second column.

Column 2. This column recovers the benzene as the ternary azeotrope and recycles it as vapor to join the overhead vapor from the first column. The bottom product from the column is essentially free of benzene (29% ethanol, 51% water). This stream is fed to the third column.

Column 3. In this column, the water is separated and sent to waste treatment. The overhead product consists of the azeotropic mixture of ethanol and water (89% ethanol, 11% water). The overheads are condensed and recycled to join the feed to the first column. The bottom product is essentially free of ethanol.

1. Draw a flowsheet for this process.
2. Estimate the stream flow rates and compositions for a production rate of 200,000 U.S. gal/d of dry (100%) ethanol.

Take the benzene losses to total 0.1 kmol/h. All the compositions given are molar percentages.

4.6. A plant is required to produce 10,000 metric tons per year of anhydrous hydrogen chloride from chlorine and hydrogen. The hydrogen source is impure: 90 mol% hydrogen, balance nitrogen.

The chlorine is essentially pure chlorine, supplied in rail tankers.

The hydrogen and chlorine are reacted in a burner at 1.5 bar pressure:

$$H_2 + Cl_2 \rightarrow 2HCl$$

Hydrogen is supplied to the burner in 3% excess over the stoichiometric amount. The conversion of chlorine is essentially 100%. The gases leaving the burner are cooled in a heat exchanger.

The cooled gases pass to an absorption column where the hydrogen chloride gas is absorbed in dilute hydrochloric acid. The absorption column is designed to recover 99.5% of the hydrogen chloride in the feed.

The unreacted hydrogen and inerts pass from the absorber to a vent scrubber where any hydrogen chloride present is neutralized by contact with a dilute, aqueous solution of sodium hydroxide. The solution is recirculated around the scrubber. The concentration of sodium hydroxide is maintained at 5% by taking a purge from the recycle loop and introducing a make-up stream of 25% concentration. The maximum concentration of hydrogen chloride discharged in the gases vented from the scrubber to atmosphere must not exceed 200 ppm by volume.

The strong acid from the absorption column (32% HCl) is fed to a stripping column where the hydrogen chloride gas is recovered from the solution by distillation. The diluted acid from the base of this column (22% HCl) is recycled to the absorption column.

The gases from the top of the stripping column pass through a partial condenser, where the bulk of the water vapor present is condensed and returned to the column as reflux. The gases leaving the column will be saturated with water vapor at 40°C.

The hydrogen chloride gas leaving the condenser is dried by contact with concentrated sulfuric acid in a packed column. The acid is recirculated over the packing. The concentration of sulfuric acid is maintained at 70% by taking a purge from the recycle loop and introducing a make-up stream of strong acid (98% H_2SO_4).

The anhydrous hydrogen chloride product is compressed to 5 bar and supplied as a feed to another process.

Using the information provided, calculate the flow rates and compositions of the main process streams, and draw a flowsheet for this process. All compositions are wt%, except where indicated.

4.7. Ammonia is synthesized from hydrogen and nitrogen. The synthesis gas is usually produced from hydrocarbons. The most common raw materials are oil or natural gas, though coal and even peat can be used.

When produced from natural gas, the synthesis gas will be impure, containing up to 5% inerts, mainly methane and argon. The reaction equilibrium and rate are favored by high pressure. The conversion is low, about 15%, and so, after removal of the ammonia produced, the gas is recycled to the converter inlet. A typical process consists of a converter (reactor) operating at 350 bar, a refrigerated system to condense out the ammonia product from the recycle loop, and compressors to compress the feed and recycle gas. A purge is taken from the recycle loop to keep the inert concentration in the recycle gas at an acceptable level.

Using the following data, draw a flow diagram of the process and calculate the process stream flow rates and compositions for the production of 600 t/d ammonia.

Data:
Composition of synthesis gas, mol fraction:

N_2	H_2	CH_4	A
24.5	73.5	1.7	0.3

Temperature and operating pressure of liquid ammonia–gas separator, 340 bar and −28°C.

Inert gas concentration in recycle gas, not greater than 15 mol%.

4.8. Methyl ethyl ketone (MEK) is manufactured by the dehydrogenation of 2-butanol.

A simplified description of the process listing the various units used is as follows:

1. A reactor in which the butanol is dehydrated to produce MEK and hydrogen, according to the reaction,

$$CH_3CH_2CH_3CHOH \rightarrow CH_3CH_2CH_3CO + H_2$$

The conversion of alcohol is 88%, and the selectivity to MEK can be taken as 100%.

2. A cooler-condenser in which the reactor off gases are cooled and most of the MEK and unreacted alcohol are condensed. Two exchangers are used, but they can be modeled as one unit. Of the MEK entering the unit, 84% is condensed, together with 92% of the alcohol. The hydrogen is noncondensable. The condensate is fed forward to the final purification column.
3. An absorption column in which the uncondensed MEK and alcohol are absorbed in water. Around 98% of the MEK and alcohol can be considered to be absorbed in this unit, giving a 10 wt% solution of MEK. The water feed to the absorber is recycled from the next unit, the extractor. The vent stream from the absorber, containing mainly hydrogen, is sent to a flare stack.
4. An extraction column in which the MEK and alcohol in the solution from the absorber are extracted into trichloroethylene (TCE). The raffinate, water containing around 0.5 wt% MEK, is recycled to the absorption column.

   The extract, which contains around 20 wt% MEK and a small amount of butanol and water, is fed to a distillation column.
5. A distillation column, which separates the MEK and alcohol from the solvent TCE. The recovery of MEK is 99.99%.

   The solvent containing a trace of MEK and water is recycled to the extraction column.
6. A second distillation column, which produces a 99.9% pure MEK product from the crude product from the first column. The residue from this column, which contains the bulk of the unreacted 2-butanol, is recycled to the reactor.

For a production rate of 1250 kg/h MEK:

1. Draw a flowsheet for the process.
2. Estimate the stream flow rates and compositions.
3. Estimate the reboiler and condenser duties of the two distillation columns.
4. Estimate the number of theoretical trays required in each column.

4.9. In the problem of Example 4.1, the feed was specified as pentane (C_5H_{12}) with a hydrogen-to-carbon ratio of 2.4:1. If the feed to the process were a heavy oil, the hydrogen-to-carbon ratio would be more like 2:1. How would the distribution of C_5 carbon compounds change if the feed had a 2:1 carbon ratio?

4.10. Example 4.1 examined the equilibrium distribution of hydrocarbon compounds within a single carbon number (C_5). In reality, cracking reactions to ethylene, propylene, and other light alkenes and alkynes will have a significant effect on the yield of a cracking process.

1. What is the effect of including C_2 and C_3 compounds on the equilibrium distribution?
2. What is the effect of including coke (carbon) as well as the C_2 and C_3 compounds?
3. What do these results tell you about cracking processes?

4.11. Optimize the heat exchanger design of Example 4.5 to minimize the total surface area required.

4.12. A stream containing 4 metric tons/h of a 20 wt% mixture of benzene in toluene is heated from 20°C to the bubble point at 4 atm pressure. The mixture is separated in a distillation column to give 99.9% recovery of benzene overhead and toluene in the bottoms.

1. If the toluene product must be cooled to 20°C, how much of the feed heat can be supplied by heat exchange with the bottoms?
2. How many heat exchange shells are needed?
3. What is the minimum total heat exchange area?
4. What is the distillation column diameter?
5. How many sieve trays are needed if the tray efficiency is 70%?

4.13. The autothermal reforming of methane to hydrogen was described in Example 4.2. The solution in the example was not optimized, and suggestions were given for how to improve the results. Optimize the process to minimize the cost of production of hydrogen, assuming

1. Cost of methane = 16¢/lb
2. Cost of oxygen = 2¢/lb
3. Cost of water = 25¢/1000 lb
4. Annualized cost of heat exchangers = \$30,000 + 3 *A*, where *A* is the area in ft^2

5. Cost of electric power = 6¢/kWh
6. Reactor and catalyst costs are the same in all cases.

Hint: First determine the optimal heat recovery and steam and oxygen to methane ratios for a given methane conversion. Repeat for different methane conversions to find the overall optimum.

4.14. The light naphtha isomerization process is more complex than the description given in Example 4.7.

1. Hydrogen is flowed through the plant to reduce catalyst deactivation. The hydrogen flow rate is typically about 2 moles per mole of hydrocarbon on a pure hydrogen basis. The hydrogen make-up gas is typically about 90 mol% hydrogen, with the balance methane.
2. Light hydrocarbon compounds are formed by cracking reactions. These compounds accumulate in the hydrogen recycle and are controlled by taking a purge stream. A stabilizer column is also required, upstream of the distillation column, to remove light hydrocarbons and hydrogen before the distillation.
3. Each of the C_6 isomers has a different blending octane value. The total octane value of the product can be found by summing the products of the mole fraction of each component and the component blending value. The blending values are: n-hexane 60; 2-methyl pentane 78.5; 3-methyl pentane 79.5; 2,2-dimethyl butane 86.3; 2,3-dimethyl butane 93.

Optimize the design of Example 4.7, subject to the following:

1. The selectivity loss due to cracking reactions can be approximated as 1% conversion of C_6 compounds to propane per reactor pass.
2. The wholesale value of gasoline can be assumed to be 2.0 + 0.05 (octane number–87) \$/U.S. gal.
3. The cost of hydrogen is \$6/1000 scf, and the fuel value of the hydrogen and propane purge stream is \$5/MMBtu.
4. The reactor plus catalyst total installed cost can be taken as \$0.5 MM per 1000 bpd of liquids processed.
5. Other costs can be estimated using the cost correlations given in Section 6.3.

Additional flowsheeting problems are given in the form of design projects in Appendices E and F.

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5 PIPING AND INSTRUMENTATION

Chapter Contents

Key Learning Objectives

- How to read a piping and instrument diagram drawn using ISA-5.1 symbols
- How valves and controllers work
- How to calculate line pressure drop and size and select pumps
- How to design control schemes for common unit operations and whole processes

5.1. INTRODUCTION

The process flowsheet shows the arrangement of the major pieces of equipment and their interconnection. It is a description of the nature of the process.

The *Piping and Instrument diagram* (P and I diagram or PID) shows the engineering details of the equipment, instruments, piping, valves, and fittings and their arrangement. It is often called the *Engineering Flowsheet* or *Engineering Line Diagram*.

This chapter covers the preparation of the preliminary P and I diagrams at the process design stage of the project.

The design of piping systems and the specification of the process instrumentation and control systems are usually done by specialist design groups, and a detailed discussion of piping design and control systems is beyond the scope of this book. Only general guide rules are given. The piping handbook edited by Nayyar et al. (2000) is particularly recommended for the guidance on the detailed design of piping systems and process instrumentation and control. The references cited in the text and listed at the end of the chapter should also be consulted.

5.2. THE P AND I DIAGRAM

The P and I diagram shows the arrangement of the process equipment, piping, pumps, instruments, valves, and other fittings. It should include

1. All process equipment, identified by an equipment number. The equipment should be drawn roughly in proportion and the location of nozzles shown.
2. All pipes, identified by a line number. The pipe size and material of construction should be shown. The material may be included as part of the line identification number.
3. All valves, control and block valves, with an identification number. The type and size should be shown. The type may be shown by the symbol used for the valve or included in the code used for the valve number.
4. Ancillary fittings that are part of the piping system, such as inline sight-glasses, strainers, and steam traps, with an identification number.
5. Pumps, identified by a suitable code number.
6. All control loops and instruments, with an identification number.

For simple processes, the utility (service) lines can be shown on the P and I diagram. For complex processes, separate diagrams should be used to show the service lines, so the information can be shown clearly, without cluttering up the diagram. The service connections to each unit should, however, be shown on the P and I diagram.

The P and I diagram will resemble the process flowsheet, but the process information is not shown. The same equipment identification numbers should be used on both diagrams.

5.2.1. Symbols and Layout

The symbols used to show the equipment, valves, instruments, and control loops will depend on the practice of the particular design office. The equipment symbols are usually more detailed than those used for the process flowsheet. A typical example of a P and I diagram is shown in Figure 5.29.

International standard symbols for instruments, controllers, and valves are given by the Instrumentation Systems and Automation Society design code ISA-5.1-1984 (R1992). Some companies use their own symbols though, and different standards are followed in some countries, such as BS 1646 in the UK and DIN 19227 and DIN 2429 in Germany (see references).

When the diagram is laid out, it is only necessary to show the relative elevation of the process connections to the equipment where they affect the process operation; for example, the net positive suction head (NPSH) of pumps, barometric legs, siphons, and the operation of thermosyphon reboilers. Full details of pipe layout are usually shown in a different drawing, known as a *piping isometric drawing*. See Figure 5.19 for an example.

Computer-aided drafting programs are available for the preparation of P and I diagrams; see the reference to the PROCEDE package in Chapter 4.

5.2.2. Basic Symbols

The symbols illustrated in this section are those given in ISA-5.1-1984 (R1992).

Control Valves

Different types of valves are discussed in section 5.3.

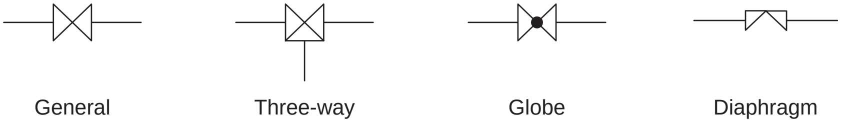


Figure 5.1. Control valves.

Actuators

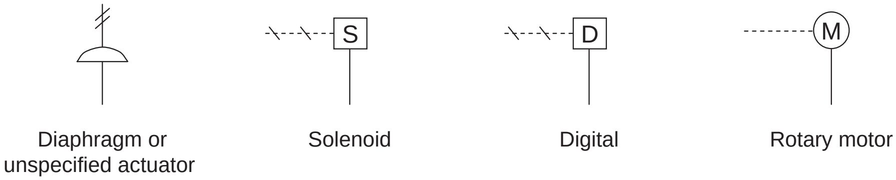
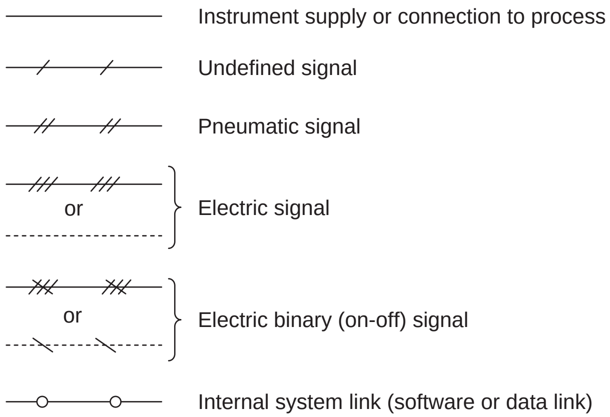


Figure 5.2. Actuators.

Most control valves (final control elements) are actuated by pneumatic signals using instrument air. Pneumatic actuators are preferred in situations in which electronic controllers might cause a process hazard or electric power is not available or reliable. Pneumatic controllers are also found in many older plants where replacement with electronic controllers has not yet occurred. Motor actuators are used for larger valves, while digital and solenoid actuators are used for valves that are switched from open to closed. Many newer controllers use a combination of these approaches. For example, a digital signal can be sent to a solenoid that opens or shuts an instrument air line that then actuates a pneumatically driven control valve.

Instrument Lines



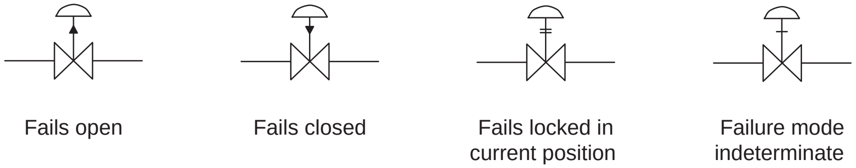
All lines should be drawn fine in relation to process piping lines

Figure 5.3. Instrument lines.

The instrument connecting lines are drawn in a manner to distinguish them from the main process lines. Process lines are drawn as solid lines and are usually drawn thicker.

Failure Mode

The direction of the arrow shows the position of the valve on failure of the power supply.



Fails open

Fails closed

Fails locked in current position

Failure mode indeterminate

Figure 5.4. Valve failure modes.

General Instrument and Controller Symbols

Locally mounted means that the controller and display are located out on the plant near to the sensing instrument location. *Main panel* means that they are located on a panel in the control room. Except on small plants, most controllers would be mounted in the control room.

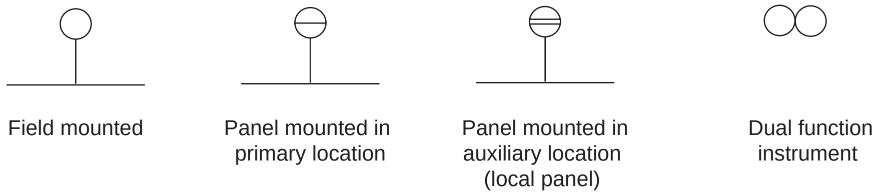


Figure 5.5. General instrument and controller symbols.

Distributed Control—Shared Display Symbols

Field mounted shared display device with limited access to adjustments

Shared display device with operator access to adjustments

Shared display device with software alarms (* is measured variable)

Figure 5.6. Distributed control—shared display symbols.

A distributed control system is a system that is functionally integrated but consists of subsystems that may be physically separate and remotely located from one another. A shared display is an operator interface device such as a computer screen or video screen that is used to display process control information from a number of sources at the command of the operator. Most plants built since 1990 (and many older plants) use shared displays instead of instrument panels.

Other Common Symbols

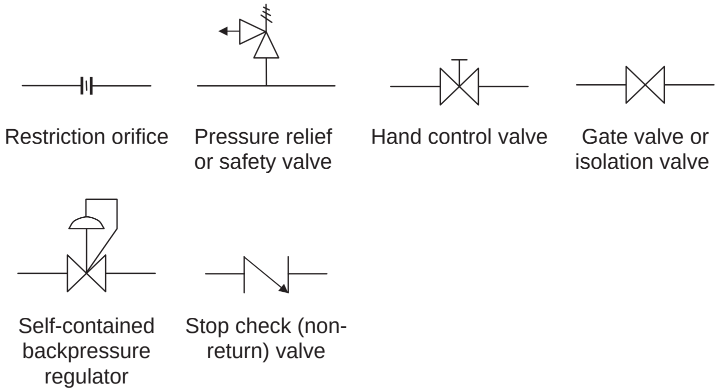


Figure 5.7. Other common symbols.

Type of Instrument

The type of instrument is indicated on the circle representing the instrument-controller by a letter code (see Table 5.1).

The first letter indicates the property measured, for example, F = flow. Subsequent letters indicate the function, for example,

I = indicating

RC = recorder controller

The letters AH or AL indicate high or low alarms.

The P and I diagram shows all the components that make up a control loop. For example, Figure 5.8 shows a field-located pressure transmitter connected to a shared display pressure indicator-controller with operator access to adjustments and high and low alarms. The pressure controller sends an electric signal to a fail-closed diaphragm-actuated pressure control valve.

Table 5.1. Letter Code for Instrument Symbols [based on ISA-5.1-1984 (R1992)]

Initiating or Measured Variable	First Letter	Indicating Only	Controllers			Transmitters	Final Control Element
			Recording	Indicating	Blind		
Analysis (composition)	A	AI	ARC	AIC	AC	AT	AV
Flow rate	F	FI	FRC	FIC	FC	FT	FV
Flow ratio	FF	FFI	FFRC	FFIC	FFC	FFT	FFV
Power	J	JI	JRC	JIC		JT	JV
Level	L	LI	LRC	LIC	LC	LT	LV
Pressure, vacuum	P	PI	PRC	PIC	PC	PT	PV
Pressure differential	PD	PDI	PDRC	PDIC	PDC	PDT	PDV
Quantity	Q	QI	QRC	QIC		QT	QZ
Radiation	R	RI	RRC	RIC	RC	RT	RZ
Temperature	T	TI	TRC	TIC	TC	TT	TV
Temperature differential	TD	TDI	TDRC	TDIC	TDC	TDT	TDV
Weight	W	WI	WRC	WIC	WC	WT	WZ

Notes:

1. The letters C, D, G, M, N, and O are not defined and can be used for any user-specified property.
2. The letter S as second or subsequent letter indicates a switch.
3. The letter Y as second or subsequent letter indicates a relay or a compute function.
4. The letter Z is used for the final control element when this is not a valve.

Consult the standard for the full set of letter codes.

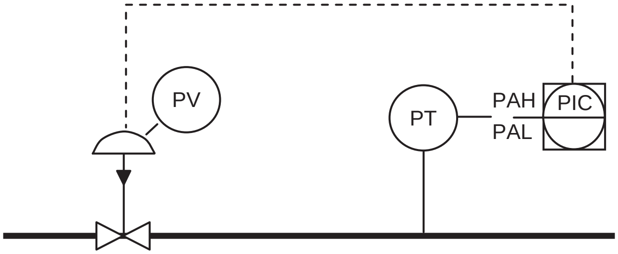


Figure 5.8. A typical control loop.

5.3. VALVE SELECTION

The valves used for a chemical process plant can be divided into two broad classes, depending on their primary function:

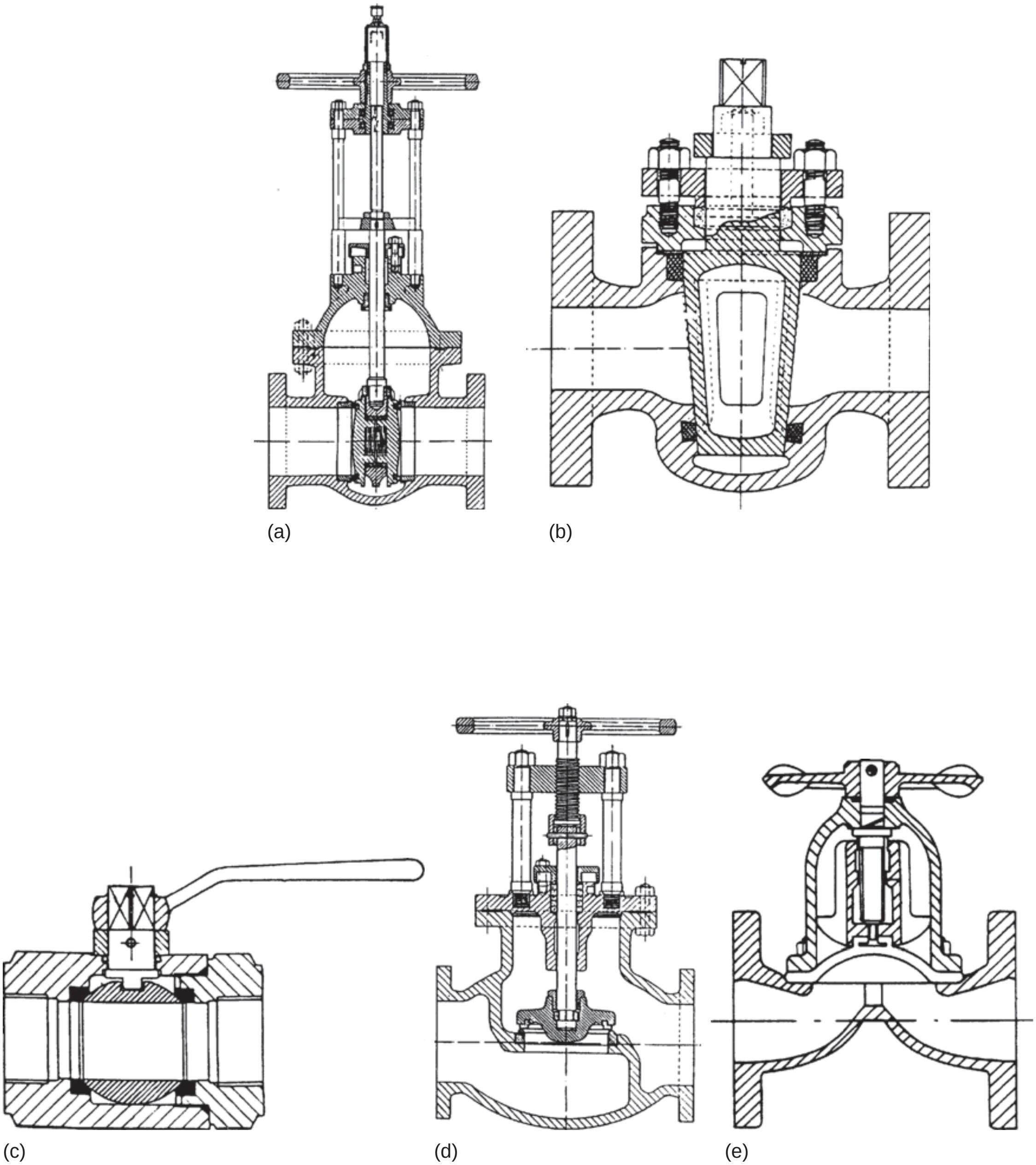
1. Shut-off valves (block valves or isolation valves), whose purpose is to close off the flow;
2. Control valves, both manual and automatic, used to regulate flow.

The main types of valves used are

Gate	Figure 5.9a
Plug	Figure 5.9b
Ball	Figure 5.9c
Globe	Figure 5.9d
Diaphragm	Figure 5.9e
Butterfly	Figure 5.9f
Nonreturn	Figure 5.9g

A valve selected for shut-off purposes should give a positive seal in the closed position and minimum resistance to flow when open. Gate, plug, and ball valves are most frequently used for this purpose. Gate valves are available in the widest range of sizes and can be operated manually or by a motor. They have a straight-through flow channel and low pressure drop when fully open. Several turns of the valve handle are usually required to close the valve, so they are best used when operated infrequently. Gate valves should not be operated partially open, as the valve seals can become deformed, causing the valve not to seal properly. Plug valves and ball valves have the advantage that they require only a quarter turn to open or close. These valves are often actuated by solenoids and are used where quick on-off switching is needed. The selection of valves is discussed by Merrick (1986, 1990), Smith and Vivian (1995), and Smith and Zappe (2003).

If flow control is required, the valve should be capable of giving smooth control over the full range of flow, from fully open to closed. Globe valves are normally used, though diaphragm valves are also common. Butterfly valves are often used for the control of gas and vapor flows. Automatic control valves are usually globe valves with special trim designs.



(a)

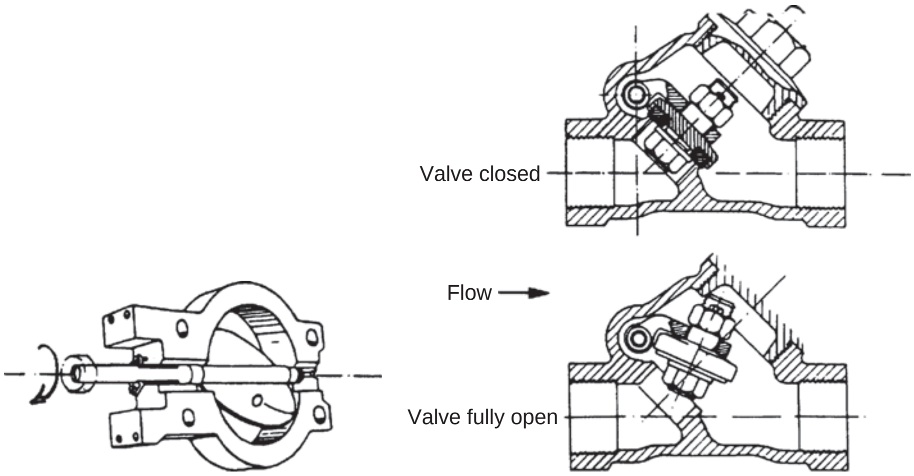
(b)

(c)

(d)

(e)

Figure 5.9. (a) Gate valve (slide valve). (b) Plug valve. (c) Ball valve. (d) Globe valve. (e) Diaphragm valve.



(f) (g)

Figure 5.9. Cont'd. (f) Butterfly valve. (g) Nonreturn valve, check valve, hinged disc type.

The careful selection and design of control valves is important; good flow control must be achieved, while keeping the pressure drop as low as possible. The valve must also be sized to avoid the flashing of hot liquids and the supercritical flow of gases and vapors. Control valve sizing is discussed by Chaflin (1974).

Nonreturn valves are used to prevent backflow of fluid in a process line. They do not normally give an absolute shut-off of the reverse flow. A typical design is shown in Figure 5.9*g*. Since swing-type check valves depend on gravity to close the valve, care must be taken to orient the valve properly when locating and installing it.

Standards for valves are set by the ASME B16 Standards Committee and can be ordered from the American Society of Mechanical Engineers. General standards are described in ASME B16.34-2004 (ASME, 2004), while valve dimensions are given in ASME B16.10-2000 (ASME, 2000). Valve design is covered by Pearson (1978).

5.4. PUMPS AND COMPRESSORS

5.4.1. Pump Selection

Pumps can be classified into two general types:

1. Dynamic pumps, such as centrifugal pumps;
2. Positive displacement pumps, such as reciprocating and diaphragm pumps.

The single-stage, horizontal, overhung, centrifugal pump is by far the most commonly used type in the chemical process industry. Other types are used where a high head or other special process considerations are specified. For example, when small flow rates of additives must be added to a process, then positive displacement metering pumps are often used.

Pump selection is made on the flow rate and head required, together with other process considerations, such as corrosion or the presence of solids in the fluid.

The chart shown in Figure 5.10 can be used to determine the type of pump required for a particular head and flow rate. This figure is based on one published by Doolin (1977).

Centrifugal pumps are characterized by their specific speed. In the dimensionless form, specific speed is given by

$$N_s = \frac{NQ^{1/2}}{(gh)^{3/4}} \tag{5.1}$$

where

N = revolutions per second;
Q = flow, m^3/s;
h = head, m;
g = gravitational acceleration m/s^2.

Pump manufacturers do not generally use the dimensionless specific speed but define the impeller specific speed by the equation

$$N'_S = \frac{N'Q^{1/2}}{h^{3/4}} \tag{5.2}$$

where

N' = revolutions per minute (rpm);
Q = flow, U.S. gal/min;
h = head, ft.

Values of the nondimensional specific speed, as defined by equation 5.1, can be converted to the form defined by equation 5.2 by multiplying by 1.72×10^4.

The impeller specific speed for centrifugal pumps (equation 5.2) usually lies between 400 and 20,000, depending on the type of impeller. Generally, pump impellers are classified as centrifugal or radial for specific speeds between 400 and 4000, mixed flow between 4000 and 9000, and axial above 9000 (Heald, 1996). Doolin (1977) states that below a specific speed of 1000, the efficiency of single-stage centrifugal pumps is low and multistage pumps should be considered.

For a detailed discussion of the factors governing the selection of the best centrifugal pump for a given duty, refer to the articles by De Santis (1976), Neerkin (1974), Jacobs (1965), or Walas (1990).

Positive displacement, reciprocating, pumps are normally used where a high head is required at a low flow rate. Holland and Chapman (1966) review the various types of positive displacement pumps available and discuss their applications.

A general guide to the selection, installation, and operation of pumps for the process industries is given by Davidson and von Bertele (1999) and Jandiel (2000).

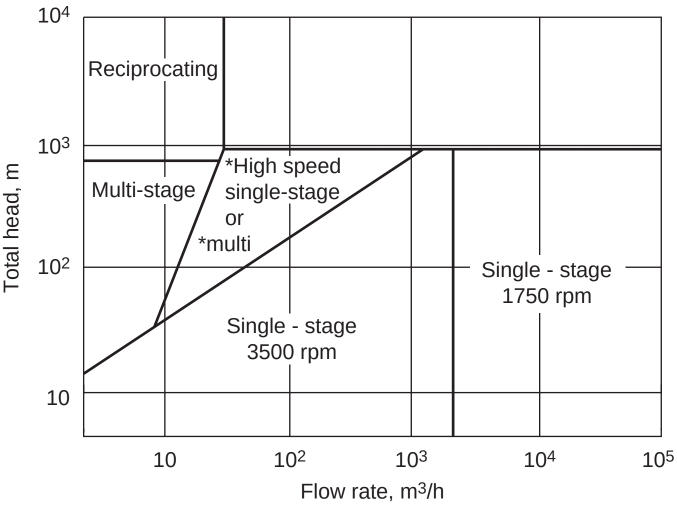


Figure 5.10. Centrifugal pump selection guide. *Single-stage >1750 rpm, multistage 1750 rpm.

The selection of the pump cannot be separated from the design of the complete piping system. The total head required will be the sum of the dynamic head due to friction losses in the piping, fittings, valves, and process equipment, and any static head due to differences in elevation.

The pressure drop required across a control valve will be a function of the valve design. Sufficient pressure drop must be allowed for when sizing the pump to ensure that the control valve operates satisfactorily over the full range of flow required. If possible, the control valve and pump should be sized together, as a unit, to ensure that the optimum size is selected for both. As a rough guide, if the characteristics are not specified, the control valve pressure drop should be taken as at least 30% of the total dynamic pressure drop through the system, with a minimum value of 50 kPa (7 psi). A good rule of thumb in the early stages of process design is to allow 70 kPa (10 psi) pressure drop for each control valve. The valve should be sized for a maximum flow rate 30% above the normal stream flow rate. Some of the pressure drop across the valve will be recovered downstream, the amount depending on the type of valve used.

Methods for the calculation of pressure drop through pipes and fittings are given in Section 5.4.2. It is important that a proper analysis is made of the system, and the use of a calculation form (worksheet) to standardize pump-head calculations is recommended. A standard calculation form ensures that a systematic method of calculation is used, and provides a checklist to ensure that all the usual factors have been considered. It is also a permanent record of the calculation. A template for a standard pump and line calculation is given in Appendix G and can be downloaded in MS Excel format from http://books.elsevier.com/companions. Example 5.8 has been set out using this calculation form. The calculation should include a check on the net positive suction head (NPSH) available; see Section 5.4.3.

Kern (1975) discusses the practical design of pump suction piping, in a series of articles on the practical aspects of piping system design published in the journal *Chemical Engineering* from December 1973 through November 1975. A detailed presentation of pipe-sizing techniques is also given by Simpson (1968), who covers liquid, gas, and two-phase systems. Line sizing and pump selection are also covered in a comprehensive article by Ludwig (1960).

5.4.2. Pressure Drop in Pipelines

The pressure drop in a pipe, due to friction, is a function of the fluid flow rate, fluid density and viscosity, pipe diameter, pipe surface roughness, and the length of the pipe. It can be calculated using the following equation:

$$\Delta P_f = 8f(L/d_i)\frac{\rho u^2}{2} \tag{5.3a}$$

where

ΔP_f = pressure drop, N/m^2;
f = friction factor;
L = pipe length, m;
d_i = pipe inside diameter, m;
ρ = fluid density, kg/m^3;
u = fluid velocity, m/s.

The friction factor is dependent on the Reynolds number and pipe roughness. The friction factor for use in equation 5.3 can be found from Figure 5.11.

$$\text{The Reynolds number is given by } Re = (\rho \times u \times d_i)/\mu \tag{5.4}$$

Values for the absolute surface roughness of commonly used pipes are given in Table 5.2. The parameter to use with Figure 5.11 is the relative roughness, given by

relative roughness, e = absolute roughness/pipe inside diameter

Note: The friction factor used in equation 5.3a is related to the shear stress at the pipe wall, R, by the equation $f = (R/\rho u^2)$. Other workers use different relationships. Their charts for friction factor will give values that are multiples of those given by Figure 5.11. So, it is important to make sure that the pressure drop equation used matches the friction factor

Table 5.2. Pipe Roughness

Material	Absolute Roughness, mm
Drawn tubing	0.0015
Commercial steel pipe	0.046
Cast iron pipe	0.26
Concrete pipe	0.3 to 3.0

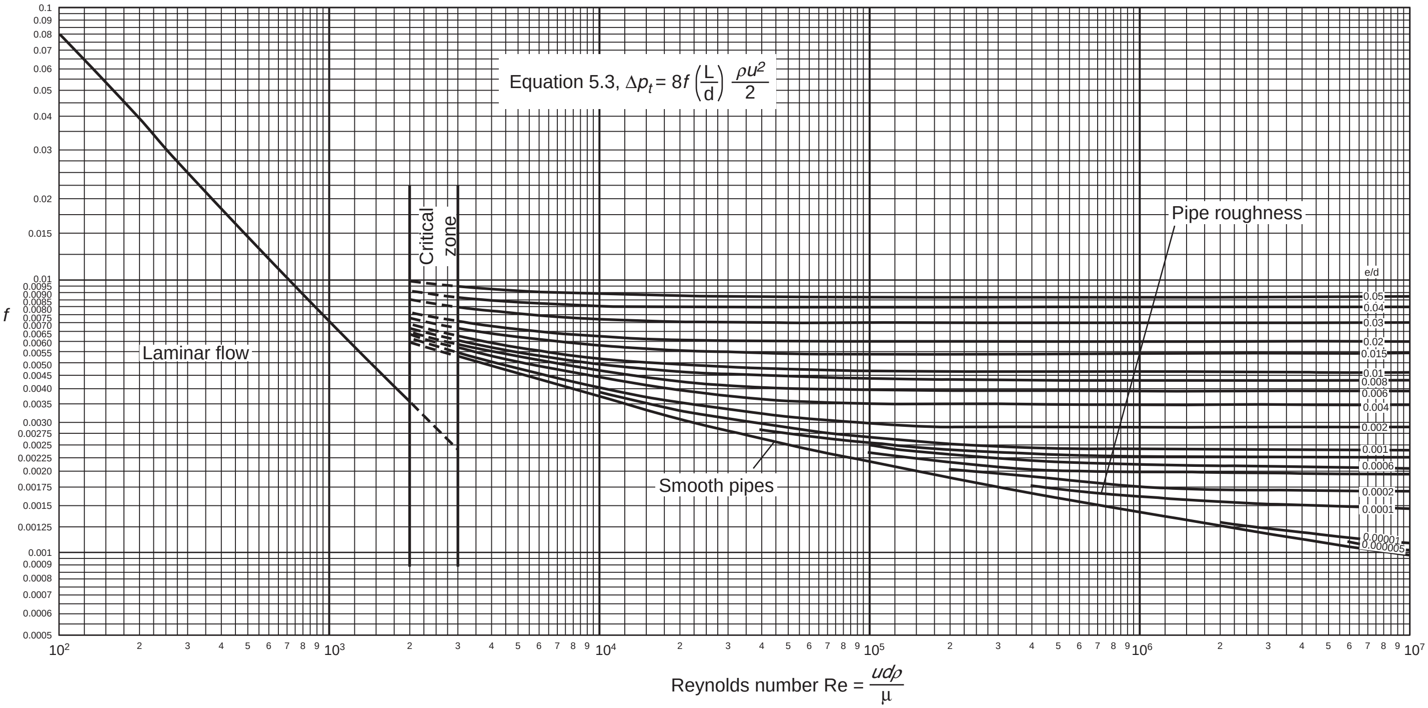


Figure 5.11. Pipe friction versus Reynolds number and relative roughness.

chart. One of the most commonly used is that of Fanning, which defines the coefficient of friction as $C_f = (2R/\rho u^2)$, i.e., $C_f = 2f$, in which case equation 5.3 becomes the following equation:

$$\Delta P_f = 4C_f(L/d_i)\frac{\rho u^2}{2} \tag{5.3b}$$

Non-Newtonian Fluids

In equation 5.3a, and when the Reynolds number is calculated for use with Figure 5.11, the fluid viscosity and density are taken to be constant. This will be true for Newtonian liquids but not for non-Newtonian liquids, where the apparent viscosity will be a function of the shear stress.

More complex methods are needed to determine the pressure drop of non-Newtonian fluids in pipelines. Suitable methods are given in Chabbra and Richardson (1999); see also Darby (2001).

Gases

When a gas flows through a pipe, the gas density is a function of the pressure and so is determined by the pressure drop. Equation 5.3 and Figure 5.11 can be used to estimate the pressure drop, but it may be necessary to divide the pipeline into short sections and sum the results.

Two-Phase Mixtures

For vapor-liquid mixtures, the pressure drop in horizontal pipes can be found using the correlation of Lockhart and Martinelli (1949), which relates the two-phase pressure drop to the pressure drop that would be calculated if each phase was flowing separately in the pipe. Details of the correlation and methods for two-phase flow in vertical pipes are given in Perry and Green (1997).

Liquid-solid mixtures that do not settle out rapidly are usually treated as non-Newtonian fluids. This will usually be the case if the solid particle size is less than about 200 microns (0.2 mm). Larger particle sizes will form settling slurries and require a critical velocity to maintain the solids in suspension. Correlations for critical velocity and pressure drop are given in Perry and Green (1997).

Gas-solid mixtures are commonly encountered in pneumatic conveying. This is discussed by Mills (2003) and Mills, Jones, and Agarwal (2004).

Miscellaneous Pressure Losses

Any obstruction to flow will generate turbulence and cause a pressure drop. So, pipe fittings such as bends, elbows, reducing or enlargement sections, and tee junctions will increase the pressure drop in a pipeline.

There will also be a pressure drop due to the valves used to isolate equipment and control the fluid flow. The pressure drop due to these miscellaneous losses can be estimated using either of two methods:

1. As the number of velocity heads, K, lost at each fitting or valve. A velocity head is $u^2/2g$, meters of the fluid, equivalent to $(u^2/2)\rho$, N/m^2. The total number of velocity heads lost due to all the fittings and valves is added to the pressure drop due to pipe friction.
2. As a length of pipe that would cause the same pressure loss as the fitting or valve. As this will be a function of the pipe diameter, it is expressed as the number of equivalent pipe diameters. The length of pipe to add to the actual pipe length is found by multiplying the total number of equivalent pipe diameters by the diameter of the pipe being used.

The number of velocity heads lost, or equivalent pipe diameter, is a characteristic of the particular fitting or type of valve used. Values can be found in handbooks and manufacturers' literature. The values for a selected number of fittings and valves are given in Table 5.3.

The two methods used to estimate the miscellaneous losses are illustrated in Example 5.1.

Pipe fittings are discussed in Section 5.5.3; see also Perry and Green (1997). Valve types and applications are discussed in Section 5.3.

Table 5.3. Pressure Loss in Pipe Fittings and Valves (for Turbulent Flow)

Fitting or Valve	K, Number of Velocity Heads	Number of Equivalent Pipe Diameters
45° standard elbow	0.35	15
45° long radius elbow	0.2	10
90° standard radius elbow	0.6–0.8	30–40
90° standard long elbow	0.45	23
90° square elbow	1.5	75
Tee-entry from leg	1.2	60
Tee-entry into leg	1.8	90
Union and coupling	0.04	2
Sharp reduction (tank outlet)	0.5	25
Sudden expansion (tank inlet)	1.0	50
Gate valve		
fully open	0.15	7.5
1/4 open	16	800
1/2 open	4	200
3/4 open	1	40
Globe valve, bevel seat-		
fully open	6	300
1/2 open	8.5	450
Globe valve, plug disk-		
fully open	9	450
1/2 open	36	1800
1/4 open	112	5600
Plug valve - open	0.4	18

Example 5.1

A pipeline connecting two tanks contains four standard elbows, a globe valve that is fully open, and a gate valve that is half open. The line is commercial steel pipe, 25 mm internal diameter, length 120 m.

The properties of the fluid are viscosity 0.99 mNm^{-2} s, density 998 kg/m^3. Calculate the total pressure drop due to friction when the flow rate is 3500 kg/h.

Solution

$$\text{Cross-sectional area of pipe} = \frac{\pi}{4}(25 \times 10^{-3})^2 = 0.491 \times 10^{-3}\,\text{m}^2$$

$$\text{Fluid velocity, } u = \frac{3500}{3600} \times \frac{1}{0.491 \times 10^{-3}} \times \frac{1}{998} = 1.98\,\text{m/s}$$

$$\text{Reynolds number, } Re = (998 \times 1.98 \times 25 \times 10^{-3})/0.99 \times 10^{-3} \qquad (5.4)$$

$$= 49{,}900 = 5 \times 10^4$$

Absolute roughness commercial steel pipe, Table 5.2 = 0.046 mm
Relative roughness = $0.046/(25 \times 10^{-3}) = 0.0018$, round to 0.002
From friction factor chart, Figure 5.11, $f = 0.0032$

Miscellaneous Losses

Fitting/Valve	Number of Velocity Heads, K	Equivalent Pipe Diameters
entry	0.5	25
elbows	(0.8 × 4)	(40 × 4)
globe valve, open	6.0	300
gate valve, 1/2 open	4.0	200
exit	1.0	50
Total	14.7	735

Method 1, Velocity Heads

$$\text{A velocity head} = u^2/2g = 1.98^2/(2 \times 9.8) = 0.20\,\text{m of liquid.}$$

$$\text{Head loss} = 0.20 \times 14.7 = 2.94\,\text{m}$$

$$\text{as pressure} = 2.94 \times 998 \times 9.8 = 28{,}754\,\text{N/m}^2$$

$$\text{Friction loss in pipe, } \Delta P_f = 8 \times 0.0032 \frac{(120)}{(25 \times 10^{-3})} 988 \times \frac{1.98^2}{2}$$

$$= 240{,}388\,\text{N/m}^2$$

$$\text{Total pressure} = 28{,}754 + 240{,}388 = 269{,}142\,\text{N/m}^2 = \underline{\underline{270\,\text{kN/m}^2}} \qquad (5.3a)$$

Method 2, Equivalent Pipe Diameters

Extra length of pipe to allow for miscellaneous losses

$$= 735 \times 25 \times 10^{-3} = 18.4\,\mathrm{m}$$

So, total length for ΔP calculation = 120 + 18.4 = 138.4 m

$$\Delta P_f = 8 \times 0.0032 \frac{(138.4)}{(25 \times 10^{-3})} 998 \times \frac{1.98^2}{2} = 277{,}247\,\mathrm{N/m^2} \tag{5.3a}$$

$$= \underline{\underline{277\,\mathrm{kN/m^2}}}$$

Note: The two methods will not give exactly the same result. The method using velocity heads is the more fundamentally correct approach, but the use of equivalent diameters is easier to apply and sufficiently accurate for use in preliminary design calculations.

5.4.3. Power Requirements for Pumping Liquids

To transport a liquid from one vessel to another through a pipeline, energy has to be supplied to

1. Overcome the friction losses in the pipes;
2. Overcome the miscellaneous losses in the pipe fittings (e.g., bends), valves, instruments etc.;
3. Overcome the losses in process equipment (e.g., heat exchangers, packed beds);
4. Overcome any difference in elevation from end to end of the pipe;
5. Overcome any difference in pressure between the vessels at each end of the pipeline.

The total energy required can be calculated from the energy equation:

$$g\Delta z + \Delta P/\rho - \Delta P_f/\rho - W = 0$$

where

W = work done by the fluid, J/kg;
Δz = difference in elevations $(z_1 - z_2)$, m;
ΔP = difference in system pressures $(P_1 - P_2)$, N/m^2;
ΔP_f = pressure drop due to friction, including miscellaneous losses, and equipment losses (see section 5.4.2), N/m^2;
ρ = liquid density kg/m^3;
g = acceleration due to gravity, m/s^2.

If W is negative, a pump is required; if it is positive, a turbine could be installed to extract energy from the system.

$$\text{The head required from the pump} = \Delta P_f/\rho g - \Delta P/\rho g - \Delta z \tag{5.5a}$$

The power is given by

$$\text{Power} = (W \times m)/\eta, \quad \text{for a pump} \tag{5.6a}$$

$$\text{and} = (W \times m) \times \eta, \quad \text{for a turbine} \tag{5.6b}$$

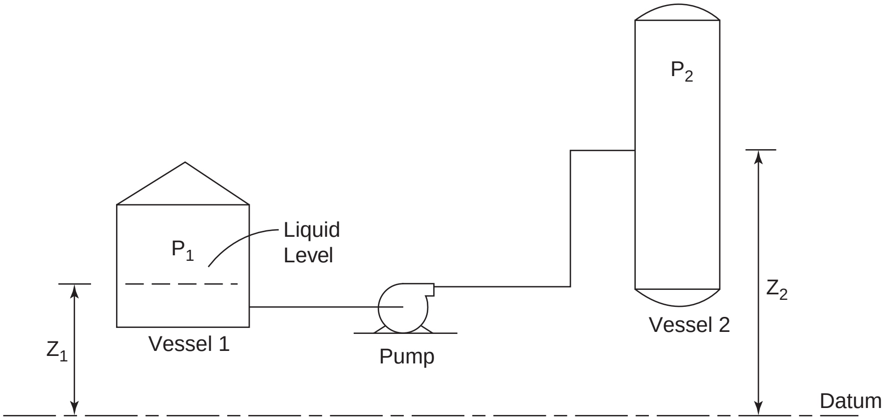


Figure 5.12. Piping system.

where

m = mass flow rate, kg/s;
η = efficiency = power out/power in.

The efficiency will depend on the type of pump used and the operating conditions. For preliminary design calculations, the efficiency of centrifugal pumps can be estimated using Figure 5.13.

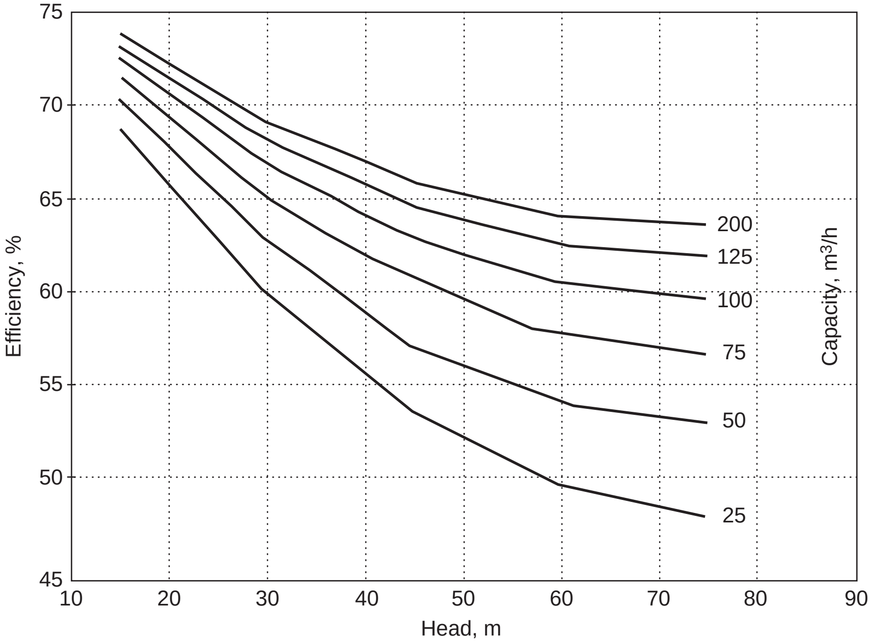


Figure 5.13. Centrifugal pump efficiency.

Example 5.2

A tanker carrying toluene is unloaded, using the ship's pumps, to an on-shore storage tank. The pipeline is 225 mm internal diameter and 900 m long. Miscellaneous losses due to fittings, valves, etc., amount to 600 equivalent pipe diameters. The maximum liquid level in the storage tank is 30 m above the lowest level in the ship's tanks. The ship's tanks are nitrogen blanketed and maintained at a pressure of 1.05 bar. The storage tank has a floating roof, which exerts a pressure of 1.1 bar on the liquid.

The ship must unload 1000 metric tons (tonnes) within 5 hours to avoid demurrage charges. Estimate the power required by the pump. Take the pump efficiency as 70%.

Physical properties of toluene: density 874 kg/m^3, viscosity 0.62 mNm^{-2} s.

Solution

$$\text{Cross-sectional area of pipe} = \frac{\pi}{4}(225 \times 10^{-3})^2 = 0.0398\,\text{m}^2$$

$$\text{Minimum fluid velocity} = \frac{1000 \times 10^3}{5 \times 3600} \times \frac{1}{0.0398} \times \frac{1}{874} = 1.6\,\text{m/s}$$

$$\text{Reynolds number} = (874 \times 1.6 \times 225 \times 10^{-3})/0.62 \times 10^{-3}$$

$$= 507{,}484 = 5.1 \times 10^5 \qquad (5.4\text{a})$$

Absolute roughness commercial steel pipe, Table 5.2 = 0.046 mm
Relative roughness = 0.046/225 = 0.0002
Friction factor from Figure 5.11, $f = 0.0019$
Total length of pipeline, including miscellaneous losses,

$$= 900 + 600 \times 225 \times 10^{-3} = 1035\,\text{m}$$

$$\text{Friction loss in pipeline, } \Delta P_f = 8 \times 0.0019 \times \left(\frac{1035}{225 \times 10^{-3}}\right) \times 874 \times \frac{1.62^2}{2} \qquad (5.3\text{a})$$

$$= 78{,}221\,\text{N/m}^2$$

Maximum difference in elevation, $(z_1 - z_2) = (0 - 30) = \underline{\underline{-30\,\text{m}}}$

Pressure difference, $(P_1 - P_2) = (1.05 - 1.1)10^5 = \underline{\underline{-5 \times 10^3}}\,\text{N/m}^2$

Energy balance

$$9.8(-30) + (-5 \times 103)/874 - (78{,}221)/874 - W = 0 \qquad (5.5)$$

$$W = \underline{\underline{-389.2}}\,\text{J/kg}$$

$$\text{Power} = (389.2 \times 55.56)/0.7 = 30{,}981\,\text{W}, \quad \text{say } \underline{\underline{31\,\text{kW}}}. \qquad (5.6\text{a})$$

Note that this is the maximum power required by the pump at the end of the unloading when the ship's tank is nearly empty and the storage tank is nearly full. Initially, the difference in elevation is lower and the power required is reduced. For design purposes the maximum power case would be the governing case and would be used to size the pump and motor.

5.4.4. Characteristic Curves for Centrifugal Pumps

The performance of a centrifugal pump is characterized by plotting the head developed against the flow rate. The pump efficiency can be shown on the same curve. A typical plot is shown in Figure 5.14. The head developed by the pump falls as the flow rate is increased. The efficiency rises to a maximum and then falls.

For a given type and design of pump, the performance will depend on the impeller diameter, the pump speed, and the number of stages. Pump manufacturers publish families of operating curves for the range of pumps they sell. These can be used to select the best pump for a given duty. A typical set of curves is shown in Figure 5.15.

5.4.5. System Curve (Operating Line)

There are two components to the pressure head that has to be supplied by the pump in a piping system:

1. The static pressure, to overcome the differences in head (height) and pressure;
2. The dynamic loss due to friction in the pipe, the miscellaneous losses, and the pressure loss through equipment.

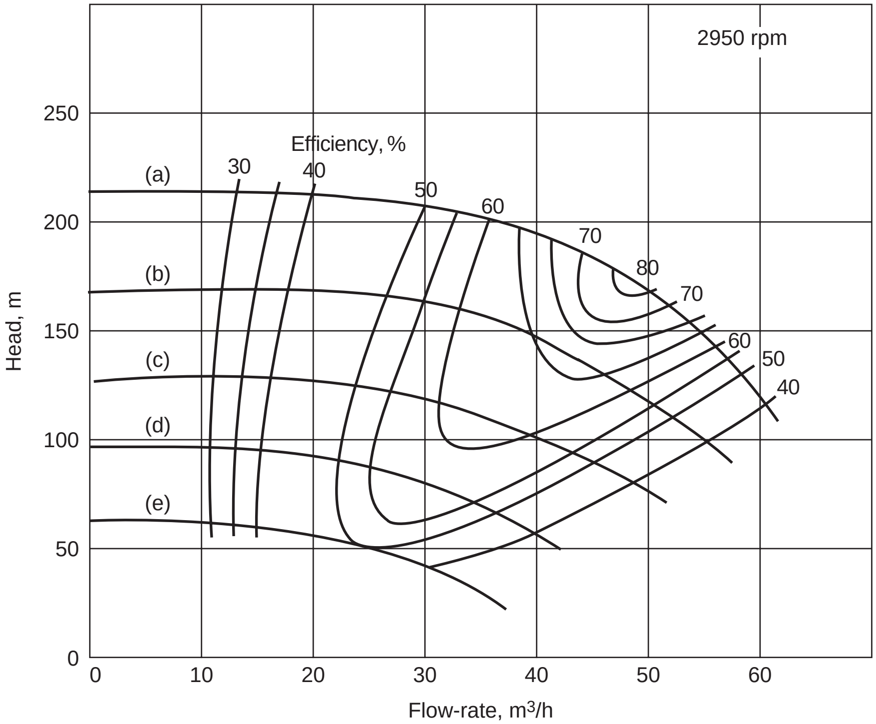


Figure 5.14. Pump characteristic for a range of impeller sizes: (a) 250 mm, (b) 225 mm, (c) 200 mm, (d) 175 mm, (e) 150 mm.

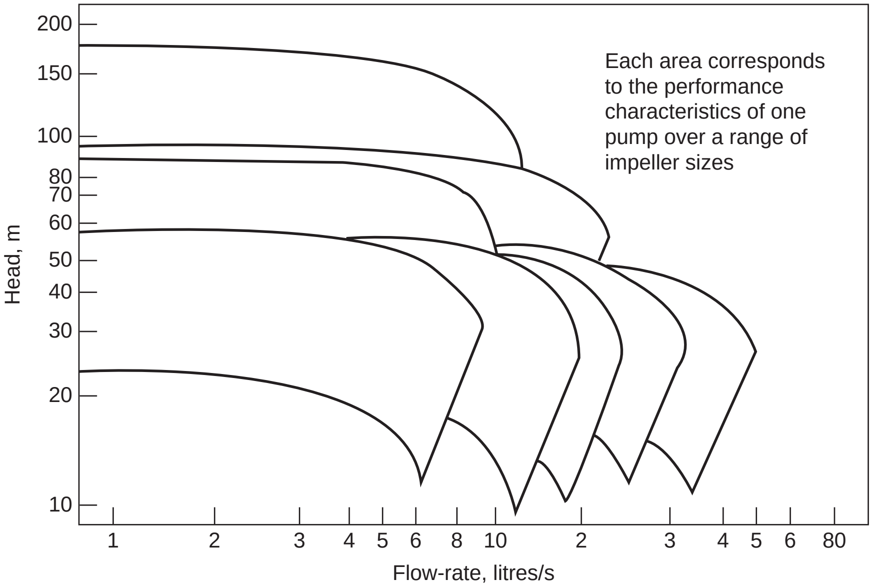


Figure 5.15. Family of pump curves.

The static pressure difference will be independent of the fluid flow rate. The dynamic loss will increase as the flow rate is increased. It will be roughly proportional to the flow rate squared; see equation 5.3. The system curve, or operating line, is a plot of the total pressure head versus the liquid flow rate. The operating point of a centrifugal pump can be found by plotting the system curve on the pump's characteristic curve; see Example 5.3. The operating point is the point where the system curve and pump curve intersect.

When a centrifugal pump is selected for a given duty, it is important to match the pump characteristic with the system curve. The operating point should be as close as is practical to the point of maximum pump efficiency, allowing for the range of flow rate over which the pump may be required to operate. This requires a good understanding of the pressure drop across the control valve if a valve is used in the line downstream of the pump. The control valve pressure drop will be proportional to the velocity squared and can range from as low as 6 to over 100 velocity heads over the range of operation of the valve, depending on the type of valve chosen (see Table 5.3). The system curve should be plotted for the case when the valve is fully open and the case when the valve is one-quarter open (or at the minimum fraction open recommended by the valve manufacturer) to determine the range over which flow can be controlled with a given combination of valve and pump. Details of valve pressure drop can be obtained from manufacturers. The equations for design of a valve are given in Perry and Green (1997).

Most centrifugal pumps are controlled by throttling the flow with a valve on the pump discharge; see Section 5.8.3. This varies the dynamic pressure loss and therefore the position of the operating point on the pump characteristic curve.

Throttling the flow results in an energy loss, which is acceptable in most applications. However, when the flow rates are large, the use of variable-speed control on the pump drive should be considered to conserve energy.

A more detailed discussion of the operating characteristics of centrifugal and other types of pump is given by Walas (1990) and Karassik et al. (2001).

Example 5.3

A process liquid is pumped from a storage tank to a distillation column using a centrifugal pump. The pipeline is 80 mm internal diameter commercial steel pipe, 100 m long. Miscellaneous losses are equivalent to 600 pipe diameters. The storage tank operates at atmospheric pressure and the column at 1.7 bara. The lowest liquid level in the tank will be 1.5 m above the pump inlet, and the feed point to the column is 3 m above the pump inlet.

Plot the system curve on the pump characteristic given in Figure 5.16 and determine the operating point and pump efficiency.

Properties of the fluid: density 900 kg/m^3, viscosity 1.36 mN m^{-2}s.

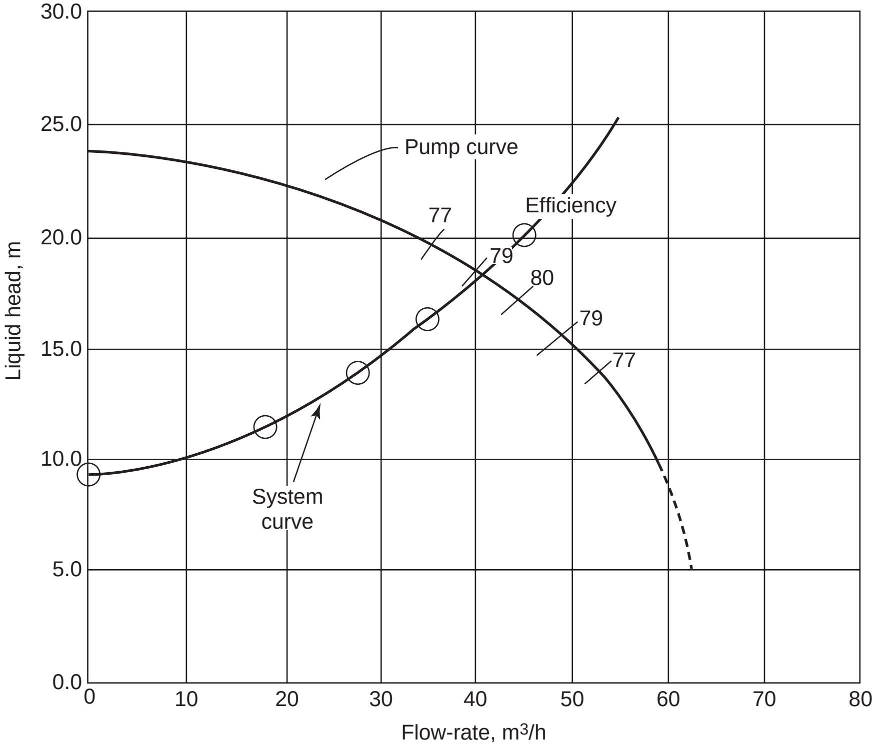


Figure 5.16 Example 5.3.

Solution

Static Head

$$\text{Difference in elevation, } \Delta z = 3.0 - 1.5 = 1.5\,\text{m}$$

$$\text{Difference in pressure, } \Delta P = (1.7 - 1.013)10^5 = 0.7 \times 10^5\,\text{N/m}^2$$

$$\text{as head of liquid} = (0.7 = 10^5)/(900 \times 9.8) = 7.9\,\text{m}$$

$$\text{Total static head} = 1.5 + 7.9 = \underline{\underline{9.4\,\text{m}}}$$

Dynamic Head

As an initial value, take the fluid velocity as 1 m/s, a reasonable value.

$$\text{Cross-sectional area of pipe} = \frac{\pi}{4}(80 \times 10^{-3})^2 = 5.03 \times 10^{-3}\text{m}^2$$

$$\text{Volumetric flow-rate} = 1 \times 5.03 \times 10^{-3} \times 3600 = 18.1\,\text{m}^3/\text{h}$$

$$\text{Reynolds number} = \frac{900 \times 1 \times 80 \times 10^{-3}}{1.36 \times 10^{-3}} = 5.3 \times 10^4 \qquad (5.4)$$

$$\text{Relative roughness} = 0.046/80 = 0.0006$$

Friction factor from Figure 5.11, $f = 0.0027$

Length including miscellaneous losses $= 100 + (600 \times 80 \times 10^{-3}) = 148\,\text{m}$

$$\text{Pressure drop, } \Delta P_f = 8 \times 0.0027 \frac{(148)}{(80 \times 10^{-3})} \times 900 \times \frac{1^2}{2} = \underline{\underline{17{,}982\,\text{N/m}^2}} \qquad (5.3)$$

$$= 17{,}982/(900 \times 9.8) = \underline{\underline{2.03}}\,\text{m liquid}$$

$$\text{Total head} = 9.4 + 2.03 = 11.4\,\text{m}$$

To find the system curve, the calculations were repeated for the velocities shown in the following table:

Velocity m/s	Flow Rate m³/h	Static Head m	Dynamic Head m	Total Head m
1	18.1	9.4	2.0	11.4
1.5	27.2	9.4	4.3	14.0
2.0	36.2	9.4	6.8	16.2
2.5	45.3	9.4	10.7	20.1
3.0	54.3	9.4	15.2	24.6

Plotting these values on the pump characteristic gives the operating point as 18.5 m at 41 m^3/h and the pump efficiency as 79%.

5.4.6. Net Positive Suction Head (NPSH)

The pressure at the inlet to a pump must be high enough to prevent cavitation occurring in the pump. Cavitation occurs when bubbles of vapor, or gas, form in the pump casing. Vapor bubbles will form if the pressure falls below the vapor pressure of the liquid.

The net positive suction head available ($NPSH_{avail}$) is the pressure at the pump suction, above the vapor pressure of the liquid, expressed as head of liquid.

The net positive head required ($NPSH_{reqd}$) is a function of the design parameters of the pump and will be specified by the pump manufacturer. As a general guide, the NPSH should be above 3 m for pump capacities up to 100 m^3/h, and 6 m above this capacity. Special impeller designs can be used to overcome problems of low suction head; see Doolin (1977).

The net positive head available is given by the following equation:

$$NPSH_{avail} = P/\rho.g + H - P_f/\rho.g - P_v/\rho.g \tag{5.7}$$

where

$NPSH_{avail}$ = net positive suction head available at the pump suction, m;
P = the pressure above the liquid in the feed vessel, N/m^2;
H = the height of liquid above the pump suction, m;
P_f = the pressure loss in the suction piping, N/m^2;
P_v = the vapor pressure of the liquid at the pump suction, N/m^2;
ρ = the density of the liquid at the pump suction temperature, kg/m^3;
g = the acceleration due to gravity, m/s^2.

The inlet piping arrangement must be designed to ensure that $NPSH_{avail}$ exceeds $NPSH_{reqd}$ under all operating conditions.

The calculation of $NPSH_{avail}$ is illustrated in Example 5.4.

Example 5.4

Liquid chlorine is unloaded from rail tankers into a storage vessel. To provide the necessary NPSH, the transfer pump is placed in a pit below ground level. Given the following information, calculate the NPSH available at the inlet to the pump, at a maximum flow rate of 16,000 kg/h.

The total length of the pipeline from the rail tanker outlet to the pump inlet is 50 m. The vertical distance from the tank outlet to the pump inlet is 10 m. Commercial steel piping, 50 mm internal diameter, is used.

Miscellaneous friction losses due to the tanker outlet constriction and the pipe fittings in the inlet piping are equivalent to 1000 equivalent pipe diameters. The vapor pressure of chlorine at the maximum temperature reached at the pump is 685 kN/m^2 and its density and viscosity, 1286 kg/m^3 and 0.364 mNm^{-2} s. The pressure in the tanker is 7 bara.

Solution

Friction Losses

$$\text{Miscellaneous losses} = 1000 \times 50 \times 10^{-3} = 50\,\text{m of pipe}$$

$$\text{Total length of inlet piping} = 50 + 50 = 100\,\text{m}$$

$$\text{Relative roughness, } e/d = 0.046/50 = 0.001$$

$$\text{Pipe cross-sectional area} = \frac{\pi}{4}(50 \times 10^{-3})^2 = 1.96 \times 10^{-3}\,\text{m}^2$$

$$\text{Velocity, } u = \frac{16{,}000}{3600} \times \frac{1}{1.96 \times 10^{-3}} \times \frac{1}{1286} = 1.76\,\text{m/s}$$

$$\text{Reynolds number} = \frac{1286 \times 1.76 \times 50 \times 10^{-3}}{0.364 \times 10^{-3}} = 3.1 \times 10^5 \qquad (5.4)$$

$$\text{Friction factor from Figure 5.11, } f = 0.00225$$

$$\Delta P_f = 8 \times 0.00225 \frac{(100)}{(50 \times 10^{-3})} \times 1286 \times \frac{1.76^2}{2} = 71{,}703\,\text{N/m}^2 \qquad (5.3)$$

$$\text{NPSH} = \frac{7 \times 10^5}{1286 \times 9.8} + 10 - \frac{71.703}{1286 \times 9.8} - \frac{685 \times 10^{-3}}{1286 \times 9.8} \qquad (5.7)$$

$$= 55.5 + 10 - 5.7 - 54.4 = \underline{\underline{5.4\,\text{m}}}$$

5.4.7. Pump and Other Shaft Seals

A seal must be made where a rotating shaft passes through the casing of a pump or the wall of a vessel. The seal must serve several functions:

1. To keep the liquid contained;
2. To prevent ingress of incompatible fluids, such as air;
3. To prevent escape of flammable or toxic materials.

Packed Glands

The simplest, and oldest, form of seal is the packed gland, or stuffing box; see Figure 5.17. Its applications range from sealing the stems of the water faucets in every home, to proving the seal on industrial pumps, agitator, and valve shafts.

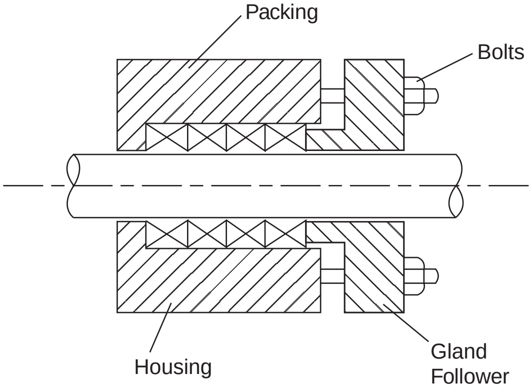


Figure 5.17. Packed gland.

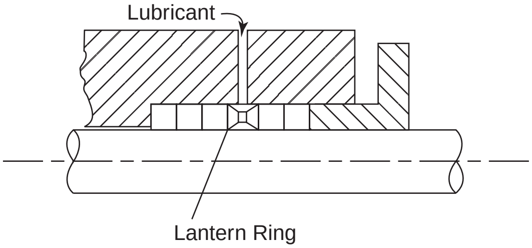


Figure 5.18. Packed gland with lantern ring.

The shaft runs through a housing (gland), and the space between the shaft and the wall of the housing is filled with rings of packing. A gland follower is used to apply pressure to the packing to ensure that the seal is tight. Proprietary packing materials are used. A summary of the factors to be considered in the selection of packing materials for packed glands is given by Hoyle (1978). To make a completely tight seal, the pressure on the packing must be 2 to 3 times the system pressure. This can lead to excessive wear on rotating shafts and lower pressures are used, allowing some leakage, which lubricates the packing. So, packed glands should be specified only for fluids that are not toxic, corrosive, or flammable.

To provide positive lubrication, a lantern ring is often incorporated in the packing and lubricant forced through the ring into the packing; see Figure 5.18. With a pump seal, a flush is often take from the pump discharge and returned to the seal, through the lantern ring, to lubricate and cool the packing. If any leakage to the environment must be avoided, a separate flush liquid can be used. A liquid must be selected that is compatible with the process fluid and the environment; water is often used.

Mechanical Seals

In the process industries the conditions at the pump seal are often harsh, and more complex seals are needed. Mechanical face seals are used; see Figure 5.19. They are generally referred to simply as *mechanical seals* and are used only on rotating shafts.

The seal is formed between two flat faces, set perpendicular to the shaft. One face rotates with the shaft; the other is stationary. The seal is made, and the faces lubricated by a very thin film of liquid, about 0.0001 μm thick. A particular advantage of this type of seal is that it can provide a very effective seal without causing any wear on the shaft. The wear is transferred to the special seal faces. Some leakage will occur, but it is small, normally only a few drops per hour.

Unlike a packed gland, a mechanical seal, when correctly installed and maintained, can be considered leak-tight.

A great variety of mechanical seal designs are available, and seals can be found to suit virtually all applications. Only the basic mechanical seal is described in this section. Full details and specifications of the range of seals available and their applications can be obtained from manufacturers' catalogues.

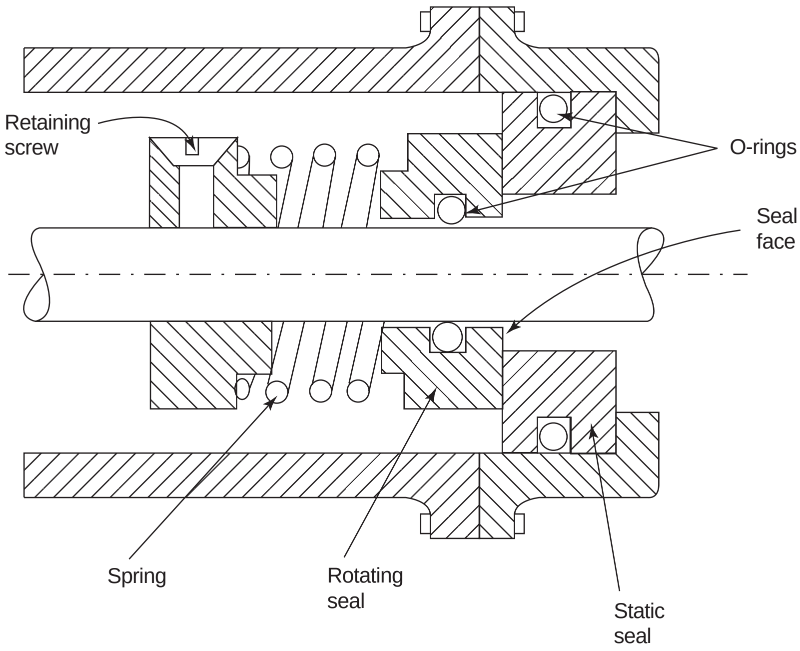


Figure 5.19. Basic mechanical seal.

The Basic Mechanical Seal

The components of a mechanical seal, as shown in Figure 5.19, are

1. A stationary sealing ring (mating ring);
2. A seal for the stationary ring, O-rings or gaskets;
3. A rotating seal ring (primary ring), mounted so that it can slide along the shaft to take up wear in the seal faces;
4. A secondary seal for the rotating ring mount, usually O-rings, or chevron seals;
5. A spring to maintain contact pressure between the seal faces, to push the faces together;
6. A thrust support for the spring, either a collar keyed to the shaft or a step in the shaft.

The assembled seal is fitted into a gland housing (stuffing box) and held in place by a retaining ring (gland plate).

Mechanical seals are classified as inside or outside, depending on whether the primary (rotating ring) is located inside the housing, running in the fluid, or outside. Outside seals are easier to maintain, but inside seals are more commonly used in the process industries, as it is easier to lubricate and flush this type.

Double Seals

Where it is necessary to prevent any leakage of fluid to the atmosphere, a double mechanical seal is used. The space between the two seals is flushed with a harmless fluid, compatible with the process fluid, and provides a buffer between the two seals.

Seal-less Pumps (Canned Pumps)

Pumps that have no seal on the shaft between the pump and the drive motor are available. They are used for severe duties, where it is essential that there is no leakage into the process fluid or the environment.

The drive motor and pump are enclosed in a single casing and the stator windings and armature are protected by metal cans; they are usually referred to as canned pumps. The motor runs in the process fluid. The use of canned pumps to control environmental pollution is discussed by Webster (1979).

5.4.8. Gas Compressors

The equipment used to compress a gas through a process piping system is different from that used for liquids. At low pressure drops, a simple fan may be adequate. At higher pressure drops, multistage compressors are commonly used. The different types of compressors and guidelines for their selection are discussed in Chapter 10, Section 10.12. Equations for the power consumed in gas compression are given in Section 3.13.

5.5. MECHANICAL DESIGN OF PIPING SYSTEMS

5.5.1. Piping System Design Codes

Design codes for pressure piping are set by the ASME B31 Committee. Different standards are required for different services, as shown in Table 5.4. Most chemical plant and oil refinery piping is designed in accordance with ASME B31.3, which will be used as reference in the following sections. The ASME B31.3 code applies to piping

Table 5.4 ASME Pipe Codes

Code No.	Scope	Latest Revision
B31.1	Power piping	2004
B31.2	Fuel gas piping	1968
B31.3	Process piping	2004
B31.4	Pipeline transportation systems for liquid hydrocarbons and other liquids	1997
B31.5	Refrigeration piping and heat transfer components	2001
B31.8	Gas transmission and distribution piping systems	2003
B31.9	Building services piping	2004
B31.11	Slurry transportation piping systems	2002

for raw, intermediate, and finished chemicals; petroleum products; gas, steam, air, and water; fluidized solids; refrigerants and cryogenic fluids. It does not apply to

1. Piping systems designed for pressures less than 15 psi gage that handle fluids that are nonflammable, nontoxic, and not damaging to human tissues and are at temperatures between −29°C (−20°F) and 186°C (366°C);
2. Power boiler piping that conforms to ASME B31.1 and power boilers that conform to ASME Boiler and Pressure Vessel Code Section I;
3. Tubes, tube headers, and manifolds of fired heaters that are internal to the heater enclosure;
4. Internal piping and external pipe connections of pressure vessels, heat exchangers, pumps, compressors, and other fluid handling or process equipment.

Note though that different design standards apply for refrigeration plants, fuel gas piping, power plants, and slurry-handling systems.

5.5.2. Wall Thickness: Pipe Schedule

The pipe wall thickness is selected to resist the internal pressure, with allowances for corrosion, erosion, and other mechanical allowances for pipe threads, etc. Process pipes can normally be considered as thin cylinders; only high-pressure pipes, such as high-pressure steam lines, are likely to be classified as thick cylinders and must be given special consideration (see Chapter 13).

The ASME B31.3 code gives the following formula for pipe thickness:

$$t_m = t_p + c$$
$$t_p = \frac{Pd}{2(SE + P\gamma)} \tag{5.8}$$

where

t_m = minimum required thickness;
t_p = pressure design thickness;
c = sum of mechanical allowances (thread depth) plus corrosion and erosion allowances;
P = internal design gage pressure, lb/in^2 (or N/mm^2);
d = pipe outside diameter;
S = basic allowable stress for pipe material, lb/in^2 (or N/mm^2);
E = casting quality factor;
γ = temperature coefficient.

Allowable stresses and values of the coefficients for different materials are given in Appendix A of the design code. Standard dimensions for stainless steel pipe are given in ASME B36.19, and for wrought steel and wrought iron pipe in ASME B36.10M. Standard pipe dimensions are also summarized by Perry and Green (1997).

Pipes are often specified by a schedule number (based on the thin cylinder formula). The schedule number is defined by

$$\text{Schedule number} = \frac{P_s \times 1000}{\sigma_s} \tag{5.9}$$

P_s = safe working pressure, lb/in^2 (or N/mm^2);
σ_s = safe working stress, lb/in^2 (or N/mm^2).

Schedule 40 pipe is commonly used for general purpose applications at low pressure.

Example 5.5

Estimate the safe working pressure for a 4 in. (100 mm) dia., schedule 40 pipe, SA53 carbon steel, butt-welded, working temperature 100°C. The maximum allowable stress for butt-welded steel pipe up to 120 °C is 11,700 lb/in^2(79.6 N/mm^2).

Solution

$$P_S = \frac{(\text{schedule no.}) \times \sigma_S}{1000} = \frac{40 \times 11700}{1000} = \underline{\underline{468\ \text{lb/in}^2}} = \underline{\underline{3180\ \text{kN/m}^2}}$$

5.5.3. Pipe Supports

Over long runs, between buildings and equipment, pipes are usually carried on pipe racks. These carry the main process and service pipes, and are laid out to allow easy access to the equipment.

Various designs of pipe hangers and supports are used to support individual pipes. Details of typical supports can be found in the books by Perry and Green (1997) and Nayyar et al. (2000). Pipe supports frequently incorporate provision for thermal expansion.

5.5.4. Pipe Fittings

Pipe runs are normally made up from lengths of pipe, incorporating standard fittings for joints, bends, and tees. Joints are usually welded, but small sizes may be screwed. Flanged joints are used where this is a more convenient method of assembly, or if the joint will have to be frequently broken for maintenance. Flanged joints are normally used for the final connection to the process equipment, valves, and ancillary equipment.

Details of the standard pipe fittings, welded, screwed, and flanged, can be found in manufacturers' catalogues and in the appropriate national standards. Standards for pipe fittings are set by the ASME B16 committee. The standards for metal pipes and fittings are discussed by Masek (1968).

5.5.5. Pipe Stressing

Piping systems must be designed so as not to impose unacceptable stresses on the equipment to which they are connected.

Loads will arise from

1. Thermal expansion of the pipes and equipment;
2. The weight of the pipes, their contents, insulation, and any ancillary equipment;
3. The reaction to the fluid pressure drop;
4. Loads imposed by the operation of ancillary equipment, such as relief valves;
5. Vibration.

Thermal expansion is a major factor to be considered in the design of piping systems. The reaction load due to pressure drop will normally be negligible. The dead-weight loads can be carried by properly designed supports.

Flexibility is incorporated into piping systems to absorb the thermal expansion. A piping system will have a certain amount of flexibility due to the bends and loops required by the layout. If necessary, expansion loops, bellows, and other special expansion devices can be used to take up expansion.

A discussion of the methods used for the calculation of piping flexibility and stress analysis are beyond the scope of this book. Manual calculation techniques and the application of computers in piping stress analysis are discussed in the handbook edited by Nayyar et al. (2000).

5.5.6. Layout and Design

An extensive discussion of the techniques used for piping system design and specification is beyond the scope of this book. The subject is covered thoroughly in the books by Sherwood (1991), Kentish (1982a, 1982b), and Lamit (1981).

5.6. PIPE SIZE SELECTION

If the motive power to drive the fluid through the pipe is available free—for instance, when pressure is let down from one vessel to another or if there is sufficient head for gravity flow—the smallest pipe diameter that gives the required flow rate would normally be used.

If the fluid has to be pumped through the pipe, the size should be selected to give the least total annualized cost.

Typical pipe velocities and allowable pressure drops, which can be used to estimate pipe sizes, are as follows:

	Velocity m/s	ΔP kPa/m
Liquids, pumped (not viscous)	1–3	0.5
Liquids, gravity flow	—	0.05
Gases and vapors	15–30	0.02% of line pressure
High-pressure steam, >8 bar	30–60	—

Rase (1953) gives expressions for design velocities in terms of the pipe diameter. His expressions, converted to SI units, are

Pump discharge	$0.06d_i + 0.4\,\text{m/s}$
Pump suction	$0.02d_i + 0.1\,\text{m/s}$
Steam or vapor	$0.2d_i\ \text{m/s}$

where d_i is the internal diameter in mm.

Simpson (1968) gives values for the optimum velocity in terms of the fluid density. His values, converted to SI units and rounded, are

Fluid Density kg/m^3	Velocity m/s
1600	2.4
800	3.0
160	4.9
16	9.4
0.16	18.0
0.016	34.0

The maximum velocity should be kept below that at which erosion is likely to occur. For gases and vapors, the velocity cannot exceed the critical velocity (sonic velocity) and would normally be limited to 30% of the critical velocity.

Economic Pipe Diameter

The capital cost of a pipe run increases with diameter, whereas the pumping costs decrease with increasing diameter. The most economic pipe diameter will be the one that gives the lowest total annualized cost. Several authors have published formulae and nomographs for the estimation of the economic pipe diameter; see Genereaux (1937), Peters and Timmerhaus (1968, 1991), Nolte (1978), and Capps (1995).

A rule of thumb for the economic pipe diameter that is widely used in oil refining is

$$\text{Economic diameter in inches} = (\text{flow rate in gpm})^{0.5}$$

In metric units:

$$d_i,\ \text{optimum} = (G/\rho)^{0.5}$$

where

G = flow rate, kg/s;
ρ = density, kg/m^3;
d_i = pipe id, m.

The formulae developed in this section are presented as an illustration of a simple optimization problem in design, and to provide an estimate of economic pipe diameter in SI units. The method used is essentially that first published by Genereaux (1937).

The cost equations can be developed by considering a 1 meter length of pipe.

The purchase cost will be roughly proportional to the diameter raised to some power.

$$\text{Purchase cost} = Bd^n \ \$/\text{m}$$

The value of the constant B and the index n depend on the pipe material and schedule.

The installed cost can be calculated by using the factorial method of costing discussed in Chapter 6:

$$\text{Installed cost} = Bd^n(1 + F)$$

where the factor F includes the cost of valves, fittings, and erection for a typical run of the pipe.

The capital cost can be included in the operating cost as an annual capital charge. There will also be an annual charge for maintenance, based on the capital cost:

$$C_C = Bd^n(1 + F)(a + b) \tag{5.10}$$

where

C_C = annualized capital cost of the piping, \$/m.yr;
a = capital annualization factor, yr^{-1};
b = maintenance costs as fraction of installed capital, yr^{-1}.

The power required for pumping is given by

$$\text{Power} = \text{volumetric flow rate} \times \text{pressure drop}.$$

Only the friction pressure drop need be considered, as any static head is not a function of the pipe diameter.

To calculate the pressure drop, we need to know the pipe friction factor. This is a function of the Reynolds number, which is in turn a function of the pipe diameter. Several expressions have been proposed for relating friction factor to the Reynolds number. For simplicity the relationship proposed by Genereaux (1937) for turbulent flow in clean commercial steel pipes will be used:

$$C_f = 0.04\, Re^{-0.16}$$

where C_f is the Fanning friction factor $= 2(R/\rho u^2)$.

Substituting this into the Fanning pressure drop equation gives

$$\Delta P = 0.125 G^{1.84} \mu^{0.16} \rho^{-1} d_i^{-4.84} \tag{5.11}$$

where

ΔP = pressure drop, N/m^2 (Pa);
μ = viscosity, Nm^{-2} s.

The annual pumping costs will be given by

$$C_w = \frac{A\,p}{1000\eta} \Delta P \frac{G}{\rho}$$

where

A = plant attainment, hours/year;
p = cost of power, \$/kWh;
η = pump efficiency.

Substituting from equation 5.11

$$C_w = \frac{A\,p}{\eta} 1.25 \times 10^{-4} G^{2.84} \mu^{0.16} \rho^{-2} d_i^{-4.84} \tag{5.12}$$

The total annual operating cost is $C_t = C_C + C_w$.

Adding equations 5.10 and 5.12, differentiating, and equating to zero to find the pipe diameter to give the minimum cost gives

$$d_i, \text{ optimum} = \left(\frac{6.05 \times 10^{-4} A\, p\, G^{2.84} \mu^{0.16}\, \rho^{-2}}{\eta\, n\, B(1+F)(a+b)} \right)^{1/(4.84+n)} \tag{5.13}$$

Equation 5.13 is a general equation and can be used to estimate the economic pipe diameter for any particular situation. It can be set up on a spreadsheet and the effect of the various factors investigated.

The equation can be simplified by substituting typical values for the constants.

A	The normal attainment for a chemical process plant will be between 90 and 95%, so take the operating hours per year as 8000.
η	Pump and compressor efficiencies will be between 50 and 70%, so take 0.6.
p	A typical wholesale cost of electric power for a large user is 0.06 \$/kWh (mid-2007).
F	This is the most difficult factor to estimate. Other authors have used values ranging from 1.5 [Peters and Timmerhaus (1968)] to 6.75 [Nolte (1978)]. It is best taken as a function of the pipe diameter, as has been done to derive the following simplified equations.
B, n	Can be estimated from the current cost of piping.
a	Will depend on the current cost of capital, and could range from 0.1 to 0.25, but is typically around 0.16. See Chapter 6 for a detailed discussion.
b	A typical figure for a process plant will be 5%; see Chapter 6.

F, B, and n are best established from a recent correlation of piping costs and should include the costs of fittings, paint, or insulation and installation. For initial estimates, the following correlations (basis January 2006) can be used:

A106 Carbon steel	1 to 8 inches,	\$/ft = 17.4(d_i in inches)$^{0.74}$
	10 to 24 inches,	\$/ft = 1.03(d_i in inches)$^{1.73}$
304 Stainless steel	1 to 8 inches,	\$/ft = 24.5(d_i in inches)$^{0.9}$
	10 to 24 inches,	\$/ft = 2.74(d_i in inches)$^{1.7}$

In metric units (d_i in meters), these become

$$\begin{array}{lll} \text{A106 Carbon steel} & 25 \text{ to } 200\,\text{mm}, & \$/\text{m} = 880\, d_i^{0.74} \\ & 250 \text{ to } 600\,\text{mm}, & \$/\text{m} = 1900\, d_i^{1.73} \\ \text{304 Stainless steel} & 25 \text{ to } 200\,\text{mm}, & \$/\text{m} = 2200\, d_i^{0.94} \\ & 250 \text{ to } 600\,\text{mm}, & \$/\text{m} = 4700\, d_i^{1.7} \end{array}$$

For small diameter carbon steel pipes, substitution in equation 5.12 gives

$$d_i,\ \text{optimum} = 0.830 G^{0.51} \mu^{0.03} \rho^{-0.36}$$

Because the exponent of the viscosity term is small, its value will change very little over a wide range of viscosity

at $\mu = 10^{-5}\ \text{Nm}^{-2}\ \text{s}\ (0.01\,\text{cp}),\ \mu^{0.03} = 0.71$

$$\mu = 10^{-2}\ \text{Nm}^{-2}\ \text{s}\ (10\,\text{cp}),\ \mu^{0.03} = 0.88$$

Taking a mean value of 0.8 gives the following equations for the optimum diameter for turbulent flow:

A106 Carbon steel pipe:

$$\begin{array}{l} 25 \text{ to } 200\,\text{mm},\ d_i,\ \text{optimum} = 0.664\ G^{0.51} \rho^{-0.36} \\ 250 \text{ to } 600\,\text{mm},\ d_i,\ \text{optimum} = 0.534\ G^{0.43} \rho^{-0.30} \end{array} \tag{5.14}$$

304 Stainless steel pipe:

$$\begin{array}{l} 25 \text{ to } 200\,\text{mm},\ d_i,\ \text{optimum} = 0.550\ G^{0.49} \rho^{-0.35} \\ 250 \text{ to } 600\,\text{mm},\ d_i,\ \text{optimum} = 0.465\ G^{0.43} \rho^{-0.31} \end{array} \tag{5.15}$$

Note that the optimum diameter for stainless steel is smaller than for carbon steel, as would be expected given the higher materials cost of the pipe. Note also that equations 5.14 and 5.15 predict optimum pipe diameters that are roughly double those given by the rule of thumb at the start of this section. This most likely reflects a change in the relative values of capital and energy since the period when the rule of thumb was deduced.

Equations 5.14 and 5.15 can be used to make an approximate estimate of the economic pipe diameter for normal pipe runs. For a more accurate estimate, or if the fluid or pipe run is unusual, the method used to develop equation 5.13 can be used, taking into account the special features of the particular pipe run.

For very long pipe systems, such as transportation pipelines, the capital costs of the required pumps should also be included.

For gases, the capital cost of compression is much more significant and should always be included in the analysis.

Equations for the optimum pipe diameter with laminar flow can be developed by using a suitable equation for pressure drop in the equation for pumping costs.

The approximate equations should not be used for steam, as the quality of steam depends on its pressure, and hence the pressure drop.

Nolte (1978) gives detailed methods for the selection of economic pipe diameters, taking into account all the factors involved. He gives equations for liquids, gases, steam, and two-phase systems. He includes in his method an allowance for the pressure drop due to fittings and valves, which was neglected in the development of equation 5.12 and by most other authors.

The use of equations 5.14 and 5.15 is illustrated in Examples 5.6 and 5.7, and the results compared with those obtained by other authors. The older correlations give lower values for the economic pipe diameters, probably due to changes in the relative values of capital and energy.

Example 5.6

Estimate the optimum pipe diameter for a water flow rate of 10 kg/s, at 20°C. Carbon steel pipe will be used. Density of water 1000 kg/m^3.

Solution

$$\begin{aligned} d_i\text{, optimum} &= 0.664 \times (10)^{0.51}\ 1000^{-0.36} \\ &= \underline{\underline{177\ \text{mm}}} \qquad (5.14) \end{aligned}$$

The resulting size, 177 mm, is 6.97 inches, which is not a standard pipe size. We can choose either 6-inch or 8-inch pipe, so try 6-inch pipe, sch 40, inside diameter 6.065 inches (154 mm).

Viscosity of water at $20°C = 1.1 \times 10^{-3}$ Ns/m^2,

$$Re = \frac{4G}{\pi \mu d} = \frac{4 \times 10}{\pi \times 1.1 \times 10^{-3} \times 154 \times 10^{-3}} = 7.51 \times 10^4$$

>4000, so flow is turbulent.

Comparison of methods:

	Economic Diameter
Equation 5.14	180 mm
Peters and Timmerhaus (1991)	4 in. (100 mm)
Nolte (1978)	80 mm

Example 5.7

Estimate the optimum pipe diameter for a flow of HCl of 7000 kg/h at 5 bar, 15°C, stainless steel pipe. Molar volume 22.4 m^3/kmol, at 1 bar, 0°C.

Solution

Molecular weight HCl = 36.5.

$$\text{Density at operating conditions} = \frac{36.5}{22.4} \times \frac{5}{1} \times \frac{273}{288} = \underline{\underline{7.72\,\text{kg/m}^3}} \qquad (5.15)$$

$$\text{Optimum diameter} = 0.465\left(\frac{7000}{3600}\right)^{0.43} \times 7.72^{-0.31} = \underline{\underline{328.4\,\text{mm}}}$$

The result, 328.4 mm, is 12.9 inches, so we can use 14-inch pipe, sch 40, with inside diameter 13.124 inch (333 mm).

Viscosity of HCl 0.013 m Ns/m^2

$$Re = \frac{4}{\pi} \times \frac{7000}{3600} \times \frac{1}{0.013 \times 10^{-3} \times 333 \times 10^{-3}} = \underline{\underline{5.71 \times 10^5}}, \quad \text{turbulent}$$

Comparison of methods:

	Economic Diameter
Equation 5.15	14 in. (333 mm)
Peters and Timmerhaus (1991)	9 in. (220 mm) carbon steel
Nolte (1978)	7 in. (180 mm) carbon steel

Example 5.8

Calculate the line size and specify the pump required for the line shown in Figure 5.20; material ortho-dichlorobenzene (ODCB), flow rate 10,000 kg/h, temperature 20°C, pipe material carbon steel.

Solution

$$\text{ODCB density at } 20\,^\circ\text{C} = 1306\,\text{kg/m}^3.$$

$$\text{Viscosity: } 0.9\,\text{mNs/m}^2 \ (0.9\,\text{cp}).$$

Estimation of Pipe Diameter Required

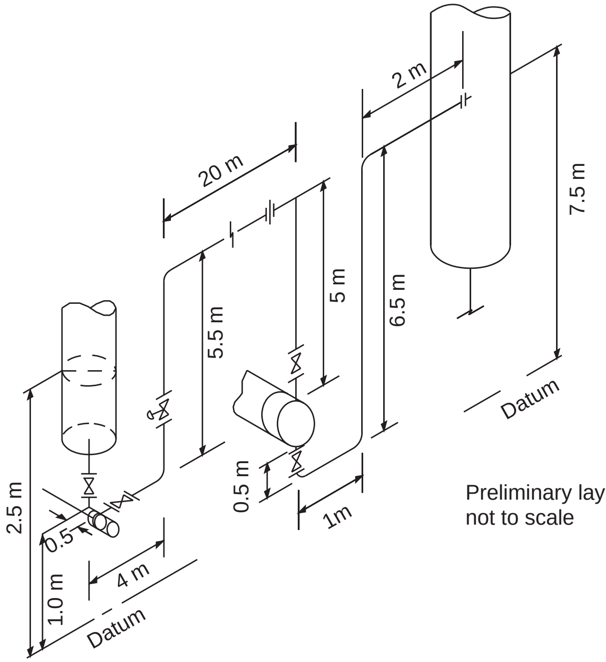
typical velocity for liquid 1 m/s

$$\text{mass flow} = \frac{10^4}{3600} = 2.78\,\text{kg/s}$$

$$\text{volumetric flow} = \frac{2.78}{1306} = 2.13 \times 10^{-3}\ \text{m}^3/\text{s}$$

$$\text{area of pipe} = \frac{\text{volumetric flow}}{\text{velocity}} = \frac{2.13 \times 10^{-3}}{1} = 2.13 \times 10^{-3}\text{m}^2$$

$$\text{diameter of pipe} = \sqrt{\left(2.13 \times 10^{-3} \times \frac{4}{\pi}\right)} = 0.052\,\text{m} = 52\,\text{mm}$$



Preliminary layout
not to scale

Figure 5.20. Piping isometric drawing (Example 5.8).

Or, use the economic pipe diameter formula:

$$d\text{, optimum} = 0.664 \times 2.78^{0.51} \times 1306^{-0.36} \qquad (5.14)$$
$$= 78.7\,\text{mm}$$

Take diameter as 77.9 mm (3-inch sch 40 pipe)

$$\text{cross-sectional area} = \frac{\pi}{4}(77.9 \times 10^{-3})^2 = 4.77 \times 10^{-3}\ \text{m}^2$$

Pressure Drop Calculation

$$\text{fluid velocity} = \frac{2.13 \times 10^{-3}}{4.77 \times 10^{-3}} = 0.45\,\text{m/s}$$

Friction loss per unit length, Δf_1:

$$Re = \frac{1306 \times 0.45 \times 77.9 \times 10^{-3}}{0.9 \times 10^{-3}} = 5.09 \times 10^4 \qquad (5.5a)$$

Absolute roughness commercial steel pipe, Table 5.2 = 0.46 mm
Relative roughness, $e/d = 0.046/80 = 0.0005$

Friction factor from Figure 5.11, $f = 0.0025$

$$\Delta f_1 = 8 \times 0.0025 \times \frac{1}{77.9 \times 10^{-3}} \times 1306 \times \frac{0.45^2}{2} = 33.95\,\text{N/m}^2 \qquad (5.3)$$

Design for a maximum flow rate of 20% above the average flow.

$$\text{Friction loss} = 0.0339 \times 1.2^2 = 0.0489\,\text{kPa/m}$$

Miscellaneous Losses

Take as equivalent pipe diameters. All bends will be taken as 90° standard radius elbow.

Line to pump suction:

$$\begin{aligned} \text{length} &= 1.5\,\text{m} \\ \text{bend, } 1 \times 30 \times 80 \times 10^{-3} &= 2.4\,\text{m} \\ \text{valve, } 1 \times 18 \times 80 \times 10^{-3} &= \underline{1.4\,\text{m}} \\ \text{total} &= 5.3\,\text{m} \end{aligned}$$

$$\text{entry loss} = \frac{\rho u^2}{2} \quad \text{(see Section 5.4.2)}$$

$$\text{at maximum design velocity} = \frac{1306(0.45 \times 1.2)^2}{2 \times 10^3} = 0.19\,\text{kPa}$$

Control valve pressure drop, allow normal	140 kPa
($\times 1.2^2$) maximum	200 kPa
Heat exchanger, allow normal	70 kPa
($\times 1.2^2$) maximum	100 kPa
Orifice, allow normal	15 kPa
($\times 1.2^2$) maximum	22 kPa

Line from pump discharge:

$$\begin{aligned} \text{length} &= 4 + 5.5 + 20 + 5 + 0.5 + 1 + 6.5 + 2 = 44.5\,\text{m} \\ \text{bends, } 6 \times 30 \times 80 \times 10^{-3} &= 14.4 = 14.4\,\text{m} \\ \text{valves, } 3 \times 18 \times 80 \times 10^{-3} &= 4.4 = \underline{4.4\,\text{m}} \\ \text{total} &= 63.4\,\text{m} \end{aligned}$$

The line pressure-drop calculation is set out on the calculation sheet shown in Table 5.5. A blank version of this calculation sheet can be found in Appendix G and is also available in MS Excel format at http://books.elsevier.com/companions.

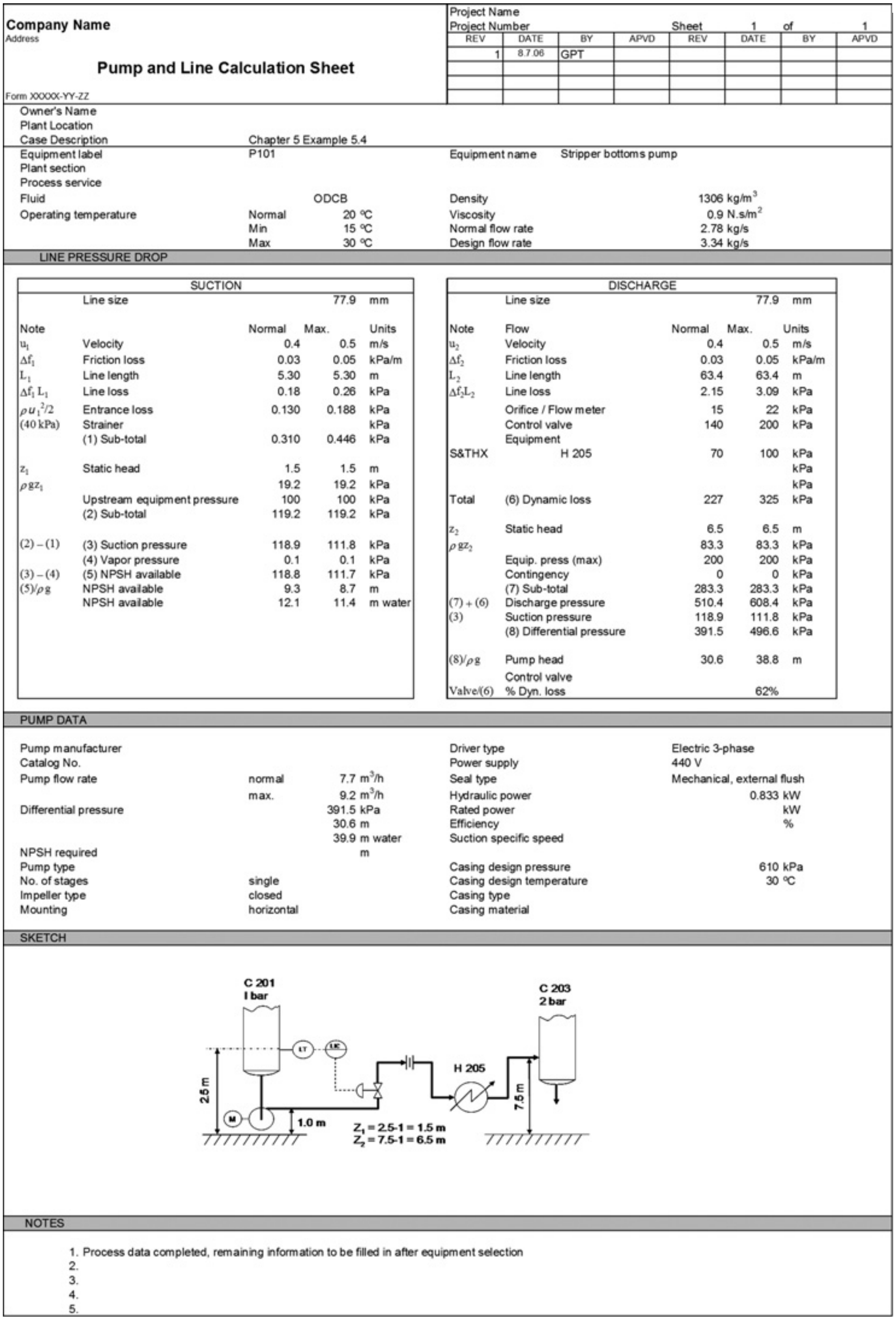
Pump selection:

flow rate $= 2.13 \times 10^{-3} \times 3600 = 7.7\,\text{m}^3/\text{h}$

differential head, maximum, $\underline{\underline{38\,\text{m}}}$

select single-stage centrifugal (Figure 5.10)

Table 5.5. Line calculation form (Example 5.8)



Company Name
Address

Pump and Line Calculation Sheet

Form XXXXX-YY-ZZ

Project Name
Project Number Sheet 1 of 1

REV	DATE	BY	APVD	REV	DATE	BY	APVD
1	8.7.06	GPT					

Owner's Name				
Plant Location				
Case Description	Chapter 5 Example 5.4			
Equipment label	P101		Equipment name	Stripper bottoms pump
Plant section				
Process service				
Fluid		ODCB	Density	1306 kg/m^3
Operating temperature	Normal	20 °C	Viscosity	0.9 N.s/m^2
	Min	15 °C	Normal flow rate	2.78 kg/s
	Max	30 °C	Design flow rate	3.34 kg/s

LINE PRESSURE DROP

SUCTION

Note		Normal	Max.	Units
	Line size	77.9		mm
u_1	Velocity	0.4	0.5	m/s
Δf_1	Friction loss	0.03	0.05	kPa/m
L_1	Line length	5.30	5.30	m
$\Delta f_1 L_1$	Line loss	0.18	0.26	kPa
$\rho u_1^2/2$	Entrance loss	0.130	0.188	kPa
(40 kPa)	Strainer			kPa
	(1) Sub-total	0.310	0.446	kPa
z_1	Static head	1.5	1.5	m
$\rho g z_1$		19.2	19.2	kPa
	Upstream equipment pressure	100	100	kPa
	(2) Sub-total	119.2	119.2	kPa
(2) – (1)	(3) Suction pressure	118.9	111.8	kPa
	(4) Vapor pressure	0.1	0.1	kPa
(3) – (4)	(5) NPSH available	118.8	111.7	kPa
(5)/ρg	NPSH available	9.3	8.7	m
	NPSH available	12.1	11.4	m water

DISCHARGE

Note			Normal	Max.	Units
	Line size		77.9		mm
	Flow				
u_2	Velocity		0.4	0.5	m/s
Δf_2	Friction loss		0.03	0.05	kPa/m
L_2	Line length		63.4	63.4	m
$\Delta f_2 L_2$	Line loss		2.15	3.09	kPa
	Orifice / Flow meter		15	22	kPa
	Control valve		140	200	kPa
	Equipment				
S&THX		H 205	70	100	kPa
					kPa
					kPa
Total	(6) Dynamic loss		227	325	kPa
z_2	Static head		6.5	6.5	m
$\rho g z_2$			83.3	83.3	kPa
	Equip. press (max)		200	200	kPa
	Contingency		0	0	kPa
	(7) Sub-total		283.3	283.3	kPa
(7) + (6)	Discharge pressure		510.4	608.4	kPa
(3)	Suction pressure		118.9	111.8	kPa
	(8) Differential pressure		391.5	496.6	kPa
(8)/ρg	Pump head		30.6	38.8	m
	Control valve				
Valve/(6)	% Dyn. loss			62%	

PUMP DATA

Pump manufacturer			Driver type	Electric 3-phase
Catalog No.			Power supply	440 V
Pump flow rate	normal	7.7 m^3/h	Seal type	Mechanical, external flush
	max.	9.2 m^3/h	Hydraulic power	0.833 kW
Differential pressure		391.5 kPa	Rated power	kW
		30.6 m	Efficiency	%
		39.9 m water	Suction specific speed	
NPSH required		m		
Pump type			Casing design pressure	610 kPa
No. of stages	single		Casing design temperature	30 °C
Impeller type	closed		Casing type	
Mounting	horizontal		Casing material	

SKETCH

NOTES

1. Process data completed, remaining information to be filled in after equipment selection
2.
3.
4.
5.

5.7. CONTROL AND INSTRUMENTATION

5.7.1. Instruments

Instruments are provided to monitor the key process variables during plant operation. They may be incorporated in automatic control loops or used for the manual monitoring of the process operation. In most modern plants, the instruments will be connected to a computer control and data logging system. Instruments monitoring critical process variables will be fitted with automatic alarms to alert the operators to critical and hazardous situations.

Details of process instruments and control equipment can be found in various handbooks; see Perry and Green (1997) and Liptak (2003). Reviews of process instruments and control equipment are published periodically in the journals *Chemical Engineering* and *Hydrocarbon Processing*. These reviews give details of instruments and control hardware available commercially.

It is desirable that the process variable to be monitored be measured directly; often, however, this is impractical, and some dependent variable that is easier to measure is monitored in its place. For example, in the control of distillation columns, the continuous, online analysis of the overhead product is desirable but difficult and expensive to achieve reliably, so temperature is often monitored as an indication of composition. The temperature instrument may form part of a control loop, controlling, say, reflux flow, with the composition of the overheads checked frequently by sampling and laboratory analysis.

5.7.2. Instrumentation and Control Objectives

The primary objectives of the designer when specifying instrumentation and control schemes are

1. Safe plant operation:
   - **a.** To keep the process variables within known safe operating limits;
   - **b.** To detect dangerous situations as they develop and to provide alarms and automatic shutdown systems;
   - **c.** To provide interlocks and alarms to prevent dangerous operating procedures.
2. Production rate:
   To achieve the design product output.
3. Product quality:
   To maintain the product composition within the specified quality standards.
4. Cost:
   To operate at the lowest production cost, commensurate with the other objectives.

These are not separate objectives and must be considered together. The order in which they are listed is not meant to imply the precedence of any objective over another, other than that of putting safety first. Product quality, production rate, and the cost of production will be dependent on sales requirements. For example, it may be a better strategy to produce a better-quality product at a higher cost.

In a typical chemical processing plant, these objectives are achieved by a combination of automatic control, manual monitoring, and laboratory and online analysis.

5.7.3. Automatic Control Schemes

The detailed design and specification of the automatic control schemes for a large project are usually done by specialists. The basic theory underlying the design and specification of automatic control systems is covered in several texts: Coughanowr (1991), Shinskey (1984, 1996) Luyben et al. (1999), Henson et al. (1996), and Perry and Green (1997). The books by Murrill (1988), Shinskey (1996), and Kalani (2002) cover many of the more practical aspects of process control system design, and are recommended.

In this chapter only the first step in the specification of the control systems for a process will be considered: the preparation of a preliminary scheme of instrumentation and control, developed from the process flowsheet. This can be drawn up by the process designer based on experience with similar plant and critical assessment of the process requirements. Many of the control loops will be conventional, and a detailed analysis of the system behavior will not be needed, nor justified. Judgment, based on experience, must be used to decide which systems are critical and need detailed analysis and design.

Some examples of typical (conventional) control systems used for the control of specific process variables and unit operations are given in the next section, and can be used as a guide in preparing preliminary instrumentation and control schemes.

Guide Rules

The following procedure can be used when drawing up preliminary P and I diagrams:

1. Identify and draw in those control loops that are obviously needed for steady plant operation, such as
   a. Level controls;
   b. Flow controls;
   c. Pressure controls;
   d. Temperature controls.
2. Identify the key process variables that need to be controlled to achieve the specified product quality. Include control loops using direct measurement of the controlled variable, where possible; if not practicable, select a suitable dependent variable.
3. Identify and include those additional control loops required for safe operation not already covered in steps 1 and 2.
4. Decide and show those ancillary instruments needed for the monitoring of the plant operation by the operators and for troubleshooting and plant development. It is well worthwhile to include additional connections for instruments

that may be needed for future troubleshooting and development, even if the instruments are not installed permanently. This would include extra thermowells, pressure tappings, orifice flanges, and extra sample points.

5. Decide on the location of sample points.
6. Decide on the type of control instrument that will be used, including whether it will be a local instrument or tied into the plant computer control system. Also decide on the type of actuator that can be used, the signal system, and whether the instrument will record data. This step should be done in conjunction with steps 1 to 4.
7. Decide on the alarms and interlocks needed; this would be done in conjunction with step 3 (see Chapter 9).

In step 1 it is important to remember the following basic rules of process control:

- There can be only a single control valve on any given stream between unit operations.
- A level controller is needed anywhere a vapor-liquid or liquid-liquid interface is maintained.
- Pressure control is more responsive when the pressure controller actuates a control valve on a vapor stream.
- Two operations cannot be controlled at different pressures unless there is a valve or other restriction (or a compressor or pump) between them.
- Temperature control is usually achieved by controlling the flow of a utility stream (such as steam or cooling water).

Some simple examples of control schemes for common unit operations are given in the next section.

5.8. TYPICAL CONTROL SYSTEMS

5.8.1. Level Control

In any equipment where an interface exists between two phases (e.g., liquid–vapor), some means of maintaining the interface at the required level must be provided. This may be incorporated in the design of the equipment, as is usually done for decanters, or by automatic control of the flow from the equipment. Figure 5.21 shows a typical arrangement for the level control at the base of a column. The control valve should be placed on the discharge line from the pump.

5.8.2. Pressure Control

Pressure control will be necessary for most systems handling vapor or gas. The method of control will depend on the nature of the process. Typical schemes are shown in Figures 5.22a, b, c, d. The scheme shown in Figure 5.22a would not be used where the vented gas was toxic or valuable. In these circumstances the vent should be taken to a vent recovery system, such as a scrubber.

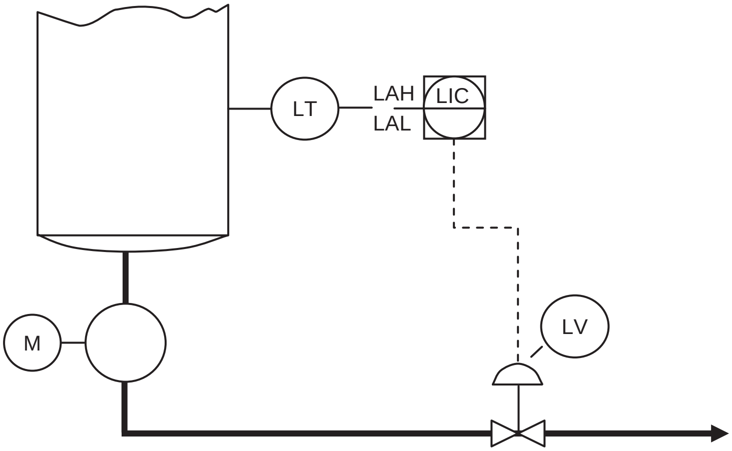


Figure 5.21. Level control.

5.8.3. Flow Control

Flow control is usually associated with inventory control in a storage tank or other equipment. There must be a reservoir to take up the changes in flow rate.

To provide flow control on a compressor or pump running at a fixed speed and supplying a near constant volume output, a bypass control would be used, as shown in Figure 5.23a. The use of variable-speed motors, as shown in Figure 5.23c, is more energy efficient than the traditional arrangement shown in Figure 5.23b and is becoming increasingly common.

5.8.4. Heat Exchangers

Figure 5.24a shows the simplest arrangement, the temperature being controlled by varying the flow of the cooling or heating medium.

If the exchange is between two process streams whose flows are fixed, bypass control will have to be used, as shown in Figure 5.24b.

For air coolers, the coolant temperature may vary widely on a seasonal (or even hourly) basis. A bypass on the process side can be used, as shown in Figure 5.24c, or else a variable-speed motor can be used, as shown in Figure 5.24d.

Condenser Control

Temperature control is unlikely to be effective for condensers, unless the liquid stream is subcooled. Pressure control is often used, as shown in Figure 5.22d, or control can be based on the outlet coolant temperature.

Reboiler and Vaporizer Control

As with condensers, temperature control is not effective, as the saturated vapor temperature is constant at constant pressure. Level control is often used for vaporizers, the controller controlling the steam supply to the heating surface, with the

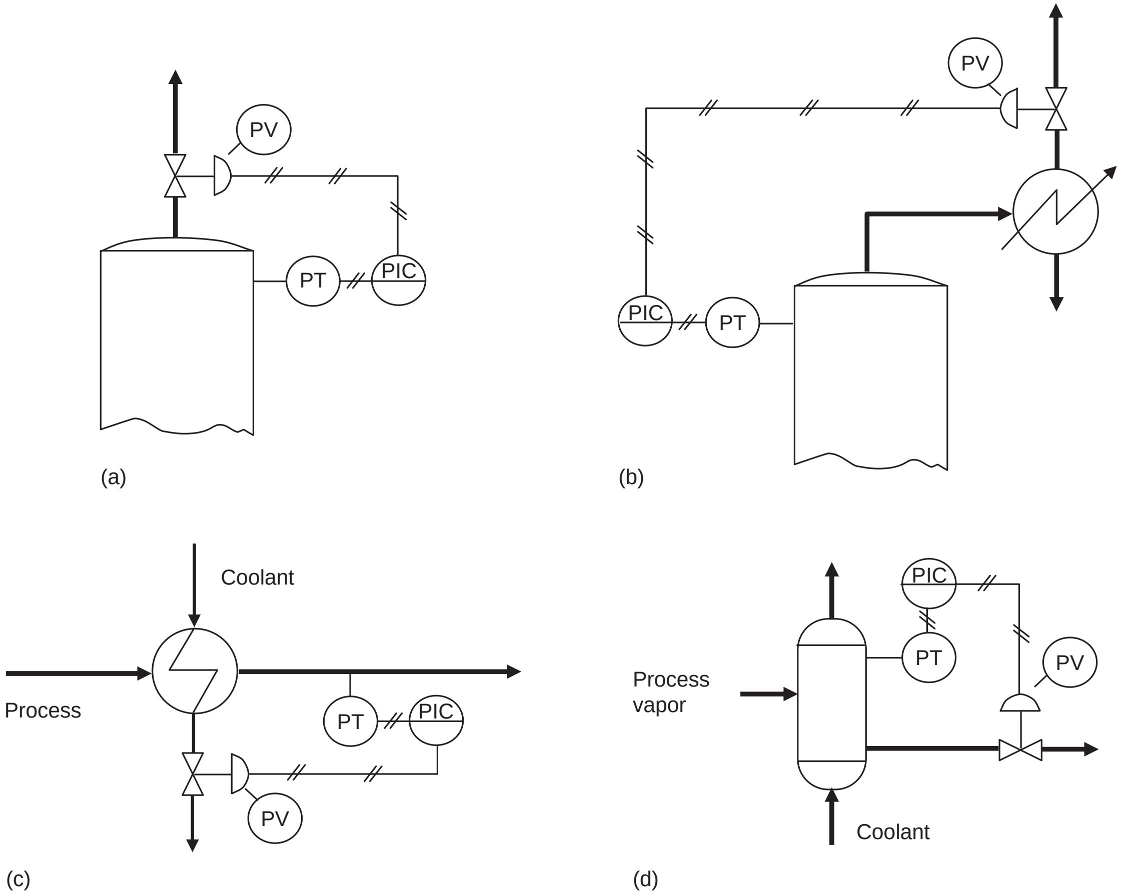


Figure 5.22. (a) Pressure control by direct venting. (b) Venting of noncondensables after a condenser. (c) Condenser pressure control by controlling coolant flow. (d) Pressure control of a condenser by varying the heat transfer area, area dependent on liquid level.

liquid feed to the vaporizer on flow control, as shown in Figure 5.25. An increase in the feed results in an automatic increase in steam to the vaporizer to vaporize the increased flow and maintain the level constant.

Reboiler control systems are selected as part of the general control system for the column and are discussed in Section 5.8.7.

5.8.5. Cascade Control

With the cascade control arrangement, the output of one controller is used to adjust the set point of another. Cascade control can give smoother control in situations in which direct control of the variable would lead to unstable operation. The "slave"

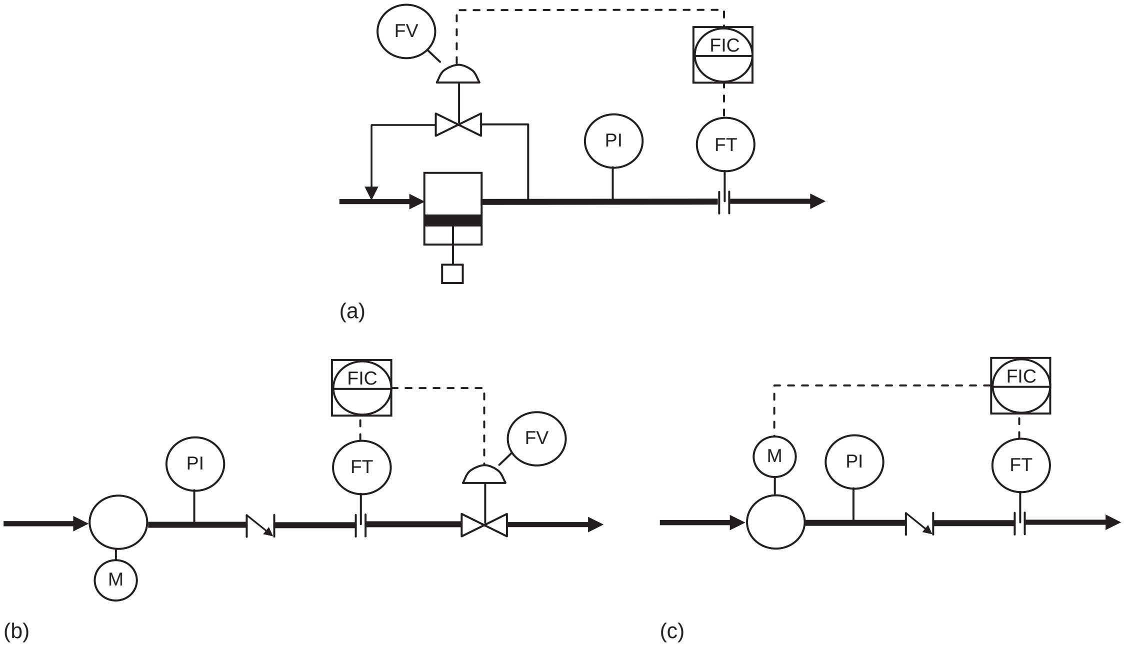


Figure 5.23. (a) Spill-back flow control for a reciprocating pump. (b) Flow control for a centrifugal pump. (c) Centrifugal pump with variable-speed drive.

controller can be used to compensate for any short-term variations in, say, a service stream flow, which would upset the controlled variable, the primary ("master") controller controlling long-term variations. Typical examples are shown in Figures 5.27e and 5.28.

5.8.6. Ratio Control

Ratio control can be used where it is desired to maintain two flows at a constant ratio, for example, reactor feeds and distillation column reflux. A typical scheme for ratio control is shown in Figure 5.26.

5.8.7. Distillation Column Control

The primary objective of distillation column control is to maintain the specified composition of the top and bottom products, and any side streams, correcting for the effects of disturbances in

1. Feed flow rate, composition, and temperature;
2. Steam supply pressure;
3. Cooling water pressure and header temperature;
4. Ambient conditions, which can cause changes in internal reflux (see Chapter 11).

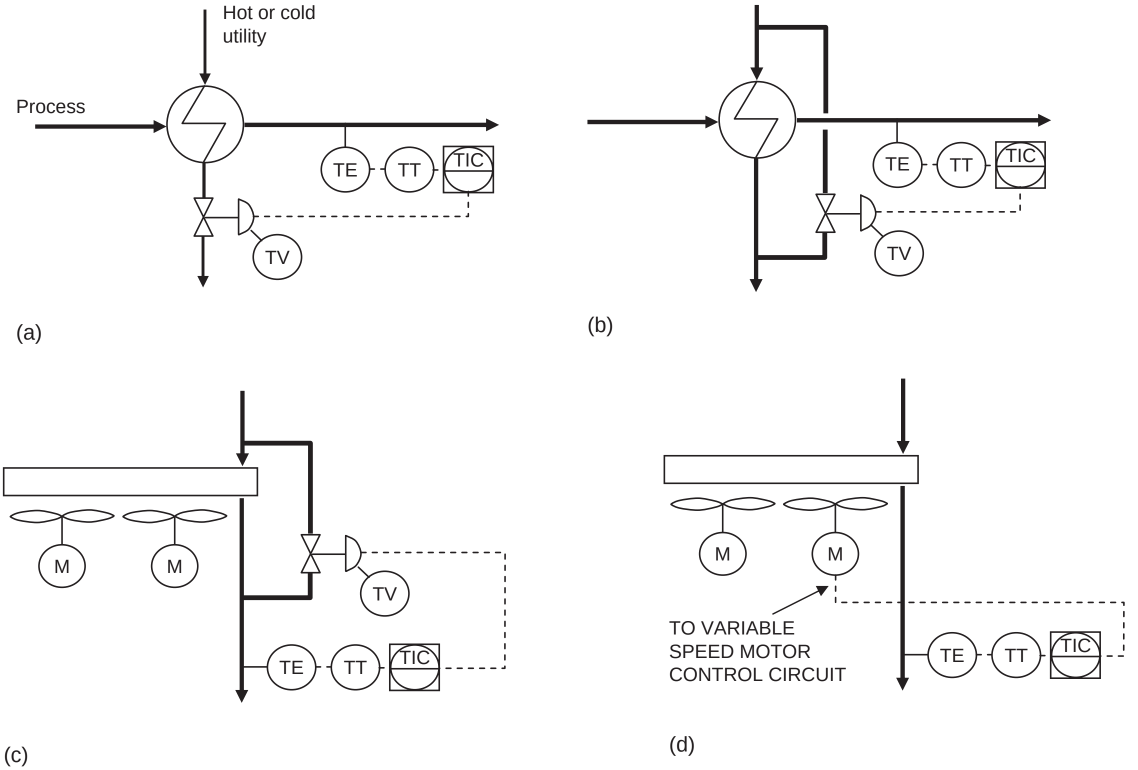


Figure 5.24. (a) Temperature control of one fluid stream. (b) Bypass control. (c) Air cooler with bypass control. (d) Air cooler with variable-speed drive.

The compositions are controlled by regulating reflux flow and boil-up. The column overall material balance must also be controlled; distillation columns have little surge capacity (hold-up), and the flow of distillate and bottom product (and side-streams) must match the feed flows.

Shinskey (1984) has shown that there are 120 ways of connecting the five main measured and controlled variables, in single loops. A variety of control schemes has been devised for distillation column control. Some typical schemes are shown in Figures 5.27a, b, c, d, e; ancillary control loops and instruments are not shown.

Distillation column control is discussed in detail by Parkins (1959), Bertrand and Jones (1961), Shinskey (1984), and Buckley et al. (1985).

Column pressure is normally controlled at a constant value. The use of variable pressure control to conserve energy has been discussed by Shinskey (1976).

The feed flow rate is often set by the level controller on a preceding column. It can be independently controlled if the column is fed from a storage or surge tank.

Feed temperature is not normally controlled, unless a feed preheater is used.

Temperature is often used as an indication of composition. The temperature sensor should be located at the position in the column where the rate of change of

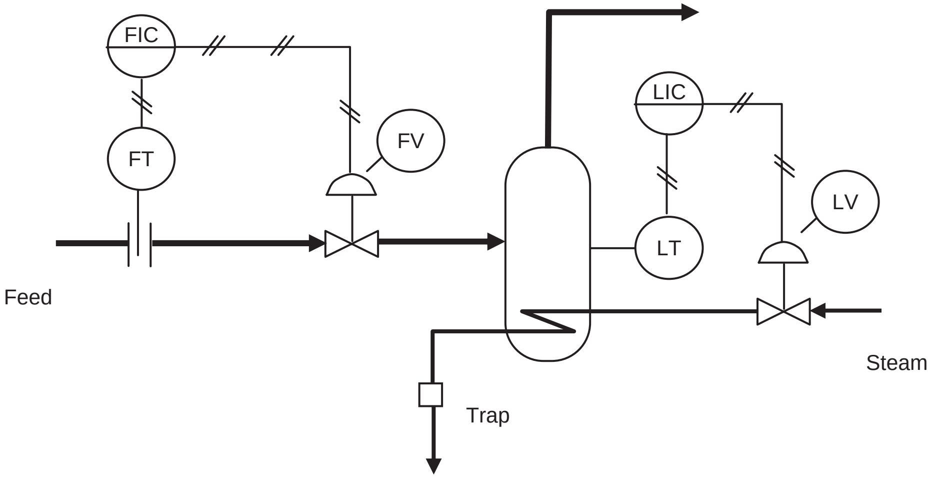


Figure 5.25. Vaporizer control.

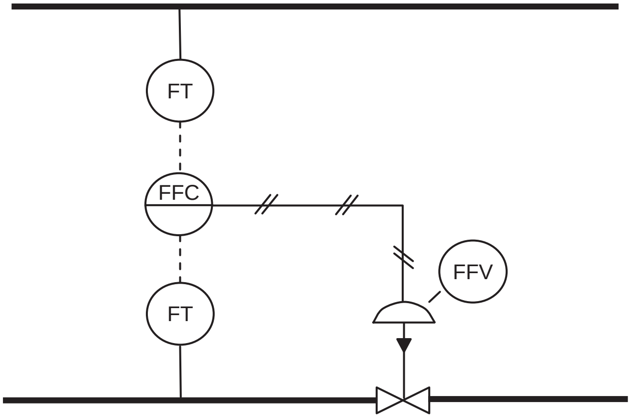


Figure 5.26. Ratio control.

temperature with change in composition of the key component is a maximum; see Parkins (1959). Near the top and bottom of the column, the change is usually small. With multicomponent systems, temperature is not a unique function of composition.

Top temperatures are usually controlled by varying the reflux ratio, and bottom temperatures by varying the boil-up rate. If reliable online analyzers are available, they can be incorporated in the control loop, but more complex control equipment will be needed.

Differential pressure control is often used on packed columns to ensure that the packing operates at the correct loading; see Figure 5.27d. Differential pressure control should not be used on trayed columns, as column pressure drop is relatively

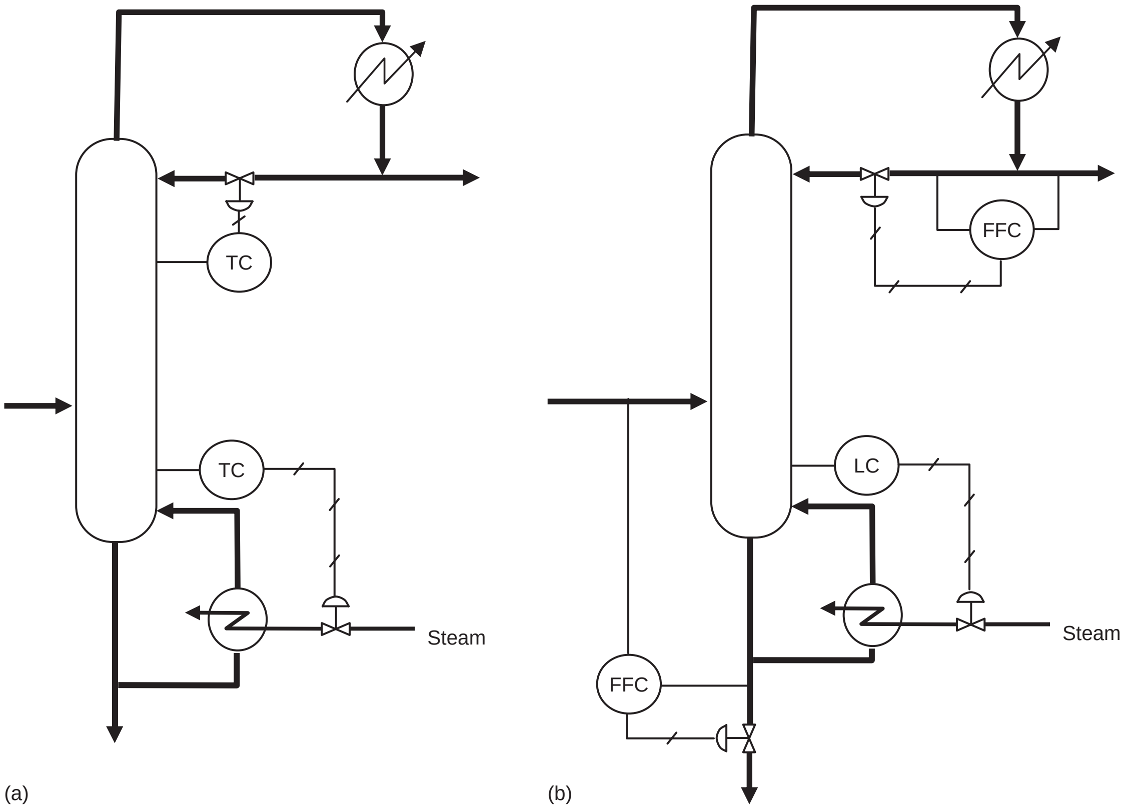


Figure 5.27. (a) Temperature pattern control. With this arrangement, interaction can occur between the top and bottom temperature controllers. (b) Composition control. Reflux ratio controlled by a ratio controller, or splitter box, and the bottom product as a fixed ratio of the feed flow.

insensitive to reboil rate unless the column is close to flooding, and such controllers are difficult to tune. See Eder (2003) for more detail.

Additional temperature indicating or recording points should be included up the column for monitoring column performance and for troubleshooting.

5.8.8. Reactor Control

The schemes used for reactor control depend on the process and the type of reactor. If a reliable online analyzer is available, and the reactor dynamics are suitable, the product composition can be monitored continuously and the reactor conditions and feed flows controlled automatically to maintain the desired product composition and yield. More often, the operator is the final link in the control loop, adjusting the

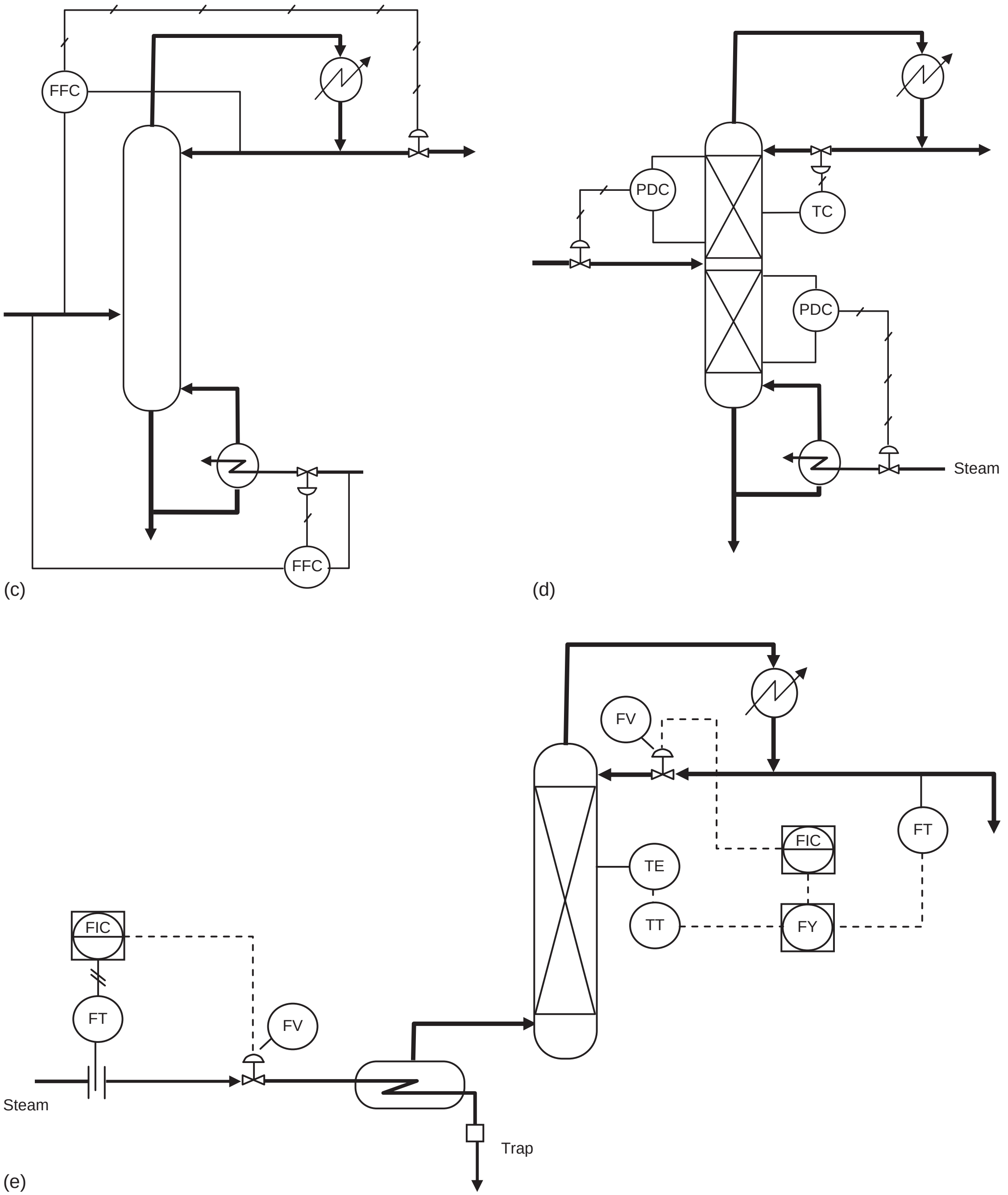


Figure 5.27. Cont'd. (c) Composition control. Top product take-off and boil-up controlled by feed. (d) Packed column, differential pressure control. Eckert (1964) discusses the control of packed columns. (e) Batch distillation, reflux flow controlled based on temperature to infer composition.

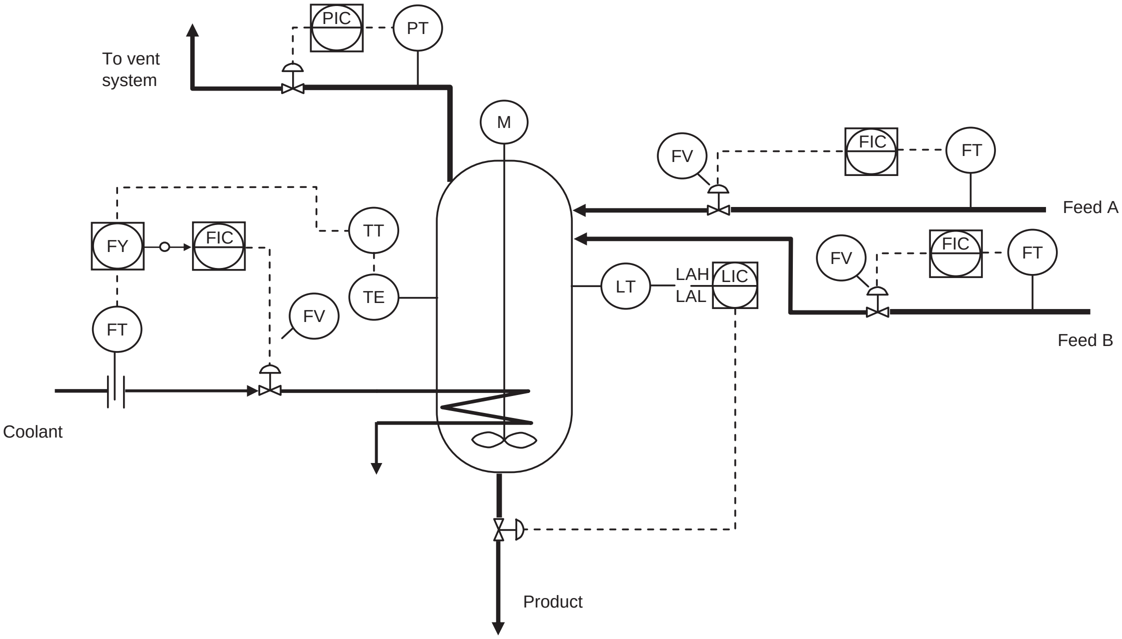


Figure 5.28. A typical stirred tank reactor control scheme, temperature cascade control of coolant flow, and flow control of reagents.

controller set points to maintain the product within specification, based on periodic laboratory analyses.

For small stirred tank reactors, temperature will normally be controlled by regulating the flow of the heating or cooling medium. For larger reactors, temperature is often controlled by recycling a part of the product stream or adding inert material to the feed to act as a heat sink. Pressure is usually held constant. For liquid phase reactors, pressure is often controlled by maintaining a vapor space above the liquid reagents. This space can be pressurized with nitrogen or other suitable gases. Material balance control will be necessary to maintain the correct flow of reactants to the reactor and the flow of products and unreacted materials from the reactor. A typical control scheme for a simple liquid phase reactor is shown in Figure 5.28.

5.9. ALARMS, SAFETY TRIPS, AND INTERLOCKS

Alarms are used to alert operators of serious and potentially hazardous deviations in process conditions. Key instruments are fitted with switches and relays to operate audible and visual alarms on the control panels and annunciator panels. Where delay or lack of response by the operator is likely to lead to the rapid development of a hazardous situation, the instrument would be fitted with a trip system to take action automatically to avert the hazard, such as shutting down pumps, closing valves, and operating emergency systems.

The basic components of an automatic trip system are

1. A sensor to monitor the control variable and provide an output signal when a preset value is exceeded (the instrument);
2. A link to transfer the signal to the actuator, usually consisting of a system of pneumatic or electric relays;
3. An actuator to carry out the required action: close or open a valve or switch off a motor.

A description of some of the equipment (hardware) used is given by Rasmussen (1975).

A safety trip can be incorporated in a control loop, as shown in Figure 5.29a. In this system the level control instrument has a built-in software alarm that alerts the operator if the level is too low and a programmed trip set for a level somewhat lower than the alarm level. However, the safe operation of such a system will be dependent on the reliability of the control equipment, and for potentially hazardous situations it is better practice to specify a separate trip system, such as that shown in Figure 5.29b, in which the trip is activated by a separate low-level switch. Provision must be made for the periodic checking of the trip system to ensure that the system operates when needed.

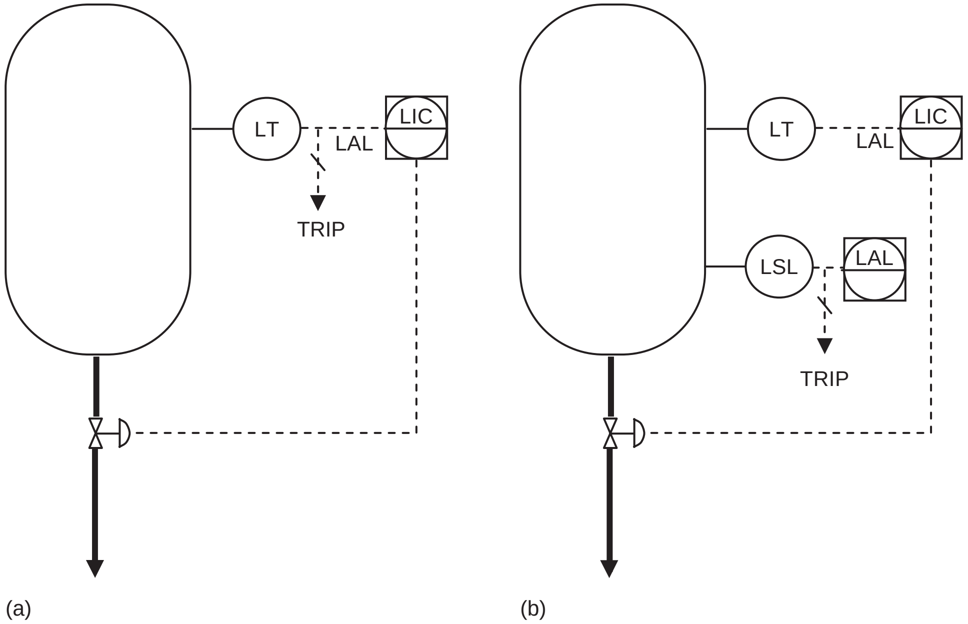


Figure 5.29. (a) Trip as part of control system. (b) Separate shutdown trip.

Interlocks

Where it is necessary to follow a fixed sequence of operations—for example, during a plant startup and shutdown, or in batch operations—interlocks are included to prevent operators departing from the required sequence. They may be incorporated in the control system design, as pneumatic or electric relays, or may be mechanical interlocks. Various proprietary special lock and key systems are also available. In most plants, programmable logic controllers are used, and the interlocks are coded into the control algorithms. Care should be taken to test all of the interlocks in the plant automation during commissioning or whenever changes are made to the plant control and automation.

5.10. COMPUTERS IN PROCESS CONTROL

Almost all process control systems installed on new plants use programmable electronic devices based on microprocessors. These range from simple digitally actuated single-loop controllers that produce a single output signal (Single Input–Single Output or SISO devices) up to complex distributed control systems that carry out control, real-time optimization, and data logging and archiving for multiple process plants across a site or even an enterprise (Multiple Input–Multiple Output or MIMO devices).

The control schemes described in Section 5.8 mainly make use of SISO controllers, since the schemes were developed for single unit operations. At the unit operation level, the primary focus of process control is usually on safe and stable operation, and it is difficult to take advantage of the capability of advanced microprocessor-based control systems. When several unit operations are put together to form a process, then the scope for use of MIMO devices increases, particularly when the devices are able to communicate with each other rapidly. The digital control system can then make use of more complex algorithms and models that enable feed-forward control (model-based predictive control) and allow data collected from upstream in the process to guide the selection of operating conditions and controller set points for downstream operations. This allows for better response to process dynamics and more rapid operation of batch, cyclic, and other unsteady state processes. Model-based predictive control is also often used as a means of controlling product quality. The reason is that devices for measuring product quality typically require analytical procedures that take several minutes to hours to run, making effective feedback control difficult to accomplish.

The use of instruments that log and archive data facilitates remote monitoring of process performance and can improve plant troubleshooting and optimization and provide high-level data for enterprise-wide supply chain management.

The electronic equipment and systems technology available for process control continues to evolve rapidly. Because of the pace of innovation, industry-wide standards have not been able to keep up; consequently different manufacturers' systems usually use proprietary technology and are often not fully compatible with each other. The implementation of the ISA SP50 Fieldbus standard is expected to substantially

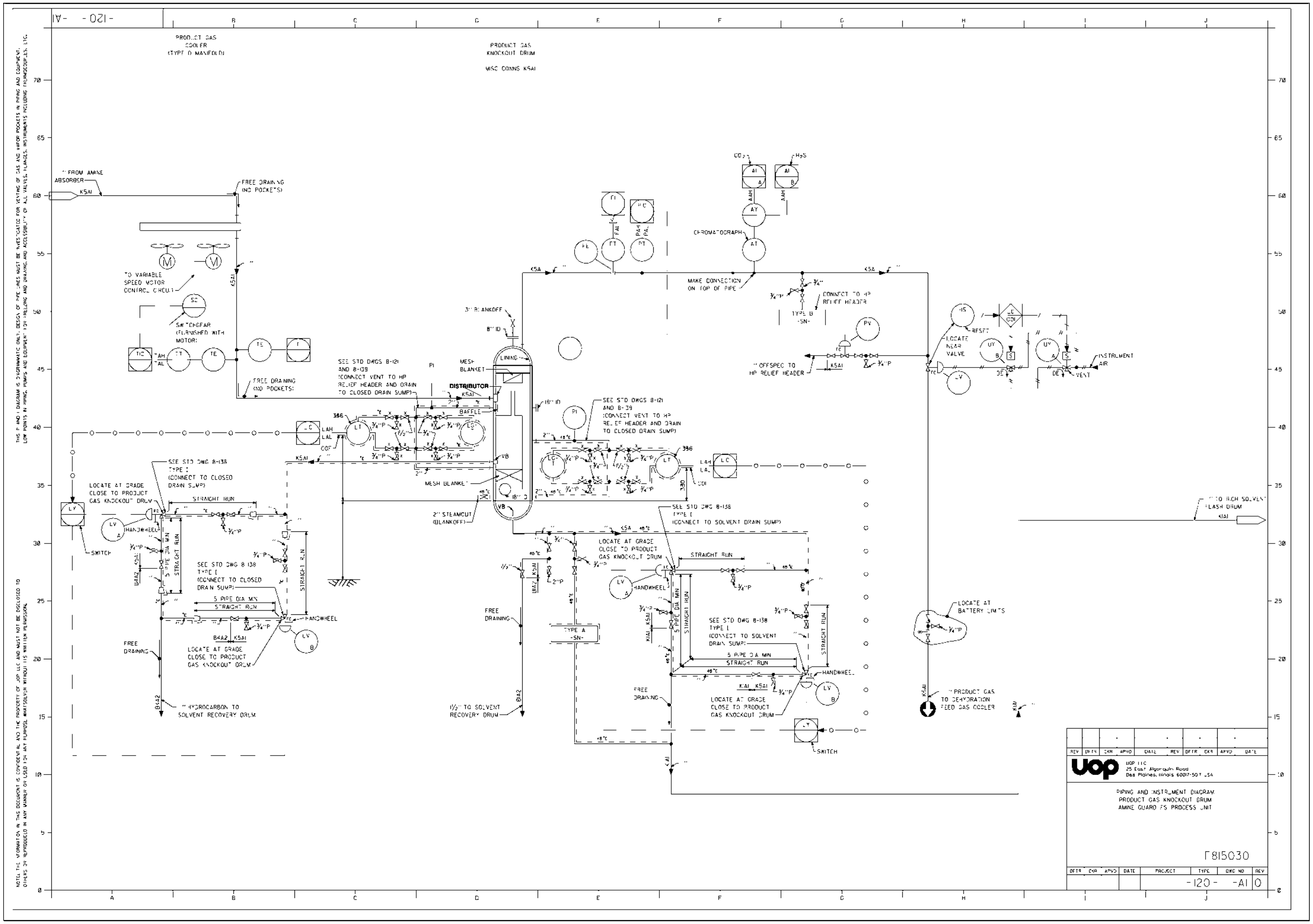


Figure 5.30. Piping and instrumentation diagram.

improve digital communications between control valve devices, leading to improved control, faster setup, better reliability through higher redundancy, and even greater distribution of functions between devices. The ISA is also developing the SP100 standard for wireless transmission. Wireless systems are beginning to be used in inventory control and maintenance management, but are not widely used yet in plant control, mainly because of problems with interference, signal blocking and signal loss. The development of more robust error checking and transmission protocols and the adoption of mesh networking approaches will probably lead to greater use of wireless instrumentation in the future.

A detailed treatment of digital technology for process control is beyond the scope of this volume. Kalani (1988), Edgar et al. (1997), and Liptak (2003) all provide excellent reviews of the subject. Mitchell and Law (2003) give a good overview of digital bus technologies.

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ASME B31.2-1968 Fuel gas piping
ASME B31.3-2004 Process piping
ASME B31.4-1997 Pipeline transportation systems for liquid hydrocarbons and other liquids
ASME B31.5-2001 Refrigeration piping and heat transfer components
ASME B31.8-2003 Gas transmission and distribution piping systems
ASME B31.9-2004 Building services piping
ASME B31.11-2002 Slurry transportation piping systems
ASME B36.19M-2004 Stainless steel pipe
ISA-5.1-1984 (R1992) Instrumentation symbols and identification

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5.12. NOMENCLATURE

		Dimensions in **MLT$**
A	Plant attainment (hours operated per year)	—
B	Purchased cost factor, pipes	$\$\$\mathbf{L}^{-1}$
a	Capital charges factor, piping	$\mathbf{T}^{-1}$
b	Maintenance cost factor, piping	$\mathbf{T}^{-1}$
c	Sum of mechanical, corrosion, and erosion allowances	$\mathbf{L}$

		Dimensions in **MLT$**
C_f	Fanning friction factor	—
C_C	Annual capital charge, piping	$\$L^{-1}T^{-1}$
C_t	Total annual cost, piping	$\$L^{-1}T^{-1}$
C_w	Annual pumping cost, piping	$\$L^{-1}T^{-1}$
d	Pipe diameter	L
d_i	Pipe inside diameter	L
E	Pipe casting quality factor	—
e	Relative roughness	—
F	Installed cost factor, piping	—
f	Friction factor	—
G	Mass flow rate	MT^{-1}
g	Gravitational acceleration	LT^{-2}
H	Height of liquid above the pump suction	L
h	Pump head	L
K	Number of velocity heads	—
L	Pipe length	L
m	Mass flow rate	MT^{-1}
N	Pump speed, revolutions per unit time	T^{-1}
N_S	Pump specific speed	—
n	Index relating pipe cost to diameter	—
P	Pressure	$ML^{-1}T^{-2}$
P_F	Pressure loss in suction piping	$ML^{-1}T^{-2}$
P_S	Safe working pressure	$ML^{-1}T^{-2}$
P_V	Vapor pressure of liquid	$ML^{-1}T^{-2}$
ΔP	Difference in system pressures ($P_1 - P_2$)	$ML^{-1}T^{-2}$
ΔP_F	Pressure drop	$ML^{-1}T^{-2}$
p	Cost of power, pumping	$\$M^{-1}L^{-2}T^{2}$
Q	Volumetric flow rate	$L^{3}T^{-1}$
R	Shear stress on surface, pipes	$ML^{-1}T^{-2}$
S	Basic allowable stress for pipe material	$ML^{-1}T^{-2}$
t	Pipe wall thickness	L
t_m	Minimum required thickness	L
t_p	Pressure design thickness	L
u	Fluid velocity	LT^{-1}
W	Work done	$L^{2}T^{-2}$
z	Height above datum	L
Δz	Difference in elevation ($z_1 - z_2$)	L
γ	Temperature coefficient	—
η	Pump efficiency	—
ρ	Fluid density	ML^{-3}
μ	Viscosity of fluid	$ML^{-1}T^{-1}$

		Dimensions in MLT$
σ_d	Design stress	$ML^{-1}T^{-2}$
σ_s	Safe working stress	$ML^{-1}T^{-2}$
Re	Reynolds number	—
$NPSH_{avail}$	Net positive suction head available at the pump suction	L
$NPSH_{reqd}$	Net positive suction head required at the pump suction	L

5.13. PROBLEMS

5.1. Select suitable valve types for the following applications:

1. Isolating a heat exchanger;
2. Manual control of the water flow into a tank used for making up batches of sodium hydroxide solution;
3. The valves need to isolate a pump and provide emergency manual control on a bypass loop;
4. Isolation valves in the line from a vacuum column to the steam ejectors producing the vacuum;
5. Valves in a line where cleanliness and hygiene are an essential requirement.

State the criterion used in the selection for each application.

5.2. Crude dichlorobenzene is pumped from a storage tank to a distillation column.

The tank is blanketed with nitrogen and the pressure above the liquid surface is held constant at 0.1 bar gauge pressure. The minimum depth of liquid in the tank is 1 m.

The distillation column operates at a pressure of 500 mmHg (500 mm of mercury, absolute). The feed point to the column is 12 m above the base of the tank. The tank and column are connected by a 50 mm internal diameter commercial steel pipe, 200 m long. The pipe run from the tank to the column contains the following valves and fittings: 20 standard radius 90° elbows; two gate valves to isolate the pump (operated fully open); an orifice plate; and a flow-control valve.

If the maximum flow rate required is 20,000 kg/h, calculate the pump motor rating (power) needed. Take the pump efficiency as 70% and allow for a pressure drop of 0.5 bar across the control valve and a loss of 10 velocity heads across the orifice.

Density of dichlorobenzene 1300 kg/m^3, viscosity 1.4 cp.

5.3. A liquid is contained in a reactor vessel at 115 bar absolute pressure. It is transferred to a storage vessel through a 50 mm internal diameter commercial steel pipe. The storage vessel is nitrogen blanketed, and pressure above the liquid surface is kept constant at 1500 N/m^2 gauge. The total run of pipe between the two vessels is 200 m. The miscellaneous losses due to entry and exit losses, fittings, valves, etc., amount to 800 equivalent pipe diameters. The liquid level in the storage vessel is at an elevation 20 m *below* the level in the reactor.

A turbine is fitted in the pipeline to recover the excess energy that is available, over that required to transfer the liquid from one vessel to the other. Estimate the power that can be taken from the turbine, when the liquid transfer rate is 5000 kg/h. Take the efficiency of the turbine as 70%.

The properties of the fluid are density 895 kg/m^3, viscosity 0.76 mNm^{-2}s.

5.4. A process fluid is pumped from the bottom of one distillation column to another, using a centrifugal pump. The line is standard commercial steel pipe 75 mm internal diameter. From the column to the pump inlet, the line is 25 m long and contains 6 standard elbows and a fully open gate valve. From the pump outlet to the second column, the line is 250 m long and contains 10 standard elbows, 4 gate valves (operated fully open), and a flow-control valve. The fluid level in the first column is 4 m above the pump inlet. The feed point of the second column is 6 m above the pump inlet. The operating pressure in the first column is 1.05 bara and that of the second column 0.3 barg.

Determine the operating point on the pump characteristic curve when the flow is such that the pressure drop across the control valve is 35 kN/m^2.

The physical properties of the fluid are density 875 kg/m^3, viscosity 1.46 mN m^{-2}s.

Also, determine the NPSH, at this flow rate, if the vapor pressure of the fluid at the pump suction is 25 kN/m^2.

Pump Characteristic							
Flow rate, m^3/h	0.0	18.2	27.3	36.3	45.4	54.5	63.6
Head, m of liquid	32.0	31.4	30.8	29.0	26.5	23.2	18.3

5.5. Revisiting the problem of example 5.3, suppose the flow was controlled using a plug-disk globe valve, and the initial design in the example assumed that the valve is fully open. What range of flow rates can be achieved if the valve can be throttled down to one-quarter open? When the valve is one-quarter open, what fraction of the pump work is lost across the valve?

5.6. Estimate the shaft work required to pump 65 gal/min of sugar solution in water (specific gravity = 1.05) if the pump inlet pressure is 25 psig and the outlet pressure required is 155 psig.

5.7. A shell and tube cooler in an aromatics complex cools 26,200 lb/h of naphtha (specific gravity 0.78, viscosity 0.007 cP). The cooler has 347 tubes, 16 ft long, 3/4 inch diameter. If the naphtha is on the tube side, estimate the tube side pressure drop.

5.8. In a detergent-making process, 1400 gal/h of water flows through a 2-inch pipe system as follows:

Exit from pump, 2 ft vertical, open gate valve, 14 ft vertical, 90° bend, 12 ft horizontal, 1/4 open globe valve, 20 ft horizontal, 90° bend, 6 ft horizontal, 90° bend, 12 ft vertical, 90° bend, 14 ft horizontal, 90° bend, 4 ft vertical, 90° bend, 28 ft horizontal, open gate valve, 3 ft horizontal, entry to tank containing 30 ft of liquid.

a. If the pump and tank are both at grade level, estimate the head that the pump must deliver.
b. If the pump inlet pressure is 25 psig, what is the outlet pressure?
c. Estimate the pump shaft work.
d. If the pump is powered by an electric motor with 85% efficiency, what is the annual electricity consumption?

5.9. A polymer is produced by the emulsion polymerization of acrylonitrile and methyl methacrylate in a stirred vessel. The monomers and an aqueous solution of catalyst are fed to the polymerization reactor continuously. The product is withdrawn from the base of the vessel as a slurry.

Devise a control system for this reactor, and draw up a preliminary piping and instrument diagram. The follow points need to be considered:

1. Close control of the reactor temperature is required.
2. The reactor runs 90% full.
3. The water and monomers are fed to the reactor separately.
4. The emulsion is a 30% mixture of monomers in water.
5. The flow of catalyst will be small compared with the water and monomer flows.
6. Accurate control of the catalyst flow is essential.

Devise a control system for the distillation column described in Chapter 11, Example 11.2. The flow to the column comes from a storage tank. The product, acetone, is sent to storage and the waste to an effluent pond. It is essential that the specifications on product and waste quality are met.

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6 COSTING AND PROJECT EVALUATION

Chapter Contents

Key Learning Objectives:

- How to estimate process capital and operating costs
- How to find and forecast prices for use in economic analysis
- How corporations finance projects
- Different criteria that companies use to compare the financial attractiveness of alternative projects, and other factors that are also taken into account in project selection
- How to allow for error in cost estimates

6.1. INTRODUCTION

Most chemical engineering design projects are carried out to provide information from which estimates of capital and operating costs can be made. Chemical plants are built to make a profit, and an estimate of the investment required and the cost of production is needed before the profitability of a project can be assessed. Cost estimation is a specialized subject and a profession in its own right, but the design engineer must be able to make rough cost estimates to decide between project alternatives and optimize the design.

This chapter introduces the components of capital and operating costs and the techniques used for estimating. Simple costing methods and some cost data are given, which can be used to make preliminary estimates of capital and operating costs in the early stages of design. Sources of cost data and methods for updating cost estimates are described. The main methods used for economic evaluation of projects are introduced, together with an overview of factors that influence project selection.

Most cost-estimating and economic analysis calculations are easily carried out using spreadsheets. Templates are introduced in the examples throughout the chapter. Blank templates are given in Appendix G and in the online material at http://books.elsevier.com/companions. The more sophisticated software that is used in industry for preliminary estimating is discussed in Section 6.3.

For a more detailed treatment of the subject, refer to the numerous specialized texts that have been published on cost estimation. The following books are particularly recommended: Happle and Jordan (1975), Guthrie (1974), Page (1996), Garrett (1989), and Humphreys (1991, 2005).

Several companies regularly publish economic analyses of chemical processes. Nexant publishes the *Process Evaluation and Research Planning* (PERP) reports (www.nexant.com/products). Roughly 10 new reports are issued each year, and almost 200 processes have been analyzed. The PERP reports provide estimates of capital and operating costs, usually for two or three process alternatives, as well as an overview of the market. SRI publishes the *Chemical Economics Handbook* (CEH) series, which contains 281 reports on a range of commodity and specialty chemicals. The CEH reports provide an overview of production technologies and analyses of several regional markets but do not provide the level of production cost detail given in the PERP reports. Various consulting firms also carry out paid economic studies of “state of the art” technology. Although there are minor variations in methodology, most of these studies estimate production costs using similar assumptions. The conventions used will be introduced in the following sections and should be followed when making preliminary economic analyses and when accurate cost information is not available.

6.2. COSTS, REVENUES, AND PROFITS

This section introduces the components of project costs and revenues.

6.2.1. Fixed Capital Investment

The *fixed capital investment* is the total cost of designing, constructing, and installing a plant and the associated modifications needed to prepare the plant site. The fixed capital investment is made up of

1. The inside battery limits (ISBL) investment—the cost of the plant itself;
2. The modifications and improvements that must be made to the site infrastructure, known as *offsite* or *OSBL investment*;
3. Engineering and construction costs;
4. Contingency charges.

ISBL Plant Costs

The *ISBL plant cost* includes the cost of procuring and installing all the process equipment that makes up the new plant.

The direct field costs include

1. All the major process equipment, such as vessels, reactors, columns, furnaces, heat exchangers, coolers, pumps, compressors, motors, fans, turbines, filters, centrifuges, dryers, etc., including field fabrication and testing if necessary;
2. Bulk items, such as piping, valves, wiring, instruments, structures, insulation, paint, lube oils, solvents, catalysts, etc.;
3. Civil works such as roads, foundations, piling, buildings, sewers, ditches, embankments, etc.;
4. Installation labor and supervision.

In addition to the direct field costs there will be indirect field costs, including

1. Construction costs such as construction equipment rental, temporary construction (rigging, trailers, etc.), temporary water and power, construction workshops, etc.;
2. Field expenses and services such as field canteens, specialists' costs, overtime pay, and adverse weather costs;
3. Construction insurance;
4. Labor benefits and burdens (Social Security, workers' compensation, etc.);
5. Miscellaneous overhead items such as agents' fees, legal costs, import duties, special freight costs, local taxes, patent fees or royalties, corporate overheads, etc.

In the early stages of a project, it is important to define the ISBL scope carefully, as other project costs are often estimated from ISBL cost. The overall project economics can be badly miscalculated if the ISBL scope is poorly defined. Methods for estimating ISBL costs are given in Section 6.3.

Offsite Costs

Offsite cost or OSBL investment includes the costs of the additions that must be made to the site infrastructure to accommodate adding a new plant or increasing the capacity of an existing plant. Offsite investments may include

- Electric main substations, transformers, switchgear, and power lines;
- Power generation plants, turbine engines, standby generators;
- Boilers, steam mains, condensate lines, boiler feed water treatment plant, supply pumps;
- Cooling towers, circulation pumps, cooling water mains, cooling water treatment;
- Water pipes, water demineralization, waste-water treatment plant, site drainage, and sewers;
- Air separation plants to provide site nitrogen for inert gas, nitrogen lines;
- Dryers and blowers for instrument air, instrument air lines;
- Pipe bridges, feed and product pipelines;
- Tanker farms, loading facilities, conveyors, docks, warehouses, railroads, lift trucks;
- Laboratories, analytical equipment, offices, canteens, changing rooms, central control rooms;
- Workshops and maintenance facilities;
- Emergency services, firefighting equipment, fire hydrants, medical facilities, etc.;
- Site security, fencing, gatehouses, and landscaping.

Offsite investments often involve interactions with utility companies such as electricity or water suppliers. They may be subject to equal or greater scrutiny than ISBL investments because of their impact on the local community through water consumption and discharge, traffic, etc.

Offsite costs are typically estimated as a proportion of ISBL costs in the early stages of design. Offsite costs are usually in the range from 10% to 100% of ISBL costs, depending on the project scope and its impact on site infrastructure. For typical petrochemical projects, offsite costs are usually between 20% and 50% of ISBL cost, and 40% is usually used as an initial estimate if no details of the site are known. For an established site with well-developed infrastructure, offsite costs will generally be lower. This is particularly true of sites that have undergone contraction, where some plants have closed, leaving underutilized infrastructure (“brownfield” sites). On the other hand, if the site infrastructure is in need of repair or upgrading to meet new regulations, or if the plant is built on a completely new site (a “greenfield” site), then offsite costs will be higher.

Once a site has been chosen for the project, then the modifications to the site infrastructure that are needed can be designed in detail in the same manner as the ISBL investments. Infrastructure upgrades are usually the first part of a project to be implemented, as they usually need to be commissioned before the plant can begin operation.

Engineering Costs

The *engineering costs*, sometimes referred to as *home office costs* or *contractor charges*, include the costs of detailed design and other engineering services required to carry out the project:

1. Detailed design engineering of process equipment, piping systems, control systems and offsites, plant layout, drafting, cost engineering, scale models, and civil engineering;
2. Procurement of main plant items and bulks;
3. Construction supervision and services;
4. Administrative charges, including engineering supervision, project management, expediting, inspection, travel and living expenses, and home office overheads;
5. Bonding;
6. Contractor's profit.

Very few operating companies retain a large enough engineering staff to carry out all of these activities internally, except for very small projects. In most cases, one or more of the major engineering contracting firms will be brought in.

Engineering costs are best estimated individually based on project scope, as they are not directly proportional to project size. A rule of thumb for engineering costs is 30% of ISBL plus OSBL cost for smaller projects and 10% of ISBL plus OSBL cost for larger projects. The actual charges paid for real industrial projects vary considerably from customer to customer and are strongly influenced by long-term client-contractor relationships and overall market demand for engineering services. Customers usually have to pay premiums or surcharges if they want to complete a project on an accelerated timeline or if they make a lot of changes once a project is under way.

Contingency Charges

Contingency charges are extra costs added into the project budget to allow for variation from the cost estimate. All cost estimates are uncertain (see Section 6.3.1), and the final installed cost of many items is not known until installation has been successfully completed. Apart from errors in the cost estimate, contingency costs also help cover

- Changes in project scope;
- Changes in prices (e.g., prices of steel, copper, catalyst, etc.);
- Currency fluctuations;
- Labor disputes;
- Subcontractor problems; and
- Other unexpected problems.

A minimum contingency charge of 10% of ISBL plus OSBL cost should be used on all projects. If the technology is uncertain, then higher contingency charges (up to 50%) are used. Contingency charges are discussed in more detail in Section 6.8.4.

6.2.2. Working Capital

Working capital is the additional money needed, above what it cost to build the plant, to start the plant up and run it until it starts earning income. Working capital typically includes

1. Value of raw material inventory–usually estimated as 2 weeks' delivered cost of raw materials;

2. Value of product and byproduct inventory–estimated as 2 weeks' cost of production;
3. Cash on hand–estimated as 1 week's cost of production;
4. Accounts receivable–products shipped but not yet paid for–estimated as 1 month's cost of production;
5. Credit for accounts payable–feedstocks, solvents, catalysts, packaging, etc. received but not yet paid for–estimated as 1 month's delivered cost;
6. Spare parts inventory–estimated as 1% to 2% of ISBL plus OSBL investment cost.

It can be seen that the sum of items 1 through 5 is roughly 7 weeks' cost of production minus 2 weeks' feedstock costs (item 5 is a credit).

Working capital can vary from as low as 5% of the fixed capital for a simple, single-product process, with little or no finished product storage, to as high as 30% for a process producing a diverse range of product grades for a sophisticated market, such as synthetic fibers. A typical figure for petrochemical plants is 15% of the fixed capital (ISBL plus OSBL cost).

Working capital is better estimated from the cost of production rather than capital investment. It is recovered at the end of the plant life.

Other methods for estimating the working capital requirement are given by Bechtel (1960), Lyda (1972), and Scott (1978).

6.2.3. Variable Costs of Production

Variable costs of production are costs that are proportional to the plant output or operation rate. These include the costs of

1. Raw materials consumed by the process;
2. Utilities—fuel burned in process heaters, steam, cooling water, electricity, raw water, instrument air, nitrogen, and other services brought in from elsewhere on the site;
3. Consumables—solvents, acids, bases, inert materials, corrosion inhibitors, additives, catalysts, and adsorbents that require continuous or frequent replacement;
4. Effluent disposal;
5. Packaging and shipping—drums, bags, tankers, freight charges, etc.

Variable costs can usually be reduced by more efficient design or operation of the plant. Methods for estimating variable costs are discussed in Section 6.4.

6.2.4. Fixed Costs of Production

Fixed production costs are costs that are incurred regardless of the plant operation rate or output. If the plant cuts back its production, these costs are not reduced. Fixed costs include

1. Operating labor—see Section 6.4.7.
2. Supervision—usually taken as 25% of operating labor.
3. Direct salary overhead—usually 40 to 60% of operating labor plus supervision.

4. Maintenance, which includes both materials and labor, and is typically estimated as 3 to 5% of ISBL investment, depending on the expected plant reliability. Plants with more moving equipment or more solids handling usually require higher maintenance.
5. Property taxes and insurance—typically 1 to 2% of ISBL fixed capital.
6. Rent of land (and/or buildings)—typically estimated as 1 to 2% of ISBL plus OSBL investment. Most projects assume land is rented rather than purchased, but in some cases the land is bought and the cost is added to the fixed capital investment and recovered at the end of the plant life.
7. General plant overhead—charges to cover corporate overhead functions such as human resources, research and development (R&D), information technology, finance, etc. Corporate overhead varies widely depending on the industry sector. Oil refining companies that carry out minimal R&D have much lower overhead than pharmaceuticals manufacturers. Plant overhead is typically taken as 65% of total labor (including supervision and direct overhead) plus maintenance.
8. Allocated environmental charges to cover superfund payments (see Chapter 14)—typically 1% of ISBL plus OSBL cost.
9. Running license fees and royalty payments—i.e., those not capitalized at the start of the project.
10. Capital charges—these include interest payments due on any debt or loans used to finance the project, but *do not* include expected returns on invested equity capital—see Section 6.6.
11. Sales and marketing costs—in some cases these are considered part of general plant overhead. They can vary from almost zero for some commodities to millions of dollars a year for branded items such as foods, toiletries, drugs, and cosmetics.

Fixed costs should never be neglected, even in the earliest stages of design, as they can have a significant impact on project economics. Very few chemical plants in the United States carry less than \$1 million (\$1 MM) of fixed costs.

Fixed costs are also a strong disincentive for building small plants. As plant size is increased, labor, supervision, and overhead costs usually do not increase; hence, the fixed cost per pound of product decreases. This, together with economies of scale in capital investment (see Section 6.3), gives larger plants more flexibility to reduce prices and hence force smaller plants out of business during downturns in the business cycle.

Fixed costs are not easily influenced by better design or operation of the plant, other than improvements that allow the plant to be operated safely with a smaller workforce. Fixed costs are more amenable to control at the corporate level than the plant level.

6.2.5. Revenues, Margins, and Profits

Revenues

The revenues for a project are the incomes earned from sales of main products and byproducts.

The production rate of main product is usually specified in the design basis and is determined based on predictions of overall market growth.

Determining which byproducts to recover, purify, and sell is usually more difficult than determining the main product. Some byproducts are produced by the main reaction stoichiometry and are unavoidable unless new chemistry can be found. These stoichiometric byproducts must usually be sold for whatever price they can get; otherwise, waste disposal costs will be excessive. Some examples of stoichiometric byproducts are given in Table 6.1. Other byproducts are produced from feed impurities or by nonselective reactions. The decision to recover, purify, and sell; recycle or otherwise attenuate; or dispose of them as wastes is an important design optimization problem and is discussed in Section 6.4.8.

Margins

The sum of product and byproduct revenues minus raw material costs is known as the *gross margin* (or sometimes *product margin* or just *margin*).

$$\text{Gross margin} = \text{Revenues} - \text{Raw materials costs} \tag{6.1}$$

Gross margin is a useful concept, as raw materials costs are almost always the largest contributor to production costs (typically 80 to 90% of total cost of production). Raw materials and product prices of commodities are often subject to high variability and can be difficult to forecast, but margins suffer less variability if producers are able to pass feedstock price increases on to their customers. Margins are therefore often used in price forecasting, as described in Section 6.4.2.

Margins vary widely between different sectors of the chemical industry. For commodities such as bulk petrochemicals and fuels, margins are typically very low (less than 10% of revenues) and may even occasionally be negative. Commodity businesses are usually cyclical because of investment cycles and experience higher margins when supply is short, as described in Section 6.4. When a product is tightly regulated (making market entry difficult) or subject to patent protection, then margins can be much higher. For example, margins on food additives, pharmaceutical products, and biomedical implants are typically more than 40% of revenues and often higher than 80% of revenues.

Table 6.1. Some Stoichiometric Byproducts

Feeds	**Main Product**	**Byproduct**
cumene + air	phenol	acetone
propylene + ethylbenzene + air	propylene oxide	styrene
ethylene + chlorine	vinyl chloride monomer	HCl
allyl chloride + HOCl + NaOH	epichlorohydrin	NaCl
methane + steam	hydrogen	carbon dioxide
glucose	ethanol (by fermentation)	carbon dioxide
acetone cyanohydrin + methanol + H_2SO_4	methyl methacrylate	ammonium sulfate
sodium chloride + electricity	chlorine	sodium hydroxide

Profits

The cash cost of production (CCOP) is the sum of the fixed and variable production costs:

$$\text{CCOP} = \text{VCOP} + \text{FCOP} \tag{6.2}$$

where

VCOP = sum of all the variable costs of production minus byproduct revenues;
FCOP = sum of all the fixed costs of production.

The cash cost of production is the cost of making products, not including any return on the equity capital invested. By convention, byproduct revenues are usually taken as a credit and included in the VCOP. This makes it easier to determine the $/lb cost of producing the main product.

The gross profit is

$$\text{Gross profit} = \text{Main product revenues} - \text{CCOP} \tag{6.3}$$

Gross profit should not be confused with gross margin, as gross profit includes all the other variable costs in addition to raw materials, and also includes fixed costs and byproduct revenues.

The profit made by the plant is usually subject to taxation. Different tax codes apply in different countries and locations, and the taxable income may not be the full gross profit. Taxes are discussed in more detail in Section 6.5. The net profit (or cash flow after tax) is the amount left after taxes are paid:

$$\text{Net profit} = \text{gross profit} - \text{taxes} \tag{6.4}$$

The net profit from the project is the money that is available as a return on the initial investments. Methods for evaluating the economic performance of investments are introduced in Sections 6.6 and 6.7.

It is sometimes useful to calculate a total cost of production (TCOP), assuming that a plant generates a specified return on investment. In this case an annual capital charge (ACC) is added to the cash cost of production:

$$\text{TCOP} = \text{CCOP} + \text{ACC} \tag{6.5}$$

Methods for calculating the annual capital charge are discussed in Section 6.7.6.

6.2.6. Cash Flows at the End of the Project

If a plant ceases operation or is “mothballed” (shut down on a semipermanent basis), then the working capital is recovered but must be reinvested if the plant is restarted. When a plant is shut down permanently, then it can be sold in its entirety or else broken up and sold as scrap. There are several companies that specialize in buying and reselling second-hand plants, and advertisements for used plants and equipment can usually be found in the classified sections of the trade journals. The scrap value can be estimated based on the equipment weight and is usually less than 10% of the ISBL investment. OSBL investments are not recovered unless the entire site is shut down. If land was purchased for the plant, which is increasingly uncommon, then the land can be sold as an additional end-of-life credit. These cash flows at the end of the project are often not included in profitability analysis, as their timing is uncertain and they are often far enough in the future that they have negligible impact on any of the measures of profitability.

6.3. ESTIMATING CAPITAL COSTS

6.3.1. Accuracy and Purpose of Capital Cost Estimates

The accuracy of an estimate depends on the amount of design detail available, the accuracy of the cost data available, and the time spent on preparing the estimate. In the early stages of a project, only an approximate estimate will be required, and justified, by the amount of information available.

The Association for the Advancement of Cost Estimating International (AACE International) is the professional association representing the cost engineering profession in the United States. AACE International classifies capital cost estimates into five types according to their accuracy and purpose:

1. Order of magnitude estimates (“ballpark estimate,” “guesstimate,” “Class 5 estimate”), accuracy typically ±30–50%, usually based on the costs of similar processes and requiring essentially no design information. These are used in initial feasibility studies and for screening purposes.
2. Preliminary (“approximate,” “study,” “feasibility,” “Class 4”) estimates, accuracy typically ±30%, which are used to make coarse choices between design alternatives. They are based on limited cost data and design detail.
3. Definitive (“authorization,” “budgeting,” “control,” “Class 3”) estimates, accuracy typically ±10–15%. These are used for the authorization of funds to proceed with the design to the point where an accurate and more detailed estimate can be made. Authorization may also include funds to cover cancellation charges on any long delivery equipment ordered at this stage of the design to avoid delay in the project. In a contracting organization this type of estimate could be used with a large contingency factor to obtain a price for tendering. Normally, however, an accuracy of about ±5% would be needed and a more detailed estimate would be made, if time permitted. With experience, and where a company has cost data available from similar projects, estimates of acceptable accuracy can be made at the flowsheet stage of the project. A rough P and I diagram and the approximate sizes of the major items of equipment would also be needed.
4. Detailed estimates (“quotation,” “tender,” “firm estimate,” “contractor’s estimate,” “Class 2 estimate”), accuracy ±5–10%, which are used for project cost control and estimates for fixed price contracts. These are based on the

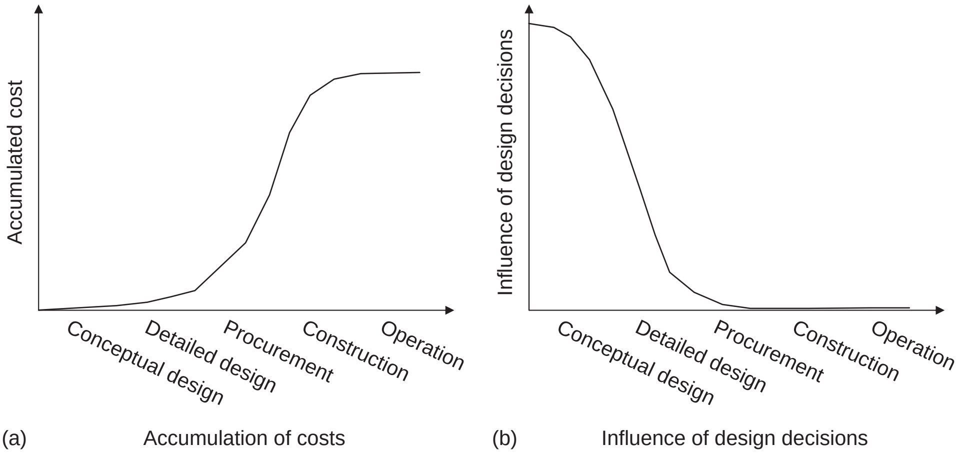


Figure 6.1. (a,b) Influence of design decisions on project cost.

completed (or near complete) process design, firm quotes for equipment, and a detailed breakdown and estimation of the construction cost. By this stage the contractor can usually present a list of all the items that must be purchased and can make a firm commitment to the client.

5. Check estimates ("tender," "as-bid," "Class 1 estimate"), accuracy ±5–10%. This is based on a completed design and concluded negotiations on procurement of specialized items and long lead-time items.

The cost of preparing an estimate increases from about 0.1% of the total project cost for ±30% accuracy, to about 3% for a detailed estimate with an accuracy of ±5%.

As a project proceeds from initial concept through detailed design to startup, costs begin to be accumulated, particularly once procurement and construction get underway (Figure 6.1a). At the same time, the ability of the design engineer to influence project cost decreases and is minimal by the time construction begins (Figure 6.1b). There is therefore a strong incentive to try to estimate project costs at as early a stage as possible, even if the design information is incomplete, so that the project can be optimized, evaluated, and abandoned if it is not attractive.

6.3.2 Rapid Cost Estimates

Historic Cost Data

The quickest way to make an order-of-magnitude estimate of plant cost is to scale it from the known cost of an earlier plant that used the same technology or from published data. This requires no design information other than the production rate.

The capital cost of a plant is related to capacity by the equation

$$C_2 = C_1 \left(\frac{S_2}{S_1}\right)^n \tag{6.6}$$

where

C_2 = ISBL capital cost of the plant with capacity S_2;
C_1 = ISBL capital cost of the plant with capacity S_1.

The exponent n is typically 0.8 to 0.9 for processes that use a lot of mechanical work or gas compression (e.g., methanol, paper pulping, solids-handling plants). For typical petrochemical processes, n is usually about 0.7. For small-scale, highly instrumented processes n is in the range 0.4 to 0.5. Averaged across the whole chemical industry, n is about 0.6, and hence equation 6.6 is commonly referred to as the "six-tenths rule." This value can be used to get a rough estimate of the capital cost if there are not sufficient data available to calculate the index for the particular process. Estrup (1972) gives a critical review of the six-tenths rule. Equation 6.6 is only an approximation, and if sufficient data are available, the relationship is best represented on a log-log plot. Garrett (1989) has published capital cost-plant capacity curves for over 250 processes.

The journal *Hydrocarbon Processing* publishes supplements on refining, petrochemical, and gas processing processes every other year. These supplements are available in print or CD format to subscribers and give approximate capital cost data for various licensed processes, which can be fitted using a rearranged form of equation 6.6:

$$C_2 = \frac{C_1}{S_1^n} \times S_2^n = a\ S_2^n \tag{6.7}$$

Values of the parameters a and n for some fuels and commodity chemical processes are given in Table 6.2. The costs in the *Hydrocarbon Processing* supplements are supplied by the technology vendors and are suitable for ballpark estimates only.

Step Count Method

If cost data for a similar process is not available, then an order-of-magnitude estimate can sometimes be made by adding contributions for different plant sections or functional units.

Experienced design engineers can often figure out costs of plant sections from historic total plant costs. For example, in many petrochemical processes, roughly 20% of ISBL capital cost is in the reactor section and 80% is in the distillation and product purification sections.

An alternative approach is Bridgewater's method, which correlates plant cost against number of processing steps (Bridgewater and Mumford, 1979). For plants primarily processing liquids and solids:

$$Q \geq 60{,}000: \quad C = 3200\,N\left(\frac{Q}{s}\right)^{0.675} \tag{6.8}$$

$$Q < 60{,}000: \quad C = 280{,}000\,N\left(\frac{Q}{s}\right)^{0.3} \tag{6.9}$$

Table 6.2. Process Cost Correlations

Process	**Licensor**	**Capacity Units**	S_{lower}	S_{upper}	a	n
ABS Resin (15% Rubber) by emulsion polymerization	Generic	MMlb/y	50	300	12.146	0.6
Acetic Acid by Cativa process	BP	MMlb/y	500	2,000	3.474	0.6
Acetic Acid by Low Water Methanol Carbonylation	Celanese	MMlb/y	500	2,000	2.772	0.6
Acrolein by propylene oxidation with Bi/Mo catalyst	Generic	MMlb/y	30	150	6.809	0.6
Adipic acid from phenol	Generic	MMlb/y	300	1,000	3.533	0.6
Alkylation (sulfuric acid effluent refrigeration process)	Stratco/DuPont	bpd	4,000	20,000	0.160	0.6
Alkylation (HF process)	UOP	bpd	5,000	12,000	0.153	0.6
Allyl chloride by propylene chlorination	Generic	MMlb/y	80	250	7.581	0.6
Alpha olefins (full-range process)	Chevron Phillips	MMlb/y	400	1,200	5.240	0.6
Alpha olefins (full-range process)	Shell	MMlb/y	400	1,000	8.146	0.6
Benzene by Sulfolane extraction	UOP/Shell	MMgal/y	50	200	7.793	0.6
Benzene by toluene hydrodealkylation	Generic	MMgal/y	50	200	7.002	0.6
Benzene reduction by Bensat	UOP	bpd	8,000	15,000	0.0275	0.6
Biodiesel (FAME) from vegetable oil	Generic	MMlb/y	100	500	2.747	0.6
bis-HET by Eastman Glycolysis	Eastman	MMlb/y	50	200	0.500	0.6
BTX Aromatics by Cyclar process	BP/UOP	tpy	200,000	800,000	0.044	0.6
BTX Aromatics by CCR Platforming	UOP	tpy	200,000	800,000	0.015	0.6
Butadiene by extractive distillation	UOP/BASF	MMlb/y	100	500	5.514	0.6
Butadiene by Oxo-D plus extractive distillation	Texas Petrochem.	MMlb/y	100	500	11.314	0.6
Butene-1 by Alphabutol ethylene dimerization	Axens	tpy	5,000	30,000	0.0251	0.6
Butene-1 by BP Process	BP	tpy	20,000	80,000	0.169	0.6
Caprolactam from nitration-grade toluene	SNIA BPD S.p.A.	tpy	40,000	120,000	0.321	0.6
Carbon monoxide by steam methane reforming	Generic	MMscf/y	2,000	6,000	0.363	0.6
Catalytic Condensation for Gasoline Production	UOP	bpd	10,000	30,000	0.222	0.6
Catalytic reforming by CCR Platforming	UOP	bpd	15,000	60,000	0.179	0.6
Coking by Flexicoking including Fluid Coking	ExxonMobil	bpd	15,000	40,000	0.343	0.6
Coking by Selective Yield Delayed Coking	Foster Wheeler/UOP	bpd	15,000	60,000	0.109	0.68
Copolymer polypropylene by INNOVENE	BP	MMlb/y	300	900	3.430	0.6
Copolymer polypropylene by Unipol	Dow	MMlb/y	300	900	3.641	0.6
Copolymer polypropylene by SPHERIPOL Bulk	Basell	MMlb/y	300	900	3.649	0.6
Copolymer polypropylene by BORSTAR	Borealis	MMlb/y	300	900	4.015	0.6
Crude distillation by D2000	TOTAL/Technip	bpd	150,000	300,000	0.151	0.6
Cumene by Q-Max	UOP	tpy	150,000	450,000	0.0120	0.6
Cyclic Olefin Copolymer by Mitsui Process	Mitsui	MMlb/y	60	120	12.243	0.6
Cyclohexane by liq-phase hydrogenation of benzene	Axens	tpy	100,000	300,000	0.0061	0.6

(*continued*)

Table 6.2. Process Cost Correlations—Cont'd

Process	**Licensor**	**Capacity Units**	**S_{lower}**	**S_{upper}**	***a***	***n***
Dewaxing by ISODEWAXING	Chevron Lummus	bpd	6,000	15,000	0.256	0.6
2,6-Dimethylnaphthalene by MeOH alkylation	Exxon Mobil/Kobe	MMlb/y	50	100	7.712	0.6
Dimethyl terephthalate by methanolysis	Generic	MMlb/y	30	80	5.173	0.6
Dimethyl terephthalate by Huels Oxidation	Huels	MMlb/y	300	800	7.511	0.6
Ethanol by ethylene hydration	Generic	Mgal/y	30	90	9.643	0.6
Ethanol (fuel grade) by Corn Dry Milling	Generic	tpy	100,000	300,000	0.0865	0.6
Ethylbenzene by EBOne	ABB Lummus/UOP	tpy	300,000	700,000	0.0085	0.6
Ethylene by ethane cracking	Generic	MMlb/y	500	2,000	9.574	0.6
Ethylene by UOP Hydro MTO	UOP/Norsk Hydro	MMlb/y	500	2,000	8.632	0.6
Ethylene: light naphtha cracker (max ethylene)	Generic	MMlb/y	1,000	2,000	16.411	0.6
Ethylene by ethane/propane cracker	Generic	MMlb/y	1,000	2,000	7.878	0.6
Ethylene by gas oil cracker	Generic	MMlb/y	1,000	2,000	17.117	0.6
Ethylene glycol via ethylene oxide hydrolysis	Shell	MMlb/y	500	1,000	5.792	0.6
Expandable polystyrene by suspension process	Generic	MMlb/y	50	100	3.466	0.6
Fischer Tropsch Process	ExxonMobil	tpy	200,000	700,000	0.476	0.6
Fluid catalytic cracking	KBR	bpd	20,000	60,000	0.210	0.6
Fluid catalytic cracking with power recovery	UOP	bpd	20,000	60,000	0.302	0.6
Gas to liquids by Syntroleum Process	Syntroleum	bpd	30,000	100,000	2.279	0.6
Gas sweetening by Amine Guard FS to pipeline spec	UOP	MMscf/d	300	800	0.386	0.6
Gasification by GE Gasification Process Maya crude	GE Energy	bpd	7,000	15,000	0.681	0.6
Gasoline desulfurization, ultra-deep by Prime-G +	Axens	bpd	7,000	15,000	0.0420	0.58
Glucose (40% Solution) by basic wet corn milling	Generic	MMlb/y	300	800	3.317	0.6
HDPE Pellets by BP Gas Phase Process	BP Amoco	MMlb/y	300	700	3.624	0.6
HDPE Pellets by Phillips Slurry Process	Phillips	MMlb/y	300	700	3.370	0.6
HDPE Pellets by Zeigler Slurry Process	Zeigler	MMlb/y	300	700	4.488	0.6
High impact polystyrene by bulk polymerization	Dow	MMlb/y	70	160	2.970	0.6
Hydrocracking by ISOCRACKING	Chevron Lummus	bpd	20,000	45,000	0.221	0.6
Hydrocracking by Unicracking, distillate	UOP	bpd	20,000	45,000	0.136	0.66
Hydrocracking	Axens	bpd	20,000	45,000	0.198	0.6
Hydrogen by steam methane reforming	Foster Wheeler	MMscf/d	10	50	1.759	0.79
Hydrotreating by Unionfining	UOP	bpd	10,000	40,000	0.0532	0.68
Isomerization by Once-through Penex	UOP	bpd	8,000	15,000	0.0454	0.6
Isomerization by Penex-Molex	UOP	bpd	8,000	15,000	0.120	0.6
Isophthalic acid by m-Xylene oxidation	Generic	MMlb/y	160	300	9.914	0.6
Isoprene via isobutylene carbonylation	IFP	MMlb/y	60	200	10.024	0.6
Isoprene by propylene dimerization and pyrolysis	Generic	MMlb/y	60	200	6.519	0.6
Linear alkylbenzene by PACOL/DeFine/PEP/Detal	UOP	MMlb/y	100	250	4.896	0.6
Linear alpha olefins	Chevron	MMlb/y	300	700	5.198	0.6

Table 6.2. Process Cost Correlations—Cont'd

Process	Licensor	Capacity Units	S_{lower}	S_{upper}	*a*	*n*
Linear alpha olefins by Linear-1	UOP	tpy	200,000	300,000	0.122	0.6
Maleic anhydride by fluid bed process	Generic	MMlb/y	70	150	7.957	0.6
Methacrylic acid by isobutylene oxidation	Generic	MMlb/y	70	150	7.691	0.6
Methanol via steam reforming & synthesis	Davy Process Tech.	tpd	3,000	7,000	2.775	0.6
m-Xylene by MX Sorbex	UOP	MMlb/y	150	300	4.326	0.6
Naphthalene by 3-stage fractional crystallizer	Generic	MMlb/y	20	50	2.375	0.6
N-Butanol from crude C4s	BASF	MMlb/y	150	300	8.236	0.6
Norbornene by Diels-Alder reaction	Generic	MMlb/y	40	90	7.482	0.6
Pentaerythritol by condensation	Generic	MMlb/y	40	90	6.220	0.6
PET resin chip with comonomer by NG3	DuPont	MMlb/y	150	300	4.755	0.6
Phenol from cumene (zeolite catalyst)	UOP/ABB Lummus	MMlb/y	200	600	6.192	0.6
Phthalic anhydride by catalytic oxidation	Generic	MMlb/y	100	200	7.203	0.6
Polycarbonate by interfacial polymerization	Generic	MMlb/y	70	150	20.680	0.6
Polyethylene terephthalate (melt phase)	Generic	MMlb/y	70	200	5.389	0.6
Polystyrene by bulk polymerization, plug flow	Generic	MMlb/y	70	200	2.551	0.6
Propylene by Oleflex	UOP	tpy	150,000	350,000	0.0943	0.6
Propylene by metathesis	Generic	MMlb/y	500	1,000	1.899	0.6
Purified terphthalic acid	EniChem/Technimont	MMlb/y	350	700	10.599	0.6
p-Xylene by Isomar and Parex	UOP	tpy	300,000	700,000	0.0230	0.6
p-Xylene by Tatoray Process	UOP	bpd	12,000	20,000	0.0690	0.6
Refined Glycerine by distillation/ adsorption	Generic	MMlb/y	30	60	2.878	0.6
Sebaccic Acid by cyclododecanone route	Sumitomo	MMlb/y	8	16	13.445	0.6
Sorbitol (70%) by continuous hydrogenation	Generic	MMlb/y	50	120	4.444	0.6
Styrene by SMART	ABB Lummus/UOP	tpy	300,000	700,000	0.0355	0.6
Vinyl acetate by Cativa Integrated Process	BP	MMlb/y	300	800	7.597	0.6
Vinyl acetate by Celanese VAntage Process	Celanese	MMlb/y	300	800	6.647	0.6
Visbreaking by coil-type visbreaker	Foster Wheeler/UOP	bpd	6,000	15,000	0.278	0.48

Note:

1. Values of *a* are in January 2006 MM$ on a U.S. Gulf Coast (USGC) basis (Nelson Farrer index = 1961.6, CE index = 478.6).
2. S_{lower} and S_{upper} indicate the bounds of the region over which the correlation can be applied.
3. *S* is based on product rate for chemicals, feed rate for fuels.
4. If the index *n* is 0.6, then the correlation is an extrapolation around a single cost point.
5. Correlations are based on data taken from *Hydrocarbon Processing* (2003, 2004a, and 2004b), except where the licensor is stated as "Generic," in which case the correlations are based on data from Nexant PERP reports (see www.Nexant.com/products for a full list of reports available).

where

C = ISBL capital cost in U.S. \$, U.S. Gulf Coast, 2000 basis;
Q = plant capacity in metric tons per year;
s = reactor conversion (=mass of desired product per mass fed to the reactor);
N = number of functional units.

(*Note:* The correlations have been updated from the original reference.)

A functional unit includes all the equipment and ancillaries needed for a significant process step or function, such as a reaction, separation, or other major unit operation. Pumping and heat exchange are not normally considered as functional units unless they have substantial cost, for example, compressors, refrigeration systems, or process furnaces.

Manufactured Products

Step-count methods such as Bridgewater's method were developed for chemical plants and do not extend well to other types of manufacturing. For large-scale production (>500,000 pieces per year) a rule of thumb is

$$\text{TCOP} = 2 \times \text{materials cost} \tag{6.10}$$

This equation can be used to make a very approximate estimate of plant cost if fixed costs and utilities can be estimated.

Example 6.1

The process for making cyclohexane by saturation of benzene consists of a feed-effluent heat exchanger, a saturation reactor, and a product stabilizer column. Estimate the cost of a plant that produces 200,000 metric tons per year (200 kMTA) of cyclohexane using the correlation in Table 6.2 and Bridgewater's method.

Solution

From Table 6.2, the cost correlation for the Axens process for benzene saturation gives

$$\begin{aligned} C &= 0.0061(S)^{0.6} \\ &= 0.0061(2 \times 10^5)^{0.6} \\ &= \underline{\underline{\$9.2\,\text{MM}}} \text{ expressed on a January 2006 USGC basis.} \end{aligned}$$

Using Bridgewater's method, we have two functional units (the reactor and product stabilizer—the heat exchanger doesn't count) and assuming that the reactor conversion is 1.0, we can substitute into equation 6.8:

$$\begin{aligned} C &= 3200 \times 2 \times (Q)^{0.675} \\ &= 3200 \times 2 \times (2 \times 10^5)^{0.675} \\ &= \$\underline{\underline{24\,\text{MM}}} \text{ expressed on a 2000 USGC basis.} \end{aligned}$$

Note that we have obtained two very different answers. Bridgewater's correlation is known to be only an approximation; however, Table 6.2 is based on data from technology vendors that may be somewhat understated. With the level of information available, it is probably safe to say that the cost is in the range \$10 MM to \$20 MM. Note also that the costs are not on the same time basis. Methods for correcting costs on different time bases will be discussed in Section 6.3.5.

6.3.3. The Factorial Method of Cost Estimation

Capital cost estimates for chemical process plants are often based on an estimate of the purchase cost of the major equipment items required for the process, the other costs being estimated as factors of the equipment cost. The accuracy of this type of estimate will depend on what stage the design has reached at the time the estimate is made and on the reliability of the data available on equipment costs. In the later stages of the project design, when detailed equipment specifications are available and firm quotes have been obtained from vendors, a relatively accurate estimation of the capital cost of the project can be made by this method.

Lang Factors

Lang (1948) proposed that the ISBL fixed capital cost of a plant is given as a function of the total purchased equipment cost by the equation

$$C = F\left(\sum C_e\right) \tag{6.11}$$

where

C = total plant ISBL capital cost (including engineering costs);
ΣC_e = total delivered cost of all the major equipment items: reactors, tanks, columns, heat exchangers, furnaces, etc.
F = an installation factor, later widely known as a Lang factor.

Lang originally proposed the following values of F, based on 1940s economics:

$F = 3.1$ for solids processing plant;
$F = 4.74$ for fluids processing plant;
$F = 3.63$ for mixed fluids-solids processing plant.

Hand (1958) suggested that better results are obtained by using different factors for different types of equipment. Examples of the factors proposed by Hand are given in Table 6.3. Hand also observed that this approach should be used only in the earliest stages of process design and in the absence of detailed design information.

Both Lang (1948) and Hand (1958) included home office costs but not offsite costs or contingency in their installation factors, so beware of double counting Engineering, Procurement, and Construction (EPC) costs when using this approach. The relative costs of materials and labor have changed substantially from when these factors were developed, and the accuracy of the correlation probably never warranted three significant figures for F. Most practitioners using this method therefore use a Lang factor of 3, 4, or 5, depending on the plant scale (larger plant = smaller factor) and type.

Table 6.3. Installation Factors Proposed by Hand (1958)

Equipment Type	Installation Factor
Compressors	2.5
Distillation columns	4
Fired heaters	2
Heat exchangers	3.5
Instruments	4
Miscellaneous equipment	2.5
Pressure vessels	4
Pumps	4

Detailed Factorial Estimates

Equation 6.11 can be used to make a preliminary estimate once the flowsheet has been drawn up and the main plant equipment has been sized. When more detailed design information is available, then the installation factor can be estimated somewhat more rigorously, by considering the cost factors that are compounded into the Lang factor individually.

The direct-cost items that are incurred in the construction of a plant, in addition to the cost of equipment, are

1. Equipment erection, including foundations and minor structural work;
2. Piping, including insulation and painting;
3. Electrical power and lighting;
4. Instruments and automatic process control (APC) systems;
5. Process buildings and structures;
6. Ancillary buildings, offices, laboratory buildings, workshops;
7. Storage for raw materials and finished product;
8. Utilities (Services), provision of plant for steam, water, air, firefighting services (if not costed separately as offsites);
9. Site preparation.

The contribution of each of these items to the total capital cost is calculated by multiplying the total purchased equipment by an appropriate factor. As with the basic Lang factor, these factors are best derived from historical cost data for similar processes. Typical values for the factors are given in several references; see Happle and Jordan (1975) and Garrett (1989). Guthrie (1974) splits the costs into the material and labor portions and gives separate factors for each.

The accuracy and reliability of an estimate can be improved by dividing the process into subunits and using factors that depend on the function of the subunits; see Guthrie (1969). In Guthrie's detailed method of cost estimation, the installation, piping, and instrumentation costs for each piece of equipment are costed separately. Detailed costing is justified only if the cost data available are reliable and the design has been taken to the point where all the cost items can be identified and included.

Table 6.4. Typical Factors for Estimation of Project Fixed Capital Cost

Item	Fluids	Process Type Fluids–Solids	Solids
1. Major equipment, total purchase cost	C_e	C_e	C_e
f_{er} Equipment erection	0.3	0.5	0.6
f_p Piping	0.8	0.6	0.2
f_i Instrumentation and control	0.3	0.3	0.2
f_{el} Electrical	0.2	0.2	0.15
f_c Civil	0.3	0.3	0.2
f_s Structures and buildings	0.2	0.2	0.1
f_l Lagging and paint	0.1	0.1	0.05
ISBL cost $C = \Sigma C_e \times$	3.3	3.2	2.5
Offsites (OS)	0.3	0.4	0.4
Design and Engineering (D&E)	0.3	0.25	0.2
Contingency (X)	0.1	0.1	0.1
Total fixed capital cost $C_{FC} = C(1 + OS)(1 + DE + X)$			
$= C\times$	1.82	1.89	1.82
$= \Sigma C_e \times$	6.00	6.05	4.55

Gerrard (2000) gives factors for individual pieces of equipment as a function of equipment cost and complexity of installation.

Typical factors for the components of the capital cost are given in Table 6.4. These can be used to make an approximate estimate of capital cost using equipment cost data published in the literature.

The installation factors given in Tables 6.3 and 6.4 are for plants built from carbon steel. When more exotic materials are used, then a materials factor f_m should also be introduced:

$$f_m = \frac{\text{purchased cost of item in exotic material}}{\text{purchased cost of item in carbon steel}} \tag{6.12}$$

Note that f_m is not equal to the ratio of the metal prices, as the equipment purchased cost also includes labor costs, overheads, fabricator's profit, and other costs that do not scale directly with metal price. Equation 6.11 can then be expanded for each piece of equipment to give

$$C = \sum_{i=1}^{i=M} C_{e,i,CS}[(1 + f_p)f_m + (f_{er} + f_{el} + f_i + f_c + f_s + f_l)] \tag{6.13}$$

or

$$C = \sum_{i=1}^{i=M} C_{e,i,A}[(1 + f_p) + (f_{er} + f_{el} + f_i + f_c + f_s + f_l)/f_m] \tag{6.14}$$

where

$C_{e,i,CS}$ = purchased equipment cost of equipment i in carbon steel;
$C_{e,i,A}$ = purchased equipment cost of equipment i in alloy;
M = total number of pieces of equipment;
f_p = installation factor for piping;
f_{er} = installation factor for equipment erection;
f_{el} = installation factor for electrical work;
f_i = installation factor for instrumentation and process control;
f_c = installation factor for civil engineering work;
f_s = installation factor for structures and buildings;
f_l = installation factor for lagging, insulation, or paint.

Failure to properly correct installation factors for materials of construction is one of the most common sources of error with the factorial method. Typical values of the materials factor for common engineering alloys are given in Table 6.5.

Summary of the Factorial Method

Many variations on the factorial method are used. The following method can be used with the data given in this chapter to make a quick, approximate estimate of the fixed capital investment needed for a project:

1. Prepare material and energy balances, draw up preliminary flowsheets, size major equipment items, and select materials of construction.
2. Estimate the purchased cost of the major equipment items. See the next section.
3. Calculate the ISBL installed capital cost, using the factors given in Table 6.4 and correcting for materials of construction using equation 6.13 or 6.14 with the materials factors given in Table 6.5.
4. Calculate the OSBL, engineering, and contingency costs using the factors given in Table 6.4.
5. The sum of ISBL, OSBL, engineering, and contingency costs is the fixed capital investment.

Table 6.5. Materials Cost Factors, f_m, Relative to Plain Carbon Steel

Material	f_m
Carbon steel	1.0
Aluminum and bronze	1.07
Cast steel	1.1
304 stainless steel	1.3
316 stainless steel	1.3
321 stainless steel	1.5
Hastelloy C	1.55
Monel	1.65
Nickel and Inconel	1.7

6. Estimate the working capital as a percentage of the fixed capital investment; 10 to 20% is typical (or better, calculate it from the cost of production if this has been estimated—see Section 6.4).
7. Add the fixed and working capital to get the total investment required.

6.3.4. Estimating Purchased Equipment Costs

The factorial method of cost estimation is based on purchased equipment costs and therefore requires good estimates for equipment costs. Costs of single pieces of equipment are also often needed for minor revamp and de-bottlenecking projects.

The best source of purchased equipment costs is recent data on actual prices paid for similar equipment. Engineers working for Engineering, Procurement, and Construction (EPC) companies (often referred to as *contractors*) have access to large amounts of high-quality data, as these companies carry out many projects globally every year. Engineers working in operating companies may have access to data from recent projects, but unless they work for a large company that carries out many capital projects, they are unlikely to be able to develop and maintain current cost correlations for more than a few basic equipment types. Most large companies recognize the difficulty of making reliable cost estimates and employ a few experienced cost engineering specialists who collect data and work closely with the EPC companies on project budgets.

Actual prices paid for equipment and bulk items may differ substantially from catalog or list prices, depending on the purchasing power of the contractor or client and the urgency of the project. Discounts and surcharges are highly confidential business information and will be closely guarded even within EPC companies.

Those design engineers who are outside the EPC sector and do not have the support of a cost-estimating department must rely on cost data from the open literature or use cost-estimating software. The most widely used software for estimating chemical plant costs is the ICARUS^{TM} suite of tools licensed by Aspen Technology Inc. ICARUS^{TM} does not use the factorial method, but instead estimates equipment costs, bulk costs, and installation costs from the costs of materials and labor, following the practice used by cost engineers for detailed estimating. The models in ICARUS^{TM} were developed by a team of cost engineers based on data collected from EPC companies and equipment manufacturers. The models are updated annually. The ICARUS Process Estimator software is included in the standard Aspen/Hsysys academic package and is available in most universities. The ICARUS^{TM} software can give reasonably good estimates when used properly and is described in more detail in Section 6.3.8.

There is an abundance of equipment cost data and cost correlations in the open literature, but much of it is of very poor quality. The relationship between size and cost given in equations 6.6 and 6.7 can also be used for equipment if a suitable size parameter is used. If the size range spans several orders of magnitude, then log-log plots usually give a better representation of the relationship than simple equations.

Some of the most reliable information on equipment costs can be found in the professional cost engineering literature. Correlations based on recent data are occasionally published in *Cost Engineering*, which is the journal of the Association for the Advancement of Cost Engineering International (AACE International). AACE

International also has an excellent website, www.aacei.org, which has cost models that members can use. There is also an extensive listing of other web resources for cost estimating at www.aacei.org/resources. The U.K. Association of Cost Engineers (ACostE) publishes the journal *The Cost Engineer* and also prints a guide to capital cost estimating (Gerrard, 2000), which gives cost curves for the main types of process equipment based on recent data. The prices are given in British pounds sterling on a U.K. basis, but this book is useful for making estimates of prices in Northwest Europe. The International Cost Engineering Council website (www.icoste.org) provides links to 46 international cost engineering societies, several of which maintain databases of local costs.

Many cost correlations can be found in chemical engineering textbooks; for example, Douglas (1988), Garrett (1989), Turton et al. (2003), Peters et al. (2003), and Ulrich and Vasudevan (2004). The references for such correlations should always be checked very carefully. When they are properly referenced, they are usually found to be based on data published by Guthrie (1969, 1974) and updated using either cost indices (as described in Section 6.3.6) or a few recent data points. Guthrie's correlations were reasonably good when published, but there have been substantial changes in the relative contributions of material and fabrication costs of most process equipment since then. Academic authors usually do not have access to sufficient high-quality cost data to be able to make reliable correlations, and most of the academic correlations predict lower costs than would be obtained using Aspen ICARUS$^{\text{TM}}$ or other detailed estimating methods. These correlations are adequate for the purposes of university design projects but should not be used in real projects. It is to be hoped that the authors of these publications will benchmark the correlations against Aspen ICARUS$^{\text{TM}}$ in future editions, which will improve the accuracy of the correlations and make them more useful to those who do not have access to costing software.

Detailed estimates are usually made by costing the materials and labor required for each item in the plant, making a full analysis of the work breakdown structure (WBS) to arrive at an accurate estimate of the labor. This method must be followed whenever cost or price data are not available, for example, when making an estimate of the cost of specialized equipment that cannot be found in the literature. For example, a reactor design is usually unique for a particular process, but the design can be broken down into standard components (vessels, heat exchange surfaces, spargers, agitators, etc.), the cost of which can be found in the literature and used to build up an estimate of the reactor cost. This method is described by Dysert (2007) and Woodward and Chen (2007) in sections of the AACE International training manual (Amos, 2007). Breakdowns of the materials and labor components for many types of process equipment are given by Page (1996). Pikulik and Diaz (1977) give a method of costing major equipment items from cost data on the basic components: shells, heads, nozzles, and internal fittings. Purohit (1983) gives a detailed procedure for estimating the cost of heat exchangers.

A large amount of vendor information is now available online and can easily be found using any of the major search engines or by starting from directories such as www.purchasing.com. Online costs are usually manufacturers' catalog prices for small order quantities. Large order sizes (as filled by contractors) are often heavily discounted. Items requiring special fabrication—for example, large vessels or compressors—may experience discounts or surcharges depending on the state of the manufacturer's order books and the purchasing power of the customer.

For those design engineers who lack access to reliable cost data or estimating software, the correlations given in Table 6.6 can be used for preliminary estimates. The correlations in Table 6.6 are of the form

$$C_e = a + bS^n \tag{6.15}$$

Table 6.6. Purchased Equipment Cost for Common Plant Equipment

Equipment	**Units for Size, S**	S_{Lower}	S_{Upper}	a	b	n	**Note**
Agitators & mixers							
Propeller	driver power, kW	5.0	75.0	4,300	1,920	0.8	
Spiral ribbon mixer	driver power, kW	5.0	35.0	11,000	420	1.5	
Static mixer	Liters/s	1.0	50.0	780	62	0.8	
Boilers							
Packaged, 15 to 40 bar	kg/h steam	5,000.0	200,000.0	4,600	62	0.8	
Field erected, 10 to 70 bar	kg/h steam	20,000.0	800,000.0	−90,000	93	0.8	
Centrifuges							
High-speed disk	diameter, m	0.26	0.49	63,000	260,000	0.8	
Atmospheric suspended basket	power, kW	2.0	20.0	37,000	1,200	1.2	
Compressors							
Blower	m^3/h	200.0	5,000.0	4,200	27	0.8	
Centrifugal	driver power, kW	132.0	29,000.0	8,400	3,100	0.6	
Reciprocating	driver power, kW	100.0	16,000.0	240,000	1.33	1.5	
Conveyors							
Belt, 0.5 m wide	length, m	10.0	500.0	21,000	340	1.0	
Belt, 1.0 m wide	length, m	10.0	500.0	23,000	575	1.0	
Bucket elevator, 0.5 m bucket	height, m	10.0	35.0	14,000	1,450	1.0	
Crushers							
Reversible hammer mill	tonne/h	20.0	400.0	400	9,900	0.5	
Pulverizers	kg/h	200.0	4,000.0	3,000	390	0.5	
Crystallizers							
Scraped surface crystallizer	length, m	7.0	280.0	41,000	40,000	0.7	
Distillation columns							
See pressure vessels, packing, and trays							
Dryers							
Direct contact rotary	area, m^2	11.0	180.0	−7,400	4,350	0.9	1
Pan	area, m^2	1.5	15.0	−5,300	24,000	0.5	2
Spray dryer	evap rate kg/h	400.0	4,000.0	190,000	180	0.9	
Evaporators							
Vertical tube	area, m^2	11.0	640.0	17,000	13,500	0.6	
Agitated falling film	area, m^2	0.5	12.0	29,000	53,500	0.6	

(*continued*)

Table 6.6. Purchased Equipment Cost for Common Plant Equipment—Cont'd

Equipment	**Units for Size, *S***	S_{Lower}	S_{Upper}	***a***	***b***	***n***	**Note**
Exchangers							
U-tube shell and tube	area, m^2	10.0	1,000.0	10,000	88	1.0	
Floating head shell and tube	area, m^2	10.0	1,000.0	11,000	115	1.0	
Double pipe	area, m^2	1.0	80.0	500	1,100	1.0	
Thermosyihon reboiler	area, m^2	10.0	500.0	13,000	95	1.0	
U-tube Kettle reboiler	area, m^2	10.0	500.0	14,000	83	1.0	
Plate and frame	area, m^2	1.0	180.0	1,100	850	0.4	3
Filters							
Plate and frame	capacity, m^3	0.4	1.4	76,000	54,000	0.5	
Vacuum drum	area, m^2	10.0	180.0	−45,000	56,000	0.3	
Furnaces							
Cylindrical	duty, MW	0.2	60.0	53,000	69,000	0.8	
Box	duty, MW	30.0	120.0	7,000	71,000	0.8	
Packings							
304 ss Raschig rings	m^3			0	3,700	1.0	
Ceramic intalox saddles	m^3			0	930	1.0	
304 ss Pall rings	m^3			0	4,000	1.0	
PVC structured packing	m^3			0	250	1.0	
304 ss structured packing	m^3			0	3,200	1.0	4
Pressure vessels							
Vertical, cs	shell mass, kg	150.0	69,200.0	−400	230	0.6	5
Horizontal, cs	shell mass, kg	250.0	69,200.0	−2,500	200	0.6	
Vertical, 304 ss	shell mass, kg	90.0	124,200.0	−10,000	600	0.6	5
Horizontal, 304 ss	shell mass, kg	170.0	114,000.0	−15,000	560	0.6	
Pumps and drivers							
Single-stage centrifugal	flow Liters/s	0.2	500.0	3,300	48	1.2	
Explosion-proof motor	power, kW	1.0	2,500.0	920	600	0.7	
Condensing steam turbine	power, kW	100.0	20,000.0	−19,000	820	0.8	
Reactors							
Jacketed, agitated	volume, m^3	0.5	100.0	14,000	15,400	0.7	
Jacketed, agitated, glass-lined	volume, m^3	0.5	25.0	13,000	34,000	0.5	
Tanks							
Floating roof	capacity, m^3	100.0	10,000.0	53,000	2,400	0.6	
Cone roof	capacity, m^3	10.0	4,000.0	5,700	700	0.7	
Trays							
Sieve trays	diameter, m	0.5	5.0	100	120	2.0	6
Valve trays	diameter, m	0.5	5.0	130	146	2.0	6
Bubble cap trays	diameter, m	0.5	5.0	200	240	2.0	6
Utilities							
Cooling tower & pumps	flow liters/s	100.0	10,000.0	61,000	650	0.9	7
Packaged mechanical refrigerator	evaporator duty, kW	50.0	1,500.0	4,900	720	0.9	
Water ion exchange plant	flow m^3/h	1.0	50.0	6,200	4,300	0.7	

where

C_e = purchased equipment cost on a U.S. Gulf Coast basis, January 2006 (CE index = 478.6, NF refinery inflation index = 1961.6);
a, b = cost constants in Table 6.6;
S = size parameter, units given in Table 6.6;
n = exponent for that type of equipment.

The correlations in Table 6.6 are valid only between the lower and upper values of S indicated. The prices are all for carbon steel equipment except where noted in the table.

Notes:

1. Direct heated;
2. Gas fired;
3. Type 304 stainless steel;
4. With surface area 350 m^2/m^3;
5. Not including heads, ports, brackets, internals, etc. (see Chapter 13 for how to calculate wall thickness);
6. Cost per tray, based on a stack of 30 trays;
7. Field assembly;
8. All costs are U.S. Gulf Coast basis, January 2006 (CE index = 478.6, NF refinery inflation index = 1961.6).

Example 6.2

A plant modification has been proposed that will allow recovery of a byproduct. The modification consists of adding the following equipment:

Distillation column, height 30 m, diameter 3 m, 50 sieve trays, operating pressure 10 bar;
U-tube heat exchanger, area 60 m^2;
Kettle reboiler, area 110 m^2;
Horizontal pressure vessel, volume 3 m^3, operating pressure 10 bar;
Storage tank, volume 50 m^3;
Two centrifugal pumps, flow rate 3.6 m^3/h, driver power 500 W;
Three centrifugal pumps, flow rate 2.5 m^3/h, driver power 1 kW (two installed plus one spare).

Estimate the installed ISBL capital cost of the modification if the plant is to be built from type 304 stainless steel. Estimate the cost using both Hand's method and the factors given in Table 6.4.

Solution

The first step is to convert the units to those required for the correlations and determine any missing design information. The distillation column can be costed as a combination of a vertical pressure vessel and internals. For both pressure vessels, we need to know the wall thickness. The details of how to calculate vessel wall thickness in accordance with the ASME Boiler and Pressure Vessel Code are given in Section 13.5, and the equation to use is equation 13.41.

The design pressure of the vessels should be 10% above the operating pressure (see Chapter 13), so the design pressure is 11 bar or roughly $1.1 \times 10^6\,\text{N/m}^2$. The maximum allowable stress for type 304 stainless steel at 500°F (260 °C) is 12.9 ksi or roughly $89\,\text{N/mm}^2$ (Table 13.2). Assuming the welds will be fully radiographed, the weld efficiency is 1.0. Substituting in equation 13.41 for the column wall thickness, t_w, then gives

$$
\begin{aligned}
t_w &= \frac{1.1 \times 10^6 \times 3}{(2 \times 89 \times 10^6 \times 1.0) - (1.2 \times 1.1 \times 10^6)} \qquad (13.41)\\
&= 0.0187\,\text{m, say } 20\,\text{mm}
\end{aligned}
$$

We can now calculate the shell mass, using the density of 304 stainless steel ($= 8{,}000\,\text{kg/m}^3$, from Table 7.2).

$$\text{Shell mass} = \pi D_c L_c t_w \rho$$

where

D_c = vessel diameter, m;
L_c = vessel length, m;
t_w = wall thickness, m;
ρ = metal density, kg/m^3.

So the shell mass for the distillation column is

$$\text{Shell mass} = \pi \times 3.0 \times 30 \times 0.02 \times 8{,}000 = 46{,}685\,\text{kg}$$

For the horizontal pressure vessel, we need to convert the volume into a length and diameter. Assuming that the vessel is a cylinder with $L_c = 2D_c$, then we can follow the same method as for the column and find $t_w = 8$ mm and shell mass = 636 kg.

Using the correlations in Table 6.6, we obtain the following purchase costs for the stainless steel pressure vessels:

Distillation column shell, cost $= -10{,}000 + 600(46685)^{0.6} = \$370{,}000$
Horizontal pressure vessel, cost $= -15{,}000 + 560(636)^{0.6} = \$12{,}000$

For the remaining equipment, we obtain the following purchase costs from the correlations in Table 6.6 based on carbon steel construction:

Distillation column trays, cost per tray $= 100 + 120(3.0)^2$ = \$1,180
Cost for 50 trays = \$59,000
U-tube heat exchanger, cost = 10,000 + 88 (60) = \$15,300
Kettle reboiler, cost = 14,000 + 83 (110) = \$23,100
Storage tank (conical head), cost $= 5{,}700 + 700(50)^{0.7}$ = \$16,500
Centrifugal pump, $3.6\,\text{m}^3/\text{h} = 1\,\text{L/s}$, so:
  Cost each $= 3{,}300 + 48(1.0)^{1.2} = \$3{,}350$, cost for two pumps = \$6,700

Driver (electric motor) cost each $= 920 + 600(0.5)^{0.7}$ = \$1,300
Cost for two drivers = \$2,600
Centrifugal pump, 2.5 m^3/h so: = 0.694 L/s,
Cost each $= 3{,}300 + 48(0.694)^{1.2}$ = \$3,330, cost for three = \$9,990
Driver (electric motor) cost each $= 920 + 600(1.0)^{0.7}$ = \$1,520
Cost for three drivers = \$4,560

Note that the pumps and drivers are at the lower end of the range of validity of the cost correlations, but their costs are small compared to the other costs, and the error introduced is therefore negligible given the overall accuracy of ±30%.

Following Hand's method, the installed cost of the distillation column is then

$$C = 4 \times 370{,}000 = \$1{,}480{,}000$$

The cost of the trays can be converted to type 304 stainless steel by multiplying by the appropriate materials factor from Table 6.5, giving

$$C = 1.3 \times 59{,}000 = \$76{,}700$$

This then gives a total cost for the column plus internals of 1,480,000 + 76,700 = \$1,560,000.

The installed cost of the horizontal pressure vessel is 4 × 12,000 = \$48,000.

The installed cost for the exchangers and storage tank in carbon steel construction is

$$C = 3.5(15{,}300 + 23{,}100) + 2.5(16{,}500) = \$176{,}000$$

so the cost in type 304 stainless steel is 1.3 × 176,000 = \$229,000.

For the pumps, we need to add the cost of the pump and driver before determining the installed cost. Only the cost of the pump needs to be converted to stainless steel. For the first set of pumps

$$C = 4 \times (2{,}600 + (1.3 \times 6{,}700)) = \$45{,}200.$$

For the second set of pumps, only two are installed (the other is a warehouse spare), so the total installed cost is

$$C = (1.3 \times 3{,}330) + 1{,}520 + (4 \times 2 \times (1{,}520 + (1.3 \times 3{,}330))) = \$52{,}600.$$

The total installed ISBL cost of the plant is then

$$C = 1{,}560{,}000 + 48{,}000 + 229{,}000 + 45{,}200 + 52{,}600 = \$1{,}930{,}000$$

or $\underline{\underline{\$1.9\,\text{MM} \pm 30\%}}$ within the accuracy of the method.

If, instead, we use the factors given in Table 6.4, then using equation 6.13, the installed cost for the exchangers, tank, and pumps is equal to

$$C = (15{,}300 + 23{,}100 + 16{,}500 + 6{,}700 + 6{,}660)[(1 + 0.8) \times 1.3 + (0.3 + 0.3 + 0.2 + 0.3 + 0.2 + 0.1)]$$

$$C = (68{,}260)[3.74] = \$255{,}300.$$

The installed cost for the pressure vessels and pump drivers (which do not require a materials conversion factor) is

$$\begin{aligned} C &= (370{,}000 + 12{,}000 + 2{,}600 + 3{,}040)[1 + 0.8 + 0.3 \\ &\quad + 0.3 + 0.2 + 0.3 + 0.2 + 0.1] \\ C &= (387{,}640)[3.2] = \$1{,}240{,}500. \end{aligned}$$

In addition to this, we require the cost of the trays in stainless steel and the cost of the spare pump and driver:

$$C = 1{,}520 + 1.3(59{,}000 + 3{,}330) = \$82{,}500.$$

The total installed ISBL cost of the plant is then

$$\begin{aligned} C &= 255{,}300 + 1{,}240{,}500 + 82{,}500 = \$1{,}580{,}000 \\ \text{or} &\quad \underline{\underline{\$1.6\,\text{MM} \pm 30\%}} \text{ within the accuracy of the method.} \end{aligned}$$

Note that although the answers obtained by the two methods are different, each is well within the range of accuracy of the other. Both estimates should be stated as being on a U.S. Gulf Coast basis, January 2006, as this is the basis for the correlations in Table 6.6.

6.3.5 Cost Escalation

All cost-estimating methods use historical data and are themselves forecasts of future costs. The prices of the materials of construction and the costs of labor are subject to inflation. Some method has to be used to update old cost data for use in estimating at the design stage and to forecast the future construction cost of the plant.

The method usually used to update historical cost data makes use of published cost indices. These relate present costs to past costs, and are based on data for labor, material, and energy costs published in government statistical digests.

$$\text{Cost in year A} = \text{Cost in year B} \times \frac{\text{Cost index in year A}}{\text{Cost index in year B}} \tag{6.16}$$

To get the best estimate, each job should be broken down into its components, and separate indices should be used for labor and materials. It is often more convenient to use the composite indices published for various industries in the trade journals. These are weighted average indices combining the various components of costs in proportions considered typical for the particular industry.

A composite index for the United States process plant industry is published monthly in the journal *Chemical Engineering*; this is the Chemical Engineering Plant Cost Index (CEPCI), usually referred to as the CE index. *Chemical Engineering* also publishes the Marshall and Swift index (M&S equipment cost index).

For oil refinery and petrochemicals projects, the *Oil and Gas Journal* publishes the Nelson-Farrer Refinery Construction Index (NF index). This index is updated monthly, and indices for 40 types of equipment are updated quarterly. The Nelson-Farrer index is on a U.S. Gulf Coast basis rather than U.S. average and is more reliable than the CE index for the types of equipment used in hydrocarbon processing.

The journal *Engineering News Record* publishes a monthly construction cost index. This is based on civil engineering projects and is sometimes used for updating offsite costs. This index has been published since 1904 and is the oldest of all the indices.

For international projects, the journal *Process Engineering* publishes monthly cost indices for several countries, including the United States, United Kingdom, Japan, Australia, and many of the EU countries.

All cost indices should be used with caution and judgment. They do not necessarily relate the true make-up of costs for any particular piece of equipment or plant, nor the effect of supply and demand on prices. The longer the period over which the correlation is made, the more unreliable the estimate. Between 1970 and 1990, prices rose dramatically. Prices then grew at a more or less steady 2 to 3% per year until 2003, when high demand for fuels projects and high energy prices caused another period of steeper price inflation. The major cost indices are plotted in Figure 6.2a. Figure 6.2b shows the same data plotted relative to the 1990 value of each index. Figure 6.2b clearly shows the NF index starting to accelerate ahead of the M&S and CE indices as fuels sector activity led price inflation from 2000 onward.

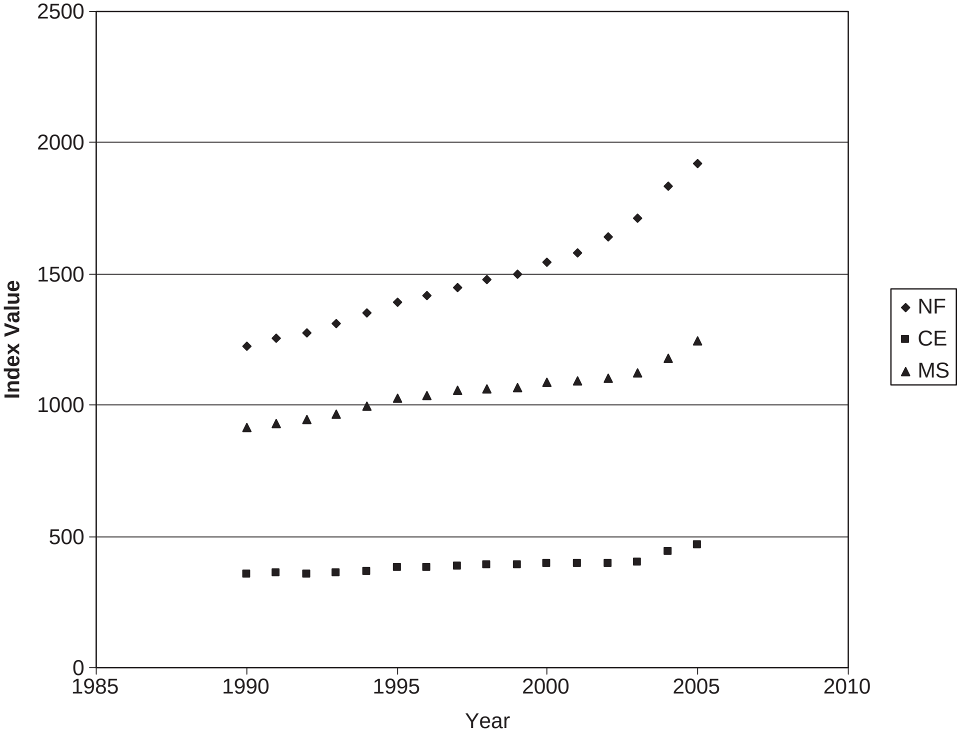


Figure 6.2a. Variation of major cost indices.

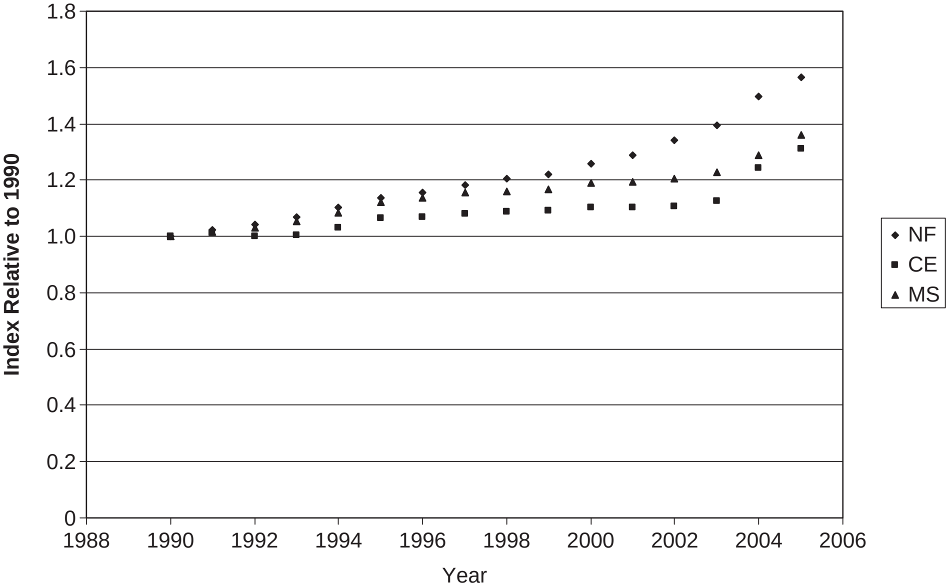


Figure 6.2b. Variation of major cost indices relative to 1990 = 1.0.

To estimate the future cost of a plant, some prediction has to be made of the future annual rate of inflation. This can be based on the extrapolation of one of the published indices, tempered by the engineer's own assessment of what the future may hold. Inflation is difficult to forecast, and allowance for inflation is often included in the contingency charges added to the project cost.

Example 6.3

The purchased cost of a shell and tube heat exchanger, carbon shell, 316 stainless steel tubes, heat transfer area 500 m^2, was \$64,000 in January 2003; estimate the cost in January 2008. Use the M&S Equipment Cost Index.

Solution

From Figure 6.2a (or by looking up the index in *Chemical Engineering*):

$$\text{Index in } 2003 = 1123.6$$
$$\text{Index in } 2005 = 1244.5$$

By extrapolation from the period 2003 to 2005, the M&S index for 2008 will be about 1426.

So, estimated cost in January 2008 = \$64,000 × 1426/1124 = $\underline{\underline{\$81,000.}}$

6.3.6. Location Factors

Most plant and equipment cost data are given on a U.S. Gulf Coast (USGC) or Northwest Europe (NWE) basis, as these are historically the main centers of the chemical industry, for which the most data are available. The cost of building a plant in any other location will depend on

- Local fabrication and construction infrastructure;
- Local labor availability and cost;
- Costs of shipping or transporting equipment to site;
- Import duties or other local tariffs;
- Currency exchange rates, which affect the relative cost of locally purchased items such as bulk materials, when converted to a conventional pricing basis such as U.S. dollars.

These differences are often captured in cost estimating by using a location factor:

$$\text{Cost of plant in location A} = \text{cost of plant on USGC} \times LF_A \tag{6.17}$$

where LF_A = location factor for location A relative to USGC basis.

Location factors for international locations are a strong function of currency exchange rates and hence fluctuate with time. Cran (1976a, b), Bridgewater (1979), Soloman (1990), and Gerrard (2000) give location factors for international locations from which this variation can be seen. It can be argued that as a result of globalization, all international installation factors are trending closer to 1.0 (Gerrard, 2000). Location factors within a country are somewhat easier to predict, and Bridgewater (1979) suggested a simple rule of thumb: add 10% for every 1,000 miles from the nearest major industrial center.

Table 6.7 gives sample location factors. These are based on data from Aspen Richardson's *International Construction Cost Factor Location Manual* (2003). More recent versions of this manual can be found by searching for Richardson Engineering Services at www.aspentech.com. The values in Table 6.7 give costs on a local basis in U.S. dollars. The location factors in Table 6.7 are based on 2003 data and can be updated by dividing by the ratio U.S. dollar/local currency in 2003 and multiplying by the ratio U.S. dollar/local currency in the year of interest. If a cost estimate for a future year is being made, then currency variation will have to be forecasted.

Example 6.4

The cost of constructing a 30,000 metric ton per year (30 kMTA) acrolein plant was estimated as \$80 million (\$80 MM) on a 2006 U.S. Gulf Coast basis. What would be the cost in U.S. dollars on a 2006 Germany basis?

Solution

From Table 6.7, the 2003 location factor for Germany was 1.11.

The exchange rate in 2003 averaged about €1 = \$1.15 and in 2006 it averaged about €1 = \$1.35.

The 2006 location factor for Germany is thus $1.11 \times 1.35/1.15 = 1.30$.

The cost of building the acrolein plant in Germany in 2006 is \$80 MM × 1.30 = $\underline{\underline{\$104\text{ MM.}}}$

Table 6.7. Location Factors

Country	Region	Location Factor
United States	Gulf Coast	1.00
	East Coast	1.04
	West Coast	1.07
	Midwest	1.02
Canada	Ontario	1.00
	Fort McMurray	1.60
Mexico		1.03
Brazil		1.14
China	imported	1.12
	indigenous	0.61
Japan		1.26
SE Asia		1.12
Australia		1.21
India		1.02
Middle East		1.07
France		1.13
Germany		1.11
Italy		1.14
Netherlands		1.19
Russia		1.53
United Kingdom		1.02

6.3.7. Offsite Costs

Improvements to the site infrastructure are almost always needed when a new plant is added to a site or a major expansion is carried out. The cost of such improvements is known as the offsite or OSBL investment, as described in Section 6.2.1.

In the early stages of designing a new process, the offsite requirements are usually not precisely known and an allowance for offsite costs is made by assuming that they will be a ratio of the ISBL investment. A typical number is 20 to 50% of ISBL investment, depending on the process and site conditions. As the design details are established and the requirements for utilities such as steam, electricity, and cooling water are determined, the site requirements can also be determined. Potential modifications to the infrastructure can then be designed to accommodate the new plant.

Many of the offsite items are designed as ‘‘packaged’’ plants or systems that are purchased from specialized suppliers. In some cases, the supplier may even offer an *over-the fence* contract, in which the supplier builds, owns, and operates the offsite plant and contracts to supply the site with the desired utility stream or service. Over-the-fence contracts are widely used for industrial gases such as nitrogen, oxygen, and hydrogen, and most plants also import electricity from the local utility company. Over-the-fence contracts for steam, cooling water, and effluent treatment are less common, but are sometimes used in smaller plants or where several companies share a site.

The question of whether to build a self-contained infrastructure for a plant or contract for offsite services is an example of a *make or buy* problem. The over-the-fence price will usually be higher than the cost of producing the utility or service internally, since the supplier needs to make a profit and recover its capital investment. On the other hand, contracting for the service reduces the project capital investment and fixed costs, since the supplier must take on the costs of labor, maintenance, and overhead. The make or buy decision is usually made by comparing annualized costs, as described in Section 6.7.6. Correlations for costs of utility plants and other offsites are given in the sources listed in Section 6.3.4.

6.3.8. Computer Tools for Cost Estimation

It is difficult for engineers outside the EPC sector to collect recent cost data from a large set of real projects and maintain accurate and up-to-date cost correlations. Instead, the most common method for making preliminary estimates in industry is to use commercial cost-estimating software.

A wide variety of cost-estimating programs is available. They include CostLink/CM (Building Systems Design, Inc.), Cost Track^{TM} (OnTrack Engineering Ltd.), ICARUS^{TM} (Aspen Technology Inc.), PRISM Project Estimator (ARES Corp.), Success Estimator (U.S. Cost), Visual Estimator (CPR International Inc.), WinEst$^{®}$ (Win Estimator$^{®}$), and others that can be found by searching on the web or looking at the listings provided by AACE International at www.aacei.org. The discussion in this section will focus on Aspen Technology's ICARUS Process Evaluator^{TM} (IPE) software, as this is probably the most widely used program and is the one with which the author is most familiar. This software is made available as part of the standard Aspen/Hysys academic license and so is available in any university that licenses Aspen Technology products. It is also available in most chemical companies.

The ICARUS^{TM} cost-estimating tools are simple to use and give quick, defensible estimates without requiring a lot of design data. Design information can be uploaded from any of the major flowsheet simulation programs, or else entered manually in the ICARUS^{TM} programs. The program allows the design to be updated as more information on design details becomes available so that a more accurate estimate can be developed. Costs can be estimated for a whole plant or for one piece of equipment at a time. Over 250 types of equipment are included, and they can be designed in a broad range of materials, including U.S., U.K., German, and Japanese standard alloys.

The ICARUS^{TM} software uses a combination of mathematical models and expert systems to develop cost estimates. Costs are based on the materials and labor required (following the practice used for detailed estimates) rather than installation factors. If design parameters are not specified by the user, then they are calculated or set to default values by the program. The user should always review the design details carefully to make sure that the default values make sense for the application. If any values are not acceptable, they can be manually adjusted and a more realistic estimate can be generated.

A detailed description of how to run the ICARUS^{TM} software is beyond the scope of this book and is unnecessary, as the program is extensively documented (AspenTech 2002a, 2002b). Some of the common issues that arise in using the software are discussed next. These or similar problems are also faced when using other cost-estimating programs.

Mapping Simulation Data

Instructions on loading data from a process simulation are given in the *Aspen ICARUS Process Evaluator*$^{\text{TM}}$ *User's Guide* (AspenTech, 2002a). When a simulator report file is loaded, IPE generates a block-flow diagram with each unit operation of the simulation shown as a block. These blocks must then be "mapped" to Icarus project components (pieces of equipment or bulk items).

Unless the user specifies otherwise, each simulator block is mapped to a default Icarus project component. The mapping defaults need to be understood properly, as large errors can be introduced if unit operations are mapped incorrectly. The default mapping specifications are given in Section 3 of the user's guide (AspenTech, 2002a). Some mappings that commonly cause problems include

1. *Reactors:* Plug-flow reactor models (PLUG in Hysys and ProII, RPLUG in AspenPlus) are mapped to a packed tower, which is fine for fixed-bed catalytic reactors, but not for other types of plug-flow reactors. All other reactor models (Gibbs, stoichiometric, equilibrium, and yield) are mapped to agitated tank reactors. Reactors that are not suitable for these mappings can be mapped to other Icarus project components or set up as user models (see below).
2. *Heaters, coolers, and heat exchangers:* The default mapping for all heat transfer equipment is the floating-head heat exchanger. ICARUS$^{\text{TM}}$ contains several different heat exchanger types, including a generic TEMA heat exchanger that can be customized to the other types, as well as fired heater and air cooler components. It is often worthwhile to change the default mapping to the TEMA exchanger to allow the exchangers to be customized in ICARUS$^{\text{TM}}$.
3. *Distillation columns:* The simulator column models include not just the column itself, but also the reboiler, condenser, overhead receiver drum, and reflux pump (but not bottoms pump). ICARUS$^{\text{TM}}$ has 10 possible configurations to which a column can be mapped. Alternatively, the column can be mapped to a packed or trayed tower, and the ancillary items can be created as separate Icarus project components.
4. *Dummy items:* Process simulations often contain models of items that are not actual plant equipment (see Chapter 4). For example, heat exchangers are sometimes modeled as a series of heaters and coolers linked by a calculator block as a means of checking for internal pinch points or allowing for heat losses to ambient. When the simulation is mapped into ICARUS$^{\text{TM}}$, dummy items should be excluded from the mapping process. In the preceding example, only the heaters should be mapped, so as to avoid double counting the heat transfer area.

The default mapping can be edited by right-clicking on "Project Component Map Specifications" in the Project Basis/Process Design folder. A simulator model can be excluded from the mapping by selecting the item and then selecting "Delete all mappings." New mappings can be specified by selecting a simulator item and adding a new mapping.

To map loaded simulator data, click the map button on the toolbar (which maps all items) or right-click on an area or plant item in the process view window (which allows items to be mapped individually). If individual items are selected, then the user is given an option to use simulator data to override the default mapping in the Component Map Specs file. This is useful for heat exchangers and other equipment where the simulator allows the equipment type to be specified.

Design Factors

All good designs include an appropriate degree of overdesign to allow for uncertainties in the design data and method (see Chapter 1). For some equipment, the design factor or margin is specified by design codes and standards, for example, in the design of pressure vessels, as described in Chapter 13. In other cases, the design engineer must specify the degree of overdesign or margin based on experience, judgment, or company policy.

The equipment sizes calculated by a process simulator will be at the design flow rate unless a higher throughput was specified by the user, and hence include no design margin. The IPE software adds an ''equipment design allowance'' to the equipment cost to allow for the design factor that will be introduced when the equipment is designed in detail. The equipment design allowance is based on the process description as follows:

New and unproven process	15%
New process	10%
Redesigned process	7%
Licensed process	5%
Proven process	3%

The process description is entered by right-clicking on ''General Specs'' in the Project Basis/Basis for Capital Costs folder.

The equipment design allowance is applied only to system-developed costs. If different design margins are needed for different equipment types, then the default should be set to ''Proven Process'' and the equipment can then be oversized appropriately. Design margins can also be added to components using the IPE custom model tool. Care should be taken to avoid adding more design margins than is necessary.

Pressure Vessels

When an estimator costs pressure vessels such as reactors and distillation columns, care must be taken to ensure that the wall thickness is adequate. The default method in IPE calculates the wall thickness required based on the ASME Boiler and Pressure Vessel Code Section VIII Division 1 method for the case where the wall thickness is governed by containment of internal pressure (see Chapter 13 for details of this method). If other loads govern the design, then the IPE software can significantly underestimate the vessel cost. This is particularly important for vessels that operate at pressures below 5 bara, where the required wall thickness is likely to be influenced by dead weight loads and bending moments from the vessel supports, and for tall vessels such as distillation columns and large packed-bed reactors, where wind loads may govern the thickness. Similarly, if the vessel is designed under a different section of the Boiler and Pressure Vessel Code, which is usually the case for vessels operated at high pressures, then IPE can overestimate the vessel cost. It is important to always remember to enter the design pressure and temperature of the vessel, not the operating pressure and temperature.

The best approach to costing pressure vessels using the IPE software is to enter all of the dimensions after completing the mechanical design of the vessel using the methods given in Chapter 13 or using suitable pressure vessel design software.

Nonstandard Components

Although IPE contains over 250 equipment types, many processes require equipment that is not on the list of available project components. Also, in some cases the user will want to specify a certain make or model of equipment that may be available only in discrete sizes (for example, gas turbine engines or large pumps and compressors). In these situations, the nonstandard equipment can be included by setting up an Equipment Model Library (EML). Many companies maintain standard EMLs listing equipment that they often specify.

A new EML can be created by selecting the "Libraries" tab in the palette and opening the folder Cost Libraries/Equipment Model Library. Right-clicking on either of the subfolders then allows the user to create a new EML in the appropriate set of units. Once an EML has been created, equipment items can be added to it. When a new item is added, a dialog box opens in which the user has to specify the sizing or costing method (linear, log-log, semi-log, or discrete) and primary sizing parameters. Two costs and sizes must also be entered to establish the cost correlation.

Equipment model libraries are useful for completing an IPE model of a process that contains nonstandard items. Care must be taken to update the EML costs so that they remain current.

Example 6.5

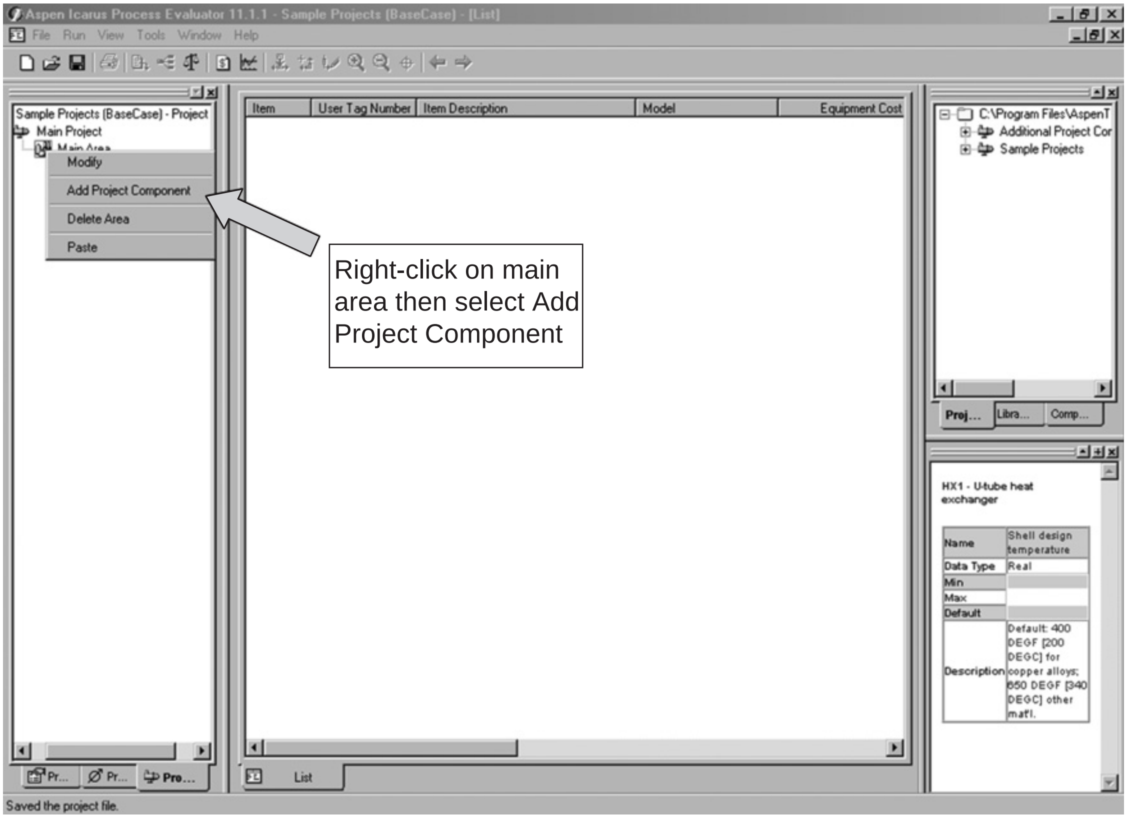
Estimate the cost of a waste heat boiler designed to produce 4,000 lb/h of steam. The exchanger area has been estimated as 1300 ft^2.

Solution

Starting from the IPE project explorer window (on the far left of the screen), right-click on the Main Area and select Add Project Component, as shown in Figure 6.3a.

Select Process Equipment, then Heat Exchangers, as shown in Figure 6.3b. Select Waste Heat Boiler and enter a name, as shown in Figure 6.3c.

Enter the size parameters and then click the Evaluate button, shown in Figure 6.3d. This runs the evaluator program and gives the results screen shown in Figure 6.3e. The purchased equipment cost is $145,900 on a January 2006 USGC basis. The installed cost is $196,225. Note that the installed cost is calculated directly by estimating bulk materials and labor rather than using an installation factor.



Right-click on main area then select Add Project Component

HX1 - U-tube heat exchanger

Name	Shell design temperature
Data Type	Real
Min	
Max	
Default	
Description	Default: 400 DEGF [200 DEGC] for copper alloys; 650 DEGF [340 DEGC] other mat'l.

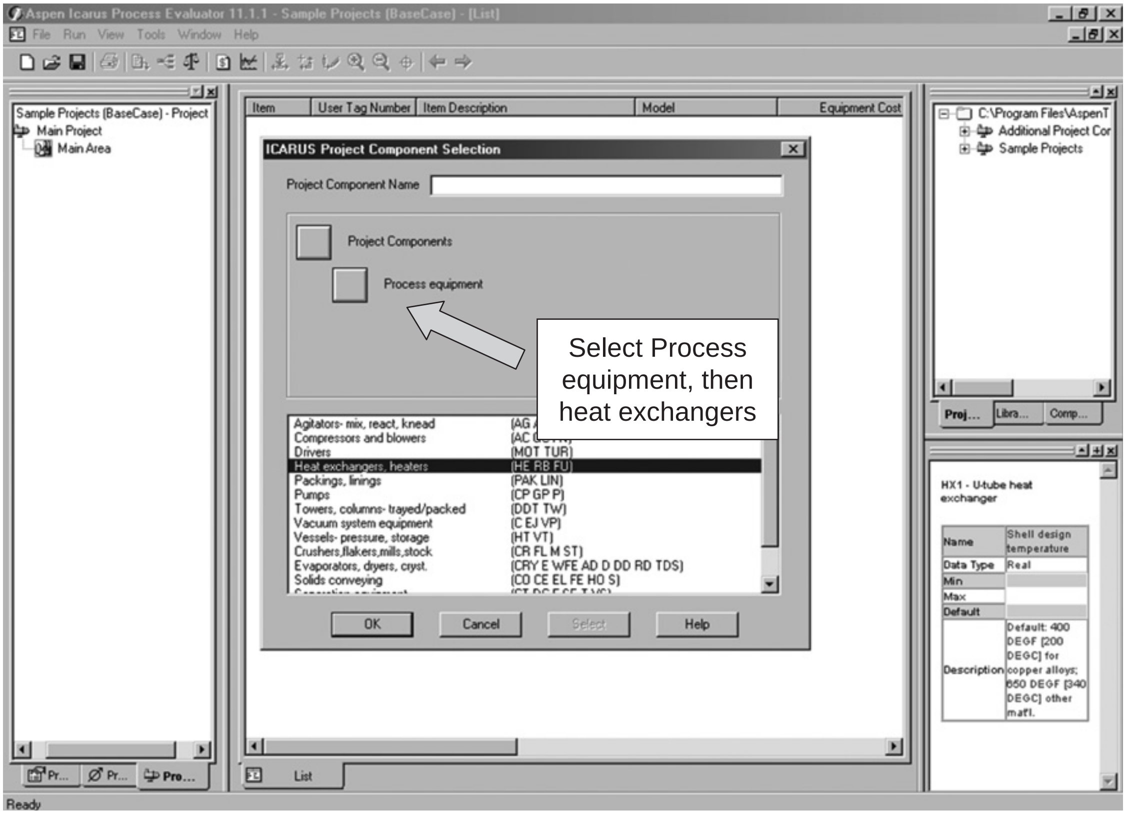
Figure 6.3a. Aspen ICARUS example.

6.3.9. Validity of Cost Estimates

It should always be remembered that cost estimates are only estimates and are subject to error. An estimate should always indicate the margin of error. The error in a cost estimate is primarily determined by the degree of design detail that is available, and even a skilled estimator cannot estimate an accurate cost for a sketchy design.

When more design information has been developed, a professional cost engineer will be able to develop a more accurate estimate. The process design engineer should compare this estimate with the preliminary estimate to gain a better understanding of where the preliminary estimate could have been improved (either through capturing missing plant items or using better costing methods). This will help the design engineer to produce better preliminary estimates in the future.

Additional resources for cost estimating are available from the various cost-estimating associations: the Association for the Advancement of Cost Engineering International (www.aacei.org); the Project Management Institute (www.pmi.org); the U.K. Association of Cost Engineers (www.acoste.org.uk); and the International Cost Engineering Council (www.icoste.org). The ICEC website has links to cost engineering societies in 46 countries.



Select Process equipment, then heat exchangers

HX1 - U-tube heat exchanger

Name	Shell design temperature
Data Type	Real
Min	
Max	
Default	
Description	Default: 400 DEGF [200 DEGC] for copper alloys; 650 DEGF [340 DEGC] other mat'l.

Figure 6.3b. Aspen ICARUS example.

6.4. ESTIMATING PRODUCTION COSTS AND REVENUES

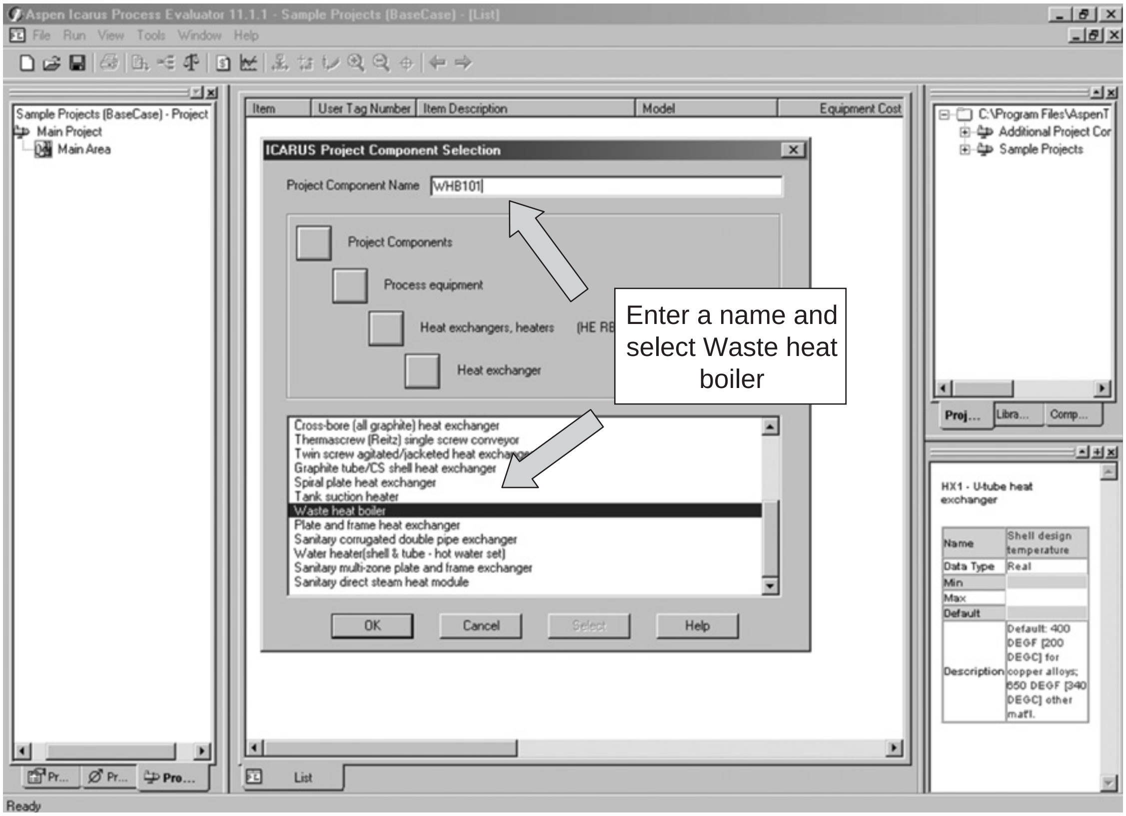
The revenues and variable costs of production are obtained by multiplying the product, feed, or utility flow rates from the flowsheet by the appropriate prices. The difficult step is usually finding good price data.

6.4.1. Sources of Price Data

This section describes the most widely used sources of price data. Some pricing terminology is given in Table 6.8.

Internal Company Forecasts

In many large companies the marketing or planning department develops official forecasts of prices for use in internal studies. These forecasts sometimes include multiple price scenarios, and projects must be evaluated under every scenario. Company forecasts are occasionally made available to the public. See, for example, Shell (2002) or Shell (2005), which can be downloaded from www.Shell.com. When an



Project Component Name: WHB101

Waste heat boiler

Enter a name and select Waste heat boiler

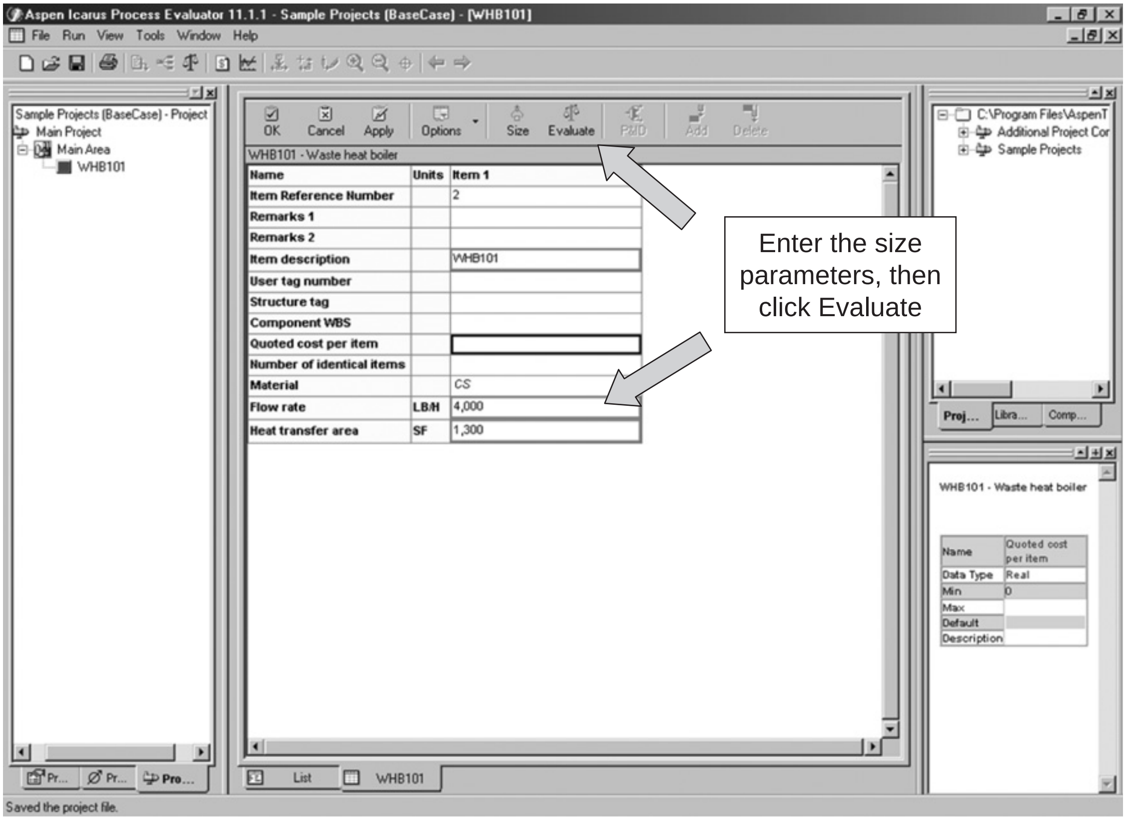
Figure 6.3c. Aspen ICARUS example.

officially approved price set exists, the design engineer should use it. The main concern is then ensuring that prices for feeds, products, or consumables that are not part of the standard forecast are put on a consistent basis.

Trade Journals

Several journals publish chemicals and fuel prices on a weekly basis.

ICIS Chemical Business Americas, formerly known as *Chemical Marketing Reporter* (ICIS Publications), previously listed prices for 757 chemicals with multiple locations and product grades for some. This list was reduced to only 85 compounds in 2006, with most of the remaining set being natural extracts. Data for 80 chemicals, 44 fuels, and 11 base oils are now provided online through the subscription service www.icispricing.com. At the time of writing, this service was very expensive compared to some of the alternatives listed later. ICIS also publishes *ICIS Chemical Business Europe* and *ICIS Chemical Business Asia*, which provide regional price data for a smaller set of compounds.



WHB101 - Waste heat boiler

Name	Units	Item 1
Item Reference Number		2
Remarks 1		
Remarks 2		
Item description		WHB101
User tag number		
Structure tag		
Component WBS		
Quoted cost per item		
Number of identical items		
Material		CS
Flow rate	LB/H	4,000
Heat transfer area	SF	1,300

Enter the size parameters, then click Evaluate

WHB101 - Waste heat boiler

Name	Quoted cost per item
Data Type	Real
Min	0
Max	
Default	
Description	

Figure 6.3d. Aspen ICARUS example.

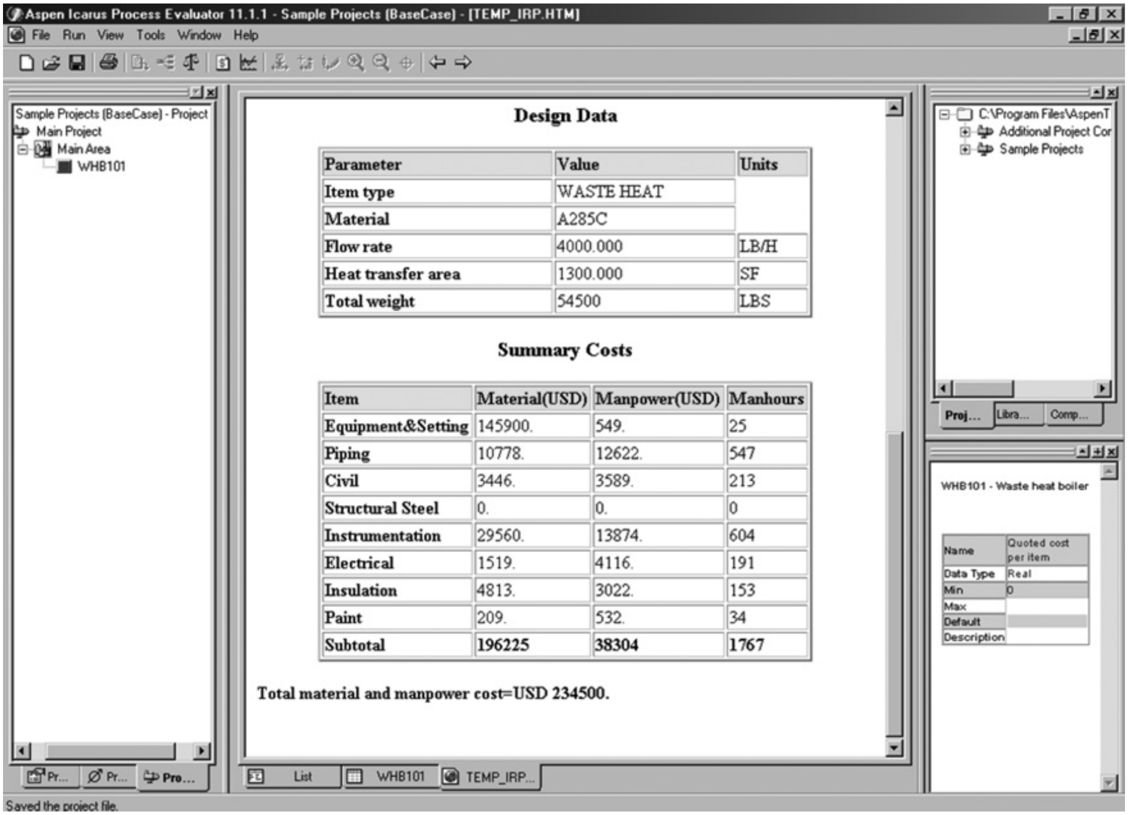
The *Oil and Gas Journal* (Pennwell) publishes prices for several crude oils and a range of petroleum products on U.S., N.W. Europe, and S.E. Asia bases, as well as natural gas prices for the United States.

Chemical Week (Access Intelligence) gives spot and contract prices for 22 commodity chemicals in U.S. and N.W. Europe markets.

Consultants

Many companies can be hired as consultants to provide economic and marketing information, or allow access to such information on a subscription basis. The information provided generally includes market surveys and technical and economic analyses of competing technologies, as well as price data and forecasts. There is not room here to list all of these companies, but some of the most widely used are

- *Purvin and Gertz*: Provides quarterly forecasts of oil, gas, and fuel prices that are widely used in the oil industry. They have a 10-year archive of historic data and forecast prices of most fuel products as well as crude oils on U.S., N.W. Europe, Middle East, and Asia bases.



Design Data

Parameter	Value	Units
Item type	WASTE HEAT	
Material	A285C	
Flow rate	4000.000	LB/H
Heat transfer area	1300.000	SF
Total weight	54500	LBS

Summary Costs

Item	Material(USD)	Manpower(USD)	Manhours
Equipment&Setting	145900.	549.	25
Piping	10778.	12622.	547
Civil	3446.	3589.	213
Structural Steel	0.	0.	0
Instrumentation	29560.	13874.	604
Electrical	1519.	4116.	191
Insulation	4813.	3022.	153
Paint	209.	532.	34
Subtotal	**196225**	**38304**	**1767**

Total material and manpower cost=USD 234500.

WHB101 - Waste heat boiler

Name	Quoted cost per item
Data Type	Real
Min	0
Max	
Default	
Description	

Figure 6.3e. Aspen ICARUS example.

- *Cambridge Energy Research Associates*: Publishes forecasts of crude oil prices based on macroeconomics and industry trends (drilling rates, etc.).
- *Chemical Market Associates Inc*. (CMAI): Maintains a large archive of historic data and future price forecasts for 70 commodity chemicals, including multiple grades, U.S., N.W. Europe, Middle East, N.E., and S.E. Asia. Spot and contract prices are given for some compounds, and in some cases margins are also estimated by formula.
- *SRI*: The *Chemical Economics Handbook* series of reports published by SRI provides overviews of the markets for 281 compounds. These reports are not updated as frequently as the others but are useful for less commoditized compounds.

Online Brokers and Suppliers

A great deal of price data is available online from suppliers' websites that can be found through directory sites such as www.purchasing.com and www.business.com/directory/chemicals.

Table 6.8. Pricing Terminology

Abbreviation	Meaning
c.i.f.	Cost, insurance, and freight
dlvd.	Delivered
f.o.b.	Free on board
frt. alld.	Freight allowed
dms.	Drums
bgs.	Bags
refy.	Refinery gate
syn.	Synthetic
t.t.	Tank truck
t.c.	Tank car (rail)
t.l.	Truck load
imp.	Imported

Some caution is needed when using price data from the web. The prices quoted are generally for spot sale of small quantity orders, and are thus much higher than the market rates for large order sizes under long-term contract. The prices listed online are also often for higher quality material such as analytical, laboratory, or USP pharmaceutical grades, which have much higher prices than bulk grades.

Reference Books

Prices for some of the more common commodity chemicals are sometimes given in process economics textbooks. These prices are usually single data points rather than forecasts. They are suitable only for undergraduate design projects.

6.4.2. Forecasting Prices

In most cases, it will take between 1 and 3 years for a project to go through the phases of design, procurement, and construction before a plant can begin operation. The plant will then operate for the project life of 10 to 20 years. The design engineer thus needs to carry out the economic analysis using prices forecasted over the next 20 or so years rather than the current price when the design is carried out.

For some compounds the only variation in price over time is minor adjustments to allow for inflation. This is the case for some specialty compounds that have relatively high prices and are not subject to competitive pressure (which tends to drive prices down). Prices can also be stable if they are controlled by governments, but this is increasingly rare. In most cases, however, prices are determined largely by feedstock prices, which are ultimately determined by fluctuations in the prices of commodity fuels and chemicals. The prices of these commodities are set by markets in response to variations in supply and demand, and vary widely over time.

Most price forecasts are based on an analysis of historic price data. Several methods are used, as illustrated in Figure 6.4. The simplest method is to use the current price, as in Figure 6.4a, but this is unsatisfactory for most commodities. Linear regression of

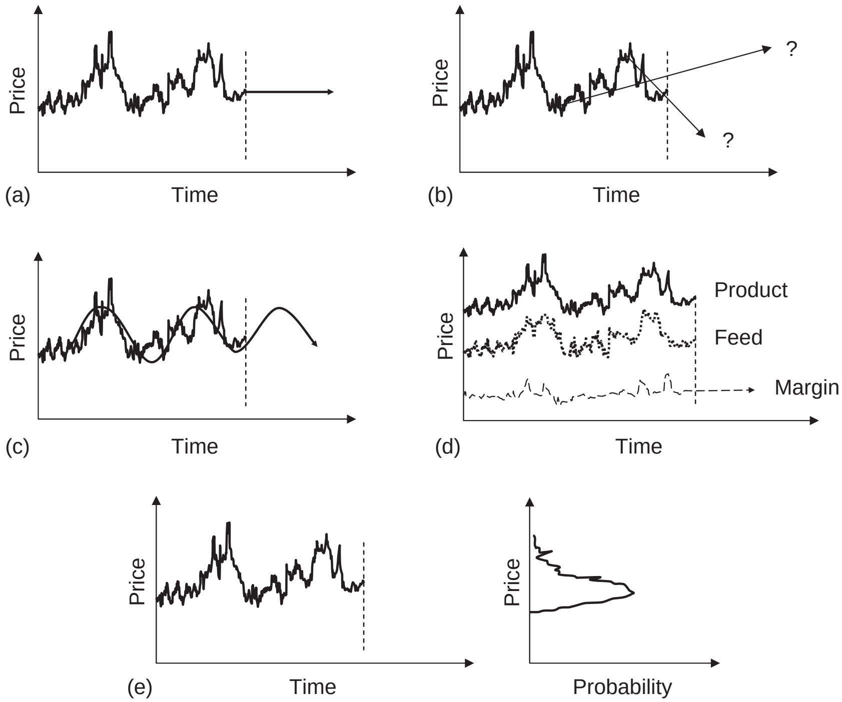


Figure 6.4. (a–e) Forecasting commodity prices.

past prices is a good method for capturing long-term trends (>10 years), but can give very different results depending on the start data chosen, as shown in Figure 6.4b. This method can be very misleading if the data set is too small.

Many commodity prices exhibit cyclic behavior due to the investment cycle, so in some cases nonlinear models can be used, as in Figure 6.4c. Unfortunately, both the amplitude and the frequency of the price peaks usually vary somewhat erratically, making it difficult to fit the cyclic price behavior with simple wave models or even advanced Fourier transform methods.

A fourth approach, illustrated in Figure 6.4d, is to recognize that feed and product prices are usually closely linked, since increases in feed costs are passed on to customers whenever possible via increases in product price. Although feed and product prices may both be variable, the gross margin is therefore subject to much less variation and can be forecasted more reliably. Forecasting of margins is the method used widely in the fuels and petrochemicals industry, as it is much easier to predict the variation in margins than the underlying variation in the prices of crude oil and natural gas. The drawbacks of this method are that it does not work very well when there are multiple routes to the same product, and it involves making assumptions about yields that may not hold true throughout the forecast period. In cases in which the gross margin is high, it can be more difficult for the manufacturer to pass on the full impact of feedstock price increases in the form of increased product prices.

In such cases, when feed prices rise rapidly, there is a drop in margins while producers wait for the market to absorb the impact of higher prices.

Another method is to model the statistical distribution of the price (or margin), as illustrated in Figure 6.4e. At its simplest, this method involves taking the average price, adjusted for inflation, over a recent period. This method can miss long-term trends in the data, and few prices follow any of the more commonly used distributions. It is useful, however, in combination with sensitivity analysis methods such as Monte Carlo Simulation (see Section 6.8).

Figure 6.5 shows North American prices from CMAI data for polyethylene terephthalate resin (PET), which is made from terephthalic acid (TPA), which in turn is made from paraxylene (PX). Several things are apparent from Figure 6.5:

1. The spot prices of PX and TPA show more volatility than the contract prices, as would be expected.
2. All the prices follow the same broad trends, with a major peak in 1995 and long recovery leading to a second peak in 2006.
3. The sharp peak in PX spot price in 1995 was not passed on to the other prices.

Figure 6.6 shows the simple margins TPA-PX and PET-PX over the same time period, all based on contract prices. The degree of variation in margins is clearly less

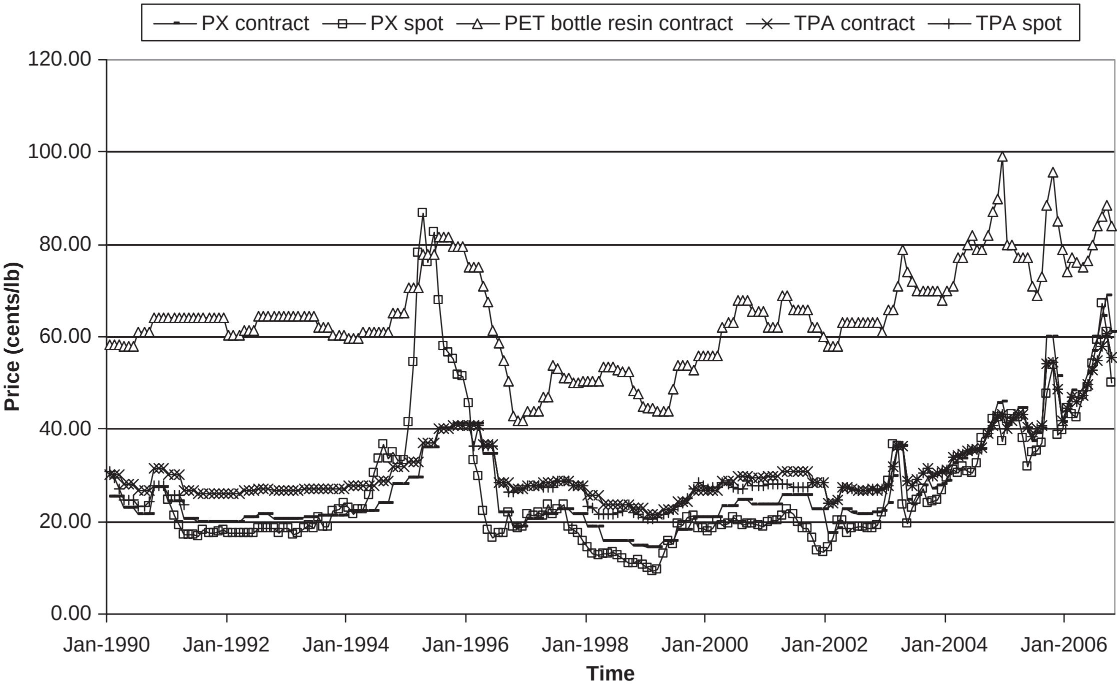


Figure 6.5. North American prices for the PET value chain.

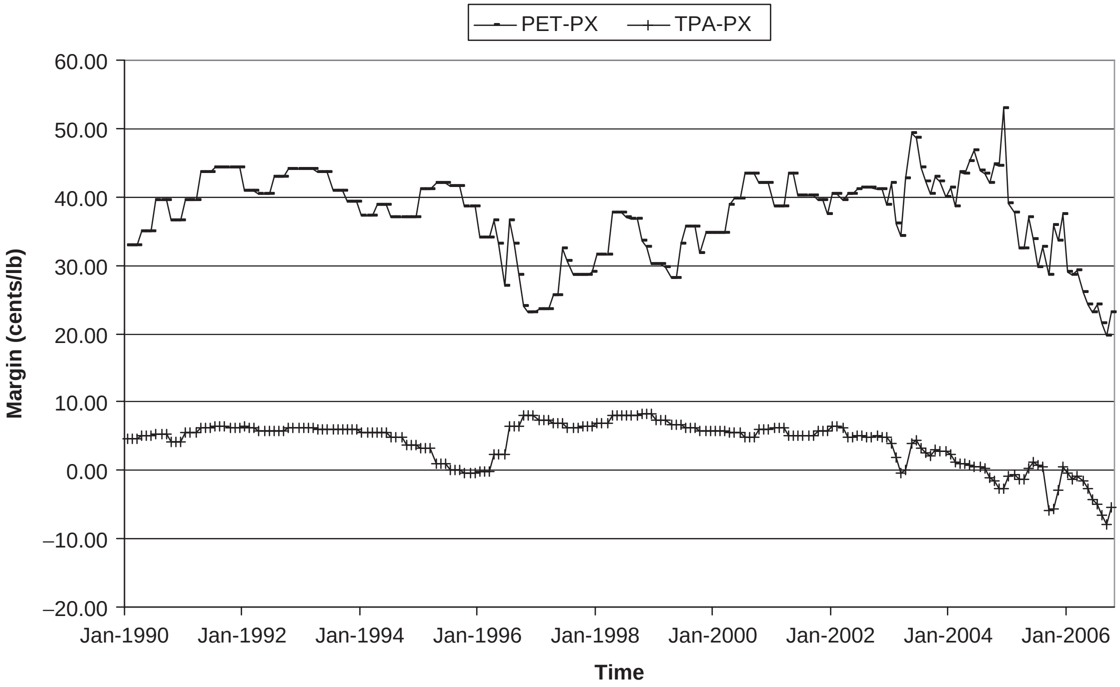


Figure 6.6. Simple margins for the PET value chain.

than the variation in the base prices. There also appears to be a long-term decline in TPA margins relative to PX.

A similar examination of feed and product prices along the value chain of a given chemical can usually provide valuable insights into the best method of forecasting. No method is perfect, and anyone capable of accurately predicting commodity prices would be well advised to pursue a more lucrative career than chemical engineering. For process design purposes, it is usually sufficient to show that the prices used for optimization and economic analysis are realistic and consistent with consensus views of the market.

6.4.3. Transfer Pricing

If the raw material for plant B is the product of plant A on the same site and owned by the same company, then the price that plant B pays to plant A is known as a "transfer price." Whenever realistic, transfer prices should be set by open market prices. This reflects the reality that plant A could sell its product on the open market or plant B could similarly buy its feed. Some cases when transfer prices do not match market prices include

1. When plant A produces material that is suitable for internal consumption but does not meet specifications for traded product. In this case, the transfer price to

plant B should be discounted to allow for the added costs incurred in plant B from handling the less pure feed.

2. When plant A is underutilized or cannot sell its product and has recovered all of its initial capital investment, then the transfer price to plant B can be set at the cash cost of production of plant A (see Section 6.2.5).
3. When the pricing of product from the upstream plant is set to drive capacity utilization or conservation, for example, by using a sliding price scale based on the amount of material used.

When transfer pricing is used, it is important to keep in mind which processes actually bring in money from customers and which do not. If unrealistic transfer prices are used, uneconomic projects may seem attractive, and poor investment decisions may be made.

6.4.4. Utility Costs

The utility consumption of a process cannot be estimated accurately without completing the material and energy balances and carrying out a pinch analysis, as described in Chapter 3. The pinch analysis gives targets for the minimum requirements of hot and cold utilities. More detailed optimization then translates these targets into expected demands for fired heat, steam, electricity, cooling water, and refrigeration. In addition to the utilities required for heating and cooling, the process may also need process water and air for applications such as washing, stripping, and instrument air supply. A good overview of methods for design and optimization of utility systems is given by Smith (2005).

The electricity demand of the process is mainly determined by the work required for pumping, compression, air coolers, and solids-handling operations, but also includes the power needed for instruments, lights, and other small users. Some plants generate their own electricity using a gas-turbine cogeneration plant with a heat recovery steam generator (waste heat boiler) to raise steam, as shown in Figure 6.7. The cogeneration plant can be sized to meet or exceed the plant electricity requirement, depending on whether the export of electricity is an attractive use of capital.

Most plants are located on sites where the utilities are provided by the site infrastructure. The price charged for a utility is mainly determined by the operating cost of generating and transmitting the utility stream. Some companies also include a capital recovery charge in the utility cost, but if this is done, then the offsite (OSBL) capital cost must be reduced to avoid double counting and biasing the project capital-energy trade-off, leading to poor use of capital.

Some smaller plants purchase utilities "over the fence" from a supplier such as a larger site or a utility company, in which case the utility prices are set by contract and are typically pegged to the price of natural gas or fuel oil.

Fired Heat

Fired heaters are used for process heating above the highest temperatures that can be reached using high-pressure steam, typically about 250°C (480°F). Process streams

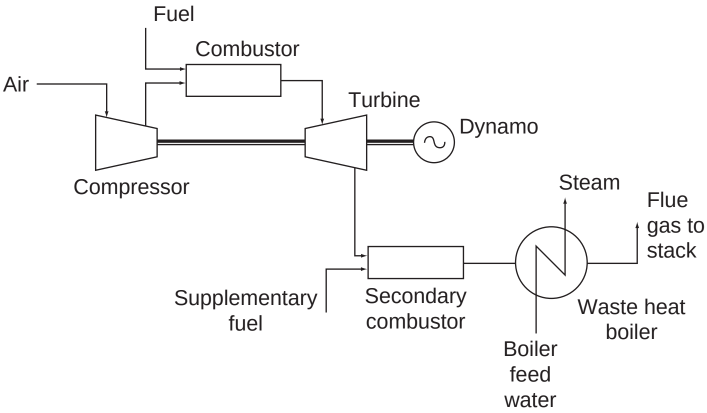


Figure 6.7. Gas-turbine-based cogeneration plant.

may be heated directly in the furnace tubes or indirectly using a hot oil circuit. The design of fired heaters is described in Chapter 12. The cost of fired heat can be calculated from the price of the fuel fired. Most fired process heaters use natural gas, as it is cleaner burning than fuel oil and therefore easier to fit NO_x control systems and obtain permits. Natural gas also requires less maintenance of burners and fuel lines, and natural gas burners can often co-fire process waste streams such as hydrogen, light hydrocarbons, or air saturated with hydrocarbons or solvents. In recent years, North American prices for natural gas have had very high midwinter peaks. This has caused some plants to revert to using heating oil as fuel.

Natural gas and heating oil are traded as commodities, and prices can be found at any online trading site or business news site (e.g., www.cnnmoney.com). Historic prices for forecasting can be found in the *Oil and Gas Journal* or from the U.S. Energy Information Administration (www.eia.doe.gov).

The fuel consumed in a fired heater can be estimated from the fired heater duty divided by the furnace efficiency. The furnace efficiency will typically be about 0.85 if both the radiant and convective sections are used (see Chapter 12) and about 0.6 if the process heating is in the radiant section only.

Steam

Steam is the most widely used heat source on most chemical plants. Steam has a number of advantages as a hot utility:

- The heat of condensation of steam is high, giving a high heat output per pound of utility at constant temperature (compared to other utilities such as hot oil and flue gas that release sensible heat over a broad temperature range).
- The temperature at which heat is released can be precisely controlled by controlling the pressure of the steam. This enables tight temperature control, which is important in many processes.
- Condensing steam has very high heat transfer coefficients, leading to cheaper heat exchangers.

- Steam is nontoxic, nonflammable, visible if it leaks externally, and inert to many (but not all) process fluids.

Most sites have a pipe network supplying steam at three or more pressure levels for different process uses. A typical steam system is illustrated in Figure 6.8. Boiler feed water at high pressure is preheated and fed to boilers where high-pressure steam is raised and superheated above the dew point to allow for heat losses in the piping. Boiler feed water preheat can be accomplished using process waste heat or convective section heating in the boiler plant. High-pressure (HP) steam is typically at about 40 bar, corresponding to a condensing temperature of 250 °C, but every site is different. Some of the HP steam is used for process heating at high temperatures. The remainder of the HP steam is expanded either through steam turbines known as *back-pressure turbines* or through let-down valves to form medium-pressure (MP) steam. The pressure of the MP steam mains varies widely from site to site, but is typically about 20 bar, corresponding to a condensing temperature of 212 °C. Medium-pressure steam is used for intermediate temperature heating or expanded to form low-pressure (LP) steam, typically at about 3 bar, condensing at 134 °C. Some of the LP steam may be used for process heating if there are low temperature heat requirements. Low-pressure (or MP or HP) steam can also be expanded in condensing turbines to generate shaft work for process drives or electricity production. A small amount of LP steam is used to strip dissolved noncondensable gases such as air from the condensate and make-up water. Low-pressure steam is also often used as "live steam" in the process, for example, as stripping vapor or for cleaning, purging, or sterilizing equipment.

When steam is condensed without coming into contact with process fluids, then the hot condensate can be collected and returned to the boiler feed water system.

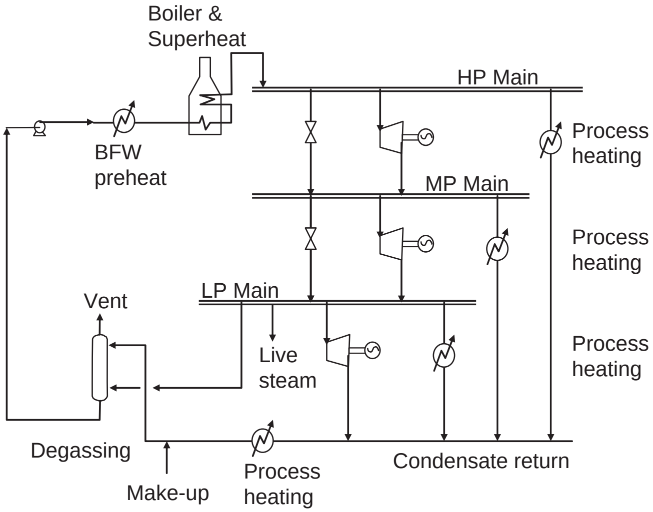


Figure 6.8. Steam system.

Condensate can also sometimes be used as a low-temperature heat source if the process requires low-temperature heat.

The price of HP steam can be estimated from the cost of boiler feed water treatment, the price of fuel, and the boiler efficiency:

$$P_{HPS} = P_F \times \frac{dH_b}{\eta_B} + P_{BFW} \tag{6.18}$$

where

P_{HPS} = price of high-pressure steam (\$/1,000 lb, commonly written \$/Mlb);
P_F = price of fuel (\$/MMBtu);
dH_b = heating rate (MMBtu/Mlb steam);
η_B = boiler efficiency;
P_{BFW} = price or cost of boiler feed water (\$/Mlb).

Package boilers typically have efficiencies similar to fired heaters, in the range 0.8 to 0.9.

The heating rate should include boiler feed water preheat, the latent heat of vaporization, and the superheat specified.

The cost of boiler feed water includes allowances for water make-up, chemical treatment, and degassing, and is typically about twice the cost of raw water (see below). If no information on the price of water is available, then 0.50 \$/Mlb can be used as an initial estimate. If the steam is condensed and the condensate is returned to the boiler feed water (which will normally be the case), then the price of steam should include a credit for the condensate. The condensate credit will often be close enough to the boiler feed water cost that the two terms cancel each other out and can be neglected.

The prices of medium- and low-pressure steam are usually discounted from the high-pressure steam price, to allow for the shaft work credit that can be gained by expanding the steam through a turbine, and also to encourage process heat recovery by raising steam at intermediate levels and using low-grade heat when possible. Several methods of discounting are used. The most rational of these is to calculate the shaft work generated by expanding the steam between levels and price this as equivalent to electricity (which could be generated by attaching the turbine to a dynamo or else would be needed to run a motor to replace the turbine if it is used as a driver). The value of the shaft work then sets the discount between steam at different levels. This is illustrated in the following example.

Example 6.6

A site has steam levels at 40 bar, 20 bar, and 6 bar. The price of fuel is \$6/MMBtu and electricity costs \$0.05/kWh. If the boiler efficiency is 0.8 and the steam turbine efficiency is 0.85, suggest prices for HP, MP, and LP steam.

Solution

The first step is to look up the steam conditions, enthalpies, and entropies in steam tables:

Steam Level	HP	MP	LP
Pressure (bar)	40	20	6
Saturation temperature (°C)	250	212	159

The steam will be superheated above the saturation temperature to allow for heat losses in the pipe network. The following superheat temperatures were set to give an adequate margin above the saturation temperature for HP steam and also to give (roughly) the same specific entropy for each steam level. The actual superheat temperatures of MP and LP steam will be higher, due to the nonisentropic nature of the expansion.

Superheat temperature (°C)	400	300	160
Specific entropy, sg (kJ/kg.K)	6.769	6.768	6.761
Specific enthalpy, hg (kJ/kg)	3214	3025	2757

We can then calculate the difference in enthalpy between levels for isentropic expansion:

Isentropic delta enthalpy (kJ/kg)	189	268

Multiplying by the turbine efficiency gives the nonisentropic enthalpy of expansion:

Actual delta enthalpy (kJ/kg)	161	228

This can be converted to give the shaft work in customary units:

Shaft work (kWh/Mlb)	20.2	28.7

Multiplying by the price of electricity converts this into a shaft work credit:

Shaft work credit ($/Mlb)	1.01	1.44

The price of high-pressure steam can be found from equation 6.18, assuming that the boiler feed water cost is canceled out by a condensate credit. The other prices can then be estimated by subtracting the shaft work credits.

Steam price($/Mlb)	6.48	5.47	4.03

For quick estimates, this example can easily be coded into a spreadsheet and updated with the current prices of fuel and power. A sample steam costing spreadsheet is available in the online material at http://books.elsevier.com/companions.

Cooling

The cost of process cooling usually depends strongly on the cost of power (electricity).

- Air coolers use electric power to run the fans. The power requirement is determined as part of the cooler design, as described in Chapter 12.

- Cooling water systems use power for pumping the cooling water through the system and for running fans (if installed) in the cooling towers. They also have costs for water make-up and chemical treatment. The power used in a typical recirculating cooling water system is usually between 1 and 2 kWh/1,000 gal of circulating water. The costs of water make-up and chemical treatment usually add about \$0.02/1,000 gal.
- Refrigeration systems use power to compress the refrigerant. The power can be estimated using the cooling duty and the refrigerator coefficient of performance (*COP*).

$$COP = \frac{\text{Refrigeration produced (Btu/hr or MW)}}{\text{Shaft work used (Btu/hr or MW)}} \tag{6.19}$$

The *COP* is a strong function of the temperature range over which the refrigeration cycle operates. For an ideal refrigeration cycle (a reverse Carnot cycle), the *COP* is

$$COP = \frac{T_1}{(T_2 - T_1)} \tag{6.20}$$

where

T_1 = evaporator absolute temperature (K);
T_2 = condenser absolute temperature (K).

The COP of real refrigeration cycles is always less than the Carnot efficiency. It is usually about 0.6 times the Carnot efficiency for a simple refrigeration cycle, but can be as high as 0.9 times the Carnot efficiency if complex cycles are used. Good overviews of refrigeration cycle design are given by Dincer (2003), Stoecker (1998), and Trott and Welch (1999).

Electricity

Chemical plants consume large enough amounts of electricity that it is often economically attractive for them to install gas turbine engines or steam turbines and generate their own electric power. This "make or buy" scenario gives chemical producers strong leverage when negotiating electric power contracts, and they are usually able to purchase electricity at or close to wholesale prices. Wholesale electricity prices vary regionally (see www.eia.doe.gov for details), but are typically about \$0.06/kWh in North America at the time of writing.

Water

Raw water is brought in to make up for losses in the steam and cooling water systems and is also treated to generate demineralized and deionized water for process use. The price of water varies strongly by location, depending on fresh water availability. Water prices are often set by local government bodies and often include a charge for waste-water rejection. This charge is usually applied on the basis of the water consumed by the plant, regardless of whether that water is actually rejected as a liquid (as opposed to being lost as vapor or incorporated into a product by reaction).

A very rough estimate of water costs can be made by assuming \$2 per 1,000 gal (\$0.5 per metric ton). Demineralized water typically costs about double the price of raw water, but this obviously varies strongly with the mineral content of the water and the disposal cost of blowdown from the demineralization system.

Air and Nitrogen

Air at 1 atmosphere pressure is freely available in most chemical plants. Compressed air can be priced based on the power needed for compression (see Chapter 3). Drying the air—for example, for instrument air—typically adds about \$0.005 per standard m^3 (\$0.14/1,000 scf). Nitrogen and oxygen are usually purchased from one of the industrial gas companies via pipeline or a small dedicated over-the-fence plant. The price varies depending on local power costs, but is typically in the range \$0.01 to \$0.03 per lb for large facilities.

Example 6.7

Estimate the annual cost of providing refrigeration to a condenser with duty 1.2 MW operating at −5°C. The refrigeration cycle rejects heat to cooling water that is available at 40 °C and has an efficiency of 80% of the Carnot cycle efficiency. The plant operates for 8,000 hours per year and electricity costs \$0.06/kWh.

Solution

The refrigeration cycle needs to operate with an evaporator temperature below −5 °C, say at −10 °C or 263 K. The condenser must operate above 40 °C, say at 45 °C (318 K).

For this temperature range, the Carnot cycle efficiency is

$$COP = \frac{T_1}{(T_2 - T_1)} = \frac{263}{318 - 263} = 4.78 \tag{6.20}$$

If the cycle is 80% efficient, then the actual coefficient of performance = 4.78 × 0.8 = 3.83.

The shaft work needed to supply 1.2 MW of cooling is given by

$$\text{Shaft work required} = \frac{\text{Cooling duty}}{COP} = \frac{1.2}{3.83} = 0.313\,\text{MW}$$

The annual cost is then = 313 kW × 8,000 h/y × 0.06 \$/kWh = $\underline{\underline{150{,}000\$/\text{y}}}$.

6.4.5. Consumables Costs

Consumables include materials such as acids, bases, sorbents, solvents, and catalysts that are used in the process. Over time these become depleted or degraded and require replacement. In some cases a continuous purge and make-up is used (for example, for acids and bases), while in other cases an entire batch is periodically replaced (for example, for sorbents and catalysts).

The prices of acids, bases, and solvents can be found from the same sources used for raw materials prices. Whenever possible, the cheapest base (NaOH) or acid (H_2SO_4)

would be used in the process, but for neutralizing spent sulfuric acid, lime (CaO) or ammonia (NH_3) are often used, as these bases react with sulfuric acid to form insoluble sulfates that can be recovered and sold as byproducts. The cost of process acid or base must always include the costs of neutralizing the spent stream.

The price of adsorbents and catalysts varies very widely depending on the nature of the material. The cheapest catalysts and adsorbents cost less than $1/lb, while more expensive catalysts containing noble metals such as platinum and palladium have costs that are mainly determined by the amount of precious metal on the catalyst. In some cases, the value of the noble metal on a load of catalyst is so high that the chemical plant rents the catalyst rather than buying it, and when the catalyst is spent, it is returned to the manufacturer for precious metal recovery.

Although small in quantity, consumables can add a lot of cost and complexity to a plant. The plant must be designed with systems for handling, storing, metering, and disposing of all the consumables used. In many chemicals plants, over half of the total pieces of equipment are associated with consumables handling.

6.4.6. Waste Disposal Costs

Materials produced by the process that cannot be recycled or sold as byproducts must be disposed of as waste. In some cases additional treatment is required to concentrate the waste stream before sending it to final disposal.

Hydrocarbon waste streams such as off-spec products, slop oils, spent solvents, and off gases (including hydrogen-rich gases) can often be incinerated or used as process fuel. This allows the fuel value of the stream to be recovered, and the waste stream can be assigned a value based on its heat of combustion:

$$P_{WFV} = P_F \times \Delta H_C^{\circ} \tag{6.21}$$

where

P_{WFV} = waste value as fuel ($/lb or $/kg);
P_F = price of fuel ($/MMBtu or $/GJ);
ΔH_C° = heat of combustion (MMBtu/lb or GJ/kg).

If additional systems such as flue gas scrubbers must be fitted to allow the waste to be combusted, then the waste stream value should be discounted to recover the extra cost.

Dilute aqueous streams are sent to waste-water treatment unless the contaminants are toxic to the bacteria in the waste-water plant. Acidic or basic wastes are neutralized prior to treatment. Neutralization is usually carried out using a base or acid that will form a solid salt that can be precipitated from the water so that the total dissolved solids (TDS) load on the waste-water plant is not excessive. The cost of waste-water treatment is typically about $6 per 1,000 gal ($1.5 per metric ton), but there may also be local charges for spent water discharge.

Inert solid wastes can be sent to landfills at a cost of about $50/ton, or in some cases used to make roads. Wastes from neutralizing spent sulfuric acid are typically calcium sulfate (gypsum) which can be used as road fill, or ammonium sulfate, which can be sold as fertilizer.

Concentrated liquid streams that cannot be incinerated locally (for example, compounds containing halogens) and noninert solids must be disposed of as hazardous waste. This entails shipping the material to a hazardous waste company for incineration in a specialized plant or long-term storage in a suitable facility. The costs of hazardous waste disposal depend strongly on the plant location, proximity to waste disposal plants, and the nature of the hazardous waste and must be evaluated on a case-by-case basis.

Additional information on waste disposal considerations is given in Chapter 14.

6.4.7. Labor Costs

The wages paid to plant operators and supervisors are a fixed cost of production, as described in Section 6.2.4. Almost all plants are operated on a shift-work basis (even batch plants), with typically 4.8 operators per shift position. This gives a four-shift rotation with allowance for weekends, vacations, and holidays and some use of overtime. Most plants require at least three shift positions: one operator in the control room, one outside, and one in the tank farm or other feed/product shipping and receiving area. Plants that use more mechanical equipment, particularly solids-handling plants, typically require more shift positions. More shift positions are also needed when handling highly toxic compounds. In some cases two or more smaller plants may be grouped together with a common control room and tank farm to reduce the number of operators needed. Very few plants run entirely unattended though, with the exception of gas processing plants, which hold no inventories of feed or product and are usually automated to allow a single control room operator to watch over several plants.

Operator salaries vary by region and experience level. For initial estimates, an average USGC salary of \$50,000 per shift position per year, not including overhead, can be used. Supervision and overhead costs are discussed in Section 6.2.4.

6.4.8. Byproduct Revenues

A good deal of process design effort is often spent analyzing byproduct recovery. Potentially valuable byproducts include

1. Materials produced in stoichiometric quantities by the reactions that form the main product (see Table 6.1 for examples). If these are not recovered as byproducts, then the waste disposal costs will be excessive.
2. Components that are produced in high yield by side reactions. Some examples include propylene, butylenes, and butadiene, all of which are byproducts of ethylene from steam cracking of naphtha feed. Orthoxylene and metaxylene are byproducts of paraxylene manufacture by catalytic reforming of naphtha.
3. Components formed in high yield from feed impurities. Most sulfur is produced as a byproduct of fuels manufacture. Crude oil and natural gas contain sulfur

compounds that are converted to H_2S during refining or gas treatment. The H_2S is then converted to elemental sulfur by the Claus process. Mannitol (a valuable hexose) is made from fructose that is present in the glucose feed to the sorbitol process.

4. Components produced in low yield that have high value. Dicyclopentadiene can be recovered from the products of steam naphtha cracking. Acetophenone is recovered as a byproduct of phenol manufacture, although it can also be made by oxidation of ethylbenzene or fermentation of cinnamic acid.
5. Degraded consumables such as solvents that have reuse value.

Prices for byproducts can be found in the same sources used for prices of main products. The difficult part is deciding whether it is worthwhile to recover a byproduct. For the byproduct to have value, it must meet the specifications for that material, which may entail additional processing costs. The design engineer must therefore assess whether the additional cost of recovering and purifying the byproduct is justified by the byproduct value and avoided waste disposal cost, before deciding whether to value the material as a byproduct or as a waste stream.

An algorithm for assessing the economic viability of recovering a byproduct X is given in Figure 6.9. Note that it is important to consider not only the cost of purifying the byproduct, but also whether it can be converted into something more valuable. This would include recycling the byproduct within the process if that might be expected to lead to a higher yield of main product or formation of a more valuable byproduct. Note also that when analyzing whether to recover a byproduct, the value created by recovering the byproduct includes not only the revenue from byproduct sales, but also the avoided byproduct disposal cost. If the byproduct has fuel value, then the fuel value should be subtracted from the revenue instead.

A rule of thumb that can be used for preliminary screening of byproducts for large plants is that for byproduct recovery to be economically viable, the net benefit must be greater than \$200,000 per year. The net benefit is the byproduct revenue plus the

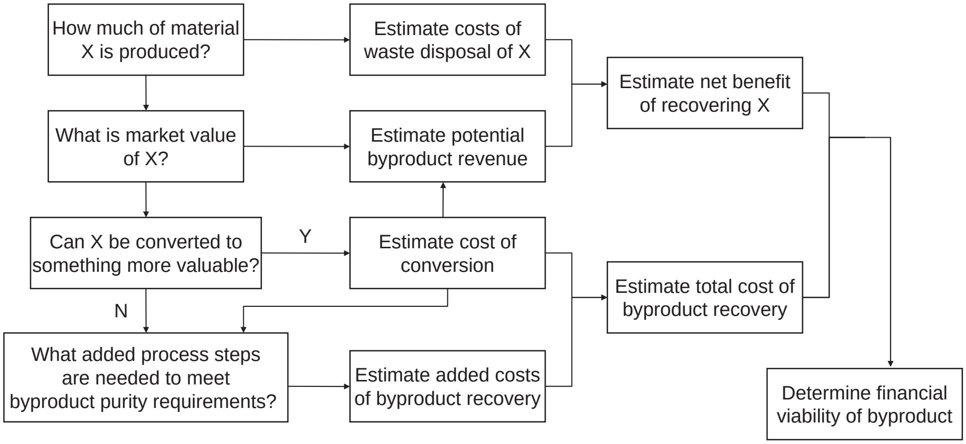


Figure 6.9. Algorithm for assessing the economic viability of byproduct recovery.

avoided waste disposal cost. (This is based on the assumption that recovering byproduct is going to add at least one separation to the process, which will cost at least \$0.5 MM of capital, or an annualized cost of about \$170,000, as described in Section 6.7.6.).

6.4.9 Summarizing Production Costs and Revenues

It is useful to create a single-page summary of all of the production costs and revenues associated with a project, as this makes it easier to review the project economics and understand the relative contribution of different components to the overall cost of production. The summary sheet usually lists the quantity per year and per unit production of product, the price, the cost per year, and the cost per unit production of product for each of the raw materials, byproducts, consumables, and utilities, as well as fixed costs and capital charges.

Most chemical companies have a preferred format for summarizing costs of production and often use standard spreadsheets. Good examples are given in the PERP reports published by Nexant (www.nexant.com/products). A template for summarizing production costs is given in Appendix G and can be downloaded in MS Excel format from the online material at http://books.elsevier.com/companions. The use of this template is illustrated in Example 6.11.

6.5. TAXES AND DEPRECIATION

The profits generated by most chemical plants are subject to taxation. Taxes can have a significant impact on the cash flows from a project. The design engineer needs to have a basic understanding of taxation and tax allowances such as depreciation in order to make an economic evaluation of the project.

6.5.1. Taxes

Individuals and corporations must pay income tax in most countries. The details of tax law can be complicated, and governments enact changes almost every year. Companies generally retain tax specialists, either as employees or as consultants, who have deep expertise in the intricacies of the field. Such specialized knowledge is not required for engineering design projects, which are usually compared on a relatively simple after-tax basis. The design engineer may occasionally need to consult a tax expert though, particularly when comparing projects in different countries with different tax laws.

Information on corporate taxes in the United States is given on the Internal Revenue Service website at www.irs.gov. At the time of writing, the top marginal rate of federal income tax on corporations in the United States is 35%, which applies to all incomes greater than \$18,333,333 (IRS Publication 542). Since almost all companies engaged in building chemical plants substantially exceed this income threshold, it is common to assume that all profits will be taxed at the marginal rate. In many locations corporations must also pay state or local income taxes.

In Canada, corporations pay income tax under the Canadian Income Tax Act. Information on the Canadian Income Tax Act can be obtained from www.fedpubs.com/subject/tax_law.htm.

The amount of tax that must be paid in a given year is calculated by multiplying the taxable income by the tax rate. The taxable income is given by:

$$\text{Taxable income} = \text{gross profit} - \text{tax allowances} \tag{6.22}$$

Various types of tax allowances are permitted in the tax laws of different countries, the most common of which is depreciation, discussed in Section 6.5.3. The after-tax cash flow is then

$$\begin{aligned} CF &= P - (P - D)t_r \\ &= P(1 - t_r) + Dt_r \end{aligned} \tag{6.23}$$

where

CF = after-tax cash flow;
P = gross profit;
D = sum of tax allowances;
t_r = rate of taxation.

It can be seen from equation 6.23 that the effect of tax allowances is to reduce taxes paid and increase cash flow.

In some countries, taxes are paid in a given year based on the previous year's income. This is true for the United States, where corporate taxes are based on a calendar year of operations and are due by March 15 of the following year. This complicates the calculations somewhat, but is easily coded into a spreadsheet.

6.5.2. Investment Incentives

National and regional governments often provide incentives to encourage companies to make capital investments, since these investments create employment, generate taxation revenue, and provide other benefits to politicians and the communities they represent.

The most common incentives used are tax allowances. Most countries allow some form of depreciation charge as a tax allowance, by which the fixed capital investment can be deducted from taxable income over a period of time, as described in Section 6.5.3. Other incentives that are often used include

1. Tax waivers or vacations, in which no taxes are paid for a fixed period of time, typically 2 to 5 years after the project begins generating revenue;
2. Investment grants or credits, in which the government makes a cash contribution toward the initial investment;
3. Low-cost loans, in which the government either loans capital directly or else subsidizes the interest due on a commercial loan;

4. Loan guarantees, in which the government agrees to underwrite loans for the project, making it easier to secure financing on advantageous terms.

An economic comparison between different process alternatives for the same site should usually be made using the same assumptions on investment incentives. This might not always be the case though, for example, if one project is eligible for a government grant because of using renewable energy and another project is not. It should also be noted that differences in incentives can have a significant impact on investment decisions when comparing investments at a company wide level in a global context.

6.5.3. Depreciation Charges

Depreciation charges are the most common type of tax allowance used by governments as an incentive for investment. Depreciation is a noncash charge reported as an expense, which reduces income for taxation purposes. There is no cash outlay for depreciation, and no money is transferred to any fund or account, so the depreciation charge is added back to the net income after taxes to give the total cash flow from operations.

$$\begin{aligned} CF &= I - (I \times t_r) + D \\ &= (P - D) - ((P - D) \times t_r) + D \\ &= P(1 - t_r) + Dt_r \end{aligned} \tag{6.24}$$

where

I = taxable income;
D = depreciation tax allowance.

It can be seen that equations 6.23 and 6.24 are equivalent.

Depreciation charges can be thought of as an allowance for the "wear and tear, deterioration or obsolescence of the property" as a result of its use (IRS publ. 946).

The book value of an asset is the original cost paid minus the accumulated depreciation charged. The book value has no connection to the resale value or current market value of the asset:

$$\text{Book value} = \text{initial cost} - \text{accumulated depreciation} \tag{6.25}$$

Note that the law usually allows depreciation only of fixed capital investments, and not total capital, since working capital is not consumed and can be recovered at the end of the project. If land was purchased for the project, then the cost of the land must be deducted from the fixed capital cost as land is assumed to retain its value and cannot be depreciated.

Over a period of time the book value of the asset or fixed investment decreases until it is fully "paid off" or "written off," at which point depreciation can no longer be charged. The schedule of how depreciation charges are taken is set by the tax law. In the United States, most investments are depreciated using the Modified Accelerated

Cost Recovery System (MACRS) described later (IRS publ. 946), but other methods are used internationally, and in a globalized economy it is necessary for design engineers to have familiarity with these also.

Straight-Line Depreciation

Straight-line depreciation is the simplest method. The depreciable value, C_d, is depreciated over n years with annual depreciation charge D_i in year i, where

$$D_i = \frac{C_d}{n} \text{ and } D_j = D_i \forall j \tag{6.26}$$

The depreciable value of the asset is the initial cost of the fixed capital investment, C, minus the salvage value (if any) at the end of the depreciable life. For chemical plants the salvage value is often taken as zero, as the plant usually continues to operate for many years beyond the end of the depreciable life.

The book value of the asset after m years of depreciation, B_m, is

$$\begin{aligned} B_m &= C - \sum_{i=1}^{m} D_i \\ &= C - \frac{mC_d}{n} \end{aligned} \tag{6.27}$$

When the book value is equal to the salvage value (or zero), then the asset is fully depreciated and no further depreciation charge can be taken.

Straight-line depreciation must be used in the United States for software (with a 36-month depreciable life), patents (with life equal to the patent term remaining), and other depreciable intangible property (IRS publ. 946).

Declining-Balance Depreciation

The declining-balance method is an accelerated depreciation schedule that allows higher charges in the early years of a project. This helps improve project economics by giving higher cash flows in the early years. In the declining-balance method, the annual depreciation charge is a fixed fraction, F_d, of the book value:

$$\begin{aligned} D_1 &= C\, F_d \qquad (6.28)\\ B_1 &= C - D_1 = C(1 - F_d) \\ D_2 &= B_1\, F = C(1 - F_d)F_d \\ B_2 &= B_1 - D_2 = C(1 - F_d)\ (1 - F_d) = C(1 - F_d)^2 \end{aligned}$$

Hence:

$$D_m = C(1 - F_d)^{m-1}\, F_d \tag{6.29}$$

$$B_m = C(1 - F_d)^m \tag{6.30}$$

The fraction F_d must be less than $2/n$, where n is the depreciable life in years. When $F_d = 2/n$, this method is known as double declining-balance depreciation.

Modified Accelerated Cost Recovery System (MACRS)

The MACRS depreciation method was established by the U.S. Tax Reform Act of 1986 and is the depreciation method used for most tangible assets in the United States. The details of the MACRS depreciation method are given in IRS publication 946, which is available online at www.irs.gov/publications. The method is basically a combination of the declining-balance method and the straight-line method. The declining-balance method is used until the depreciation charge becomes less than it would be under the straight-line method, at which point the MACRS method switches to charge the same amount as the straight-line method.

Under MACRS depreciation, different recovery periods are assigned to different kinds of assets, based on a usable life ("class life") designated by the U.S. Internal Revenue Service (IRS). For chemical plants and most other processing equipment, the class life is 10 to 16 years and the recovery period is 7 years. It should be noted, however, that for roads, docks, and other civil infrastructure, a 15-year recovery period is used, so some offsite investments are depreciated on a different schedule from that used for the ISBL investment.

Another important convention within MACRS depreciation is that the method assumes that all property is acquired mid-year and hence assigns half of the full-year depreciation in the first and last years of the recovery period. The result is the schedule of depreciation charges given in Table 6.9.

Other details of MACRS depreciation are not discussed here, and at the time of writing, the tax law also allows assets to be depreciated by the straight-line method (over the class life, not the recovery period and still following the half-year convention). The tax law is revised frequently and the most recent version of IRS publication

Table 6.9. MACRS Depreciation Charges

	Depreciation Rate ($F_i = D_i/C_d$)	
Recovery Year	**7-Year Recovery**	**15-Year Recovery**
1	14.29	5.00
2	24.49	9.50
3	17.49	8.55
4	12.49	7.70
5	8.93	6.93
6	8.92	6.23
7	8.93	5.90
8	4.46	5.90
9		5.91
10		5.90
11		5.91
12		5.90
13		5.91
14		5.90
15		5.91
16		2.95

946 should be consulted for the current regulations. Similarly, when international projects are analyzed, the appropriate national and regional tax laws must be checked to ensure that the correct depreciation rules are followed. Several other less widely used depreciation methods are not discussed here. A good overview of these is given by Humphreys (1991).

Example 6.8

A chemical plant with a fixed capital investment of $100 million generates an annual gross profit of $50 million. Calculate the depreciation charge, taxes paid, and after-tax cash flows for the first 10 years of plant operation using straight-line depreciation over 10 years and using MACRS depreciation with a 7-year recovery period. Assume the plant is built at time zero and begins operation at full rate in year 1. Assume the rate of corporate income tax is 35%, and taxes must be paid based on the previous year's income.

Solution

The solution is easily coded into a spreadsheet. The results are shown in the tables below:

Year	Gross profit (MM$)	Depreciation charge (MM$)	Taxable income (MM$)	Taxes paid (MM$)	Cash Flow (MM$)
0	0	0	0	0	–100
1	50	10	40	0	50
2	50	10	40	14	36
3	50	10	40	14	36
4	50	10	40	14	36
5	50	10	40	14	36
6	50	10	40	14	36
7	50	10	40	14	36
8	50	10	40	14	36
9	50	10	40	14	36
10	50	10	40	14	36

Year	Gross profit (MM$)	Depreciation charge (MM$)	Taxable income (MM$)	Taxes paid (MM$)	Cash Flow (MM$)
0	0	0	0	0	–100
1	50	14.29	35.71	0	50
2	50	24.49	25.51	12.50	37.50
3	50	17.49	32.51	8.93	41.07
4	50	12.49	37.51	11.38	38.62
5	50	8.93	41.07	13.13	36.87
6	50	8.92	41.08	14.37	35.63
7	50	8.93	41.07	14.38	35.62
8	50	4.46	45.54	14.37	35.63
9	50	0	50	15.94	34.06
10	50	0	50	17.50	32.50

6.6. PROJECT FINANCING

The construction and operation of chemical plants require large amounts of capital. Corporations engaged in the production of chemicals must raise the finances to support such investments. Like taxation, corporate financing is a specialized subject with many intricacies that require expert knowledge. The design engineer needs a superficial awareness of this subject to carry out economic analysis and optimization of the design.

6.6.1. Basics of Corporate Accounting and Finance

The purpose of financial accounting is to report the economic performance and financial condition of a company to its owners (shareholders), lenders, regulatory agencies, and other stakeholders. The primary means for financial reporting is the annual report to shareholders. The annual reports for companies in the chemical, pharmaceutical, and fuels industries generally contain

1. A letter from the chief executive officer (CEO) describing the past year's operations, significant acquisitions, divestitures and restructuring, and plans for the short and long term;
2. Financial information:
   - **a.** Balance sheet;
   - **b.** Income statement;
   - **c.** Cash flow statement;
   - **d.** Notes to the financial statements;
   - **e.** Comments from the independent auditors.
3. Information on the directors and executive management of the company;
4. A report on the health, safety, and environmental performance of the company (sometimes published separately).

The annual report of any publicly traded company will usually be available online and can easily be found by visiting the company's website. The site will usually have a prominent link to "information for investors" or something similar. No attempt has been made to create fictitious financial statements for the purposes of this book, as an abundance of real examples is readily available online. The reader is encouraged to search online for real examples.

Balance Sheet

The balance sheet is a snapshot of the financial condition of the company. It lists all the assets owned by the company and all the liabilities or amounts owed by the company. The difference between assets and liabilities is the stockholder's equity, i.e., notionally the amount of money the stockholders would have available to share out if they decided to liquidate the company.

$$\text{Stockholder's equity} = \text{assets} - \text{liabilities} \tag{6.31}$$

Assets are typically listed in order of decreasing liquidity. Liquidity is a measure of how easily the asset could be turned into cash. Assets include

- Cash and cash equivalents;
- Notes and accounts receivable, i.e., money owed to the company for goods shipped but not yet paid for;
- Inventories of raw materials, products, spare parts, and other supplies;
- Prepaid taxes and expenses;
- Investments such as equity stakes in other companies or joint ventures;
- Property, plant, and equipment. This is listed at book value, i.e., cost less accumulated depreciation. The actual market value of these assets may be considerably higher;
- Intangible assets such as patents, trademarks, goodwill, etc.

Liabilities are usually listed in the order in which they are due, starting with current liabilities. Liabilities include

- Accounts payable, i.e., payment owed on goods already received by the company;
- Notes and loans that are due for repayment;
- Accrued liabilities and expenses such as legal settlements, amounts set aside for warranties, guarantees, etc.;
- Deferred income taxes;
- Long-term debt.

The difference between assets and liabilities is the shareholder's equity. This consists of the capital paid in by the owners of common and preferred stocks, together with earnings retained and reinvested in the business. The capital paid in by the shareholders is often listed as the par value of the stock (typically 25¢ to $1 per share) plus the additional capital paid in when the stock was initially sold by the company. Note that this reflects only the capital raised by the company and has no relation to subsequent increases or decreases in the value of the stock that may have resulted from trading.

Income Statement

The income statement or consolidated statement of operations is a summary of the incomes, expenditures, and taxes paid by the company over a fixed period of time. Results are usually presented for the past three calendar years.

The income statement lists the following items:

1. Sales and operating revenues (positive);
2. Income from equity holdings in other companies (positive);
3. Cost of goods sold (negative);
4. Selling, general, and administrative expenses (negative);
5. Depreciation (negative on the income statement but will be added back on the cash flow statement);
6. Interest paid on debt (negative);

7. Taxes other than income tax, such as excise duties (negative);
8. Income taxes (negative).

The sum of items 1 through 5 is sometimes listed as *earnings before interest and taxes* (EBIT). The sum of items 1 through 7 is listed as income before taxes or taxable income, and is usually positive. The net income is the sum of items 1 through 8, i.e., income before taxes minus taxes paid. Net income is also usually expressed as earnings per share of common stock.

The income statement gives a good insight into the overall profitability and margins of a business. It has to be read carefully though, as several items listed are noncash charges such as depreciation that do not affect the cash flow of the business. Corrections for these items are made in the cash flow statement.

Cash Flow Statement

The cash flow statement gives a summary of overall cash flows into and out of the business as a result of operating activities, investments, and financing activities. It is also usually reported for the past three calendar years.

The cash flow from operating activities section starts with the net income. Adjustments are made for noncash transactions (depreciation and deferred taxes are added back in), and changes in assets and liabilities.

The cash flow from investing activities section lists the cash spent on acquiring fixed assets such as property, plant, and equipment, less any revenues from sale of fixed assets. It also lists acquisitions or divestitures of subsidiary businesses.

The cash flow from financing activities section summarizes changes in the company's long-term and short-term debt, proceeds from issues of common stock, repurchase of stocks, and dividends paid to stockholders.

The sum of cash flows from operations, investments, and financing gives the net change in cash and cash equivalents. This is then added to the cash and cash equivalents from the beginning of the year to give the cash and cash equivalents at the end of the year, which appears on the balance sheet.

Summary

The business and accounting literature contain a wealth of information on how to read and analyze corporate financial statements. Most engineers work for or with corporations and have a direct personal interest in understanding financial performance; however, a detailed treatment of the subject is beyond the scope of this book. Excellent introductions to finance and accounting are given in the books by Spiro (1996) and Shim and Henteleff (1995).

6.6.2. Debt Financing and Repayment

Most debt capital is raised by issuing long-term bonds. A *mortgage* is a bond that is backed by pledging a specific real asset as security against the loan. An unsecured bond is called a *debenture*. The ratio of total debt divided by total assets is known as the *debt ratio* (DR) or leverage of the company.

All debt contracts require payment of interest on the loan and repayment of the principal (either at the end of the loan period or amortized over the period of the loan). Interest payments are a fixed cost, and if a company defaults on these payments, then its ability to borrow money will be drastically reduced. Since interest is deducted from earnings, the greater the leverage of the company, the higher the risk to future earnings, and hence to future cash flows and the financial solvency of the company. In the worst case, the company could be declared bankrupt and the assets of the company sold off to repay the debt. Finance managers therefore carefully adjust the amount of debt owed by the company so that the cost of servicing the debt (the interest payments) does not place an excessive burden on the company.

The rate of interest owed on debt depends on the bond markets, government central banks, and the creditworthiness of the company. When new bonds are issued, they must be offered at a competitive interest rate; otherwise, they will not sell. If the bond issuer has a high credit rating, then it will be able to issue bonds at close to the interest rates set by the government. (U.S. Treasury bonds are not rated, as it is assumed that they will be backed by the federal government). If the credit rating of the issuer is lower, then there is a higher chance that the debt may not be repaid, in which case it must be offered at a higher interest rate to offset this risk. Credit rating services such as Moody's and Standard and Poor's study the finances of corporations and publish credit ratings. These ratings are usually not advertised by issuers unless they are very high, but they are published in the financial papers. The difference in interest rate between low-rated and high-rated bonds issued at the same time is typically 2 to 3%.

Once they have been issued, bonds are traded on the New York Stock Exchange or the American Stock Exchange. Although the price of the bond in subsequent trading may vary from the offer price (or face value), the interest rate remains fixed. The *Wall Street Journal* reports prices daily for the most actively traded corporate bonds. Bond prices can also be found at www.investinginbonds.com, together with much other useful information on bond markets. The interest rate is listed as the "coupon" and the date on which the bond expires is the "maturity." Bonds are also assigned a unique nine-digit identification number by the American Bankers' Association Committee on Uniform Security Identification Procedures (CUSIP). For example, in 2006 Honeywell Inc. issued a 30-year bond CUSIP #438516AR7 with coupon 5.700 and maturity 03/15/2036.

6.6.3. Equity Financing

Equity capital consists of the capital contributed by stockholders, together with earnings retained for reinvestment in the business. Stockholders purchase stocks in the expectation of getting a return on their investment. This return can come from the dividends paid annually to stockholders (the part of earnings returned to the owners) or from growth of the company that is recognized by the stock market and leads to an increase in the price of the stock. Most stock is usually held by sophisticated institutional investors such as banks, mutual funds, insurance companies, and pension funds. These investors employ expert analysts to assess the performance of companies relative to other companies in the same sector and to the market as a whole. If the management of a company does not effectively deliver the financial return expected by investors, the stock price will suffer and the management will soon be replaced.

Simple measures of the effectiveness of management are the return on equity and earnings per share. Return on equity (ROE) is defined as

$$\text{ROE} = \frac{\text{net annual profit}}{\text{stockholder's equity}} \times 100\% \tag{6.32}$$

The stockholders' expectation of return on their equity can be expressed as an interest rate and is known as the *cost of equity capital*. The cost of equity required to meet the expectations of the market is usually substantially higher than the interest rate owed on debt because of the riskier nature of equity finance (since debt holders are paid first and hence have the primary right to any profit made by the business). For most corporations in the United States at the time of writing, the cost of equity is in the range 25 to 30%.

6.6.4. Cost of Capital

Very few companies operate entirely on debt or equity financing alone, and most use a balance of both. The overall cost of capital is simply the weighted average of the cost of debt and the cost of equity:

$$i_c = (DR \times i_d) + ((1 - DR) \times i_e) \tag{6.33}$$

where

i_c = cost of capital;
DR = debt ratio;
i_d = interest rate due on debt;
i_e = cost of equity.

For example, if a company were financed 55% with debt at an average 8% interest and 45% with equity that carried an expectation of a 25% return, then the overall cost of capital would be

$$\begin{aligned} i_c &= (0.55 \times 0.08) + (0.45 \times 0.25) \\ &= 0.1565 \end{aligned}$$

Since the equity is by definition (equation 6.31) the assets minus the liabilities (debt), the overall return on assets (ROA) can be expressed as

$$\text{ROA} = \frac{\text{net annual profit}}{\text{total assets}} \times 100\% \tag{6.34}$$

It follows that:

$$\frac{\text{ROA}}{\text{ROE}} = \frac{\text{stockholder's equity}}{\text{total assets}} = 1 - DR \tag{6.35}$$

The overall cost of capital sets the interest rate that is used in economic evaluation of projects. The total portfolio of projects funded by a company must meet or exceed this interest rate if the company is to achieve its targeted return on equity and hence satisfy the expectations of its owners.

6.7. ECONOMIC EVALUATION OF PROJECTS

As the purpose of investing money in a chemical plant is to earn money, some means of comparing the economic performance of projects is needed. Before a company agrees to spend a large amount of capital on a proposed project, the management must be convinced that the project will provide a sound investment compared to other alternatives. This section introduces the principal methods used for making economic comparisons between projects.

6.7.1. Cash Flow and Cash Flow Diagrams

During any project, cash initially flows out of the company to pay for the costs of engineering, equipment procurement, and plant construction. Once the plant is constructed and begins operation, then the revenues from sale of product begin to flow into the company. The *net cash flow* at any time is the difference between the earnings and expenditure. A cash flow diagram, such as that shown in Figure 6.10, shows the forecast cumulative net cash flow over the life of a project. The cash flows are based on the best estimates of investment, operating costs, sales volume, and sales price that can be made for the project. A cash flow diagram gives a clear picture of the resources required for a project and the timing of the earnings. The diagram can be divided into the following characteristic regions:

A–B The investment required to design the plant.
B–C The heavy flow of capital to build the plant and provide funds for startup, including working capital.
C–D The cash flow curve turns up at C, as the process comes on stream and income is generated from sales. The net cash flow is now positive, but the cumulative amount remains negative until the investment is paid off, at point D.

Point D is known as the *break-even point* and the time to reach the break-even point is called the *payback time*. (In a different context, the term *break-even point* is also sometimes used for the percentage of plant capacity at which the income equals the cost for production.)

D–E In this region the cumulative cash flow is positive. The project is earning a return on the investment.
E–F Toward the end of project life, the rate of cash flow may tend to fall off, due to increased operating costs and falling sales volume and price due to obsolescence of the plant, and the slope of the curve changes.

The point F gives the final cumulative net cash flow at the end of the project life.

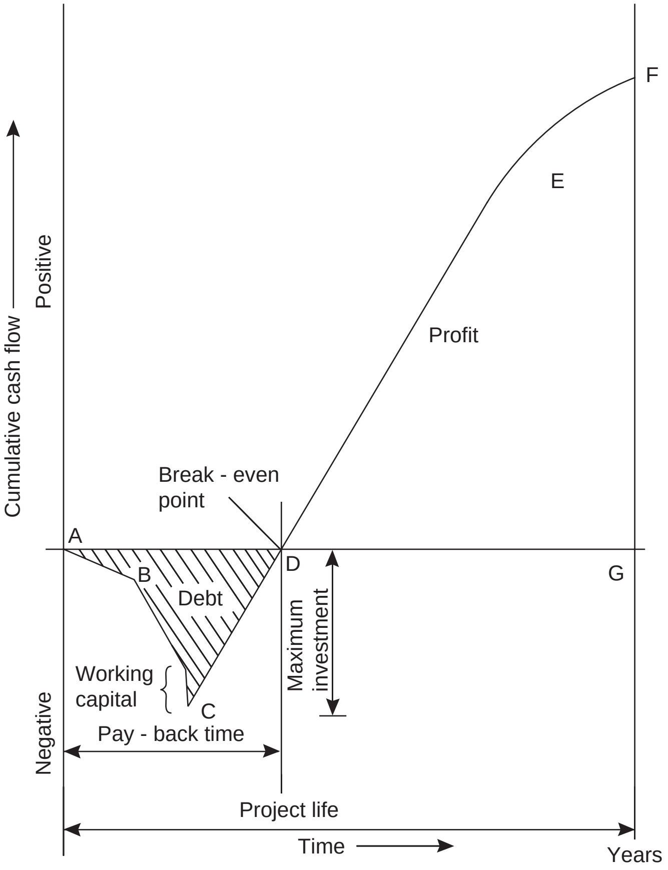


Figure 6.10. Project cash flow diagram.

Net cash flow is a relatively simple and easily understood concept, and it forms the basis for the calculation of other, more complex measures of profitability. Taxes and the effect of depreciation are usually not considered in cash flow diagrams.

6.7.2. Simple Methods for Economic Analysis

Payback Time

A simple method for estimating the payback time is to divide the total initial capital (fixed capital plus working capital) by the average annual cash flow:

$$\text{simple pay-back time} = \frac{\text{total investment}}{\text{average annual cash flow}} \tag{6.36}$$

This is not the same payback time indicated by the cash flow diagram, as it assumes that all the investment is made in year 0 and revenues begin immediately. For most chemical plant projects, this is not realistic as investments are typically spread over 1 to 3 years, and revenues may not reach 100% of design basis until the second year of operation. The simple payback time also neglects taxes and depreciation.

Return on Investment

Another simple measure of economic performance is the return on investment (ROI). The ROI is defined in a similar manner to ROA and ROE:

$$\text{ROI} = \frac{\text{net annual profit}}{\text{total investment}} \times 100\% \tag{6.37}$$

If ROI is calculated as an average over the whole project, then

$$\text{ROI} = \frac{\text{cumulative net profit}}{\text{plant life} \times \text{initial investment}} \times 100\% \tag{6.38}$$

Calculation of the after-tax ROI is complicated if the depreciation term is less than the plant life and if an accelerated method of depreciation such as MACRS is used. In such cases, it is just as easy to calculate one of the more meaningful economic criteria such as net present value or discounted cash flow rate of return, described later. Because of this complication, a pre-tax ROI is often used instead:

$$\text{pre-tax ROI} = \frac{\text{pre-tax cash flow}}{\text{total investment}} \times 100\% \tag{6.39}$$

Note that pre-tax ROI is based on cash flow, not profit or taxable income, and therefore does not include a depreciation charge.

Return on investment is also sometimes calculated for incremental modifications to a large project, as described in Section 6.9.3.

6.7.3. Time Value of Money

In Figure 6.10 the net cash flow is shown at its value in the year in which it occurred. So the figures on the ordinate show the *future worth* of the project. The cumulative value is the *net future worth* (NFW).

The money earned in any year can be reinvested as soon as it is available and can start to earn a return. So money earned in the early years of the project is more valuable than that earned in later years. This ‘‘time value of money’’ can be allowed for by using a variation of the familiar compound interest formula. The net cash flow in each year of the project is brought to its ‘‘present value’’ at the start of the project by discounting it at some chosen compound interest rate.

The future worth of an amount of money, P, invested at interest rate, i, for n years is

$$\text{Future worth in year } n = P(1 + i)^n$$

Hence, the present value of a future sum is

$$\text{present value of future sum} = \frac{\text{future worth in year } n}{(1 + i)^n} \tag{6.40}$$

The interest rate used in discounting future values is known as the *discount rate* and is chosen to reflect the earning power of money. In most companies the discount rate is set at the cost of capital (see Section 6.6.4).

Discounting of future cash flows should not be confused with allowing for price inflation. Inflation is a general increase in prices and costs, usually caused by imbalances between supply and demand. Inflation raises the costs of feed, products, utilities, labor, and parts but does not affect depreciation charges, which are based on original cost. Discounting, on the other hand, is a means of comparing the value of money that is available now (and can be reinvested) with money that will become available at some time in the future. All of the economic analysis methods can be modified to allow for inflation. See, for example, Humphreys (1991), Chapter 6. In practice, most companies assume that although prices may suffer inflation, margins and hence cash flows will be relatively insensitive to inflation. Inflation can therefore be neglected for the purposes of comparing the economic performance of projects.

6.7.4. Net Present Value

The *net present value* (NPV) of a project is the sum of the present values of the future cash flows:

$$\text{NPV} = \sum_{n=1}^{n=t} \frac{CF_n}{(1+i)^n} \tag{6.41}$$

where

CF_n = cash flow in year n;
t = project life in years;
i = interest rate (= cost of capital, percent /100).

The net present value is always less than the total future worth of the project because of the discounting of future cash flows. Net present value is easily calculated using spreadsheets, and most spreadsheet programs have an NPV function.

The net present value is a strong function of the interest rate used and the time period studied. When different time periods are analyzed, the time period is sometimes denoted by a subscript. For example, NPV_{10} would denote the NPV over a 10-year period.

Net present value is a more useful economic measure than simple payback and ROI, since it allows for the time value of money and also for annual variation in expenses and revenues. Few large projects are completed in a single year and immediately begin production at full capacity. A more typical startup schedule is given in Table 6.10. Net present value is also a more appropriate method to use when considering after-tax income using an accelerated depreciation method such as MACRS.

6.7.5. Discounted Cash Flow Rate of Return (DCFROR)

When the NPV is calculated at various interest rates, it is possible to find an interest rate at which the cumulative net present value at the end of the project is zero.

Table 6.10. Typical Startup Schedule

Year	Costs	Revenues	Explanation
1st year	30% of fixed capital	0	Engineering + long lead-time items
2nd year	40–60% of fixed capital	0	Procurement and construction
3rd year	10–30% of fixed capital + working capital +		Remaining construction
	FCOP + 30% VCOP	30% of design basis revenue	Initial production
4th year	FCOP + 50–90% VCOP	50–90% of design basis revenue	Shake-down of plant
5th year +	FCOP + VCOP	100% of design basis revenue	Full production at design rates

This particular rate is called the *discounted cash flow rate of return* (DCFROR) and is a measure of the maximum interest rate that the project could pay and still break even by the end of the project life:

$$\sum_{n=1}^{n=t} \frac{CF_n}{(1+i')^n} = 0 \tag{6.42}$$

where

CF_n = cash flow in year n;
t = project life in years;
i' = the discounted cash flow rate of return (percent/100).

The value of i' is found by trial-and-error calculations or by using the appropriate function in a spreadsheet. A more profitable project will be able to pay a higher DCFROR.

DCFROR provides a useful way of comparing the performance of capital for different projects, independent of the amount of capital used, the life of the plant, or the actual interest rates prevailing at any time. DCFROR is a more useful method than NPV when comparing projects of very different size. The NPV of large projects is usually greater than that of small projects, but then the investment is also much greater. DCFROR is independent of project size, and the project with the highest DCFROR always provides the best ‘‘bang for the buck.’’ When DCFROR is used as an investment criterion, companies usually expect projects to have a DCFROR greater than the cost of capital.

DCFROR can also be compared directly with interest rates. Because of this, it is sometimes known as the *interest rate of return* or *internal rate of return* (IRR).

Example 6.9

Estimate the NPV at a 12% interest rate and the DCFROR for the project described in Example 6.8, using the MACRS depreciation method.

Solution

Calculating the present values of the cash flows from the previous example requires adding two columns to the spreadsheet. We first calculate the discount factor $(1+i)^{-n}$ and then multiply this by the cash flow in year n to give the present value of the cash flow. The present values can then be summed to give the net present value:

Year	Gross profit (MM$)	Depreciation charge (MM$)	Taxable income (MM$)	Taxes paid (MM$)	Cash Flow (MM$)	Discount factor	Present value of CF (MM$)
0	0	0	0	0	–100	1	–100
1	50	14.29	35.71	0	50	0.893	44.64
2	50	24.49	25.51	12.50	37.50	0.797	29.90
3	50	17.49	32.51	8.93	41.07	0.712	29.23
4	50	12.49	37.51	11.38	38.62	0.636	24.54
5	50	8.93	41.07	13.13	36.87	0.567	20.92
6	50	8.92	41.08	14.37	35.63	0.507	18.05
7	50	8.93	41.07	14.38	35.62	0.452	16.11
8	50	4.46	45.54	14.37	35.63	0.404	14.39
9	50	0	50	15.94	34.06	0.361	12.28
10	50	0	50	17.50	32.50	0.322	10.46
				Interest rate		12%	
				Total = Net present value =			120.54

Note that we could also have calculated NPV directly using the NPV function. In MS Excel, the NPV function starts at the end of year 1, so any cash flows in year 0 should not be included in the function range.

The DCFROR can then be found by adjusting the interest rate until the NPV is equal to zero. This is easily accomplished in the spreadsheet using the "Goal Seek" tool, giving DCFROR = 40%.

6.7.6. Annualized Cost Methods

An alternative method of comparing the magnitude of a capital investment in current dollars with a revenue stream in the future is to convert the capital cost into a future annual capital charge.

If an amount P is invested at an interest rate i, then after n years of compound interest, it matures to the sum $P(1+i)^n$.

If, instead, an amount A is invested each year, also at interest rate i, then it matures to a sum, S, where

$$S = A + A(1+i) + A(1+i)^2 + \ldots + A(1+i)^{n-1} \tag{6.43}$$

so

$$S(1+i) = A(1+i) + A(1+i)^2 + \ldots + A(1+i)^n \tag{6.44}$$

Hence, subtracting equation 6.43 from equation 6.44:

$$Si = A[(1+i)^n - 1] \tag{6.45}$$

If the annual payments A have matured to give the same final sum that would have been obtained by investing the principal P at the same interest rate, then

$$S = P\ (1 + i)^n = \frac{A}{i}[(1 + i)^n - 1]$$

Hence

$$A = P\frac{[i(1 + i)^n]}{[(1 + i)^n - 1]} \tag{6.46}$$

and we can define an annual capital charge ratio (*ACCR)* as

$$ACCR = \frac{A}{P} = \frac{[i(1 + i)^n]}{[(1 + i)^n - 1]} \tag{6.47}$$

The annual capital charge ratio is the fraction of the principal that must be paid out each year to fully repay the principal and all accumulated interest over the life of the investment. This is the same formula used for calculating payments on home mortgages and other loans where the principal is amortized over the loan period.

If the cost of capital is used as the interest rate (see Section 6.6.4), then the annual capital charge ratio can be used to convert the initial capital expense into an annual capital charge, or annualized capital cost, as described in Section 6.2.5.

$$\text{Annual capital charge (ACC)} = ACCR \times \text{total capital cost} \tag{6.48}$$

The annual capital charge can be added to the operating costs to give a total annualized cost (TAC):

$$\text{TAC} = \text{operating costs} + ACCR \times \text{total capital cost} \tag{6.49}$$

The TAC can be compared with forecasted future revenues. The TAC is also sometimes referred to as *total cost of production* (TCOP).

Table 6.11 shows values of *ACCR* for different values of i and n. For a typical cost of capital of about 15% and a plant life of 10 years, the value of *ACCR* is 0.199, or about one-fifth of the capital investment.

Table 6.11. Values of Annual Capital Charge Ratio (*ACCR*) for Different Interest Rates

Interest Rate, *i*	***ACCR:* 10-Year Life**	***ACCR:* 20-Year Life**
0.1	0.163	0.117
0.12	0.177	0.134
0.15	0.199	0.16
0.2	0.239	0.205
0.25	0.280	0.253
0.3	0.323	0.302

There are a few important things that should be noted when using the annualized cost method:

1. The method assumes investment and cash flows begin immediately and so does not capture information on the timing of early expenditures and revenues.
2. The method does not take into account taxes or depreciation and assumes that all of the revenue from the project is available to provide a return on the initial investment.
3. Working capital is recovered at the end of the project, and so strictly only the fixed capital should be annualized. Equations 6.46 and 6.47 can be modified for the case where an additional sum becomes available at the end of the investment term, but this modified version is seldom used in practice and working capital is often either neglected in the annualized cost method or else (wrongly) thrown in with fixed capital. A simple way around this problem is to assume that the working capital is entirely funded by debt, in which case the cost of carrying the working capital is reduced to an interest payment that appears as part of the fixed costs of production. At the end of the project life the working capital will be released and will be available to repay the principal on the debt.
4. As described in Section 6.2.4, several of the fixed costs of production are proportional to the fixed capital invested (*FC*). If we assume annual charges of 3% of *FC* for maintenance, 2% of *FC* for property tax, and 65% plant overhead, then the annual capital charge ratio is increased by $0.02 + (1.65 \times 0.03) = 0.07$.
5. If we also assume engineering costs are 10% of (ISBL + OSBL) capital investment and add 15% of (ISBL + OSBL) capital as contingency, then with a 10-year plant life and a 15% interest rate, the annual capital charge ratio is

$$\begin{aligned} ACCR &= [0.199 \times (1.0 + 0.1 + 0.15) + 0.07] \times [\text{Installed ISBL} \\ &\quad + \text{OSBL capital cost}] = 0.32 \times [\text{Installed ISBL} + \text{OSBL capital cost}] \end{aligned} \tag{6.50}$$

Equation 6.50 is the basis for the widely used rule of thumb of annualizing capital cost by dividing by three. When this rule of thumb is used, it is important to remember that some, but not all, of the fixed costs have been counted in the annual capital charge.

The annualized cost method involves more assumptions than calculating NPV or DCFROR, but it is widely used as a quick way of comparing investments with the resulting benefits. Annualized cost is also useful as a method for analyzing small projects and modifications that lead to reduced operating costs (for example, heat recovery projects), since the annualized capital outlay can be directly traded off against the expected annual savings and there is usually no change in working capital, operating labor, or other fixed costs of production. Small projects usually can be executed quickly, so the error introduced by neglecting the timing of investments and revenues is less important than it is when designing a new plant.

The annualized cost method is also used when comparing the costs of equipment with different expected operating life. Annualization of the costs allows equipment with different service life to be compared on the same annual basis. This is illustrated in the example that follows.

Example 6.10

A carbon steel heat exchanger that costs \$140,000 is expected to have a service life of 5 years before it requires replacement. If type 304 stainless steel is used, then the service life will be increased to 10 years. Which exchanger is the most economical if the cost of capital is 12%?

Solution

With a 12% interest rate and 5-year life, the annual capital charge ratio is

$$ACCR = \frac{[i(1+i)^n]}{[(1+i)^n - 1]} = \frac{[0.12(1.12)^5]}{[(1.12)^5 - 1]} = 0.277 \tag{6.47}$$

The annualized capital cost of the carbon steel exchanger is then = \$140,000 × 0.277 = $\underline{\underline{\$38,780/\mathrm{y}}}$.

From Table 6.5, we can estimate the cost of the type 304 stainless steel exchanger to be \$140,000 × 1.3 = \$182,000. From Table 6.11 (or equation 6.47), with a 10-year life and 12% interest rate, the annual capital charge ratio is 0.177, so the annualized cost of the stainless steel exchanger is

$$= \$182{,}000 \times 0.177 = \underline{\underline{\$32{,}210/\mathrm{y}}}$$

In this case, it would be more economical to buy the stainless steel heat exchanger.

6.7.7. Summary

There is no single best criterion for economic evaluation of projects. Each company uses its own preferred methods and sets criteria for the minimum performance that will allow a project to be funded (see Section 6.9). The design engineer must be careful to ensure that the method and assumptions used are in accordance with company policy and that projects are compared on a fair basis. Projects should always be compared using the same economic criterion but do not have to be compared on *the exact same* basis, since in a global economy there may be significant regional advantages in feed and product pricing, capital costs, financing, or investment incentives.

As well as economic performance, many other factors have to be considered when evaluating projects, such as the following:

1. Safety;
2. Environmental problems (waste disposal);
3. Political considerations (government policies);
4. Location of customers and suppliers (supply chain);
5. Availability of labor and supporting services;
6. Corporate growth strategies;
7. Company experience in the particular technology.

Example 6.11

Adipic acid is used in the manufacture of nylon 6,6. It is made by hydrogenation of phenol to a mixture of cyclohexanol and cyclohexanone (known as KA oil–ketone and alcohol), followed by oxidation with nitric acid. The overall reaction can be written approximately as

$$C_6H_5OH + 2H_2 \rightarrow C_6H_{10}O$$

$$C_6H_{10}O + H_2 \rightarrow C_6H_{11}OH$$

$$C_6H_{11}OH + 2HNO_3 \rightarrow HOOC(CH_2)_4COOH + N_2O + 2H_2O$$

The actual process requirements of phenol, hydrogen, nitric acid, and utilities and consumables have been determined to be

Material	Amount	Units
Phenol	0.71572	lb/lb product
Hydrogen	0.0351	lb/lb product
Nitric acid (100% basis)	0.71778	lb/lb product
Byproduct off gas	0.00417	lb/lb product
Various catalysts and chemicals	32.85	$/metric ton product
Electric power	0.0939	kWh/lb product
Cooling water	56.1	gal/lb product
HP steam	0.35	lb/lb product
MP steam	7.63	lb/lb product
Boiler feed water	0.04	gal/lb product

These yields were taken from Chem Systems PERP report 98/99-3 Adipic acid (Chem Systems, 1999). The nitric acid consumption is given on a 100% basis, but 60% nitric acid is used in the process.

Estimate the fixed capital cost, the working capital, the cash cost of production, and total cost of production for a new 400,000 metric ton per year (400 kMTA) adipic acid plant located in Northeast Asia. The prices of adipic acid, phenol, hydrogen, and nitric acid have been forecasted for Northeast Asia as $1400/MT, $1000/MT, $1100/MT, and $380/MT, respectively. Assume a 15% cost of capital and a 10-year project life.

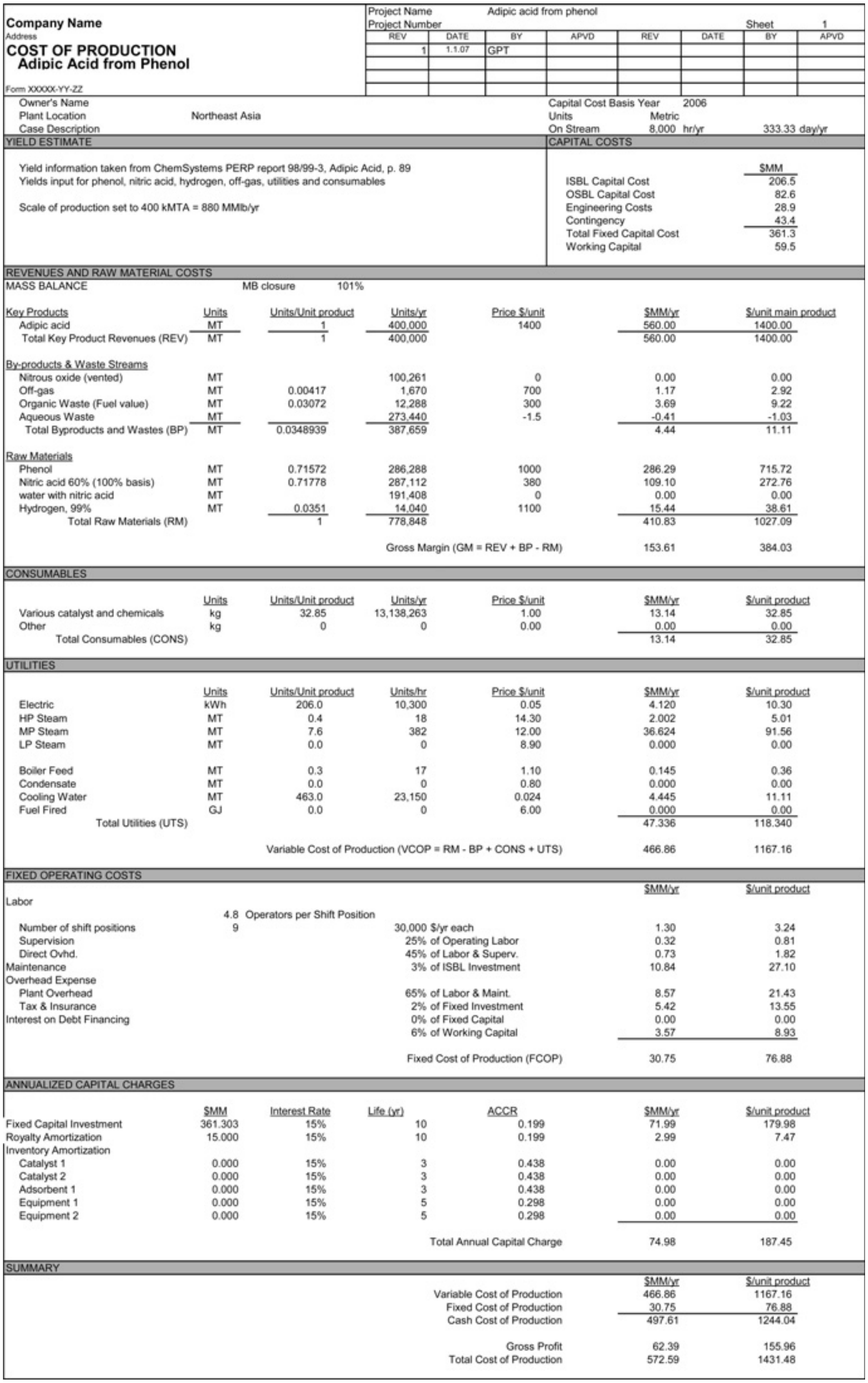
Solution

It is convenient to summarize costs of production in a spreadsheet, as discussed in Section 6.4.9. The template from Appendix G has been used in this example and is given in Figure 6.11. In addition to entering the information from the problem statement into the spreadsheet (with any necessary conversion of units), a few additional calculations are needed, as described next.

Estimating Capital Cost

The capital cost of the process can be estimated based on historic data using the correlation given in Table 6.2. The correlation is based on the plant capacity in MMlb/y, so we need to convert the capacity: 400 kMTA is equal to 880 MMlb/y:

$$\text{ISBL capital cost} = 3.533S^{0.6} = 3.533(880)^{0.6} = \$206.5\text{ MM}$$



Company Name
Address
COST OF PRODUCTION
Adipic Acid from Phenol
Form XXXXX-YY-ZZ

Project Name Adipic acid from phenol
Project Number
Sheet 1

REV	DATE	BY	APVD	REV	DATE	BY	APVD
1	1.1.07	GPT					

Owner's Name		Capital Cost Basis Year	2006	
Plant Location	Northeast Asia	Units	Metric	
Case Description		On Stream	8,000 hr/yr	333.33 day/yr

YIELD ESTIMATE

Yield information taken from ChemSystems PERP report 98/99-3, Adipic Acid, p. 89
Yields input for phenol, nitric acid, hydrogen, off-gas, utilities and consumables

Scale of production set to 400 kMTA = 880 MMlb/yr

CAPITAL COSTS

	$MM
ISBL Capital Cost	206.5
OSBL Capital Cost	82.6
Engineering Costs	28.9
Contingency	43.4
Total Fixed Capital Cost	361.3
Working Capital	59.5

REVENUES AND RAW MATERIAL COSTS

MASS BALANCE MB closure 101%

Key Products	Units	Units/Unit product	Units/yr	Price $/unit	$MM/yr	$/unit main product
Adipic acid	MT	1	400,000	1400	560.00	1400.00
Total Key Product Revenues (REV)	MT	1	400,000		560.00	1400.00
By-products & Waste Streams						
Nitrous oxide (vented)	MT		100,261	0	0.00	0.00
Off-gas	MT	0.00417	1,670	700	1.17	2.92
Organic Waste (Fuel value)	MT	0.03072	12,288	300	3.69	9.22
Aqueous Waste	MT		273,440	-1.5	-0.41	-1.03
Total Byproducts and Wastes (BP)	MT	0.0348939	387,659		4.44	11.11
Raw Materials						
Phenol	MT	0.71572	286,288	1000	286.29	715.72
Nitric acid 60% (100% basis)	MT	0.71778	287,112	380	109.10	272.76
water with nitric acid	MT		191,408	0	0.00	0.00
Hydrogen, 99%	MT	0.0351	14,040	1100	15.44	38.61
Total Raw Materials (RM)		1	778,848		410.83	1027.09
Gross Margin (GM = REV + BP - RM)					153.61	384.03

CONSUMABLES

	Units	Units/Unit product	Units/yr	Price $/unit	$MM/yr	$/unit product
Various catalyst and chemicals	kg	32.85	13,138,263	1.00	13.14	32.85
Other	kg	0	0	0.00	0.00	0.00
Total Consumables (CONS)					13.14	32.85

UTILITIES

	Units	Units/Unit product	Units/hr	Price $/unit	$MM/yr	$/unit product
Electric	kWh	206.0	10,300	0.05	4.120	10.30
HP Steam	MT	0.4	18	14.30	2.002	5.01
MP Steam	MT	7.6	382	12.00	36.624	91.56
LP Steam	MT	0.0	0	8.90	0.000	0.00
Boiler Feed	MT	0.3	17	1.10	0.145	0.36
Condensate	MT	0.0	0	0.80	0.000	0.00
Cooling Water	MT	463.0	23,150	0.024	4.445	11.11
Fuel Fired	GJ	0.0	0	6.00	0.000	0.00
Total Utilities (UTS)					47.336	118.340
Variable Cost of Production (VCOP = RM - BP + CONS + UTS)					466.86	1167.16

FIXED OPERATING COSTS

			$MM/yr	$/unit product
Labor				
	4.8	Operators per Shift Position		
Number of shift positions	9	30,000 $/yr each	1.30	3.24
Supervision		25% of Operating Labor	0.32	0.81
Direct Ovhd.		45% of Labor & Superv.	0.73	1.82
Maintenance		3% of ISBL Investment	10.84	27.10
Overhead Expense				
Plant Overhead		65% of Labor & Maint.	8.57	21.43
Tax & Insurance		2% of Fixed Investment	5.42	13.55
Interest on Debt Financing		0% of Fixed Capital	0.00	0.00
		6% of Working Capital	3.57	8.93
		Fixed Cost of Production (FCOP)	30.75	76.88

ANNUALIZED CAPITAL CHARGES

	$MM	Interest Rate	Life (yr)	ACCR	$MM/yr	$/unit product
Fixed Capital Investment	361.303	15%	10	0.199	71.99	179.98
Royalty Amortization	15.000	15%	10	0.199	2.99	7.47
Inventory Amortization						
Catalyst 1	0.000	15%	3	0.438	0.00	0.00
Catalyst 2	0.000	15%	3	0.438	0.00	0.00
Adsorbent 1	0.000	15%	3	0.438	0.00	0.00
Equipment 1	0.000	15%	5	0.298	0.00	0.00
Equipment 2	0.000	15%	5	0.298	0.00	0.00
Total Annual Capital Charge					74.98	187.45

SUMMARY

	$MM/yr	$/unit product
Variable Cost of Production	466.86	1167.16
Fixed Cost of Production	30.75	76.88
Cash Cost of Production	497.61	1244.04
Gross Profit	62.39	155.96
Total Cost of Production	572.59	1431.48

Figure 6.11. Cost of production worksheet for Example 6.11.

The ISBL cost is on a U.S. Gulf Coast basis, so we need to convert to a Northeast Asia basis. If we look up the location factor in Table 6.7, then it is not clear what factor we should use. The location factor for Japan is 1.26, while for China it varies from 0.6 to 1.1, depending on the amount of indigenous vs. imported equipment used. Since the exact location of the plant has not yet been specified, we are not able to make a definitive assessment of what the location factor should be. As a first approximation, we therefore assume it is 1.0 and note that this should be revisited as part of the sensitivity analysis.

The OSBL capital cost is estimated as 40% of ISBL cost. The engineering cost and contingency are estimated as 10% and 15% of the sum (ISBL + OSBL) cost, respectively, giving a total fixed capital cost of $\underline{\underline{\$361.3\text{ MM}}}$.

Closing Mass Balance

The first thing that is apparent when entering the yield data is that the mass balance for the process does not close properly with the information given. This suggests that we still need to account for some waste streams.

The first waste stream is apparent from the process stoichiometry. Nitric acid is recycled in the process until it is eventually converted to N_2O and vented to the atmosphere. The yield of N_2O can therefore be found by a mass balance on nitrogen:

$$\text{Nitrogen fed} = \text{nitrogen purged}$$

$$400{,}000 \times 0.71778 \times \frac{14}{63} = m_{N2O} \times \frac{2 \times 14}{44}$$

where m_{N2O} is the flow rate of N_2O, which can be calculated as 100,261 MT/y. As a first approximation, there is no cost for handling this stream, although we might revisit this at a more detailed design stage if we need to fit vent scrubbers or other equipment to handle this off gas.

The second waste stream is also apparent from the overall stoichiometry. Phenol has a molecular weight of 100 and adipic acid has a molecular weight of 146, so the stoichiometric requirement of phenol is 100/146 = 0.68493 lb/lb product. The actual process consumption has been estimated as 0.71572 lb/lb product, so the difference (0.71572 − 0.68493 = 0.03079 lb/lb) must be converted into organic byproducts. It is possible that some of the organic byproduct may be material that is lost with the hydrogen-rich fuel gas, but as a first approximation we can assume that we recover an organic liquid waste product from the process. It is also possible (in fact quite likely) that some of the material that we are calling organic byproduct is actually losses of organics in the nitrous oxide vent stream. Since this stream probably must be scrubbed before discharge, it is fair to assume as a first approximation that any organic material in it would be collected as an organic waste. This assumption should be revisited at a later stage in the design process when better information on process yields is available. The organic waste stream is priced at a typical fuel value of $300/MT, assuming that it can be burned as process fuel.

The third waste stream is an aqueous waste. This consists of the water that is brought in with the nitric acid, the water formed by the reaction stoichiometry, and any other water consumed, for example, in vent scrubbers or process water washes.

The water brought in with the nitric acid is easily found by mass balance, since it is equal to the mass flow rate of nitric acid (100% basis) × 40/60 = 400,000 × 0.71778 × 4/6 = 191,408 MT/y.

The water formed by reaction stoichiometry can be estimated as 1 mole per mole nitric acid consumed, i.e., 18 MT per 63 MT consumed, giving 400,000 × 0.71778 × 18/63 = 82,032 MT/y. Note that we could also have estimated this as 2 moles per mole product, but that would give an overestimate of the water production as the amount of nitric acid consumed is less than the apparent stoichiometric requirement. The reason is that the overall reaction given above is only an approximation and does not include the reaction of cyclohexanone.

The water consumed in process washes and scrubbers is harder to estimate, but since no process water consumption was listed under utilities, we can assume as a first approximation that all the process water needs are met by internal recycles. This gives a total waste-water flow of 191,408 + 82,032 = 273,440 MT/y. The waste-water stream is assigned a cost of $1.5/MT (see Section 6.4.6)

When the values above for nitrous oxide, organic waste, and aqueous waste are entered in the spreadsheet, the mass balance shows 101 MT of product for every 100 MT of feed. This is not perfectly closed but is good enough at this stage in the analysis. The error is most likely in the organic or aqueous waste streams and will have little impact on the economic analysis. This should, of course, be revisited when better process yield data and a converged process simulation are available.

Estimating Utility Costs

The amounts of utilities consumed are easily estimated from the production rate and the information in the problem statement (with conversion to metric units).

The prices of steam at different levels can be taken from Example 6.6, since the costs of fuel and natural gas are the same.

The prices of boiler feed water, condensate, and cooling water are estimated as described in Section 6.4.4.

The utility cost is about 10% of the variable cost of production. This is typical for many commodity chemical processes.

Estimating Fixed Costs

The adipic acid process is a relatively complex process and essentially contains two plants: phenol hydrogenation and KA oil oxidation. We should therefore assume at least four shift positions for each plant, say nine total. For a Northeast Asia basis, we expect that the salary cost per shift position will be lower than the typical $50,000 per year that we would assume for a U.S. Gulf Coast plant. As a first approximation this is estimated as $30,000/y. The remaining salary and overhead costs are fixed following the assumptions given in Section 6.2.4.

Interest charges are not included for the fixed capital (since we will calculate an annualized charge based on overall cost of capital later). An interest charge is included for the working capital, as working capital is recovered at the end of the project and so should not be amortized, as discussed in Section 6.7.6.

The total fixed cost of production is calculated to be $31 MM/y, which is low, compared to the variable cost of production ($467 MM/y). It is not uncommon for fixed costs to make a relatively minor contribution to the total cost of production for a world-scale plant.

Estimating Working Capital

The working capital is estimated as 7 weeks' cash cost of production minus 2 weeks' feedstock costs plus 1% of the fixed capital investment, as described in Section 6.2.2. Because the cash cost of production includes the interest payable on the working capital, this sets up a circular reference in the spreadsheet. The spreadsheet options must be adjusted to ensure that the calculation iterates to convergence. The converged result is $\underline{\underline{\$59.5\ \text{MM}}}$. Note that the value calculated is about 10% greater than it would have been had we estimated the working capital as 15% of fixed capital investment.

Estimating Annualized Capital Costs

The fixed capital investment is to be annualized over 10 years at a 15% interest rate. For this interest rate and recovery period, the annual capital charge ratio is 0.199, so the annual capital charge is $0.199 \times 361.3 = \$71.99$ MM/y, or \$179.98 /MT of product. As a quick check, we can see that this is roughly 10% of the total cost of production, which is typical for commodity chemical processes.

In addition to the fixed capital investment, we should also make an allowance for a process royalty. The problem statement did not specify whether the plant was to be built using proprietary technology, but it is reasonable to assume that a royalty will need to be paid. If a \$15 MM royalty is added, then this annualizes to a cost of \$3 MM/y, or roughly 0.5% of revenues, which is a reasonable initial estimate. This should be revisited during more detailed design when discussions with technology vendors take place.

Estimating Cost of Production

The cash cost of production is the sum of the fixed and variable production costs (equation 6.2):

$$\text{CCOP} = \text{VCOP} + \text{FCOP} = 466.86 + 30.75 = \underline{\underline{\$497.61\ \text{MM/y}}}$$

The total cost of production is the sum of the cash cost of production and the annual capital charge (equation 6.5):

$$\text{TCOP} = \text{CCOP} + \text{ACC} = 497.61 + 74.98 = \underline{\underline{\$572.59\ \text{MM/y}}}$$

It is worth noting that the calculated total cost of production is greater than the projected annual revenue of \$560 MM/y. This suggests that the project would not earn the expected 15% interest rate. This is explored further in the following example and in problems 6.14 and 6.15.

Example 6.12

The adipic acid plant in Example 6.11 is built with 30% of the fixed investment in year 1 and 70% in year 2, and the plant operates at 50% of capacity in year 3 before reaching full capacity in year 4. The plant can be depreciated by the straight-line method over 10 years and profits can be assumed to be taxed at 35% per year, payable the next year. Assume that losses cannot be offset against revenues from other operations for tax purposes (i.e., no tax credits in years when the plant makes a loss). Estimate the following:

1. The cash flow in each year of the project;
2. The simple payback period;
3. The net present value with a 15% cost of capital for 10 years and 15 years of production at full capacity;
4. The DCFROR for 15 years of production at full capacity.

Is this an attractive investment?

Solution

The solution requires calculating the cash flows in each year of the project. This is easily coded into a spreadsheet, as illustrated in Figure 6.12. A blank template of this spreadsheet is given in Appendix G and is available in MS Excel format in the online material at http://books.elsevier.com/companions.

Cash Flow Table

In years 1 and 2 of the project, there are capital expenses but no revenues or operating costs. The capital expenses are not operating losses, so they have no effect on taxes or depreciation. They are negative cash flows.

In year 3 the plant operates at 50% capacity and generates 50% of the design basis revenue. All of the working capital must be invested. The plant incurs 100% of the fixed cost of production but only 50% of the variable cost. Because the plant makes a profit, depreciation can be charged. Using the straight-line method of depreciation with a 10-year recovery period, the annual depreciation charge is one-tenth of the total fixed capital investment $= 361.3/10 = \$36.1$ MM. Since the gross profit in year 3 is only \$12.8 MM, the effect of charging depreciation is that the taxable income is negative, so no taxes are owed in year 4 (taxes are paid based on the previous year's income).

In year 4 the plant operates at full capacity and generates 100% of the design basis revenues with 100% of the VCOP. From here onwards, the plant makes a gross profit of \$59.4 MM each year.

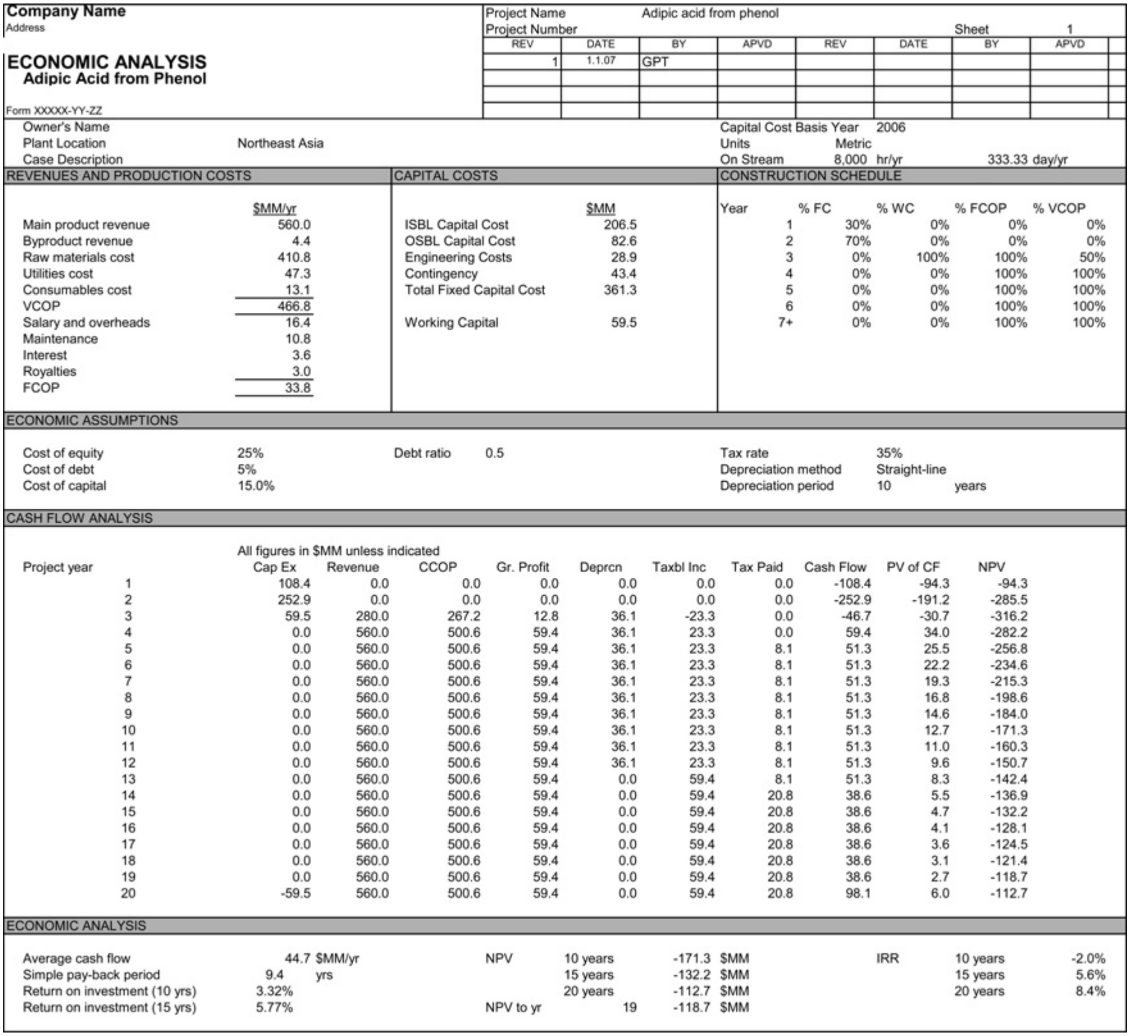
Depreciation is charged for 10 years, i.e., until year 12. The taxable income therefore increases in year 13 and the taxes paid increase in year 14, giving a reduction in cash flow from \$51.3 MM to \$38.6 MM.

In the final year of the project, the working capital is released and should be taken as a positive increment to the cash flow. This is shown as occurring in year 20 in Figure 6.12, but should be adjusted when the length of the project is varied, as described later.

The present value of the cash flow in year n can be found by multiplying by $(1 + i)^{-n}$, as described in equation 6.40. The net present value up to year n is the cumulative sum of all the present values of cash flow up to that year.

Simple Payback Period

The simple payback is calculated from the fixed investment and the average annual cash flow (equation 6.36). The average annual cash flow should be based only on the



Company Name
Address

ECONOMIC ANALYSIS
Adipic Acid from Phenol

Form XXXXX-YY-ZZ

Project Name Adipic acid from phenol
Project Number Sheet 1

REV	DATE	BY	APVD	REV	DATE	BY	APVD
1	1.1.07	GPT					

Owner's Name
Plant Location Northeast Asia
Case Description

Capital Cost Basis Year 2006
Units Metric
On Stream 8,000 hr/yr 333.33 day/yr

REVENUES AND PRODUCTION COSTS

	$MM/yr
Main product revenue	560.0
Byproduct revenue	4.4
Raw materials cost	410.8
Utilities cost	47.3
Consumables cost	13.1
VCOP	466.8
Salary and overheads	16.4
Maintenance	10.8
Interest	3.6
Royalties	3.0
FCOP	33.8

CAPITAL COSTS

	$MM
ISBL Capital Cost	206.5
OSBL Capital Cost	82.6
Engineering Costs	28.9
Contingency	43.4
Total Fixed Capital Cost	361.3
Working Capital	59.5

CONSTRUCTION SCHEDULE

Year	% FC	% WC	% FCOP	% VCOP
1	30%	0%	0%	0%
2	70%	0%	0%	0%
3	0%	100%	100%	50%
4	0%	0%	100%	100%
5	0%	0%	100%	100%
6	0%	0%	100%	100%
7+	0%	0%	100%	100%

ECONOMIC ASSUMPTIONS

Cost of equity 25%
Cost of debt 5%
Cost of capital 15.0%
Debt ratio 0.5
Tax rate 35%
Depreciation method Straight-line
Depreciation period 10 years

CASH FLOW ANALYSIS

All figures in $MM unless indicated

Project year	Cap Ex	Revenue	CCOP	Gr. Profit	Deprcn	Taxbl Inc	Tax Paid	Cash Flow	PV of CF	NPV
1	108.4	0.0	0.0	0.0	0.0	0.0	0.0	-108.4	-94.3	-94.3
2	252.9	0.0	0.0	0.0	0.0	0.0	0.0	-252.9	-191.2	-285.5
3	59.5	280.0	267.2	12.8	36.1	-23.3	0.0	-46.7	-30.7	-316.2
4	0.0	560.0	500.6	59.4	36.1	23.3	0.0	59.4	34.0	-282.2
5	0.0	560.0	500.6	59.4	36.1	23.3	8.1	51.3	25.5	-256.8
6	0.0	560.0	500.6	59.4	36.1	23.3	8.1	51.3	22.2	-234.6
7	0.0	560.0	500.6	59.4	36.1	23.3	8.1	51.3	19.3	-215.3
8	0.0	560.0	500.6	59.4	36.1	23.3	8.1	51.3	16.8	-198.6
9	0.0	560.0	500.6	59.4	36.1	23.3	8.1	51.3	14.6	-184.0
10	0.0	560.0	500.6	59.4	36.1	23.3	8.1	51.3	12.7	-171.3
11	0.0	560.0	500.6	59.4	36.1	23.3	8.1	51.3	11.0	-160.3
12	0.0	560.0	500.6	59.4	36.1	23.3	8.1	51.3	9.6	-150.7
13	0.0	560.0	500.6	59.4	0.0	59.4	8.1	51.3	8.3	-142.4
14	0.0	560.0	500.6	59.4	0.0	59.4	20.8	38.6	5.5	-136.9
15	0.0	560.0	500.6	59.4	0.0	59.4	20.8	38.6	4.7	-132.2
16	0.0	560.0	500.6	59.4	0.0	59.4	20.8	38.6	4.1	-128.1
17	0.0	560.0	500.6	59.4	0.0	59.4	20.8	38.6	3.6	-124.5
18	0.0	560.0	500.6	59.4	0.0	59.4	20.8	38.6	3.1	-121.4
19	0.0	560.0	500.6	59.4	0.0	59.4	20.8	38.6	2.7	-118.7
20	-59.5	560.0	500.6	59.4	0.0	59.4	20.8	98.1	6.0	-112.7

ECONOMIC ANALYSIS

Average cash flow	44.7 $MM/yr	NPV	10 years	-171.3 $MM	IRR	10 years	-2.0%
Simple pay-back period	9.4 yrs		15 years	-132.2 $MM		15 years	5.6%
Return on investment (10 yrs)	3.32%		20 years	-112.7 $MM		20 years	8.4%
Return on investment (15 yrs)	5.77%	NPV to yr	19	-118.7 $MM			

Figure 6.12. Economic analysis worksheet for Example 6.12.

years in which the plant generates revenue, i.e., years 3 to 20, and is found to be \$44.7 MM/y. Note that it does not matter if this range includes the year in which working capital is invested, as long as it also includes the year in which working capital is recovered. The working capital thereby cancels out and is not included in the average cash flow.

The simple payback period is then found from

$$\text{simple pay-back time} = \frac{\text{total investment}}{\text{average annual cash flow}} = \frac{361.3}{44.7} = \underline{\underline{8.08 \text{ years}}} \qquad (6.36)$$

Net Present Value

The net present value with a 15% cost of capital after 10 years of production is the NPV at the end of year 13. This can be looked up in the cash flow table and is \$–142.4 MM. If the plant is closed after 10 years of production and the working capital is released, then there would be an additional cash flow of \$59.1 MM in year 13, increasing the NPV to \$–132.7 MM.

The net present value after 15 years of production is the NPV at the end of year 18, which can also be found from the cash flow table and is \$–121.4 MM. If the plant is closed after 15 years of production and the working capital is released, then there would be an additional cash flow of \$59.1 MM in year 18, increasing the NPV to \$–116.6 MM.

In all cases the NPV for this project is negative, so it is not an attractive investment with a 15% cost of capital. We already knew this would be the case based on the cost of production analysis in Example 6.11, which showed that the TCOP with capital recovered at a 15% interest rate was greater than the expected revenue.

Internal Rate of Return (DCFROR)

The DCFROR (IRR) of the project after 15 years of production at full capacity can be found by either adjusting the interest rate (manually or using the goal seek function) until the NPV at the end of year 18 is equal to zero, or by using the IRR function in the spreadsheet over the range year 1 to year 18. The working capital should be included as a recovered cost in year 18.

The answer obtained in either case is DCFROR = 7.85%. This is the maximum interest rate at which this project can be financed to break even in 15 years of production.

Summary

None of the economic measures indicates that this is an attractive project with the projected costs, revenues, and capital expenses. It should perhaps be noted, though, that this analysis was based on a class 5 estimate of the capital cost (±50%). If we had any technical improvement in mind that could reduce either the capital investment or the cost of production, then we might want to develop the design further to assess if the economic analysis was sufficiently improved.

Example 6.13

A plant is producing 10,000 metric tons per year (10 kMTA) of a product. The overall yield is 70%, on a mass basis (kg of product per kg raw material). The raw material costs \$500/metric ton, and the product sells for \$900/metric ton. A process modification has been devised that will increase the yield to 75%. The additional investment required is \$1,250,000, and the additional operating costs are negligible. Is the modification worth making?

Solution

There are two ways of looking at the earnings to be gained from the modification:

1. If the additional production given by the yield increase can be sold at the current price, the earnings on each additional ton of production will equal the sales price less the raw material cost.

2. If the additional production cannot be readily sold, the modification results in a reduction in raw material requirements, rather than increased sales, and the earnings (savings) are from the reduction in annual raw material costs.

The second way gives the lowest figures and is the safest basis for making the evaluation. At 10 kMTA production

$$\text{Raw material requirements at 70\% yield} = \frac{10{,}000}{0.7} = 14{,}286$$

$$\text{at 75\% yield} = \frac{10{,}000}{0.75} = 13{,}333$$

$$\text{Cost savings} = 953 \text{ metric tons/y, which is worth } 953 \times 500 = \$476{,}500/\text{y}$$

$$\text{Pre-tax ROI} = \frac{476{,}500}{1{,}250{,}000} = \underline{\underline{38\%}}$$

As the annual savings are constant, the simple payback period is the inverse of the pre-tax ROI:

$$\text{Simple payback period} = \frac{1{,}250{,}000}{476{,}500} = \underline{\underline{2.62 \text{ years}}}$$

Based on the attractive ROI and payback period, this investment would seem to be worth pursuing further. Whether or not it was implemented would depend on the hurdle rate set for investments by the company.

6.8. SENSITIVITY ANALYSIS

6.8.1. Simple Sensitivity Analysis

The economic analysis of a project can only be based on the best estimates that can be made of the investment required and the cash flows. The actual cash flows achieved in any year will be affected by changes in raw materials costs and other operating costs and will be very dependent on the sales volume and price. A sensitivity analysis is a way of examining the effects of uncertainties in the forecasts on the viability of a project. To carry out the analysis, the investment and cash flows are first calculated using what are considered the most probable values for the various factors; this establishes the base case for analysis. Various parameters in the cost model are then adjusted, assuming a range of error for each factor in turn. This will show how sensitive the cash flows and economic criteria are to errors in the forecast figures. A sensitivity analysis gives some idea of the degree of risk involved in making judgments on the forecast performance of the project.

The results of a sensitivity analysis are usually presented as plots of an economic criterion such as NPV or DCFROR vs. the parameter studied. Several plots are sometimes shown on the same graph using a scale from 0.5 × base value to 2 × base value as the abscissa.

6.8.2. Parameters to Study

The purpose of sensitivity analysis is to identify those parameters that have a significant impact on project viability over the expected range of variation of the parameter. Typical parameters investigated and the range of variation that is usually assumed are given in Table 6.12.

Varying the production rate (while keeping investment and fixed costs constant) investigates the effects of unexpectedly high downtime due to maintenance or operations problems, as well as unexpected difficulties in selling the full volume of product that could be produced. An increase in production rate beyond the design capacity might also be possible if the plant design margins allow some extra capacity or if the yields can be improved by use of a better catalyst, etc.

The choice of which feed and product prices to use in the sensitivity analysis depends strongly on the method of price forecasting that has been used. Typically, total raw material cost is studied rather than treating each feed separately, but if raw material costs are found to be the dominant factor, then they may be broken out into the costs of individual raw materials.

6.8.3. Statistical Methods for Risk Analysis

In a simple sensitivity analysis, each parameter is varied individually, and the output is a qualitative understanding of which parameters have the most impact on project viability. In a more formal risk analysis, statistical methods are used to examine the effect of variation in all of the parameters simultaneously and hence quantitatively determine the range of variability in the economic criteria. This allows the design engineer to estimate the degree of confidence with which the chosen economic criterion can be said to exceed a given threshold.

A simple method of statistical analysis was proposed by Piekarski (1984) and is described in Humphreys (2005). Each item in the estimate is expressed as a most likely value, *ML;* an upper value, *H;* and a lower value, *L*. The upper and lower values

Table 6.12. Sensitivity Analysis Parameters

Parameter	**Range of Variation**
Sales price	± 20% of base (larger for cyclic commodities)
Production rate	± 20% of base
Feed cost	− 10% to + 30% of base
Fuel cost	− 50% to + 100% of base
Fixed costs	− 20% to + 100% of base
ISBL capital investment	− 20% to + 50% of base
OSBL capital investment	− 20% to + 50% of base
Construction time	− 6 months to + 2 years
Interest rate	base to base + 2 percentage points

can be estimated using the ranges of variation given in Table 6.12. The mean and standard deviation are then estimated as

$$\text{mean value,} \quad \bar{x} = \frac{(H + 2ML + L)}{4} \tag{6.51}$$

$$\text{standard deviation,} \; S_x = \frac{(H - L)}{2.65} \tag{6.52}$$

Note that the mean is not necessarily equal to the most likely value if the distribution is skewed. This is often the case for cost functions.

The mean and standard deviation of other parameters can then be estimated by combination of the individual means and standard deviations using the mathematics of statistics given in Table 6.13.

This allows relatively easy estimation of the overall error in a completed cost estimate, and with a little more difficulty can be extended to economic criteria such as NPV, TAC, or ROI.

Rather than build the preceding simple method into a spreadsheet, a more sophisticated approach is to take the economic model and subject it to analysis using Monte Carlo simulation. In Monte Carlo simulation, random numbers are generated and used to establish the value of each parameter within its allowed range. For example, each parameter could be set equal to $L + (R \times (H - L)/10)$, where R is a random number between 1 and 10. The overall probability distribution in the calculated parameter (economic criterion) can be estimated by performing a large number of such simulations. Several commercial programs for Monte Carlo simulation are available, for example, REP/PC (Decision Sciences Corp.), @RISK (Palisade Corp.), and CRYSTAL BALL® (Decisioneering® Corp.).

Table 6.13. Mathematics of Statistics

If: $y = f(\bar{x}, \bar{z})$, then the standard deviation of y, S_y is given as a function of S_x and S_z.

Function y of $\bar{x}$, $\bar{z}$	Standard deviation S_y
$y = a\bar{x} + b\bar{z}$	$S_y = \sqrt{a^2\ S_x^2 + b^2\ S_z^2}$
$y = \bar{x}\bar{z}$	$S_y = \bar{x}\bar{z}\sqrt{\frac{S_x^2}{\bar{x}^2} + \frac{S_z^2}{\bar{z}^2}}$
$y = \frac{\bar{x}}{\bar{z}}$	$S_y = \frac{\bar{x}}{\bar{z}}\sqrt{\frac{S_x^2}{\bar{x}^2} + \frac{S_z^2}{\bar{z}^2}}$

Notes:

1. These formulae are strictly true only when the covariance of x and z is 0—i.e., there is no statistical interrelation between x and z—and when x and z have been estimated from a small set of data points.
2. For a more general description of the formulae, see Ku (1966).

Care must be taken in formulating Monte Carlo simulation problems. The Monte Carlo method implicitly assumes that all parameters vary randomly and independently. If two parameters are correlated (for example, feedstock and product prices or feedstock and energy prices), then they should not be varied independently. The correct approach is to vary one of the parameters and then predict the other by correlation, imposing a random error on the predicted parameter to reflect the accuracy of the correlation.

The cost-estimating literature contains a lot of information on risk analysis. Good introductions to the use of statistics in risk analysis are given by Humphreys (2005) and Sweeting (1997).

6.8.4. Contingency Costs

The concept of a contingency charge to allow for variation in the capital cost estimate was introduced in Section 6.2.1, where it was suggested that a minimum contingency charge of 10% of ISBL plus OSBL fixed capital should be used.

If the confidence interval of the estimate is known, then the contingency charges can also be estimated based on the desired level of certainty that the project will not overrun the projected cost. For example, if the cost estimate is normally distributed, then the estimator has the following confidence levels:

- 90% confidence that the cost is less than $\bar{x} + 1.3S_x$.
- 95% confidence that the cost is less than $\bar{x} + 1.65S_x$.
- 98% confidence that the cost is less than $\bar{x} + 2.05S_x$.
- 99% confidence that the cost is less than $\bar{x} + 2.33S_x$.

Although many of the components of a cost estimate are skewed distributions, when these are combined the resulting distribution is often approximately normal. The preceding guidelines can thus be used to determine the amount of contingency charge needed for a given level of confidence.

Note also that a 10% contingency charge gives 98% confidence of the cost coming in under estimate if the estimate has accuracy ±6.5% (using the approximate method of calculating S_x given in equation 6.52). This illustrates that a 10% contingency charge should really be viewed as a minimum level and is only appropriate for detailed estimates (Class 1 and Class 2), when the technology is well understood.

Example 6.14

A preliminary (Class 4) estimate of the ISBL capital cost of building a 200,000 ton per year ethanol plant by corn dry milling has been stated as \$130 MM −30%/+50%. The plant is to be built on a green-field site, and offsite costs are estimated to be between \$40 MM and \$60 MM. Estimate a value for the total project cost that will give 98% confidence that the project can be carried out within the amount estimated.

Solution

For the ISBL cost, H = \$195 MM, L = \$91 MM, and ML = \$130 MM, so

$$\bar{x}_{ISBL} = \frac{(H + 2ML + L)}{4} = \frac{(195 + 260 + 91)}{4} = \$136.5\text{ MM} \qquad (6.51)$$

$$S_{x,ISBL} = \frac{(H - L)}{2.65} = \frac{195 - 91}{2.65} = \$39.2\,\text{MM} \qquad (6.52)$$

Similarly, for the OSBL costs, assuming the most likely value is in the middle of the range given

$$\bar{x}_{OSBL} = \frac{(H + 2ML + L)}{4} = \frac{(40 + 100 + 60)}{4} = \$50\,\text{MM} \qquad (6.51)$$

$$S_{x,OSBL} = \frac{(H - L)}{2.65} = \frac{60 - 40}{2.65} = \$7.55\,\text{MM} \qquad (6.52)$$

Both mean values should be increased by 10% to allow for engineering costs, so combining the means gives

$$\bar{x}_{Total} = 1.1\bar{x}_{ISBL} + 1.1\bar{x}_{OSBL} = \$205.2\,\text{MM}$$

$$S_{x,Total} = \sqrt{(1.1S_{x,ISBL})^2 + (1.1S_{x,OSBL})^2} = \$43.9\,\text{MM}$$

We have 98% confidence that the cost is less than $\bar{x} + 2.05S_x = 205.2 + (2.05 \times 43.9) = \underline{\underline{\$295\,\text{MM}}}$. If we budget the project for this amount (or tender a contract), then we are accepting a 1 in 50 risk that the project will exceed the given budget.

6.9. PROJECT PORTFOLIO SELECTION

A typical company involved in the chemical, pharmaceutical, or fuels industries will evaluate many projects each year. Only a few of these projects are selected for implementation. This section discusses some of the criteria and methods used in making that selection.

6.9.1. Types of Projects

Investment projects are carried out for a variety of reasons.

Regulatory compliance projects are often required as a result of changes in environmental or other legislation. If the government changes the rules on plant safety, emissions, or product specifications, then unless an exemption can be obtained, the plant must be modified or closed down. Regulatory compliance projects often have poor financial performance unless the costs of going out of business are considered.

Cost-reduction projects are aimed at reducing the cost of production of an existing plant. The most common cost-reduction investments are for *preventive maintenance*, in which equipment is replaced, repaired, or cleaned after a planned interval and before the equipment deteriorates to the point where it could impact process performance or safety. Most preventive maintenance projects are small and are handled through the plant maintenance budget, but some can be very large, expensive projects requiring a major plant shutdown, for example, replacing the fired tubes in a main plant furnace. Another common type of cost-reduction project is *heat recovery* or *heat integration projects*, in which the plant heat exchange network or utility system is upgraded to reduce energy costs.

Whenever possible, companies also seek to fund *growth projects* that can be expected to give high returns on the capital invested. Growth projects include expansions of existing units, often referred to as *debottlenecking* or *revamp projects,* as well as construction of entirely new plants in *grassroots projects*.

In all cases except grassroots projects, a large amount of information about the existing plant, site, and products is usually needed before the project can be designed. Much effort is usually spent on reconciling simulation or other models to the plant performance so as to be useful for designing the plant modifications. Grassroots projects are typically used as undergraduate design projects because they are self-contained and do not require model reconciliation; however, in industrial practice they make up less than 10% of all projects.

6.9.2. Limits on the Project Portfolio

The most obvious limit on the portfolio of projects that can be funded is the availability of capital, which is in turn limited by the financing arrangements of the company (see Section 6.6).

Capital spending is often set in proportion to sales, operating profit, or total assets. Table 6.14 shows recent information on capital spending for some of the largest chemical companies in the world. It can be seen from Table 6.14 that most of the companies' capital spending was between 4 and 6% of sales and also between 4 and 6% of assets. The major exceptions to this were the chemical businesses of oil companies (ExxonMobil Chemical and Chevron Phillips) and Sinopec. The oil companies are primarily involved in the manufacture of commodity chemicals, and during 2005 this sector was at a cyclic peak, causing a high ratio of sales to investment. The case of Sinopec is a little different. In 2005, Sinopec was still partly owned by the communist government of the People's Republic of China and was beginning to generate additional capital by offering shares to international investors. The extremely high proportion of sales revenue invested in capital expansion therefore partly reflects political pressures that a free-market company would not experience and partly reflects investment resulting from the influx of outside capital.

A second important constraint on the number of projects that can be carried out is the availability of critical resources. Companies with small engineering staffs will be able to carry out only a few projects at one time. Even if extensive use is made of Engineering, Procurement, and Construction (EPC) contractors, the owners will still need to provide some engineering support to each project. The availability of EPC contractors can also be an issue during times of peak industry construction. Projects that require extensive research and development work may be delayed because of constraints on the availability of researchers and pilot plant facilities.

Often the most important constraint is set by regulatory timelines. Regulatory compliance projects must be completed in time for the plant or product to comply

Table 6.14. Capital Spending of Large Chemical Companies

Company	Sales (MM$)	Net Profit (MM$)	Total Assets (MM$)	Capital Spending (MM$)	Capital/ Sales	Capital/ Net Profit	Capital/ Assets
BASF	50,629	3,562	42,249	2,592	0.051	0.728	0.061
Dow	46,307	–	45,934	1,597	0.034	–	0.035
Bayer	32,434	1,892	43,495	1,644	0.051	0.869	0.038
ExxonMobil Chemical	26,777	3,403	–	654	0.024	0.192	–
DuPont	26,639	2,053	33,250	1,340	0.050	0.653	0.040
Sinopec	22,167	–	–	11,635	0.525	–	–
Mitsubishi Chemical	20,490	728	18,089	832	0.041	1.143	0.046
Lyondell	18,606	531	14,980	249	0.013	0.469	0.017
Akzo Nobel	15,398	1,138	14,717	609	0.040	0.535	0.041
Degussa	13,920	–582	15,988	964	0.069	–1.656	0.060
Sumitomo Chemical	13,240	–	18,529	1,063	0.080	–	0.057
Asahi Kasei	12,747	508	11,705	564	0.044	1.110	0.048
Mitsui Chemical	12,524	375	11,304	692	0.055	1.845	0.061
Solvay	10,141	967	13,312	2,286	0.225	2.364	0.172
Chevron Phillips	10,707	853	6,960	177	0.017	0.208	0.025
DSM	9,707	624	11,874	475	0.049	0.761	0.040
Shin–Etsu	9,594	979	14,216	1,019	0.106	1.041	0.072
Johnson–Matthey	8,772	–	3,995	229	0.026	–	0.057
Lanxess	8,469	–75	5,142	297	0.035	–3.960	0.058
Air Products	8,144	712	10,409	1,043	0.128	1.465	0.100
Syngenta	8,104	622	11,608	174	0.021	0.280	0.015
Rohm & Haas	7,994	637	9,727	333	0.042	0.523	0.034

Notes:

1. Source: Davis (2006).
2. Numbers are based on 2005 financial data.

with the new law. This may dictate a narrow window of typically less than 5 years, in which the project must be planned, designed, and constructed, giving the company little choice on when the project must be begun.

Regulatory timelines are extremely important for pharmaceutical products. A new drug is protected by patent for 20 years from the date the patent is filed. Beyond that time, competitors are able to sell generic versions of the drug, and the price usually falls significantly. Before a new drug can be marketed, both the product and the manufacturing process must be approved by the Food and Drug Administration. Pharmaceutical manufacturers thus seek to maximize the revenue that they can obtain from a drug between FDA approval and patent expiration. This requires making advance preparations during the approvals process so that the rate of production can be ramped up quickly when final approval is obtained. The portfolio of investment projects for a pharmaceutical company will be strongly influenced by the expected outcomes of the regulatory approval process for new products.

6.9.3. Decision Criteria

Different types of projects are often judged using different economic criteria.

At the plant or site scale, management may have been given a small discretionary capital budget that can be used for preventive maintenance and cost-reduction projects (if it is not swallowed up by regulatory compliance projects). These projects are often ranked using simple measures such as payback, ROI, or total annualized cost. For a project to be considered for funding, it must meet a minimum (or maximum) criterion, known as a *hurdle rate*. For example, a company may dictate that projects should not be funded unless the payback period is less than 2 years. Regulatory compliance projects are often evaluated based on minimum incremental total annual cost, since it is implicitly assumed that there will be no additional revenue. If there is additional revenue, for example, from sale of a byproduct, then this can be offset against the costs. If the cost of compliance is excessive, then the alternative costs of closing down or selling the site will also be evaluated.

Small projects or modifications to ongoing projects are often evaluated based on an incremental ROI defined as

$$\text{Incremental ROI} = \frac{\text{incremental profit}}{\text{incremental investment}} \times 100\% \tag{6.53}$$

A separate hurdle rate is set for incremental ROI to ensure that modifications to a large project pay out in their own right and do not get funded just because of the attractiveness (or size) of the base project. This helps to prevent creep of project expenses.

Major growth and expansion projects that require significant investment are usually evaluated at the corporate level. Most companies look at the internal rate of return (IRR or DCFROR), the fixed and working capital, and the NPV with the interest rate set equal to the cost of capital. The selection of projects is constrained by the factors described in Section 6.9.2. The set of projects chosen may also be strongly influenced by strategic factors such as the desire to expand a particular business or product line, or a desire to expand the presence of the company in a region that is experiencing rapid economic growth, such as India or China.

Two means of simplifying the selection problem are usually used so that the company senior management is not faced with a list of thousands of potential projects. The first is to set internal hurdle rates based on simple measures such as IRR or payback so that unattractive projects are weeded out at an early stage of the evaluation process. The second method is to divide the available capital budget into categories (sometimes referred to as *buckets*) so as to balance the competing needs of different regions and businesses, growth areas vs. established products, etc. The various strategic business units or regional subsidiaries (depending on how the company is organized) each submit their proposed capital budgets and a ranked list of projects. Corporate senior management then makes strategic adjustments between the different categories and determines where to draw the line in each list such that the overall portfolio is balanced in accordance with the strategic objectives that they have set for the company. In a large corporation, this process may be repeated at two or more levels of management, with the list of selected projects being passed up to a higher level for further review and approval before the capital is authorized.

The problem of portfolio selection is easily expressed numerically as a constrained optimization: maximize economic criterion subject to constraint on available capital. This is a form of the "knapsack problem," which can be formulated as a mixed-integer linear program (MILP), as long as the project sizes are fixed. (If not, then it becomes a mixed-integer nonlinear program.) In practice, numerical methods are very rarely used for portfolio selection, as many of the strategic factors considered are difficult to quantify and relate to the economic objective function.

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6.11. NOMENCLATURE

		Dimensions in $\$\mathbf{MLT}\boldsymbol{\theta}$
A	Annual amount invested in equations 6.43 to 6.47	\$
ACC	Annual capital charge	\$
$ACCR$	Annual capital charge ratio	—
a	Constant in equation 6.7 or equation 6.15	\$
B_m	Book value in after *m* years of depreciation	\$
b	Constant in equation 6.15	\$
C	Capital cost	\$
C_d	Depreciable value	\$
C_e	Purchased equipment cost	\$
$C_{e,i,A}$	Purchased cost of equipment *i* in alloy	\$
$C_{e,i,CS}$	Purchased cost of equipment *i* in carbon steel	\$
C_1	Capital cost of plant with capacity S_1	\$
C_2	Capital cost of plant with capacity S_2	\$
CCOP	Cash cost of production	$\$\mathbf{M}^{-1}$ or $\$\mathbf{T}^{-1}$
CF	Cash flow	\$
CF_n	Cash flow in year *n*	\$
COP	Coefficient of performance of a refrigeration cycle	—
D	Sum of tax allowances, depreciation	\$
D_c	Diameter of distillation column	**L**
D_i	Depreciation charge in year *i*	\$
DR	Debt ratio (leverage)	—
dH_b	Boiler heating rate	$\mathbf{L}^{-2}\mathbf{T}^{2}$
F	Installation (Lang) factor	—
FCOP	Fixed cost of production	$\$\mathbf{M}^{-1}$ or $\$\mathbf{T}^{-1}$
F_d	Fraction of book value depreciated each year in declining balance method	—
f_c	Installation factor for civil engineering work	—
f_{el}	Installation factor for electrical work	—
f_{er}	Installation factor for equipment erection	—
f_i	Installation factor for instrumentation and control	—
f_l	Installation factor for lagging, insulation, and paint	—
f_m	Materials factor	—
f_p	Installation factor for piping	—
f_s	Installation factor for structures and buildings	—

		Dimensions in $\$\mathbf{MLT}\boldsymbol{\theta}$
H	High value of range (equation 6.51)	\$
I	Taxable income	\$
i	Interest rate	—
i'	Discounted cash flow rate of return (internal rate of return)	—
i_c	Cost of capital	—
i_d	Interest rate due on debt	—
i_e	Cost of equity	—
L	Low value of range (equation 6.51)	\$
L_c	Vessel length	$\mathbf{L}$
LF_A	Location factor for location A relative to U.S. Gulf Coast basis	—
M	Total number of pieces of equipment	—
ML	Most likely value of range (equation 6.51)	\$
m	Number of years	$\mathbf{T}$
N	Number of significant processing steps (functional units)	—
NPV	Net present value	S
n	Capital cost exponent in equations 6.6 and 6.15	—
n	Number of years	$\mathbf{T}$
P	Gross profit, or principle invested in equations 6.43 to 6.47	\$
P_{BFW}	Price of boiler feed water	$\$\mathbf{M}^{-1}$
P_F	Price of fuel	$\$\mathbf{M}^{-1}\mathbf{L}^{-2}\mathbf{T}^{2}$
P_{HPS}	Price of high-pressure steam	$\$\mathbf{M}^{-1}$
P_{WFV}	Value of waste as fuel	$\$\mathbf{M}^{-1}$
Q	Plant capacity	$\mathbf{MT}^{-1}$
ROA	Return on assets	—
ROE	Return on equity	—
ROI	Return on investment	—
S	Plant or equipment capacity	*
S	Matured sum in equations 6.43 to 6.47	\$
S_x	Standard deviation	\$
S_1	Capacity of plant 1	*
S_2	Capacity of plant 2	*
s	Reactor conversion	—
T_1	Evaporator absolute temperature	$\boldsymbol{\theta}$
T_2	Condenser absolute temperature	$\boldsymbol{\theta}$
TAC	Total annualized cost	\$
TCOP	Total cost of production	$\$\mathbf{M}^{-1}$ or $\$\mathbf{T}^{-1}$
t	Time, project life in years	$\mathbf{T}$

		Dimensions in \$MLT$\boldsymbol{\theta}$
t_r	Tax rate	—
t_w	Vessel wall thickness	L
VCOP	Variable cost of production	\$$\mathbf{M}^{-1}$ or \$$\mathbf{T}^{-1}$
$\bar{x}$	Mean value	\$
ΔH_C°	Heat of combustion	$\mathbf{L}^{-2}\mathbf{T}^{2}$
η_B	Boiler efficiency	—
ρ	Metal density	$\mathbf{ML}^{-3}$

Note: Asterisk (*) indicates that the dimensions are dependent on the type of equipment or process.

6.12. PROBLEMS

6.1. Estimate the capital cost of a plant that produces 80,000 metric tons per year of caprolactam.

6.2. The process used in the manufacture of aniline from nitrobenzene is described in Appendix F, design problem F.8. The process involves six significant stages:

Vaporization of the nitrobenzene;
Hydrogenation of the nitrobenzene;
Separation of the reactor products by condensation;
Recovery of crude aniline by distillation;
Purification of the crude nitrobenzene;
Recovery of aniline from waste-water streams.
Estimate the capital cost of a plant to produce 20,000 metric tons per year.

6.3. A reactor vessel cost \$365,000 in June 1998; estimate the cost in January 2008.

6.4. The cost of a distillation column was \$225,000 in early 1998; estimate the cost in January 2009.

6.5. Using the data on equipment costs given in this chapter or commercial cost-estimating software, estimate the cost of the following equipment:

1. A shell and tube heat exchanger, heat transfer area 50 m^2, floating-head type, carbon steel shell, stainless steel tubes, operating pressure 25 bar;
2. A kettle reboiler, heat transfer area 25 m^2, carbon steel shell and tubes, operating pressure 10 bar;
3. A horizontal, cylindrical, storage tank, 3 m diameter, 12 m long, used for liquid chlorine at 10 bar, material carbon steel;
4. A plate column, diameter 2 m, height 25 m, stainless clad vessel, 20 stainless steel sieve plates, operating pressure 5 bar.

6.6. Compare the cost the following types of heat exchangers, each with a heat transfer area of 10 m^2. Take the construction material as carbon steel:
1. Shell and tube, fixed head;
2. Double-pipe.

6.7. Estimate the cost of the following items of equipment:
1. A packaged boiler to produce 20,000 kg/h of steam at 40 bar;
2. A centrifugal compressor, driver power 75 kW;
3. A plate and frame filter press, filtration area 10 m^2;
4. A floating-roof storage tank, capacity 50,000 m^3;
5. A cone-roof storage tank, capacity 35,000 m^3.

6.8. A storage tank is purged continuously with a stream of nitrogen. The purge stream leaving the tank is saturated with the product stored in the tank. A major part of the product lost in the purge could be recovered by installing a scrubbing tower to absorb the product in a solvent. The solution from the tower could be fed to a stage in the production process, and the product and solvent recovered without significant additional cost. A preliminary design of the purge recovery system has been made. It would consist of
1. A small tower 0.5 m diameter, 4.0 m high, packed with 25 mm ceramic saddles, packed height 3.0 m;
2. A small storage tank for the solution, 5 m^3 capacity;
3. The necessary pipe work, pump, and instrumentation.

All the equipment can be constructed from carbon steel.

Using the following data, evaluate whether it would be economical to install the recovery system:
1. Cost of product \$5 per lb;
2. Cost of solvent \$0.5 per lb;
3. Additional solvent make-up 10 kg/d;
4. Current loss of product 0.7 kg/h;
5. Anticipated recovery of product 80%;
6. Additional utility costs, negligible.

Other operating costs will be insignificant.

6.9. Make a rough estimate of the cost of steam per ton, produced from a packaged boiler. At 15 bar, 10,000 kg per hour of steam are required. Natural gas will be used as the fuel, calorific value 39 MJ/m^3 (roughly 1 MMBtu/1000 scf). Take the boiler efficiency as 80%. No condensate will be returned to the boiler.

6.10. The production of methyl ethyl ketone (MEK) is described in Appendix F, problem F.3. A preliminary design has been made for a plant to produce 10,000 metric tons (tonnes or te) per year. The major equipment items required are as follows. The plant operating rate will be 8,000 hours per year.

Estimate the capital required for this project and the cash cost of production. The plant will be built on an existing site with adequate infrastructure to provide the ancillary requirements of the new plant (no offsite investment is needed).

Major equipment items:

1. Butanol vaporizer: shell and tube heat exchanger, kettle type, heat transfer area 15 m^2, design pressure 5 bar, material carbon steel;
2. Reactor feed heaters, (two): shell and tube, fixed head, heat transfer area 25 m^2, design pressure 5 bar, material stainless steel;
3. Reactors, (three): shell and tube construction, fixed tube sheets, heat transfer area 50 m^2, design pressure 5 bar, material stainless steel;
4. Condenser: shell and tube heat exchanger, fixed tube sheets, heat transfer area 25 m^2, design pressure 2 bar, material stainless steel;
5. Absorption column: packed column, diameter 0.5 m, height 6.0 m, packing height 4.5 m, packing 25 mm ceramic saddles, design pressure 2 bar, material carbon steel;
6. Extraction column: packed column, diameter 0.5 m, height 4 m, packed height 3 m, packing 25 mm stainless steel pall rings, design pressure 2 bar, material carbon steel;
7. Solvent recovery column: plate column, diameter 0.6 m, height 6 m, 10 stainless steel sieve plates, design pressure 2 bar, column material carbon steel;
8. Recovery column reboiler: thermosiphon, shell and tube, fixed tube sheets, heat transfer area 4 m^2, design pressure 2 bar, material carbon steel;
9. Recovery column condenser: double-pipe, heat transfer area 1.5 m^2, design pressure 2 bar, material carbon steel;
10. Solvent cooler: double pipe exchanger, heat transfer area 2 m^2, material stainless steel;
11. Product purification column: plate column, diameter 1 m^2, height 20 m, 15 sieve plates, design pressure 2 bar, material stainless steel;
12. Product column reboiler: kettle type, heat transfer area 4 m^2, design pressure 2 bar, material stainless steel;
13. Product column condenser: shell and tube, floating head, heat transfer area 15 m^2, design pressure 2 bar, material stainless steel;
14. Feed compressor: centrifugal, rating 750 kW;
15. Butanol storage tank: cone roof, capacity 400 m^3, material carbon steel;
16. Solvent storage tank: horizontal, diameter 1.5 m, length 5 m, material carbon steel;
17. Product storage tank: cone roof, capacity 400 m^3, material carbon steel.

Raw materials

1. 2-butanol, 1.045 kg per kg of MEK, price $800 per metric ton.
2. Solvent (trichloroethane) make-up 7,000 kg per year, price $1.0/kg.

Utilities

1. Fuel oil, 3,000 metric tons per year, heating value 45 GJ/metric ton;
2. Cooling water, 120 metric tons per hour;
3. Steam, low pressure, 1.2 metric tons per hour;
4. Electrical power, 1 MW.

The fuel oil is burned to provide flue gases for heating the reactor feed and the reactor. Some of the fuel requirements could be provided by using the byproduct hydrogen. Also, the exhaust flue gases could be used to generate steam. The economics of these possibilities need not be considered.

6.11. A plant is proposing to install a combined heat and power system to supply electrical power and process steam. Power is currently taken from a utility company, and steam is generated using onsite boilers.

The capital cost of the CHP plant is estimated to be $23 million. Combined heat and power are expected to give net savings of $10 million per year. The plant is expected to operate for 10 years after the completion of construction.

Calculate the cumulative net present value of the project, at a discount rate of 12%, using MACRS depreciation with a 7-year recovery term. Also, calculate the discounted cash flow rate of return.

Construction will take 2 years, and the capital will be paid in two equal increments, at the end of the first and second years. The savings (income) can be taken as paid at the end of each year. Production will start on the completion of construction.

6.12. A process heat recovery study identifies five potential modifications, none of which are mutually exclusive, with the costs and energy savings as follows:

Project	Capital Cost (MM$)	Fuel Savings (MMBtu/h)
A	1.5	15
B	0.6	9
C	1.8	16
D	2.2	17
E	0.3	8

If fuel costs $6/MMBtu and the plant operates for 350 days/year, which projects have a simple payback period less than 1 year?

What is the maximum 10-year NPV that can be achieved with a 15% interest rate and a 35% tax rate? Assume all the projects can be built immediately and use MACRS depreciation with a 7-year recovery term. What combination of projects is selected to meet the maximum NPV?

6.13. An electronics company wants to fit a solvent recovery system on the vent gas from its circuit board manufacturing line. The solvent recovery system consists of a chiller, a knockout drum, and an adsorbent bed. The adsorbent is periodically regenerated by circulating hot air over the bed and to the chiller and knockout. After consultation with equipment vendors, the following purchased prices are estimated for the major plant equipment:

Item	Cost ($)
Chiller	4,000
Knockout drum	1,000
Packaged refrigeration plant	3,000
Adsorbent vessel (×2)	1,500 each
Air blower	4,000
Air heater	3,000

Estimate the ISBL cost of the plant and the total project cost. If the annual operating costs are $38,000 and the annual savings in recovered solvent are $61,500, what is the IRR of this project?

6.14. Carry out a sensitivity analysis of the adipic acid project described in Examples 6.11 and 6.12.

6.15. The adipic acid plant described in Examples 6.11 and 6.12 is to be built in China, with a location factor of 0.85. Up to 45% of the total investment can be secured as a low-cost loan at an interest rate of 1%.

1. What is the cost of capital if the cost of equity is 40%?
2. What is the NPV for 15 years of production?
3. What is the IRR if the debt must be amortized over 15 years as a fixed cost of production?

7 MATERIALS OF CONSTRUCTION

Chapter Contents

Key Learning Objectives

- Mechanical and chemical properties that must be considered when selecting materials of construction for a chemical plant
- Relative costs of common materials of construction
- Properties of alloys commonly used in engineering
- When to use polymers or ceramic materials

7.1. INTRODUCTION

This chapter covers the selection of materials of construction for process equipment and piping.

Many factors have to be considered when selecting engineering materials, but for the chemical process plant, the overriding considerations are usually high temperature strength and the ability to resist corrosion. The process designer will be responsible for recommending materials that will be suitable for the process conditions. The process engineer must also consider the requirements of the mechanical design engineer; the material selected must have sufficient strength and be easily worked. The most economical material that satisfies both process and mechanical requirements should be selected; this will be the material that gives the lowest cost over the working life of the plant, allowing for maintenance and replacement. Other factors, such as product contamination and process safety, must also be considered. The mechanical properties that are important in the selection of materials are discussed briefly in this chapter. Several books have been published on the properties of materials, and the metal-working processes used in equipment fabrication, and a selection suitable for further study is given in the list of references at the end of this chapter. The mechanical design of process equipment is discussed in Chapter 13.

A detailed discussion of the theoretical aspects of corrosion is not given in this chapter, as this subject is covered comprehensively in several books: Revie (2005), Fontana (1986), Dillon (1986), and Schweitzer (1989).

An extensive set of corrosion data for different materials is given by Craig and Anderson (1995).

7.2. MATERIAL PROPERTIES

The most important characteristics to be considered when selecting a material of construction are

1. Mechanical properties;
    a. Strength–tensile strength;
    b. Stiffness–elastic modulus (Young's modulus);
    c. Toughness–fracture resistance;
    d. Hardness–wear resistance;
    e. Fatigue resistance;
    f. Creep resistance.
2. The effect of high temperature, low temperature, and thermal cycling on the mechanical properties;
3. Corrosion resistance;
4. Any special properties required, such as thermal conductivity, electrical resistance, magnetic properties;
5. Ease of fabrication—forming, welding, casting (see Table 7.1);
6. Availability in standard sizes—plates, sections, tubes;
7. Cost.

Table 7.1. A Guide to the Fabrication Properties of Common Metals and Alloys

	Machining	Cold Working	Hot Working	Casting	Welding	Annealing Temp.°C
Mild steel	S	S	S	D	S	750
Low alloy steel	S	D	S	D	S	750
Cast iron	S	U	U	S	D/U	—
Stainless steel (18Cr, 8Ni)	S	S	S	D	S	1050
Nickel	S	S	S	S	S	1150
Monel	S	S	S	S	S	1100
Copper (deoxidized)	D	S	S	S	D	800
Brass	S	D	S	S	S	700
Aluminum	S	S	S	D	S	550
Dural	S	S	S	—	S	350
Lead	—	S	—	—	S	—
Titanium	S	S	U	U	D	—

S—Satisfactory; D—Difficult, special techniques needed; U—Unsatisfactory.

7.3. MECHANICAL PROPERTIES

Typical values of the mechanical properties of the more common materials used in the construction of chemical process equipment are given in Table 7.2.

7.3.1. Tensile Strength

The *tensile strength* (tensile stress) is a measure of the basic strength of a material. It is the maximum stress that the material will withstand, measured by a standard tensile test.

Table 7.2. Mechanical Properties of Common Metals and Alloys (Typical Values at Room Temperature)

	Tensile Strength (N/mm^2)	0.1% Proof Stress (N/mm^2)	Modulus of Elasticity (kN/mm^2)	Hardness Brinell	Specific Gravity
Mild steel	430	220	210	100–200	7.9
Low alloy steel	420–660	230–460	210	130–200	7.9
Cast iron	140–170	—	140	150–250	7.2
Stainless steel (18Cr, 8Ni)	>540	200	210	160	8.0
Nickel (>99% Ni)	500	130	210	80–150	8.9
Monel	650	170	170	120–250	8.8
Copper (deoxidized)	200	60	110	30–100	8.9
Brass (Admiralty)	400–600	130	115	100–200	8.6
Aluminum (>99%)	80–150	—	70	30	2.7
Dural	400	150	70	100	2.7
Lead	30	—	15	5	11.3
Titanium	500	350	110	150	4.5

Note: Tensile stress and proof stress are not the same as the maximum allowable stress permitted by design code. See Tables 7.5 and 7.7 for maximum allowable stress values.

The older name for this property, which is more descriptive of the property, was Ultimate Tensile Strength (UTS).

Proof stress is the stress to cause a specified permanent extension, usually 0.1%.

The maximum allowable stress specified by the ASME Boiler and Pressure Vessel (BPV) Code is calculated from these and other material properties at the design temperature, and allows for suitable safety factors. The basis for establishing maximum allowable stress values is discussed in Chapter 13 and is described in detail in the ASME BPV Code Section II Part D, Mandatory Appendix 1.

7.3.2. Stiffness

Stiffness is the ability to resist bending and buckling. It is a function of the elastic modulus of the material and the shape of the cross-section of the member (the second moment of area).

7.3.3. Toughness

Toughness is associated with tensile strength, and is a measure of the material's resistance to crack propagation. The crystal structure of ductile materials, such as steel, aluminum, and copper, is such that they stop the propagation of a crack by local yielding at the crack tip. In other materials, such as the cast irons and glass, the structure is such that local yielding does not occur and the materials are brittle. Brittle materials are weak in tension but strong in compression. Under compression, any incipient cracks present are closed up. Various techniques have been developed to allow the use of brittle materials in situations in which tensile stress would normally occur. For example, the use of prestressed concrete and glass-fiber-reinforced plastics in pressure vessels construction.

A detailed discussion of the factors that determine the fracture toughness of materials can be found in the books by Institute of Metallurgists (1960) and Boyd (1970). Gordon (1976) gives an elementary, but very readable, account of the strength of materials in terms of their macroscopic and microscopic structure.

7.3.4. Hardness

The surface *hardness*, as measured in a standard test, is an indication of a material's ability to resist wear. This will be an important property if the equipment is being designed to handle abrasive solids, or liquids containing suspended solids which are likely to cause erosion.

7.3.5. Fatigue

Fatigue failure is likely to occur in equipment subject to cyclic loading; for example, rotating equipment, such as pumps and compressors, and equipment subjected to temperature or pressure cycling. A comprehensive treatment of this subject is given by Harris (1976).

7.3.6. Creep

Creep is the gradual extension of a material under a steady tensile stress, over a prolonged period of time. It is usually important only at high temperatures, for instance, with steam and gas turbine blades. For a few materials, notably lead, the rate of creep is significant at moderate temperatures. Lead will creep under its own weight at room temperature, and lead linings must be supported at frequent intervals.

The creep strength of a material is usually reported as the stress to cause rupture in 100,000 hours at the test temperature.

7.3.7. Effect of Temperature on the Mechanical Properties

The tensile strength and elastic modulus of metals decrease with increasing temperature. For example, the tensile strength of mild steel (low carbon steel, $C < 0.25\%$) is $450\,N/mm^2$ at 25°C falling to 210 at 500°C, and the value of Young's modulus $200{,}000\,N/mm^2$ at 25°C falling to $150{,}000\,N/mm^2$ at 500°C. The ASME BPV Code Section II Part D specifies maximum temperatures for each material. For example, SA-285 plain carbon steel plate cannot be used to construct a pressure vessel that meets the specifications of ASME BPV Code Section VIII Div. 1 with a design temperature greater than 900°F (482°C). Any pressure vessel that is designed for use above this temperature must be made from killed steel or alloy. The maximum allowable stress used in design is always based on the design temperature. Materials must be chosen that have sufficient strength at the design temperature to give an economic and mechanically feasible wall thickness. The stainless steels are superior in this respect to plain carbon steels.

Creep resistance will be important if the material is subjected to high stresses at elevated temperatures. Special alloys, such as Inconel 600 (UNS N06600) or Incoloy 800 (UNS N08800) (both trademarks of International Nickel Co.) are used for high-temperature equipment such as furnace tubes in environments that do not contain sulfur. The selection of materials for high-temperature applications is discussed by Day (1979) and Lai (1990).

At low temperatures, less than 10°C, metals that are normally ductile can fail in a brittle manner. Serious disasters have occurred through the failure of welded carbon steel vessels at low temperatures. The phenomenon of brittle failure is associated with the crystalline structure of metals. Metals with a body-centered-cubic (bcc) lattice are more liable to brittle failure than those with a face-centered-cubic (fcc) or hexagonal lattice. For low-temperature equipment, such as cryogenic plant and liquefied-gas storages, austenitic stainless steel (fcc) or aluminum alloys (hex) should be specified; see Wigley (1978).

V-notch impact tests, such as the Charpy test, are used to test the susceptibility of materials to brittle failure: see Wells (1968) and ASME BPV Code Sec. VIII Div. 1 Part UG-84.

The brittle fracture of welded structures is a complex phenomenon and is dependent on plate thickness and the residual stresses present after fabrication, as well as the operating temperature. A comprehensive discussion of brittle fracture in steel structures is given by Boyd (1970).

7.4. CORROSION RESISTANCE

The conditions that cause corrosion can arise in a variety of ways. For this brief discussion on the selection of materials, it is convenient to classify corrosion into the following categories:

1. General wastage of material–uniform corrosion;
2. Galvanic corrosion–dissimilar metals in contact;
3. Pitting–localized attack;
4. Intergranular corrosion;
5. Stress corrosion;
6. Erosion–corrosion;
7. Corrosion fatigue;
8. High-temperature oxidation and sulfidation;
9. Hydrogen embrittlement.

Metallic corrosion is essentially an electrochemical process. Four components are necessary to set up an electrochemical cell:

1. Anode—the corroding electrode;
2. Cathode—the passive, noncorroding electrode;
3. The conducting medium—the electrolyte—the corroding fluid;
4. Completion of the electrical circuit—through the material;

Cathodic areas can arise in many ways:

i. Dissimilar metals;
ii. Corrosion products;
iii. Inclusions in the metal, such as slag;
iv. Less well-aerated areas;
v. Areas of differential concentration;
vi. Differentially strained areas.

7.4.1. Uniform Corrosion

The term *uniform corrosion* describes the more or less uniform wastage of material by corrosion, with no pitting or other forms of local attack. If the corrosion of a material can be considered to be uniform, the life of the material in service can be predicted from experimentally determined corrosion rates.

Corrosion rates are usually expressed as penetration rates in inches per year (ipy), or mills per year (mpy) (where a mill $= 10^{-3}$ inches). They are also expressed as a weight loss in milligrams per square decimeter per day (mdd). In corrosion testing, the corrosion rate is measured by the reduction in weight of a specimen of known area over a fixed period of time.

$$\text{ipy} = \frac{12w}{tA\rho} \tag{7.1}$$

where

w = mass loss in time t, lb;
t = time, years;
A = surface area, ft^2;
ρ = density of material, lb/ft^3;

as most of the published data on corrosion rates are in imperial units.

In SI units 1 ipy = 25 mm per year.

When corrosion rates expressed in mdd are judged, it must be remembered that the penetration rate depends on the density of the material. For ferrous metals, 100 mdd = 0.02 ipy.

What can be considered as an acceptable rate of attack will depend on the cost of the material; the duty, particularly as regards to safety; and the economic life of the plant. For the more commonly used inexpensive materials, such as the carbon and low alloy steels, a guide to what is considered acceptable is given in Table 7.3. For the more expensive alloys, such as the high alloy steels, the brasses and aluminum, the figures given in Table 7.3 should be divided by 2.

If the predicted corrosion rate indicates only short exposures, then the design engineer should allow for frequent inspection of the plant and periodic replacement of the affected equipment. This affects process economics in two ways, as it reduces the on-stream factor (number of days of production per year) and increases the maintenance costs. Usually the economic impact of frequent shutdown and replacement is so negative that use of a more expensive alloy with better corrosion resistance can be justified.

Allowances for expected corrosion over the plant life or time between replacements must be added to the minimum vessel wall thicknesses calculated to comply with the ASME BPV Code. These corrosion allowances can be economically or mechanically prohibitive if the corrosion rate is high. Guidance on corrosion allowances is given in the ASME BPV Code Sec. VIII Div. 1 Non-mandatory Appendix E. The corrosion allowance should at least equal the expected corrosion loss during the desired life of the vessel.

The corrosion rate will be dependent on the temperature and concentration of the corrosive fluid. An increase in temperature usually results in an increased rate of corrosion, though not always. The rate will depend on other factors that are affected by temperature, such as oxygen solubility.

Table 7.3. Acceptable Corrosion Rates

	Corrosion Rate	
	ipy	**mm/y**
Completely satisfactory	<0.01	0.25
Use with caution	<0.03	0.75
Use only for short exposures	<0.06	1.5
Completely unsatisfactory	>0.06	1.5

The effect of concentration can also be complex; for example, the corrosion of mild steel in sulfuric acid, where the rate is unacceptably high in dilute acid and at concentrations above 70%, but is acceptable at intermediate concentrations.

7.4.2. Galvanic Corrosion

If dissimilar metals are placed in contact, in an electrolyte, the corrosion rate of the anodic metal will be increased, as the metal lower in the electrochemical series will readily act as a cathode. The galvanic series in sea water for some of the more commonly used metals is shown in Table 7.4. Some metals under certain conditions form a natural protective film, for example, stainless steel in oxidizing environments. This state is denoted by "passive" in the series shown in Table 7.4. Active indicates the absence of the protective film, for example, where the surface of the metal is subject to wear due to moving parts or abrasion by the fluid. Minor shifts in position in the series can be expected in other electrolytes, but the series for sea water is a good indication of the combinations of metals to be avoided. If metals that are widely separated in the galvanic series have to be used together, they should be electrically insulated from each other, breaking the conducting circuit. Alternatively, if sacrificial loss of the anodic material can be accepted, the thickness of this material can be increased to allow for the increased rate of corrosion. The corrosion rate will depend on the relative areas of the anodic and cathodic metals. A high cathode to anode area should be avoided. Sacrificial anodes are used to protect underground steel pipes.

7.4.3. Pitting

Pitting is the term given to very localized corrosion that forms pits in the metal surface. If a material is liable to pitting, penetration can occur prematurely, and corrosion rate data are not a reliable guide to the equipment life.

Table 7.4. Galvanic Series in Sea Water

Noble end (protected end)	18/8 stainless steel (passive)
	Monel
	Inconel (passive)
	Nickel (passive)
	Copper
	Aluminum bronze (Cu 92%, Al 8%)
	Admiralty brass (Cu 71%, Zn 28%, Sn 1%)
	Nickel (active)
	Inconel (active)
	Lead
	18/8 stainless steel (active)
	Cast iron
	Mild steel
	Aluminum
	Galvanized steel
	Zinc
	Magnesium

Pitting can be caused by a variety of circumstances; any situation that causes a localized increase in corrosion rate may result in the formation of a pit. In an aerated medium, the oxygen concentration will be lower at the bottom of a pit, and the bottom will be anodic to the surrounding metal, causing increased corrosion and deepening of the pit. A good surface finish will reduce this type of attack. Pitting can also occur if the composition of the metal is not uniform, for example, the presence of slag inclusions in welds. The impingement of bubbles can also cause pitting, the effect of cavitation in pumps, which is an example of erosion-corrosion.

7.4.4. Intergranular Corrosion

Intergranular corrosion is the preferential corrosion of material at the grain (crystal) boundaries. Though the loss of material will be small, intergranular corrosion can cause the catastrophic failure of equipment. Intergranular corrosion is a common form of attack on alloys but occurs rarely with pure metals. The attack is usually caused by a differential couple being set up between impurities existing at the grain boundary. Impurities will tend to accumulate at the grain boundaries after heat treatment. The classic example of intergranular corrosion in chemical plants is the weld decay of unstabilized stainless steel. This is caused by the precipitation of chromium carbides at the grain boundaries in a zone adjacent to the weld, where the temperature has been between 500–800°C during welding. Weld decay can be avoided by annealing after welding, if practical (post-weld heat treatment); or by using low carbon grades ($<0.3\%$ C); or by using grades stabilized by the addition of titanium or niobium.

7.4.5. Effect of Stress

Corrosion rate and the form of attack can be changed if the material is under stress. Generally, the rate of attack will not change significantly within normal design stress values. However, for some combinations of metal, corrosive media, and temperature, the phenomenon called *stress corrosion cracking* can occur. This is the general name given to a form of attack in which cracks are produced that grow rapidly, and can cause premature, brittle failure of the metal. The conditions necessary for stress corrosion cracking to occur are

1. Simultaneous stress and corrosion;
2. A specific corrosive substance; in particular the presence of Cl^-, OH^-, NO_3^-, or NH_4^+ ions.

Mild stress can cause cracking; the residual stresses from fabrication and welding are sufficient.

For a general discussion of the mechanism of stress corrosion cracking, see Fontana (1986).

Some classic examples of stress corrosion cracking are

The season cracking of brass cartridge cases;
Caustic embrittlement of steel boilers;
The stress corrosion cracking of stainless steels in the presence of chloride ions.

Stress corrosion cracking can be avoided by selecting materials that are not susceptible in the specific corrosion environment or, less certainly, by stress relieving by post-weld heat treatment.

Comprehensive tables of materials susceptible to stress corrosion cracking in specific chemicals are given by Moore (1979). Moore's tables are taken from the corrosion data survey published by NACE (1974). See also ASME BPV Code Sec. II Part D Appendix A-330.

The term *corrosion fatigue* is used to describe the premature failure of materials in corrosive environments caused by cyclic stresses. Even mildly corrosive conditions can markedly reduce the fatigue life of a component. Unlike stress corrosion cracking, corrosion fatigue can occur in any corrosive environment and does not depend on a specific combination of corrosive substance and metal. Materials with a high resistance to corrosion must be specified for critical components subjected to cyclic stresses.

7.4.6. Erosion-Corrosion

The term *erosion-corrosion* is used to describe the increased rate of attack caused by a combination of erosion and corrosion. If a fluid stream contains suspended particles, or where there is high velocity or turbulence, erosion will tend to remove the products of corrosion and any protective film, and the rate of attack will be markedly increased. If erosion is likely to occur, more resistant materials must be specified, or the material surface protected in some way. For example, plastic inserts can be used to prevent erosion-corrosion at the inlet to heat exchanger tubes.

7.4.7. High-Temperature Oxidation and Sulfidation

Corrosion is normally associated with aqueous solutions but oxidation can occur in dry conditions. Carbon and low alloy steels will oxidize rapidly at high temperatures, and their use is limited to temperatures below 480°C (900°F).

Chromium is the most effective alloying element to give resistance to oxidation, forming a tenacious oxide film. Chromium alloys should be specified for equipment subject to temperatures above 480°C in oxidizing atmospheres. For example, type 304L stainless steel (18% Cr) can be used up to 650°C (1200°F). For temperatures above 700°C, additional stabilization is needed. Type 347 stainless steel is stabilized with niobium and can be used up to 850°C. High nickel alloys can also be used as long as sulfur is not present, and high chromium content Ni alloys are used at the highest temperatures. For example, Inconel 600 (15.5% Cr) can be used up to 650°C (1200°F) and Incoloy 800 (21% Cr) can be used up to 850°C (1500°F).

Sulfur is a very common corrosive contaminant in gas processing, oil refining, and energy conversion. In reducing environments sulfur is present as H_2S, which causes sulfidation of metals. The metal chosen must often withstand a sulfidizing environment on one side and an oxidizing environment on the other side, all at high temperature (for example, in a furnace tube). Sulfur can attack the chromium oxide scale that protects the alloy, causing breakaway corrosion, particularly for high nickel alloys. Lai (1990) gives high-temperature corrosion data for various sulfidizing and mixed-gas environments and recommends the use of high-chromium high-silicon alloys such as HR-160 in this service.

7.4.8. Hydrogen Embrittlement

Hydrogen embrittlement is the name given to the loss of ductility caused by the absorption (and reaction) of hydrogen in a metal. It is of particular importance when specifying steels for use in hydrogen reforming plant. Alloy steels have a greater resistance to hydrogen embrittlement than the plain carbon steels. A chart showing the suitability of various alloy steels for use in hydrogen atmospheres, as a function of hydrogen partial pressure and temperature, is given in the NACE (1974) corrosion data survey. Below 500°C (930°F), plain carbon steel can be used.

7.5. SELECTION FOR CORROSION RESISTANCE

In order to select the correct material of construction, the process environment to which the material will be exposed must be clearly defined. In addition to the main corrosive chemicals present, the following factors must be considered:

1. Temperature—affects corrosion rate and mechanical properties;
2. Pressure;
3. pH;
4. Presence of trace impurities—stress corrosion;
5. The amount of aeration—differential oxidation cells;
6. Stream velocity and agitation—erosion-corrosion;
7. Heat transfer rates—differential temperatures.

The conditions that may arise during abnormal operation, such as at startup and shutdown, must be considered, in addition to normal, steady-state operation.

Corrosion Charts

The resistance of some commonly used materials to a range of chemicals is shown in Appendix B. More comprehensive corrosion data, covering most of the materials used in the construction of a process plant, in a wide range of corrosive media, are given by Rabald (1968), NACE (1974), Hamner (1974), Perry et al. (1997), Lai (1990), and Schweitzer (1976, 1989, 1998).

The 12-volume *Dechema Corrosion Handbook* is an extensive guide to the interaction of corrosive media with materials (Dechema, 1987). The ASM *Handbook of Corrosion Data* also has extensive data (Craig and Anderson, 1995).

These corrosion guides can be used for the preliminary screening of materials that are likely to be suitable, but the fact that published data indicate that a material is satisfactory cannot be taken as a guarantee that it will be suitable for the process environment being considered. Slight changes in the process conditions, or the presence of unsuspected trace impurities, can markedly change the rate of attack or the nature of the corrosion. The guides will, however, show clearly those materials that are manifestly unsuitable. Judgment, based on experience with the materials in similar process environments, must be used when assessing published corrosion data.

Pilot plant tests and laboratory corrosion tests under simulated plant conditions will help in the selection of suitable materials if actual plant experience is not available. Preliminary tests can be carried out by inserting coupons of different materials into an apparatus that is known to resist corrosion before testing plant components. This reduces the likelihood of component failure and possible release of chemicals during testing. Care is needed in the interpretation of laboratory tests.

The advice of the technical service department of the company supplying the materials should also be sought.

7.6. MATERIAL COSTS

An indication of the cost of some commonly used metals is given in Table 7.5. The actual cost of metals and alloys will fluctuate quite widely, depending on movements in the world metal exchanges.

Current metals prices can be found at

www.steelonthenet.com free site with monthly carbon steel prices
www.steelbb.com steel business briefing—subscription site with weekly carbon steel and stainless steel prices
www.steelweek.com subscription site with weekly international prices
www.metalprices.com/freesite/metals great alloy calculator—3-month-old prices are free; current prices subscription only

The quantity of a material used will depend on the material density and strength (maximum allowable stress) and these must be taken into account when comparing

Table 7.5. Relative Cost of Metals (July 2006)

Metal	Type or Grade	Price ($/lb)	Max Allowable Stress (ksi = 1,000 psi)	Relative Cost Rating
Carbon steel	A-285	0.27	12.9	1
Austenitic stainless steel	304	0.90	20	2.2
	316	1.64	20	4
Aluminum alloy	A03560	1.27	8.6	2.4
Copper	C10400	3.34	6.7	27
Nickel	99%Ni	8.75	10	48
Incoloy	N08800	3.05	20	7.5
Monel	N04400	6.76	18.7	20
Titanium	R50250	9.62	10	27

Note: The maximum allowable stress values are at 40°C (100°F) and are taken from ASME BPV Code Sec. II Part D. The code should be consulted for values at other temperatures. Several other grades exist for most of the materials listed.

material costs. Moore (1970) compares costs by calculating a cost rating factor defined by the equation

$$\text{Cost rating} = \frac{C \times \rho}{\sigma_d} \tag{7.2}$$

where

C = cost per unit mass, \$/kg;
ρ = density, kg/m^3;
σ_d = maximum allowable stress, N/mm^2.

Cost ratings, relative to the rating for mild steel (low carbon), are shown in Table 7.5 for mid-2006 prices. Materials with a relatively high maximum allowable stress, such as stainless and low alloy steels, can be used more efficiently than carbon steel. Note that the simplified formula given in equation 7.2 does not take into account different corrosion allowances for the different materials.

The relative cost of equipment made from different materials will depend on the cost of fabrication, as well as the basic cost of the material. Unless a particular material requires special fabrication techniques, the relative cost of the finished equipment will be lower than the relative bare material cost. For example, the purchased cost of a stainless-steel storage tank will be 2 to 3 times the cost of the same tank in carbon steel, whereas the relative cost of the metals is from 5 to 8.

If the corrosion rate is uniform, then the optimum material can be selected by calculating the annual costs for the possible candidate materials. The annual cost will depend on the predicted life, calculated from the corrosion rate, and the purchased cost of the equipment. In a given situation, it may prove more economic to install a cheaper material with a high corrosion rate and replace it frequently, rather than select a more resistant but more expensive material. This strategy would be considered only for relatively simple equipment with low fabrication costs, and where premature failure would not cause a serious hazard. For example, carbon steel could be specified for an aqueous effluent line in place of stainless steel, accepting the probable need for replacement. The pipe wall thickness would be monitored *in situ* frequently to determine when replacement was needed.

The more expensive, corrosion-resistant alloys are frequently used as a cladding on carbon steel. If a thick plate is needed for structural strength, as for pressure vessels, the use of clad materials can substantially reduce the cost. The design requirements for pressure vessels with cladding or applied internal linings are given in ASME BPV Code Sec. VIII Div. 1 Part UCL.

7.7. CONTAMINATION

With some processes, the prevention of the contamination of a process stream, or a product, by certain metals, or the products of corrosion, overrides any other considerations when selecting suitable materials. For instance, in textile processes, stainless steel or aluminum is often used in preference to carbon steel, which would be quite suitable except that any slight rusting will mark the textiles (iron staining).

With processes that use catalysts, care must be taken to select materials that will not cause contamination and poisoning of the catalyst.

Some other examples that illustrate the need to consider the effect of contamination by trace quantities of other materials are

1. For equipment handling acetylene, the pure metals, or alloys containing copper, silver, mercury, or gold must be avoided to prevent the formation of explosive acetylides.
2. The presence of trace quantities of mercury in a process stream can cause the catastrophic failure of brass heat exchanger tubes, from the formation of a mercury-copper amalgam. Incidents have occurred in which the contamination has come from unsuspected sources, such as the failure of mercury-in-steel thermometers.
3. In the Flixborough disaster (see Chapter 9), there was evidence that the stress corrosion cracking of a stainless-steel pipe had been caused by zinc contamination from galvanized wire supporting lagging.

7.7.1. Surface Finish

In the food, pharmaceutical, biochemical, and textile industries, for example, the surface finish of the material is as important as the choice of material, to avoid contamination.

Stainless steel is widely used, and the surfaces, inside and out, are given a high finish by abrasive blasting and mechanical polishing. This is done for the purposes of hygiene, to prevent material adhering to the surface, and to aid cleaning and sterilization. The surface finishes required in food processing are discussed by Timperley (1984) and Jowitt (1980).

A good surface finish is important in textile fiber processing to prevent the fibers snagging.

7.8. COMMONLY USED MATERIALS OF CONSTRUCTION

The general mechanical properties, corrosion resistance, and typical areas of use of some of the materials commonly used in the construction of chemical plants are given in this section. The values given are for a typical, representative grade of the material or alloy. The alloys used in chemical plant construction are known by a variety of trade names, and code numbers are designated in the various national standards. With the exception of the stainless steels, no attempt has been made in this book to classify the alloys discussed by using one or another of the national standards; the commonly used, generic names for the alloys have been used. For the full details of the properties and compositions of the different grades available in a particular class of alloy and the designated code numbers, reference should be made to the appropriate national code, to the various handbooks, or to manufacturers' literature. See, for example, ASME BPV

Code Sec. II Part D for a full listing of materials properties and ASME BPV Code Sec. VIII Div.1 for material-specific fabrication guidelines.

The U.S. trade names and codes are given by Perry et al. (1997). A comprehensive review of the engineering materials used for chemical and process plant can be found in the book by Evans (1974).

7.8.1. Iron and Steel

Low carbon steel (mild steel) is the most commonly used engineering material. It is cheap, is available in a wide range of standard forms and sizes, and can be easily worked and welded. It has good tensile strength and ductility.

The carbon steels and iron are not resistant to corrosion, except in certain specific environments, such as concentrated sulfuric acid and the caustic alkalis. They are suitable for use with most organic solvents, except chlorinated solvents, but traces of corrosion products may cause discoloration.

Mild steel is susceptible to stress corrosion cracking in certain environments.

The corrosion resistance of the low alloy steels (less than 5% of alloying elements), where the alloying elements are added to improve the mechanical strength and not for corrosion resistance, is not significantly different from that of the plain carbon steels.

A comprehensive reference covering the properties and application of steels, including the stainless steels, is the book by Llewellyn (1992). The use of carbon steel in the construction of chemical plants is discussed by Clark (1970).

The high silicon irons (14 to 15% Si) have a high resistance to mineral acids, except hydrofluoric acid. They are particularly suitable for use with sulfuric acid at all concentrations and temperatures. They are, however, very brittle.

7.8.2. Stainless Steel

The stainless steels are the most frequently used corrosion-resistant materials in the chemical industry.

To impart corrosion resistance, the chromium content must be above 12%, and the higher the chromium content, the more resistant the alloy to corrosion in oxidizing conditions. Nickel is added to improve the corrosion resistance in nonoxidizing environments.

Types

A wide range of stainless steels is available, with compositions tailored to give the properties required for specific applications. They can be divided into three broad classes according to their microstructure:

1. Ferritic: 13–20% Cr, <0.1% C, with no nickel
2. Austenitic: 18–20% Cr, >7% Ni
3. Martensitic: 12–14% Cr, 0.2 to 0.4% C, up to 2% Ni

The uniform structure of Austenite (face-centered cubic, with the carbides in solution) is the structure desired for corrosion resistance, and it is these grades that are widely used in the chemical industry. The composition of the main grades of austenitic steels are shown in Table 7.6. Their properties are discussed below.

Type 304 (the so-called 18/8 stainless steels): The most generally used stainless steel. It contains the minimum Cr and Ni that give a stable austenitic structure. The carbon content is low enough for heat treatment not to be normally needed with thin sections to prevent weld decay (see Section 7.4.4).

Type 304L: Low-carbon version of type 304 (<0.03% C) used for thicker welded sections, where carbide precipitation would occur with type 304.

Type 321: A stabilized version of 304, stabilized with titanium to prevent carbide precipitation during welding. It has a slightly higher strength than 304L and is more suitable for high-temperature use.

Type 347: Stabilized with niobium.

Type 316: In this alloy, molybdenum is added to improve the corrosion resistance in reducing conditions, such as in dilute sulfuric acid and, in particular, to solutions containing chlorides.

Type 316L: A low-carbon version of type 316, which should be specified if welding or heat treatment is liable to cause carbide precipitation in type 316.

Types 309/310: Alloys with a high chromium content, to give greater resistance to oxidation at high temperatures. Alloys with greater than 25% Cr are

Table 7.6. Commonly Used grades of Austenitic Stainless Steel

Specification No./	Composition %							
AISI No.	**C max**	**Si max**	**Mn max**	**Cr Range**	**Ni Range**	**Mo Range**	**Ti**	**Nb**
304	0.08	—	2.00	17.5	8.0	—	—	—
				20.0	11.0			
304L	0.03	1.00	2.00	17.5	8.0	—	—	—
				20.0	12.0			
321	0.12	1.00	2.00	17.0	9.0	—	4 × C	—
				20.0	12.0			
347	0.08	1.00	2.00	17.0	9.0	—	—	10 × C
				20.0	13.0			
316	0.08	1.00	2.00	16.0	10.0	2.0	—	—
				18.0	14.0	3.0		
316L	0.03	1.0	2.0	16.0	10.0	2.0	—	—
				18.0	14.0	3.0		
309	0.20	—	—	22.0	12.0	—	—	—
				24.0	15.0			
310	0.25	—	—	24.0	19.0	—	—	—
				26.0	22.0			

S and P = 0.045% all grades.
AISI = American Iron and Steel Institute.

susceptible to embrittlement due to sigma phase formation at temperatures above 500°C. Sigma phase is an intermetallic compound, FeCr. The formation of the sigma phase in austenitic stainless steels is discussed by Hills and Harries (1960).

Mechanical Properties

The austenitic stainless steels have greater strength than the plain carbon steels, particularly at elevated temperatures (see Table 7.7).

As was mentioned in Section 7.3.7, the austenitic stainless steels, unlike the plain carbon steels, do not become brittle at low temperatures. It should be noted that the thermal conductivity of stainless steel is significantly lower than that of mild steel.

Typical values at 100°C are	type 304 (18/8)	16 W/m°C
	mild steel	60 W/m°C

Austenitic stainless steels are nonmagnetic in the annealed condition.

General Corrosion Resistance

The higher the alloying content, the better the corrosion resistance over a wide range of conditions, strongly oxidizing to reducing, but the higher the cost. A ranking in order of increasing corrosion resistance, taking type 304 as 1, is as follows:

304	304L	321	316	316L	310
1.0	1.1	1.1	1.25	1.3	1.6

Intergranular corrosion (weld decay) and stress corrosion cracking are problems associated with the use of stainless steels and must be considered when selecting types suitable for use in a particular environment. Stress corrosion cracking in stainless steels can be caused by a few ppm of chloride ions (see Section 7.4.5).

In general, stainless steels are used for corrosion resistance when oxidizing conditions exist. Special types, or other high nickel alloys, should be specified if reducing conditions are likely to occur. The properties, corrosion resistance, and uses of the various grades of stainless steel are discussed fully by Peckner and Bernstein (1977). A comprehensive discussion of the corrosion resistance of stainless steels is given in Sedriks (1979).

Stress corrosion cracking in stainless steels is discussed by Turner (1989).

High Alloy Content Stainless Steels

Super austenitic, high nickel stainless steels containing between 29 to 30% nickel and 20% chromium have a good resistance to acids and acid chlorides. They are more expensive than the lower alloy content, 300 series, of austenitic stainless steels.

Table 7.7. Comparative Strength of Carbon Steel and Stainless Steel

Temperature °F		100	300	500	700	900
Maximum allowable stress (1,000 psi)	Carbon steel (A285 plate)	12.9	12.9	12.9	11.5	5.9
	Stainless steel (304L plate)	16.7	16.7	14.7	13.5	11.9

Maximum allowable stress values from ASME BPV Code Sec. II Part D.

Duplex and super-duplex stainless steels contain high percentages of chromium. They are called *duplex* because their structure is a mixture of the austenitic and ferritic phases. They have a better corrosion resistance than the austenitic stainless steels and are less susceptible to stress corrosion cracking. The chromium content of duplex stainless steels is around 20% and around 25% in the super-duplex grades. The super-duplex steels were developed for use in aggressive offshore environments.

The duplex range of stainless steels can be readily cast, wrought, and machined. Problems can occur in welding, due to the need to keep the correct balance of ferrite and austenite in the weld area, but this can be overcome using the correct welding materials and procedures.

The cost of the duplex grades is comparable with the 316 steels. Super-duplex costs around 50% higher than the cost of duplex.

The selection and properties of duplex stainless steels are discussed by Bendall and Guha (1990) and Warde (1991).

7.8.3. Nickel

Nickel has good mechanical properties and is easily worked. The pure metal (>99%) is not generally used for chemical plants, its alloys being preferred for most applications. The main use is for equipment handling caustic alkalis at temperatures above that at which carbon steel could be used; above 70°C. Nickel is not subject to corrosion cracking like stainless steel.

7.8.4. Monel

Monel, the classic nickel-copper alloy with the metals in the ratio 2:1, is probably, after the stainless steels, the most commonly used alloy for chemical plants. It is easily worked and has good mechanical properties up to 500°C. It is more expensive than stainless steel but is not susceptible to stress corrosion cracking in chloride solutions. Monel has good resistance to dilute mineral acids and can be used in reducing conditions, where the stainless steels would be unsuitable. It may be used for equipment handling alkalis, organic acids and salts, and sea water.

7.8.5. Inconel and Incoloy

Inconel (typically 76% Ni, 7% Fe, 15% Cr) is used primarily for acid resistance at high temperatures. It maintains its strength at elevated temperature and is resistant to furnace gases, if sulfur free. It is not suitable for use in sulfidizing environments. Nickel alloys with higher chromium content such as Incoloy 800 (21% Cr) and RA-33 (25% Cr) have better oxidation resistance at higher temperatures.

7.8.6. The Hastelloys

The trade name *Hastelloy* covers a range of nickel, chromium, molybdenum iron alloys that were developed for corrosion resistance to strong mineral acids, particularly HCl. The corrosion resistance and use of the two main grades, Hastelloy B (65% Ni, 28% Mo, 6% Fe) and Hastelloy C (54% Ni, 17% Mo, 15% Cr, 5% Fe), are discussed in papers by Weisert (1952a,b).

7.8.7. Copper and Copper Alloys

Pure copper is not widely used for chemical equipment. It has been used traditionally in the food industry, particularly in brewing. Copper is a relatively soft, very easily worked metal and is used extensively for small-bore pipes and tubes.

The main alloys of copper are the brasses, alloyed with zinc, and the bronzes, alloyed with tin. Other, so-called bronzes are the aluminum bronzes and the silicon bronzes.

Copper is attacked by mineral acids, except cold, dilute, unaerated sulfuric acid. It is resistant to caustic alkalis, except ammonia, and to many organic acids and salts. The brasses and bronzes have a similar corrosion resistance to the pure metal. Their main use in the chemical industry is for valves and other small fittings, and for heat exchanger tubes and tube sheets. If brass is used, a grade must be selected that is resistant to dezincification.

The cupro-nickel alloys (70% Cu) have a good resistance to corrosion-erosion and are used for heat exchanger tubes, particularly where sea water is used as a coolant.

7.8.8. Aluminum and Its Alloys

Pure aluminum lacks mechanical strength but has higher resistance to corrosion than its alloys. The main structural alloys used are the Duralumin (Dural) range of aluminum-copper alloys (typical composition 4% Cu, with 0.5% Mg) which have a tensile strength equivalent to that of mild steel. The pure metal can be used as a cladding on Dural plates, to combine the corrosion resistance of the pure metal with the strength of the alloy. The corrosion resistance of aluminum is due to the formation of a thin oxide film (as with the stainless steels). It is therefore most suitable for use in strong oxidizing conditions. It is attacked by mineral acids and by alkalis, but is suitable for concentrated nitric acid, greater than 80%. It is widely used in the textile and food industries, where the use of mild steel would cause contamination. It is also used for the storage and distribution of demineralized water.

7.8.9. Lead

Lead was one of the traditional materials of construction for chemical plants but has now, due to its price, been largely replaced by other materials, particularly plastics. It is a soft, ductile material and is mainly used in the form of sheets (as linings) or pipe. It has a good resistance to acids, particularly sulfuric.

7.8.10. Titanium

Titanium is now used quite widely in the chemical industry, mainly for its resistance to chloride solutions, including sea water and wet chlorine. It is rapidly attacked by dry chlorine, but the presence of as low a concentration of moisture as 0.01% will prevent attack. Like the stainless steels, titanium depends for its resistance on the formation of an oxide film. Titanium is also used in other halide services, for example, in liquid phase oxidation processes, such as the manufacture of terephthalic acid, that use bromide as catalyst or promoter.

Alloying with palladium (0.15%) significantly improves the corrosion resistance, particularly to HCl. Titanium is being increasingly used for heat exchangers, for both shell and tube, and plate exchangers, replacing cupro-nickel for use with sea water.

The use of titanium for corrosion resistance is discussed by Deily (1997).

7.8.11. Tantalum

The corrosion resistance of tantalum is similar to that of glass, and it has been called a metallic glass. It is expensive, about five times the cost of stainless steel, and is used for special applications, where glass or a glass lining would not be suitable. Tantalum plugs are used to repair glass-lined equipment.

The use of tantalum as a material of construction in the chemical industry is discussed by Fensom and Clark (1984) and Rowe (1994) (1999).

7.8.12. Zirconium

Zirconium and zirconium alloys are used in the nuclear industry because of their low neutron absorption cross-section and resistance to hot water at high pressures.

In the chemical industry, zirconium is finding use where resistance to hot and boiling acids is required: nitric, sulfuric, and particularly hydrochloric. Its resistance is equivalent to that of tantalum, but zirconium is less expensive, similar in price to high nickel steel. Rowe (1999) gives a brief review of the properties and use of zirconium for chemical plants.

7.8.13. Silver

Silver linings are used for vessels and equipment handling hydrofluoric acid. It is also used for special applications in the food and pharmaceutical industries where it is vital to avoid contamination of the product.

7.8.14. Gold

Because of its high cost, gold is rarely used as a material of construction. It is highly resistant to attack by dilute nitric acid and hot concentrated sulfuric acid, but is dissolved by aqua regia (a mixture of concentrated nitric and sulfuric acids). It is attacked by chlorine and bromine, and it forms an amalgam with mercury.

It has been used as thin plating on condenser tubes and other surfaces.

7.8.15. Platinum

Platinum has a high resistance to oxidation at high temperature. One of its main uses has been, in the form of an alloy with copper, in the manufacture of the spinnerets used in synthetic textile spinning processes.

7.9. PLASTICS AS MATERIALS OF CONSTRUCTION FOR CHEMICAL PLANTS

Plastics are being increasingly used as corrosion-resistant materials for chemical plant construction. They are also widely used in food processing and biochemical plants. They can be divided into two broad classes:

1. Thermoplastic materials, which soften with increasing temperature; for example, polyvinyl chloride (PVC) and polyethylene.
2. Thermosetting materials, which have a rigid, cross-linked structure; for example, the polyester and epoxy resins.

Details of the chemical composition and properties of the wide range of plastics used as engineering materials can be found in the books by Butt and Wright (1980), Evans (1974), and Harper (2001).

The biggest use of plastics is for piping; sheets are also used for lining vessels and for fabricated ducting and fan casings. Moldings are used for small items, such as pump impellers, valve parts, and pipe fittings.

The mechanical strength and operating temperature of plastics are low compared with metals. The mechanical strength and other properties can be modified by the addition of fillers and plasticizers. When reinforced with glass or carbon fibers, thermosetting plastics can have a strength equivalent to mild steel and are used for pressure vessels and pressure piping. Guidelines for the design of fiber-reinforced plastic pressure vessels are given in the ASME BPV Code Sec. X Part RD. Unlike metals, plastics are flammable. Plastics can be considered to complement metals as corrosion-resistant materials of construction. They generally have good resistance to dilute acids and inorganic salts, but suffer degradation in organic solvents that would not attack metals. Unlike metals, plastics can absorb solvents, causing swelling and softening. The properties and typical areas of use of the main plastics used for chemical plants are reviewed briefly in the following sections. A comprehensive discussion of the use of plastics as corrosion-resistant materials is given in a book by Fontana (1986). Information on selection of plastics for different applications is also given by Harper (2001). The mechanical properties and relative cost of plastics are given in Table 7.8.

Table 7.8. Mechanical Properties and Relative Cost of Polymers

Material	Tensile Strength (N/mm^2)	Elastic Modulus (kN/mm^2)	Density (kg/m^3)	Relative Cost
PVC	55	3.5	1400	1.5
Polyethylene (low density)	12	0.2	900	1.0
Polypropylene	35	1.5	900	1.5
PTFE	21	1.0	2100	30.0
GRP polyester	100	7.0	1500	3.0
GRP epoxy	250	14.0	1800	5.0

Approximate cost relative to polyethylene, volumetric basis.

7.9.1. Polyvinyl Chloride (PVC)

PVC is probably the most commonly used thermoplastic material in the chemical industry. Of the available grades, rigid (unplasticized) PVC is the most widely used. It is resistant to most inorganic acids, except strong sulfuric and nitric, and inorganic salt solutions. It is unsuitable, due to swelling, for use with most organic solvents. The maximum operating temperature for PVC is low, 60°C. The use of PVC as a material of construction in chemical engineering is discussed in a series of articles by Mottram and Lever (1957).

7.9.2. Polyolefins

Low-density polyethylene is a relatively cheap, tough, flexible plastic. It has a low softening point and is not suitable for use above about 60°C. The higher density polymer (950 kg/m^3) is stiffer and can be used at higher temperatures. Polypropylene is a stronger material than the polyethylenes and can be used at temperatures up to 120°C.

The chemical resistance of the polyolefins is similar to that of PVC.

7.9.3. Polytetrafluoroethylene (PTFE)

PTFE, known under the trade names Teflon and Fluon, is resistant to all chemicals, except molten alkalis and fluorine, and can be used at temperatures up to 250°C. It is a relatively weak material, but its mechanical strength can be improved by the addition of fillers (glass and carbon fibers). It is expensive and difficult to fabricate. PTFE is used extensively for gaskets, gland packings (for example, on valve stems), and demister pads. As a coating, it is used to confer nonstick properties to surfaces, such as filter plates. It can also be used as a liner for vessels.

7.9.4. Polyvinylidene Fluoride (PVDF)

PVDF has properties similar to PTFE but is easier to fabricate. It has good resistance to inorganic acids and alkalis and organic solvents. It is limited to a maximum operating temperature of 140°C.

7.9.5. Glass-Fiber-Reinforced Plastics (GRP)

The polyester resins, reinforced with glass fiber, are the most common thermosetting plastics used for chemical plant. Complex shapes can be easily formed using the techniques developed for working with reinforced plastics. Glass-reinforced plastics are relatively strong and have a good resistance to a wide range of chemicals. The mechanical strength depends on the resin used, the form of the reinforcement (chopped mat or cloth), and the ratio of resin to glass.

Through the use of special techniques, in which the reinforcing glass fibers are wound in the form of a continuous filament, high strength can be obtained, and this method is used to produce pressure vessels.

The polyester resins are resistant to dilute mineral acids, inorganic salts, and many solvents. They are less resistant to alkalis.

Glass-fiber-reinforced epoxy resins are also used for chemical plants but are more expensive than the polyester resins. In general they are resistant to the same range of chemicals as the polyesters but are more resistant to alkalis.

The chemical resistance of GRP is dependent on the amount of glass reinforcement used. High ratios of glass to resin give higher mechanical strength but generally lower resistance to some chemicals. The design of chemical plant equipment in GRP is the subject of a book by Malleson (1969); see also Shaddock (1971), Baines (1984), and ASME BPV Code Sec. X.

7.9.6. Rubber

Rubber, particularly in the form of linings for tanks and pipes, has been extensively used in the chemical industry for many years. Natural rubber is most commonly used because of its good resistance to acids (except concentrated nitric) and alkalis. It is unsuitable for use with most organic solvents.

Synthetic rubbers are also used for particular applications. Hypalon (trademark, E. I. du Pont de Nemours) has a good resistance to strongly oxidizing chemicals and can be used with nitric acid. It is unsuitable for use with chlorinated solvents. Viton (trademark, E. I. du Pont de Nemours) has a better resistance to solvents, including chlorinated solvents, than other rubbers. Both Hypalon and Viton are expensive, compared with other synthetic and natural rubbers.

The use of natural rubber lining is discussed by Saxman (1965), and the chemical resistance of synthetic rubbers by Evans (1963).

Butt and Wright (1980) give an authoritative account of the application and uses of rubber and plastic linings and coatings.

7.10. CERAMIC MATERIALS (SILICATE MATERIALS)

Ceramics are compounds of nonmetallic elements and include the following materials used for chemical plant:

Glass, the borosilicate glasses (hard glass);
Stoneware;
Acid-resistant bricks and tiles;
Refractory materials;
Cements and concrete;

Ceramic materials have a cross-linked structure and are therefore brittle.

7.10.1. Glass

Borosilicate glass (known by several trade names, including Pyrex) is used for chemical plants, as it is stronger than the soda glass used for general purposes; it is more resistant to thermal shock and chemical attack. Glass equipment is often used in small-scale manufacture of specialty chemicals. Glass can be used up to moderately high temperatures (700°C) but is not suitable for pressures above atmospheric unless used as a lining.

Glass equipment is available from several specialist manufacturers. Pipes and fittings are produced in a range of sizes, up to 0.5 m. Special equipment, such as heat exchangers, is available and, together with the larger sizes of pipe, can be used to construct distillation and absorption columns. Teflon gaskets are normally used for jointing glass equipment and pipe.

Where failure of the glass could cause injury, pipes and equipment should be protected by external shielding or wrapping with plastic tape. Glass apparatus should allow adequate venting to the atmosphere to handle anticipated relief scenarios without accumulating high pressure.

Glass linings, also known as glass enamel, have been used on steel and iron vessels for many years. Borosilicate glass is used, and the thickness of the lining is about 1 mm. The techniques used for glass lining and the precautions to be taken in the design and fabrication of vessels to ensure a satisfactory lining are discussed by Landels and Stout (1970) and by the ASME BPV Code Sec. VIII Div. 1, Mandatory Appendix 27. Borosilicate glass is resistant to acids, salts, and organic chemicals. It is attacked by the caustic alkalis and fluorine.

7.10.2. Stoneware

Chemical stoneware is similar to the domestic variety, but of higher quality—stronger and with a better glaze. It is available in a variety of shapes for pipe runs and columns. As for glass, it is resistant to most chemicals, except alkalis and fluorine. The composition and properties of chemical stoneware are discussed by Holdridge (1961). Stoneware and porcelain shapes are used for packing absorption and distillation columns (see Chapter 11).

7.10.3. Acid-Resistant Bricks and Tiles

High-quality bricks and tiles are used for lining vessels, ditches, and to cover floors. The linings are usually backed with a corrosion-resistant membrane of rubber or plastic, placed behind the tiles, and special acid-resistant cements are used for the joints. Brick and tile linings are covered in a book by Falcke and Lorentz (1985).

7.10.4. Refractory Materials (Refractories)

Refractory bricks and cements are needed for equipment operating at high temperatures, such as fired heaters, high-temperature reactors, and boilers.

The refractory bricks in common use are composed of mixtures of silica (SiO_2) and alumina (Al_2O_3). The quality of the bricks is largely determined by the relative amounts of these materials and the firing temperature. Mixtures of silica and alumina form a eutectic (94.5% SiO_2, 1545°C), and for a high refractoriness under load (the ability to resist distortion at high temperature), the composition must be well removed from the eutectic composition. The highest quality refractory bricks, for use in load-bearing structures at high temperatures, contain high proportions of silica or alumina. "Silica bricks," containing greater than 98% SiO_2, are used for general furnace construction. High alumina bricks, 60% Al_2O_3, are used for special furnaces where resistance to attack by alkalis is important; such as lime and cement kilns. Fire bricks, typical composition 50% SiO_2, 40% Al_2O_3, balance CaO and Fe_2O_3, are used for general furnace construction. Silica can exist in a variety of allotropic forms, and bricks containing a high proportion of silica undergo reversible expansion when heated up to working temperature. The higher the silica content, the greater the expansion, and this must be allowed for in furnace design and operation.

Ordinary fire bricks, fire bricks with a high porosity, and special bricks composed of diatomaceous earths are used for insulating walls.

Full details of the refractory materials used for process and metallurgical furnaces can be found in the books by Norton (1968) and Lyle (1947). Additional information on refractories can be found in the books by Schacht (1995, 2004) and Routschka (1997).

7.11. CARBON

Impervious carbon, impregnated with chemically resistant resins, is used for specialized equipment, particularly heat exchangers. It has a high conductivity and a good resistance to most chemicals, except oxidizing acids of concentrations greater than 30%. Carbon tubes can be used in conventional shell and tube exchanger arrangements, or proprietary designs can be used, in which the fluid channels are formed in blocks of carbon; see Hilland (1960) and Denyer (1991).

7.12. PROTECTIVE COATINGS

A wide range of paints and other organic coatings is used for the protection of mild steel structures. Paints are used mainly for protection from atmospheric corrosion. Special chemically resistant paints have been developed for use on chemical process equipment. Chlorinated rubber paints and epoxy-based paints are used. In the application of paints and other coatings, good surface preparation is essential to ensure good adhesion of the paint film or coating.

Brief reviews of the paints used to protect chemical plants are given by Ruff (1984) and Hullcoop (1984).

7.13. DESIGN FOR CORROSION RESISTANCE

The life of equipment subjected to corrosive environments can be increased by proper attention to design details. Equipment should be designed to drain freely and completely. The internal surfaces should be smooth and free from crevices where corrosion products and other solids can accumulate. Butt joints should be used in preference to lap joints. The use of dissimilar metals in contact should be avoided, or care taken to ensure that they are effectively insulated to avoid galvanic corrosion. Fluid velocities and turbulence should be high enough to avoid the deposition of solids, but not so high as to cause erosion-corrosion. The design and operating procedures should make allowance for changes in the environment to which the materials are exposed. For example, heating and cooling rates should be slow enough to prevent thermal shocks, and care should be taken during maintenance not to damage corrosion-resistant films that have developed during operation.

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7.15. NOMENCLATURE

		Dimensions in **MLT$**
A	Area	$\mathbf{L}^2$
C	Cost of material	**$/M**
t	Time	**T**
w	Mass loss	**M**
ρ	Density	$\mathbf{ML}^{-3}$
σ_d	Maximum allowable stress	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$

7.16. PROBLEMS

7.1. A pipeline constructed of carbon steel failed after 3 years of operation. On examination it was found that the wall thickness had been reduced by corrosion to about half the original value. The pipeline was constructed of nominal 100 mm (4 in) schedule 40, pipe, inside diameter 102.3 mm (4.026 in), outside diameter 114.3 mm (4.5 in). Estimate the rate of corrosion in ipy and mm per year.

7.2. The pipeline described in question 7.1 was used to carry wastewater to a hold-up tank. The effluent is not hazardous. A decision has to be made on what material to use to replace the pipe. Three suggestions have been made:

1. Replace with the same schedule carbon steel pipe and accept renewal at 3-year intervals.
2. Replace with a thicker pipe, schedule 80, outside diameter 114.3 mm (4.5 in), inside diameter 97.2 mm (3.826 in).
3. Use stainless steel pipe, which will not corrode.

The estimated cost of the pipes, per unit length is schedule 40 carbon steel $5, schedule 80 carbon steel $8.3, stainless steel (304) schedule 40 $24.8.

Installation and fittings for all the materials adds $16.5 per unit length.

The downtime required to replace the pipe does not result in a loss of production.

If the expected future life of the plant is 7 years, recommend which pipe to use.

7.3. Choose a suitable material of construction for the following duties:

1. 98% w/w sulfuric acid at 70°C;
2. 5% w/w sulfuric acid at 30°C;
3. 30% w/w hydrochloric acid at 50°C;
4. 5% aqueous sodium hydroxide solution at 30°C;
5. Concentrated aqueous sodium hydroxide solution at 50°C;
6. 5% w/w nitric acid at 30°C;
7. Boiling concentrated nitric acid;
8. 10% w/w sodium chloride solution;
9. A 5% w/w solution of cuprous chloride in hydrochloric acid;
10. 10% w/w hydrofluoric acid.

In each case, select the material for a 50 mm pipe operating at approximately 2 bar pressure.

7.4. Suggest suitable materials of construction for the following applications:

1. A 10,000 m^3 storage tank for toluene;
2. A 5.0 m^3 tank for storing a 30% w/w aqueous solution of sodium chloride;
3. A 2 m diameter, 20 m high distillation column, distilling acrylonitrile;
4. A 100 m^3 storage tank for strong nitric acid;
5. A 500 m^3 aqueous waste hold-up tank. The wastewater pH can vary from 1 to 12. The wastewater will also contain traces of organic material;
6. A packed absorption column 0.5 m diameter, 3 m high, absorbing gaseous hydrochloric acid into water. The column will operate at essentially atmospheric pressure.

7.5. Aniline is manufactured by the hydrogenation of nitrobenzene in a fluidized bed reactor. The reactor operates at 250°C and 20 bar. The reactor vessel is approximately 3 m diameter and 9 m high. Suggest suitable materials of construction for this reactor.

7.6. Methyl ethyl ketone (MEK) is manufactured by the dehydrogenation of 2-butanol using a shell and tube type reactor. Flue gases are used for heating and pass through the tubes. The flue gases will contain traces of sulfur dioxide. The reaction products include hydrogen.

The reaction takes place in the shell at a pressure of 3 bar and temperature of 500°C. Select suitable materials for the tubes and shell.

7.7. In the manufacture of aniline by the hydrogenation of nitrobenzene, the off gases from the reactor are cooled and the products and unreacted nitrobenzene condensed in a shell and tube exchanger. A typical composition of the condensate is kmol/h: aniline 950, cyclo-hexylamine 10, water 1920, nitrobenzene 40. The gases enter the condenser at 230°C and leave at 50°C. The cooling water enters the tubes at 20°C and leaves at 50°C. Suggest suitable materials of construction for the shell and the tubes.

7.8. A slurry of acrylic polymer particles in water is held in storage tanks prior to filtering and drying. Plain carbon steel would be a suitable material for the tanks, but it is essential that the polymer does not become contaminated with iron in storage. Suggest some alternative materials of construction for the tanks.

7.9. Coal gasification is carried out at 850°C and 40 atmospheres pressure, by reaction of coal with steam and oxygen. The empirical formula of the coal is roughly $CH_{0.8}S_{0.013}$. What materials of construction would you recommend for

1. The coal addition system;
2. The oxygen injection system;
3. The gasification reactor;
4. The product gas transfer line.

8 DESIGN INFORMATION AND DATA

Chapter Contents

Key Learning Objectives

- How to obtain the chemical and physical properties needed for design calculations
- How commercial process simulators predict properties for compounds when little or no data are available
- How to select a suitable phase equilibrium model

8.1. INTRODUCTION

Information on manufacturing processes, equipment parameters, materials of construction, costs, and the physical properties of process materials are needed at all stages of design, from the initial screening of possible processes to the plant startup and production.

Sources of data on costs were discussed in Chapter 6 and materials of construction in Chapter 7. This chapter covers sources of information on manufacturing processes and physical properties, and the estimation of physical property data. Information on the types of equipment (unit operations) used in chemical process plants is given in Chapters 10, 11, and 12, which are concerned with equipment selection and design.

When a project is largely a repeat of a previous project, the data and information required for the design will be available in the company's process files, if proper detailed records are kept. For a new project or process, the design data must be obtained from the literature, or by experiment (research laboratory and pilot plant), or purchased from other companies. The information on manufacturing processes available in the general literature can be of use in the initial stages of process design, for screening potential processes, but is usually mainly descriptive and too superficial to be of much use for detailed design and evaluation.

The literature on the physical properties of elements and compounds is extensive, and reliable values for common materials can usually be found. The principal sources of physical property data are listed in the references at the end of this chapter.

Where values cannot be found, the data required must be measured experimentally or estimated. Methods of estimating (predicting) the more important physical properties required for design are given in this chapter. A physical property data bank is given in Appendix C and is available in MS Excel format in the online material at http://books.elsevier.com/companions.

Readers who are unfamiliar with the sources of information and the techniques used for searching the literature should consult one of the many guides to the technical literature that have been published, such as those by Lord (2000) and Maizell (1998).

8.2. SOURCES OF INFORMATION ON MANUFACTURING PROCESSES

In this section, the sources of information available in the open literature on commercial processes for the production of chemicals and related products are reviewed.

The chemical process industries are competitive, and the information that is published on commercial processes is restricted. The articles on particular processes published in the technical literature and in textbooks invariably give only a superficial account of the chemistry and unit operations used. They lack the detailed information on reaction kinetics, process conditions, equipment parameters, and physical properties that is needed for process design. The information that can be found in the general literature is, however, useful in the early stages of a project, when searching for possible process routes. It is often sufficient for a flowsheet of the process to be drawn up and a rough estimate of the capital and production costs made.

The most comprehensive collection of information on manufacturing processes is probably the *Encyclopedia of Chemical Technology* edited by Kirk (2003) and Kirk and Othmer (2001), which covers the whole range of chemical and associated products. Another encyclopedia covering manufacturing processes is that edited by McKetta (2001). Several books have also been published that give brief summaries of the production processes used for the commercial chemicals and chemical products. The best known of these is probably Shreve's book on the chemical process industries, now updated by Austin and Basta (1998). Comyns (1993) lists named chemical manufacturing processes, with references.

The extensive German reference work on industrial processes, *Ullman's Encyclopedia of Industrial Technology*, is now available in an English translation (Ullman, 2002).

Specialized texts have been published on some of the more important bulk industrial chemicals, such as that by Miller (1969) on ethylene and its derivatives; these are too numerous to list but should be available in the larger reference libraries and can be found by reference to the library catalogue. Meyers (2003) gives a good introduction to the processes used in oil refining. Kohl and Nielsen (1997) provide an excellent overview of the processes used for gas treating and sulfur recovery.

Books quickly become outdated, and many of the processes described are obsolete or at best obsolescent. More up-to-date descriptions of the processes in current use can be found in the technical journals. The journal *Hydrocarbon Processing* publishes an annual review of petrochemical processes, which was titled *Petrochemical Developments* and is now called *Petrochemicals Notebook*; this gives flow diagrams and brief process descriptions of new process developments.

Patents

Patents can be useful sources of information, but some care is needed in extracting information from them. To obtain a patent, an inventor is legally obliged to disclose the best mode of practice of the invention; failure to do so could render the patent invalid if it were contested. Most patents therefore include one or more examples illustrating how the invention is practiced and differentiating it from the prior art. The examples given in a patent often give an indication of the process conditions used, though they are frequently examples of laboratory preparations, rather than of the full-scale manufacturing processes. Many process patents also include examples based on computer simulations, in which case the data should be viewed with suspicion. When data from patents is used, it is important to carefully read the section that describes the experimental procedure to be sure that the experiments were run under appropriate conditions.

A patent gives its owner the right to sue anyone who practices the technology described in the patent claims without a license from the patent owner. Patent attorneys generally try to write patents to claim broad ranges of process conditions, so as to maximize the range of validity and make it hard for competitors to avoid the patent by making a slight change in temperature, pressure, or other process parameters. Very often, a patent will say something along the lines of "the reaction is carried out at a temperature in the range 50 to 500°C, more preferably in the range 100 to

300°C and most preferably in the range 200 to 250°C.” It is usually possible to use engineering judgment to determine the optimal conditions from such ranges. The best conditions will usually be at or near the upper or lower end of the narrowest defined range. The examples in the patent will often indicate the best operating point.

Patents can be downloaded free from the website of the U.S. patent office, www.uspto.gov. The USPTO website also has limited search capability. Most large companies subscribe to more sophisticated patent search services such as Delphion (www.delphion.com), PatBase (www.patbase.com) or GetthePatent (www.getthepatent.com).

Several guides have been written to help engineers understand the use of patents for the protection of inventions and as sources of information, such as those by Auger (1992) and Gordon and Cookfair (2000).

The Internet

It is worthwhile searching online for information on processes, equipment, products, and physical properties. Many manufacturers and government departments maintain websites. In particular, up-to-date information can be obtained on the health and environmental effects of products.

Many university libraries or engineering departments provide information guides for students, and these are available on the Internet. A search using the key words such as “chemical engineering information” will usually find them. Some examples are

- The University of Manchester, UK, Heriot-Watt University, Edinburgh, UK and the Joint Information Systems Committee: www.intute.ac.uk/sciences/
- University of Florida Web Virtual Library: www.che.ufl.edu/www-che/
- Karlsburg University, Germany: International Directory of Chemical Engineering URLs: www.ciw.uni-karlsruhe.de/links.php

Many of the important sources of engineering information are subscription services. The American Chemical Society’s Chemical Abstracts Service is the best source for chemical properties and reaction kinetics data. Chemical abstracts can be searched online through the SciFinder subscription service (www.cas.org). This is available in most university libraries.

Another important source of information is Knovel. Knovel provides online access to most standard reference books. It is a subscription service but can be accessed through many libraries, including those of the professional engineering institutions and some universities. At the time of writing, Knovel is available free to members of the AIChE and IChemE. In addition to having many reference books in .pdf format, Knovel has interactive graphs and lookup tables for books such as *Perry’s Chemical Engineers Handbook* and the *International Critical Tables*.

8.3. GENERAL SOURCES OF PHYSICAL PROPERTIES

In this section, those references that contain comprehensive compilations of physical property data are reviewed. Sources of data on specific physical properties are given in the remaining sections of the chapter.

International Critical Tables (1933) is still probably the most comprehensive compilation of physical properties and is available in most reference libraries. Though it was first published in 1933, physical properties do not change, except in as much as experimental techniques improve, and ICT is still a useful source of engineering data. ICT is now available as an e-book and can be referenced on the Internet through Knovel (2003).

Tables and graphs of physical properties are given in many handbooks and textbooks on chemical engineering and related subjects. Many of the data given are duplicated from book to book, but the various handbooks do provide quick, easy access to data on the more commonly used substances.

An extensive compilation of thermophysical data has been published by Plenum Press (Touloukian, 1970–1977). This multiple-volume work covers conductivity, specific heat, thermal expansion, viscosity, and radiative properties (emittance, reflectance, absorptance, and transmittance).

Elsevier have published a series of volumes on physical property and thermodynamic data. Those of use in design are included in the Bibliography at the end of this chapter.

The Engineering Sciences Data Unit (ESDU, www.ihsesdu.com) was set up to provide validated data for engineering design, developed under the guidance and approval of engineers from industry, the universities, and research laboratories. ESDU data include equipment design data and software and extensive high-quality physical property data—mostly for pure fluids that are in use in the oil and process industries.

Caution should be exercised when taking data from the literature, as typographical errors often occur. If a value looks doubtful, it should be cross-checked in an independent reference or by estimation.

The values of some properties are dependent on the method of measurement; for example, surface tension and flash point, and the method used should be checked, by reference to the original paper if necessary, if an accurate value is required.

The results of research work on physical properties are reported in the general engineering and scientific literature. The *Journal of Chemical Engineering Data* specializes in publishing physical property data for use in chemical engineering design. A quick search of the literature for data can be made by using the abstracting journals, such as *Chemical Abstracts* (American Chemical Society) and *Engineering Index* (Engineering Index Inc., New York). *Engineering Index* is now called *Engineering Information (Ei)* and is a web-based reference source owned by Elsevier Information (www.ei.org).

Computerized physical property data banks have been set up by various organizations to provide a service to the design engineer. They can be incorporated into computer-aided design programs and are increasingly being used to provide reliable, authenticated design data. Examples of such programs are the PPDS and the DIPPR^{TM} databases.

PPDS (Physical Property Data Service) was originally developed in the United Kingdom by the Institution of Chemical Engineers and the National Physical Laboratory. It is now available as a Microsoft^{TM} Windows version from NEL, a division of the TUV Suddeutschland Group (www.tuvnel.com/content/ppds.aspx). PPDS is made available to universities at a discount.

The DIPPR^{TM} databases were developed in the United States by the Design Institute for Physical Properties of the American Institute of Chemical Engineers. The DIPPR^{TM} projects are aimed at providing evaluated process design data for the design of chemical processes and equipment (www.aiche.org/TechnicalSocieties/DIPPR/index.aspx). The DIPPR Project 801 has been made available to university departments; see Rowley et al. (2004).

8.4. ACCURACY REQUIRED OF ENGINEERING DATA

The accuracy needed depends on the use to which the data will be put. Before spending time and money searching for the most accurate value or arranging for special measurements to be made, the designer must decide what accuracy is required; this will depend on several factors:

1. *The level of design:* Less accuracy is obviously needed for rough screening calculations made to sort out possible alternative designs than in the final stages of design, when money will be committed to purchase equipment.
2. *The reliability of the design methods:* If there is some uncertainty in the techniques to be used, it is clearly a waste of time to search out highly accurate physical property data that will add little or nothing to the reliability of the final design.
3. *The sensitivity to the particular property:* How much will a small error in the property affect the design calculation? For example, it was shown in Chapter 5 that the estimation of the optimum pipe diameter is insensitive to viscosity. The sensitivity of a design method to errors in physical properties and other data can be checked by repeating the calculation using slightly altered values.

It is often sufficient to estimate a value for a property (sometimes even to make an intelligent guess) if the value has little effect on the final outcome of the design calculation. For example, in calculating the heat load for a reboiler or vaporizer, an accurate value of the liquid specific heat is seldom needed, as the latent heat load is usually many times the sensible heat load and a small error in the sensible heat calculation will have little effect on the design. The designer must, however, exercise caution when deciding to use less-reliable data and must be sure that they are sufficiently accurate for the design purpose. For example, it would be correct to use an approximate value for density when calculating the pressure drop in a pipe system where a small error could be tolerated, considering the other probable uncertainties in the design, but it would be quite unacceptable in the design of a decanter, where the operation depends on small differences in density.

Consider the accuracy of the equilibrium data required to calculate the number of equilibrium stages needed for the separation of a mixture of acetone and water by distillation (see Chapter 11, Example 11.2). Several investigators have published vapor-liquid equilibrium data for this system: Othmer et al. (1952), York and Holmes (1942), Kojima et al. (1968), Reinders and De Minjer (1947).

If the purity of the acetone product required is less than 95%, inaccuracies in the VLE plot have little effect on the estimate of the number of stages required, as the relative volatility is very high. If a high purity is wanted, say >99%, then reliable data are needed in this region as the equilibrium line approaches the operating line (a pinch point occurs). Of the references cited, none gives values in the region above 95%, and only two give values above 90%; more experimental values are needed to design with confidence. There is a possibility that the system forms an azeotrope in this region. An azeotrope does form at higher pressure (Othmer et al., 1952).

8.5. PREDICTION OF PHYSICAL PROPERTIES

Whenever possible, experimentally determined values of physical properties should be used. If reliable values cannot be found in the literature and if time or facilities are not available for their determination, then to proceed with the design, the designer must resort to estimation. Techniques are available for the prediction of most physical properties with sufficient accuracy for use in process and equipment design. A detailed review of all the different methods available is beyond the scope of this book; selected methods are given for the more commonly needed properties. The criterion used for selecting a particular method for presentation in this chapter was to choose the most easily used, simplest method that had sufficient accuracy for general use. If highly accurate values are required, then specialized texts on physical property estimation should be consulted, such as those by Reid et al. (1987), Poling et al. (2000), Bretsznajder (1971), Sterbacek et al. (1979), and AIChE (1983, 1985).

A quick check on the probable accuracy of a particular method can be made by using it to estimate the property for an analogous compound, for which experimental values are available.

The techniques used for prediction are also useful for the correlation, and extrapolation and interpolation, of experimental values.

Group contribution techniques are based on the concept that a particular physical property of a compound can be considered to be made up of contributions from the constituent atoms, groups, and bonds, the contributions being determined from experimental data. They provide the designer with simple, convenient methods for physical property estimation, requiring only a knowledge of the structural formula of the compound.

Also useful, and convenient to use, are prediction methods based on the use of reduced properties (corresponding states), providing that values for the critical properties are available or can be estimated with sufficient accuracy; see Sterbacek et al. (1979).

In most cases, the methods described in the following sections, or their equivalents, are available in commercial process simulation programs such as AspenPlus^{TM}, ChemCAD^{TM}, Pro II^{TM}, and UniSim^{TM}. The easiest way to estimate mixture properties is usually to set up a stream with the desired temperature, pressure, and composition in one of the simulators. The design engineer should always check the results from the simulation against any available data. If no experimental data are available, then it is usually a good idea to make an independent estimate of any parameters that have a strong influence on the design, to be satisfied that the results from the simulator are credible. If the independent estimate does not agree with the simulation result, then it may be worthwhile to conduct some experiments to collect real data.

8.6. DENSITY

8.6.1. Liquids

Values for the density of pure liquids can usually be found in the handbooks. It should be noted that the density of most organic liquids, other than those containing a halogen or other "heavy atom," usually lies between 800 and 1000 kg/m^3. Liquid densities are given in Appendix C.

An approximate estimate of the density at the normal boiling point can be obtained from the molar volume (see Table 8.6)

$$\rho_b = \frac{M}{V_m} \tag{8.1}$$

where

ρ_b = density, kg/m^3;
M = molecular mass;
V_m = molar volume, m^3/kmol.

For mixtures, it is usually sufficient to take the specific volume of the components as additive, even for nonideal solutions, as is illustrated by Example 8.1.

The densities of many aqueous solutions are given by Perry et al. (1997).

Example 8.1

Calculate the density of a mixture of methanol and water at 20°C, composition 40% w/w methanol.

Density of water at 20°C	998.2 kg/m^3
Density of methanol at 20°C	791.2 kg/m^3

Solution

Basis: 1000 kg

$$\text{Volume of water} = \frac{0.6 \times 1000}{998.2} = 0.601\ \text{m}^3$$

$$\text{Volume of methanol} = \frac{0.4 \times 1000}{791.2} = \underline{0.506\ \text{m}^3}$$

$$\text{Total} = 1.107\ \text{m}^3$$

$$\text{Density of mixture} = \frac{1000}{1.107} = \underline{\underline{903.3\ \text{kg/m}^3}}$$

$$\text{Experimental value} = 934.5\ \text{kg/m}^3$$

$$\text{Error} = \frac{934.5 - 903.3}{903.3} = 3\%, \text{ which would be acceptable for most engineering purposes}$$

If data on the variation of density with temperature cannot be found, they can be approximated for nonpolar liquids from Smith's equation for thermal expansion (Smith et al., 1954):

$$\beta = \frac{0.04314}{(T_c - T)^{0.641}} \tag{8.2}$$

where

β = coefficient of thermal expansion, K^{-1};
T_c = critical temperature, K;
T = temperature, K.

8.6.2. Gas and Vapor Density (Specific Volume)

For general engineering purposes it is often sufficient to consider that real gases and vapors behave ideally and to use the gas law:

$$PV = n\mathrm{R}T \tag{8.3}$$

where

P = absolute pressure N/m^2 (Pa);
V = volume m^3;
n = mols of gas;
T = absolute temperature, K;
R = universal gas constant, 8.314 J K^{-1} mol^{-1} (or kJ K^{-1} $kmol^{-1}$).

$$\text{Specific volume} = \frac{\mathrm{R}T}{P} \tag{8.4}$$

These equations will be sufficiently accurate up to moderate pressures, in circumstances in which the value is not critical. If greater accuracy is needed, the simplest method is to modify equation 8.3 by including the compressibility factor z:

$$PV = zn\mathrm{R}T \tag{8.5}$$

The compressibility factor can be estimated from a generalized compressibility plot, which gives z as a function of reduced pressure and temperature (Chapter 3, Figure 3.8).

The pseudocritical properties of mixtures should be used to obtain the compressibility factor:

$$P_{c,m} = P_{c,a}y_a + P_{c,b}y_b + \ldots \tag{8.6}$$

$$T_{c,m} = T_{c,a}y_a + T_{c,b}y_b + \ldots \tag{8.7}$$

where

P_c = critical pressure;
T_c = critical temperature;
y = mol fraction;

suffixes
m = mixture;
a, b, etc. = components.

8.7. VISCOSITY

Viscosity values are needed for any design calculations involving the transport of fluids or heat. Values for pure substances can usually be found in the literature; see Yaws (1993–1994). Liquid viscosities are given in Appendix C. Methods for the estimation of viscosity are given in following sections.

8.7.1. Liquids

A rough estimate of the viscosity of a pure liquid at its boiling point can be obtained from the modified Arrhenius equation:

$$\mu_b = 0.01\rho_b^{0.5} \tag{8.8}$$

where

μ_b = viscosity, mNs/m^2;
ρ_b = density at boiling point, kg/m^3.

A more accurate value can be obtained if reliable values of density are available or can be estimated with sufficient accuracy, from Souders' equation (Souders, 1938):

$$\log(\log 10\mu) = \frac{I}{M}\rho \times 10^{-3} - 2.9 \tag{8.9}$$

where

μ = viscosity, mNs/m^2;
M = molecular mass;
I = Souders' index, estimated from the group contributions given in Table 8.1;
ρ = density at the required temperature, kg/m^3.

Example 8.2

Estimate the viscosity of toluene at 20°C.

Solution

Toluene

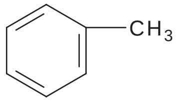
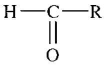
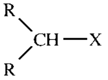
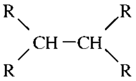
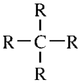


Table 8.1. Contributions for Calculating the Viscosity Constant I in Souders' Equation

Atom	H	O	C	N	Cl	Br	I
Contribution	+2.7	+29.7	+50.2	+37.0	+60	+79	+110

Contributions of groups and bonds

Double bond	−15.5	 $\text{H—}\overset{\displaystyle \text{O}}{\underset{}{\text{C}}}\text{—R}$	+10
Five-member ring	−24		
Six-member ring	−21		
Side groups on a six-member ring:		$\text{—CH=CH—CH}_2\text{—X}^{\dagger}$	+4
Molecular weight <17	−19		+6
Molecular weight >16	−17		
Ortho or *para* position	+3		
Meta position	−1		
	+8	OH	+57.1
		COO	+90
		COOH	+104.4
		NO_2	+80
	+10		
$\text{—CH}_2\text{—}$	+55.6		

[†] X is a negative group.

Contributions from Table 8.1:

7 carbon atoms	$7 \times 50.2 =$	351.4
8 hydrogen atoms	$8 \times 2.7 =$	21.6
3 double bonds	$3(-15.5) =$	−46.5
1 six-membered ring		−21.1
1 side group		−9.0
	Total, $I =$	296.4

Density at 20°C = 866 kg/m^3
Molecular weight 92

$$\log(\log 10\,\mu) = \frac{296.4 \times 866 \times 10^{-3}}{92} - 2.9 = -0.11$$

$$\log 10\,\mu = 0.776$$

$$\mu = 0.597, \quad \text{rounded} = 0.6\,\text{mNs/m}^2$$

experimental value, 0.6 cp = 0.6 mNs/m^2

Author's note: The fit obtained in this example is rather fortuitous; the usual accuracy of the method for organic liquids is around ±10%.

Variation with Temperature

If the viscosity is known at a particular temperature, the value at another temperature can be estimated with reasonable accuracy (within ±20%) by using the generalized

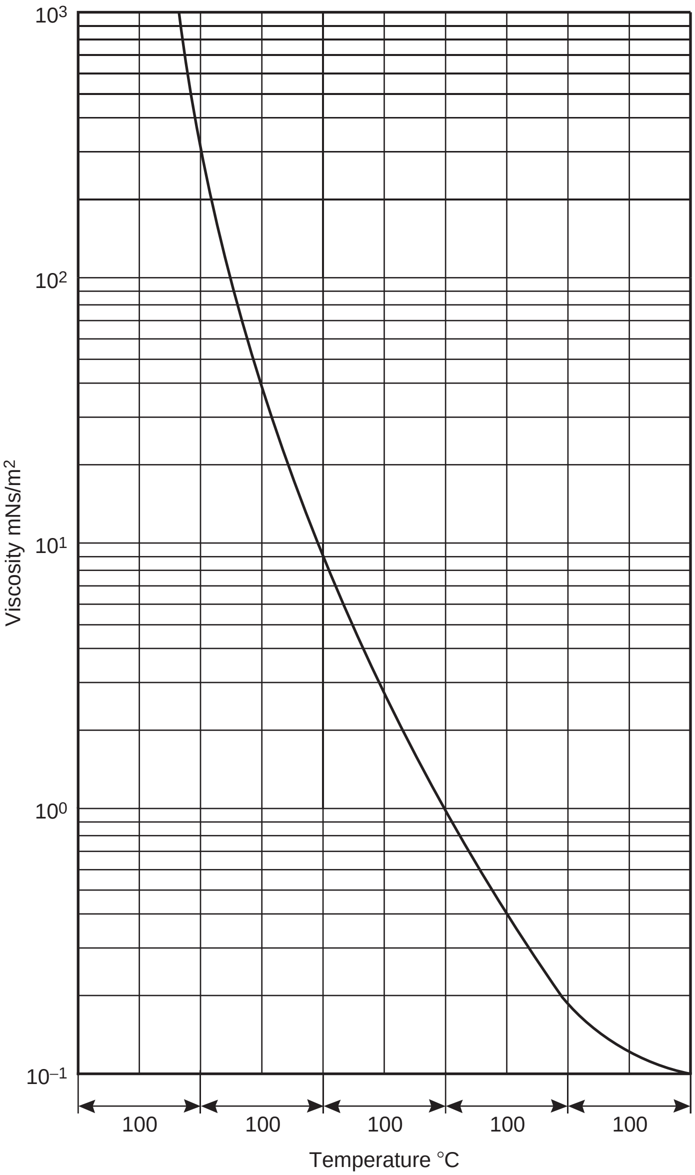


Figure 8.1. Generalized viscosity vs. temperature curve for liquids.

plot of Lewis and Squires (1934); see Figure 8.1. The scale of the temperature ordinate is obtained by plotting the known value, as illustrated in Example 8.3.

Example 8.3

Estimate the viscosity of toluene at 80°C, using the value at 20°C given in Example 8.2.

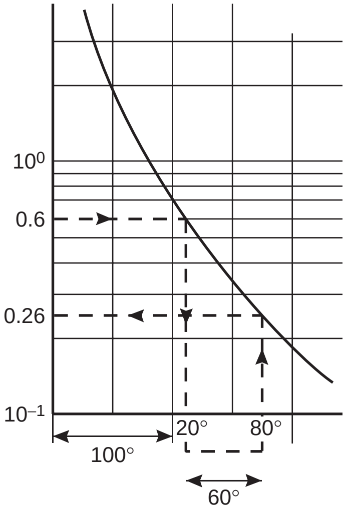


Figure 8.1 Cont'd.

Solution

Temperature increment $80 - 20 = 60°\text{C}$.

From Figure 8.1, viscosity at $80°\text{C} = 0.26\,\text{mNs/m}^2$.

Effect of Pressure

The viscosity of a liquid is dependent on pressure as well as temperature, but the effect is not significant except at very high pressures. A rise in pressure of 300 bar is roughly equivalent to a decrease in temperature of 1°C.

Mixtures

It is difficult to predict the viscosity of mixtures of liquids. Viscosities are rarely additive, and the shape of the viscosity-concentration curve can be complex. The viscosity of the mixture may be lower or, occasionally, higher than that of the pure components. A rough check on the magnitude of the likely error in a design calculation, arising from uncertainty in the viscosity of a mixture, can be made by using the smallest and largest values of the pure components in the calculation and noting the result.

As an approximation, the variation can be assumed to be linear, if the range of viscosity is not very wide, and a weighted average viscosity calculated. For organic liquid mixtures a modified form of Souders' equation can be used, using a mol fraction weighted average value for the viscosity constant for the mixture I_m and the average molecular weight.

For a binary mixture, equation 8.9 becomes

$$\log(\log 10\,\mu_m) = \rho_m\left[\frac{x_1 I_1 + x_2 I_2}{x_1 M_1 + x_2 M_2}\right] \times 10^{-3} - 2.9 \tag{8.10}$$

where

μ_m = viscosity of mixture;
ρ_m = density of mixture;
x_1, x_2 = mol fraction of components;
M_1, M_2 = molecular masses of components.

Bretsznajder (1971) gives a detailed review of the methods that have been developed for estimating the viscosity of mixtures, including methods for aqueous solutions and dispersions.

For heat transfer calculations, Kern (1950) gives a rough rule of thumb for organic liquid mixtures:

$$\frac{1}{\mu_m} = \frac{w_1}{\mu_1} + \frac{w_2}{\mu_2} \tag{8.11}$$

where

w_1, w_2 = mass fractions of the components 1 and 2;
μ_1, μ_2 = viscosities of components 1 and 2.

8.7.2 Gases

Reliable methods for the prediction of gas viscosities and the effect of temperature and pressure are given by Bretsznajder (1971) and Reid et al. (1987).

Where an estimate of the viscosity is needed to calculate Prandtl numbers, the methods developed for the direct estimation of Prandtl numbers should be used.

For gases at low pressure, Bromley (1952) has suggested the following values:

	Prandtl Number
Monatomic gases (e.g., Ar, He)	0.67 ± 5%
Nonpolar, linear molecules (e.g., O_2, Cl_2)	0.73 ± 15%
Nonpolar, nonlinear molecules (e.g., CH_4, C_6H_6)	0.79 ± 15%
Strongly polar molecules (e.g., CH_3OH, SO_2, HCl)	0.86 ± 8%

Note: The Prandtl number for gases varies only slightly with temperature.

8.8 THERMAL CONDUCTIVITY

The experimental methods used for the determination of thermal conductivity are described by Tsederberg (1965), who also lists values for many substances. The four-volume handbook by Yaws (1995–1997) is a useful source of thermal conductivity data for hydrocarbons and inorganic compounds.

8.8.1. Solids

The thermal conductivity of a solid is determined by its form and structure, as well as composition. Values for the commonly used engineering materials are given in various handbooks.

8.8.2. Liquids

The data available in the literature up to 1973 have been reviewed by Jamieson et al. (1975). The Weber equation (Weber, 1880) can be used to make a rough estimate of the thermal conductivity of organic liquids for use in heat transfer calculations:

$$k = 3.56 \times 10^{-5} C_p \left(\frac{\rho^4}{M}\right)^{1/3} \tag{8.12}$$

where

k = thermal conductivity, W/m°C;
M = molecular mass;
C_p = specific heat capacity, kJ/kg°C;
ρ = density, kg/m^3.

Bretsznajder (1971) gives a group contribution method for estimating the thermal conductivity of liquids.

Example 8.4

Estimate the thermal conductivity of benzene at 30°C.

Solution

Density at 30°C = 875 kg/m^3
Molecular mass = 78
Specific heat capacity = 1.75 kJ/kg°C

$$k = 3.56 \times 10^{-5} \times 1.75 \left(\frac{875^4}{78}\right)^{1/3} = \underline{\underline{0.12\ \text{W/m°C}}} \tag{8.12}$$

Experimental value, 0.16 W/m°C, error 25%.

8.8.3. Gases

Approximate values for the thermal conductivity of pure gases, up to moderate pressures, can be estimated from values of the gas viscosity, using Eucken's equation (Eucken, 1912):

$$k = \mu \left(C_p + \frac{10.4}{M}\right) \tag{8.13}$$

where

μ = viscosity, mNs/m^2;
C_p = specific heat capacity, kJ/kg°C;
M = molecular mass.

Example 8.5

Estimate the thermal conductivity of ethane at 1 bar and 450°C.

Solution

Viscosity $= 0.0134\,\mathrm{mNs/m^2}$
Specific heat capacity $= 2.47\,\mathrm{kJ/kg^\circ C}$

$$k = 0.0134\left(2.47 + \frac{10.4}{30}\right) = 0.038\ \mathrm{W/m^\circ C} \tag{8.13}$$

Experimental value, 0.043 W/m°C, error 12%.

8.8.4. Mixtures

In general, the thermal conductivities of liquid mixtures and gas mixtures are not simple functions of composition and the thermal conductivity of the components. Bretsznajder (1971) discusses the methods that are available for estimating the thermal conductivities of mixtures from a knowledge of the thermal conductivity of the components.

If the components are all nonpolar, a simple weighted average is usually sufficiently accurate for design purposes:

$$k_m = k_1 w_1 + k_2 w_2 + \dots \tag{8.14}$$

where

k_m = thermal conductivity of mixture;
k_1, k_2 = thermal conductivity of components;
w_1, w_2 = component mass fractions.

8.9. SPECIFIC HEAT CAPACITY

The specific heats of the most common organic and inorganic materials can usually be found in the handbooks.

8.9.1. Solids and Liquids

Approximate values can be calculated for solids and liquids by using a modified form of Kopp's law, which is given by Werner (1941). The heat capacity of a compound is taken as the sum of the heat capacities of the individual elements of which it is composed. The values attributed to each element for liquids and solids, at room temperature, are given in Table 8.2; the method is illustrated in Example 8.6.

Table 8.2. Heat Capacities of the Elements, J/mol°C

Element	Solids	Liquids
C	7.5	11.7
H	9.6	18.0
B	11.3	19.7
Si	15.9	24.3
O	16.7	25.1
F	20.9	29.3
P and S	22.6	31.0
all others	26.0	33.5

Example 8.6

Estimate the specific heat capacity of urea, CH_4N_2O.

Solution

Element	mol. Mass	Heat capacity	
C	12	7.5	= 7.5
H	4	4×9.6	= 38.4
N	28	2×26.0	= 52.0
O	16	16.7	= 16.7
Total	60		114.6 J/mol°C

$$\text{Specific heat capacity} = \frac{114.6}{60} = \underline{\underline{1.91\ \text{J/g°C}}}(\text{kJ/kg°C})$$

Experimental value 1.34 kJ/kg°C, error 43%.

Kopp's rule does not take into account the arrangement of the atoms in the molecule and, at best, gives only very approximate, "ballpark" values.

For organic liquids, the group contribution method proposed by Chueh and Swanson (1973a, b) gives reasonably accurate predictions. The contributions to be assigned to each molecular group are given in Table 8.3, and the method is illustrated in Examples 8.7 and 8.8.

Liquid specific heats do not vary much with temperature, at temperatures well below the critical temperature (reduced temperature <0.7).

The specific heats of liquid mixtures can be estimated, with sufficient accuracy for most technical calculations, by taking heat capacities as the mass (or mole) weighted sum of the pure component heat capacities.

For dilute aqueous solutions, it is usually sufficient to take the specific heat of the solution as that of water.

Exceptions to the above 18.84 rule:

1. No such extra 18.84 additions for —CH_3 groups.

Table 8.3. Group Contributions for Liquid Heat Capacities at 20°C, kJ/kmol°C (Chueh and Swanson, 1973a, b)

Group	Value	Group	Value
Alkane		$-\overset{O}{\overset{\Vert}{C}}-O-$	60.71
$-CH_3$	36.84	$-CH_2OH$	73.27
$-CH_2-$	30.40	$-\overset{\vert}{C}HOH$	76.20
$-\overset{\vert}{C}H-$	20.93	$-\overset{\vert}{\underset{\vert}{C}}OH$	111.37
$-\overset{\vert}{\underset{\vert}{C}}-$	7.37	$-OH$	44.80
Olefin		$-ONO_2$	119.32
$=CH_2$	21.77	Halogen	
$=\overset{\vert}{C}-H$	21.35	$-Cl$ (first or second on a carbon)	36.01
$=\overset{\vert}{C}-$	15.91	$-Cl$ (third or fourth on a carbon)	25.12
Alkyne		$-Br$	37.68
$-C\equiv H$	24.70	$-F$	16.75
$-C\equiv$	24.70	$-I$	36.01
In a ring		Nitrogen	
$-\overset{\vert}{C}H=$	18.42	$H-\overset{H}{\overset{\vert}{N}}-$	58.62
$-\overset{\vert}{C}=$ or $-\overset{\vert}{\underset{\vert}{C}}-$	12.14	$-\overset{H}{\overset{\vert}{N}}-$	43.96
$-C=$	22.19	$-\overset{\vert}{N}-$	31.40
$-CH_2-$	25.96	$-N=$(in a ring)	18.84
Oxygen		$-C\equiv N$	58.70
$-O-$	35.17	Sulphur	
$>C=O$	53.00	$-SH$	44.80
$-\underset{H}{\underset{\vert}{C}}-O$	53.00	$-S-$	33.49
$-\overset{O}{\overset{\Vert}{C}}-OH$	79.97	Hydrogen	
		$H-$ (for formic acid, formates, hydrogen cyanide, etc.)	14.65

Add 18.84 for any carbon group which fulfills the following criterion: a carbon group which is joined by a single bond to a carbon group connected by a double or triple bond with a third carbon group. In some cases a carbon group fulfills the above criterion in more ways than one; 18.84 should be added each time the group fulfills the criterion.

2. For a $-CH_2-$ group fulfilling the 18.84 addition criterion, add 10.47 instead of 18.84. However, when the $-CH_2-$ group fulfills the addition criterion in more ways than one, the addition should be 10.47 the first time and 18.84 for each subsequent addition.
3. No such extra addition for any carbon group in a ring.
   mol. wt. = 109

Example 8.7

Using Chueh and Swanson's method, estimate the specific heat capacity of ethyl bromide at 20°C.

Solution

Ethyl bromide CH_3CH_2Br

Group	Contribution	No. of	
$-CH_3$	36.84	1	= 36.84
$-CH_2-$	30.40	1	= 30.40
$-Br$	37.68	1	= 37.68
		Total	104.92 kJ/kmol°C

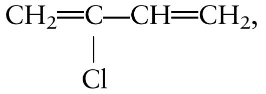
$$\text{Specific heat capacity} = \frac{104.92}{109} = \underline{\underline{0.96\,\text{kJ/kg°C}}}$$

Experimental value 0.90 kJ/kg°C

Example 8.8

Estimate the specific heat capacity of chlorobutadiene at 20°C, using Chueh and Swanson's method.

Solution

Structural formula  $CH_2{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH{=}CH_2$, mol. wt. 88.5

Group	Contribution	No. of	Addition Rule	Total
$=CH_2$	21.77	2	—	= 43.54
$=\underset{\mid}{C}-$	15.91	1	18.84	= 34.75
$=\overset{\mid}{CH}$	21.35	1	18.84	= 40.19
$-Cl$	36.01	1	—	= 36.01
			Total	154.49 kJ/kmol°C

$$\text{Specific heat capacity} = \frac{154.49}{88.5} = \underline{\underline{1.75\,\text{kJ/kg°C}}}$$

8.9.2. Gases

The dependence of gas-specific heats on temperature was discussed in Chapter 3, Section 3.5. For a gas in the ideal state the specific heat capacity at constant pressure is given by

$$C_p^o = a + bT + cT^2 + dT^3 \qquad \text{(equation 3.19)}$$

Values for the constants in this equation for the more common gases can be found in the handbooks and in Appendix C.

Several group contribution methods have been developed for the estimation of the constants, such as that by Rihani and Doraiswamy (1965) for organic compounds. Their values for each molecular group are given in Table 8.4, and the method is illustrated in Example 8.9. The values should not be used for acetylenic compounds.

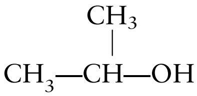
The correction of the ideal gas heat capacity to account for real conditions of temperature and pressure was discussed in Chapter 3, Section 3.7.

Example 8.9

Estimate the specific heat capacity of isopropyl alcohol at 500 K.

Solution

Structural formula



$$\mathrm{CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}OH}$$

Group	No. of	a	$b \times 10^2$	$c \times 10^4$	$d \times 10^6$
$-\mathrm{CH_3}$	2	5.0970	17.9480	−0.7134	0.0095
$-\overset{\vert}{\underset{\vert}{\mathrm{C}}}\mathrm{H}$	1	−14.7516	14.3020	−1.1791	0.03356
—OH	1	27.2691	−0.5640	0.1733	−0.0068
Total		17.6145	31.6860	−1.7190	0.0363

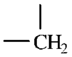
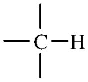
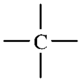
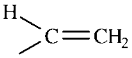
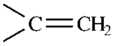
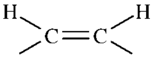
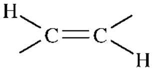
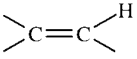
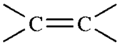
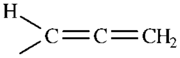
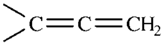
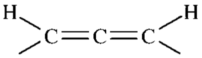
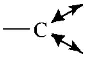
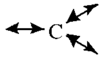
$$C_p^o = 17.6145 + 31.6860 \times 10^{-2}T - 1.7192 \times 10^{-4}T^2 + 0.0363 \times 10^{-6}T^3.$$

At 500 K, substitution gives

$$C_p = \underline{\underline{137.6\ \mathrm{kJ/kmol^\circ C}}}$$

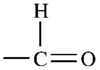
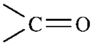
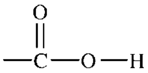
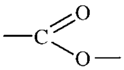
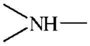
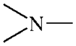
Experimental value, 31.78 cal/mol°C = 132.8 kJ/kmol°C, error 4%.

Table 8.4. Group Contributions to Ideal Gas Heat Capacities, kJ/kmol°C (Rihani and Doraiswamy, 1965)

Group	a	$b \times 10^2$	$c \times 10^4$	$d \times 10^6$
Aliphatic hydrocarbon groups				
$-CH_3$	2.5485	8.9740	−0.3567	0.004752
 $-\overset{\vert}{CH_2}$	1.6518	8.9447	−0.5012	0.0187
$=CH_2$	2.2048	7.6857	−0.3994	0.008264
 $-\overset{\vert}{\underset{\vert}{C}}-H$	−14.7516	14.3020	−1.1791	0.03356
 $-\overset{\vert}{\underset{\vert}{C}}-$	−24.4131	18.6493	−1.7619	0.05288
	1.1610	14.4786	−0.8031	0.01792
	−1.7472	16.2694	−1.1652	0.03083
	−13.0676	15.9356	−0.9877	0.02305
	3.9261	12.5208	−0.7323	0.01641
	−6.161	14.1696	−0.9927	0.02594
	1.9829	14.7304	−1.3188	0.03854
	9.3784	17.9597	−1.07433	0.02474
	11.0146	17.4414	−1.1912	0.03047
	−13.0833	20.8878	−1.8018	0.05447
Aromatic hydrocarbon groups				
	−6.1010	8.0165	−0.5162	0.01250
	−5.8125	6.3468	−0.4476	0.01113
	0.5104	5.0953	−0.3580	0.00888
Contributions due to ring formation				
Three-membered ring	−14.7878	−0.1256	0.3129	−0.02309
Four-membered ring	−36.2368	4.5134	0.1779	−0.00105
Five-membered ring:				
Pentane	−51.4348	7.7913	−0.4342	0.00898
Pentene	−28.8106	3.2732	−0.1445	0.00247
Six-membered ring:				
Hexane	−56.0709	8.9564	−0.1796	−0.00781
Hexene	−33.5941	9.3110	−0.80118	0.02291

(*continued*)

Table 8.4. Group Contributions to Ideal Gas Heat Capacities, kJ/kmol°C (Rihani and Doraiswamy, 1965)—Cont'd

Group	a	$b \times 10^2$	$c \times 10^4$	$d \times 10^6$
	Oxygen-containing groups			
$—OH$	27.2691	−0.5640	0.1733	−0.00680
$—O—$	11.9161	−0.04187	0.1901	−0.01142
 $—\overset{H}{C}=O$	14.7308	3.9511	0.2571	−0.02922
	4.1935	8.6931	−0.6850	0.01882
 $—\overset{O}{\overset{\Vert}{C}}—O—H$	5.8846	14.4997	−1.0706	0.02883
	11.4509	4.5012	0.2793	−0.03864
	−15.6352	5.7472	−0.5296	0.01586
	Nitrogen-containing groups			
$—C\equiv N$	18.8841	2.2864	0.1126	−0.01587
$—N\equiv C$	21.2941	1.4620	0.1084	−0.01020
$—NH_2$	17.4937	3.0890	0.2843	−0.03061
	−5.2461	9.1825	−0.6716	0.01774
	−14.5186	12.3230	−1.1191	0.03277
	10.2401	1.4386	0.07159	−0.01138
$—NO_2$	4.5638	11.0536	−0.7834	0.01989
	Sulphur-containing groups			
$—SH$	10.7170	5.5881	−0.4978	0.01599
$—S—$	17.6917	0.4719	−0.0109	−0.00030
	17.0922	−0.1260	0.3061	−0.02546
$—SO_3H$	28.9802	10.3561	0.7436	−0.09397
	Halogen-containing groups			
$—F$	6.0215	1.4453	−0.0444	−0.00014
$—Cl$	12.8373	0.8885	−0.0536	0.00116
$—Br$	11.5577	1.9808	−0.1905	0.0060
$—I$	13.6703	2.0520	−0.2257	0.00746

8.10. ENTHALPY OF VAPORIZATION (LATENT HEAT)

The latent heats of vaporization of the more commonly used materials can be found in the handbooks and in Appendix C.

A very rough estimate can be obtained from Trouton's rule (Trouton, 1884), one of the oldest prediction methods:

$$\frac{L_v}{T_b} = \text{constant} \tag{8.15}$$

where

L_v = latent heat of vaporization, kJ/kmol;
T_b = normal boiling point, K.

For organic liquids the constant can be taken as 100.

More accurate estimates, suitable for most engineering purposes, can be made from knowledge of the vapor pressure-temperature relationship for the substance. Several correlations have been proposed; see Reid et al. (1987).

The equation presented here, due to Haggenmacher (1946), is derived from the Antoine vapor pressure equation (see Section 8.11):

$$L_v = \frac{8.32BT^2\Delta z}{(T + C)^2} \tag{8.16}$$

where

L_v = latent heat at the required temperature, kJ/kmol;
T = temperature, K;
B, C = coefficients in the Antoine equation (equation 8.20);
Δz = $z_{\text{gas}} - z_{\text{liquid}}$ (where z is the compressibility constant), calculated from the equation:

$$\Delta z = \left[1 - \frac{P_r}{T_r^3}\right]^{0.5} \tag{8.17}$$

P_r = reduced pressure;
T_r = reduced temperature.

If an experimental value of the latent heat at the boiling point is known, the Watson equation (Watson, 1943) can be used to estimate the latent heat at other temperatures:

$$L_v = L_{v,b}\left[\frac{T_c - T}{T_c - T_b}\right]^{0.38} \tag{8.18}$$

where

L_v = latent heat at temperature T, kJ/kmol;
$L_{v,b}$ = latent heat at the normal boiling point, kJ/kmol;
T_b = boiling point, K;
T_c = critical temperature, K;
T = temperature, K.

Over a limited range of temperature, up to 100°C, the variation of latent heat with temperature can usually be taken as linear.

8.10.1. Mixtures

For design purposes it is usually sufficiently accurate to take the latent heats of the components of a mixture as additive:

$$L_v \text{ mixture} = L_{v1}x_1 + L_{v2}x_2 + \ldots \tag{8.19}$$

where

L_{v1}, L_{v2} = latent heats of the components kJ/kmol;
x_1, x_2 = mol fractions of components.

Example 8.10

Estimate the latent heat of vaporization of acetic anhydride, $C_4H_6O_3$, at its boiling point, 139.6°C (412.7 K), and at 200°C (473 K).

Solution

For acetic anhydride $T_c = 569.1$ K, $P_c = 46$ bar,

Antoine constants $A = 16.3982$
$B = 3287.56$
$C = -75.11$

Experimental value at the boiling point 41,242 kJ/kmol.
From Trouton's rule:

$$L_{v,b} = 100 \times 412.7 = \underline{\underline{41{,}270 \text{ kJ/kmol}}}$$

Note: The close approximation to the experimental value is fortuitous; the rule normally gives only a very approximate estimate.

From Haggenmacher's equation:

$$\text{at the b.p. } P_r = \frac{1}{46} = 0.02124$$

$$T_r = \frac{412.7}{569.1} = 0.7252$$

$$\Delta z = \left[1 - \frac{0.02124}{0.7252^3}\right]^{0.5} = 0.972$$

$$L_{v,b} = \frac{8.32 \times 3287.6 \times (412.7)^2 \times 0.972}{(412.7 - 75.11)^2} = \underline{\underline{39{,}733 \text{ kJ/mol}}}$$

At 200°C, the vapor pressure must first be estimated from the Antoine equation:

$$\ln P = A - \frac{B}{T + C}$$

$$\ln P = 16.3982 - \frac{3287.56}{473 - 75.11} = 8.14$$

$$P = 3421.35\ \text{mmHg} = 4.5\ \text{bar}$$

$$P_c = \frac{4.5}{46} = 0.098$$

$$T_c = \frac{473}{569.1} = 0.831$$

$$\Delta z = \left[1 - \frac{0.098}{0.831^3}\right]^{0.5} = 0.911$$

$$L_v = \frac{8.32 \times 3287.6 \times (473)^2 \times 0.911}{(473 - 75.11)^2} = \underline{\underline{35{,}211\ \text{kJ/kmol}}}$$

Using Watson's equation and the experimental value at the b.p.

$$L_v = 41{,}242\left[\frac{569.1 - 473}{569.1 - 412.7}\right]^{0.38} = \underline{\underline{34{,}260\ \text{kJ/kmol}}}$$

8.11. VAPOR PRESSURE

If the normal boiling point (vapor pressure = 1 atm) and the critical temperature and pressure are known, then a straight line drawn through these two points on a plot of log-pressure versus reciprocal absolute temperature can be used to make a rough estimation of the vapor pressure at intermediate temperatures.

Several equations have been developed to express vapor pressure as a function of temperature. One of the most commonly used is the three-term Antoine equation (Antoine, 1888):

$$\ln P = A - \frac{B}{T + C} \tag{8.20}$$

where

P = vapor pressure, mmHg;
A, B, C = the Antoine coefficients;
T = temperature, K.

Vapor pressure data, in the form of the constants in the Antoine equation, are given in several references; the compilations by Ohe (1976), Dreisbach (1952), Hala et al. (1968), and Hirata et al. (1975) give values for several thousand compounds. Antoine vapor pressure coefficients for the elements are given by Nesmeyanov (1963). Care must be taken when using Antoine coefficients taken from the literature in equation 8.20, as the equation is often written in different and ambiguous forms; the logarithm of the pressure may be to the base 10, instead of the natural logarithm, and the temperature may be degrees Celsius, not absolute temperature. Also, occasionally, the minus sign shown in equation 8.20 is included in the constant B and the equation written with a plus sign. The pressure may also be in units other than mm Hg. Always check the actual form of the equation used in the particular reference. Antoine constants for use in equation 8.20 are given in Appendix C. A spreadsheet for calculating vapor pressure is available in MS Excel format in the online material at http://books.elsevier.com/companions. Vapor pressure data for hydrocarbons can be found in the four-volume handbook by Yaws (1994–1995).

8.12. DIFFUSION COEFFICIENTS (DIFFUSIVITIES)

Diffusion coefficients are needed in the design of mass transfer processes, such as gas absorption, distillation, and liquid-liquid extraction, as well as in catalytic reactions where mass transfer can limit the rate of reaction.

Experimental values for the more common systems can be often found in the literature, but for most design work the values must be estimated.

8.12.1. Gases

The equation developed by Fuller et al. (1966) is easy to apply and gives reliable estimates:

$$D_v = \frac{1.013 \times 10^{-7} T^{1.75} \left(\dfrac{1}{M_a} + \dfrac{1}{M_b} \right)^{1/2}}{P\left[\left(\sum_a v_i \right)^{1/3} + \left(\sum_b v_i \right)^{1/3} \right]^2} \tag{8.21}$$

where

D_v = diffusivity, m^2/s,
T = temperature, K;
M_a, M_b = molecular masses of components *a* and *b;*
P = total pressure, bar;

$\sum_a v_i, \sum_b v_i$ = the summation of the special diffusion volume coefficients

for components *a* and *b*, given in Table 8.5.

The method is illustrated in Example 8.11.

Example 8.11

Estimate the diffusivity of methanol in air at atmospheric pressure and 25°C.

Solution

Diffusion volumes from Table 8.5; methanol:

Element	v_i No. of	
C	$16.50 \times 1 =$	16.50
H	$1.98 \times 4 =$	7.92
O	$5.48 \times 1 =$	5.48
	$\sum_a v_i$	29.90

Table 8.5. Special Atomic Diffusion Volumes (Fuller *et al.*, 1966)

Atomic and Structural Diffusion Volume Increments			
C	16.5	Cl	19.5*
H	1.98	S	17.0*
O	5.48	Aromatic or heterocyclic rings	−20.0
N	5.69*		

Diffusion Volumes of Simple Molecules			
H_2	7.07	CO	18.9
D_2	6.70	CO_2	26.9
He	2.88	N_2O	35.9
N_2	17.9	NH_3	14.9
O_2	16.6	H_2	12.7
Air	20.1	CCL_2F_2	114.8*
Ne	5.59	SF_6	69.7*
Ar	16.1	Cl_2	37.7*
Kr	22.8	Br_2	67.2*
Xe	37.9*	SO_2	41.1*

*Value based on only a few data points.

Diffusion volume for air = 20.1.
1 standard atmosphere = 1.013 bar.
Molecular mass CH_3OH = 32, air = 29.

$$D_v = \frac{1.013 \times 10^{-7} \times 298^{1.75}(1/32 + 1/29)^{1/2}}{1.013[(29.90)^{1/3} + (20.1)^{1/3}]^2} \qquad (8.21)$$
$$= \underline{\underline{16.2 \times 10^{-6} \mathrm{m}^2/\mathrm{s}}}$$

Experimental value, 15.9×10^{-6} m^2/s.

8.12.2. Liquids

The equation developed by Wilke and Chang (1955) can be used to predict liquid diffusivity:

$$D_L = \frac{1.173 \times 10^{-13}(\phi M)^{0.5} T}{\mu V_m^{0.6}} \qquad (8.22)$$

where

D_L = liquid diffusivity, m^2/s;
ϕ = an association factor for the solvent;
= 2.6 for water (some workers recommend 2.26);
= 1.9 for methanol;
= 1.5 for ethanol;
= 1.0 for unassociated solvents;

M = molecular mass of solvent;
μ = viscosity of solvent, mN s/m^2;
T = temperature, K;
V_m = molar volume of the solute at its boiling point, m^3/kmol. This can be estimated from the group contributions given in Table 8.6.

The method is illustrated in Example 8.12.

The Wilke-Chang correlation is shown graphically in Figure 8.2. This figure can be used to determine the association constant for a solvent from experimental values for D_L in the solvent.

The Wilke-Chang equation gives satisfactory predictions for the diffusivity of organic compounds in water but not for water in organic solvents.

Example 8.12

Estimate the diffusivity of phenol in ethanol at 20°C (293 K).

Solution

Viscosity of ethanol at 20°C, 1.2 mNs/m^2.

Molecular mass, 46.

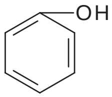
Molar volume of phenol  from Table 8.6:

Table 8.6. Structural Contributions to Molar Volumes, m^3/kmol (Gambill, 1958)

Molecular Volumes							
Air	0.0299	CO_2	0.0340	H_2S	0.0329	NO	0.0236
Br_2	0.0532	COS	0.0515	I_2	0.0715	N_2O	0.0364
Cl_2	0.0484	H_2	0.0143	N_2	0.0312	O_2	0.0256
CO	0.0307	H_2O	0.0189	NH_3	0.0258	SO_2	0.0448
Atomic Volumes							
As	0.0305	F	0.0087	P	0.0270	Sn	0.0423
Bi	0.0480	Ge	0.0345	Pb	0.0480	Ti	0.0357
Br	0.0270	H	0.0037	S	0.0256	V	0.0320
C	0.0148	Hg	0.0190	Sb	0.0342	Zn	0.0204
Cr	0.0274	I	0.037	Si	0.0320		

Cl, terminal, as in RCl	0.0216	in higher esters, ethers	0.0110
medial, as in R—CHCl—R	0.0246	in acids	0.0120
Nitrogen, double-bonded	0.0156	in union with S, P, N	0.0083
triply bonded, as in nitriles	0.0162	three-membered ring	− 0.0060
in primary amines, RNH_2	0.0105	four-membered ring	− 0.0085
in secondary amines, R_2NH	0.012	five-membered ring	− 0.0115
in tertiary amines, R_3N	0.0108	six-membered ring as in benzene, cyclohexane, pyridine	− 0.0150
Oxygen, except as noted below	0.0074		
in methyl esters	0.0091	Naphthalene ring	− 0.0300
in methyl ethers	0.0099	Anthracene ring	− 0.0475

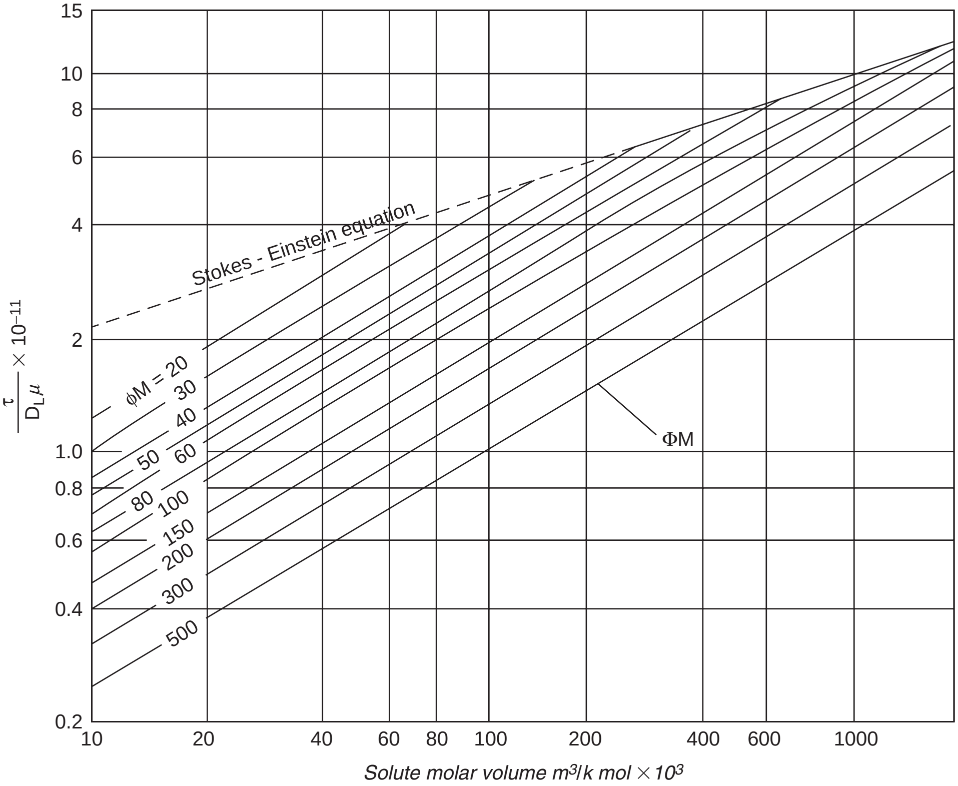


Figure 8.2. The Wilke-Chang correlation.

Atom	Vol.	No. of		
C	0.0148	× 6	=	0.0888
H	0.0037	× 6	=	0.0222
O	0.0074	× 1	=	0.0074
Ring	−0.015	× 1	=	−0.015
		Total	=	0.1034 m^3/k mol

$$D_L = \frac{1.173 \times 10^{-13}(1.5 \times 46)^{0.5} 293}{1.2 \times 0.1034^{0.6}} = \underline{\underline{9.28 \times 10^{-10} \mathrm{m}^2/\mathrm{s}}} \tag{8.22}$$

Experimental value, 8 × 10^{-10} m^2/s, error 16%.

8.13. SURFACE TENSION

It is usually difficult to find experimental values for surface tension for any but the more commonly used liquids. A useful compilation of experimental values is that by

Jasper (1972), which covers over 2000 pure liquids. Othmer *et al*. (1968) give a nomograph covering about 100 compounds.

If reliable values of the liquid and vapor density are available, the surface tension can be estimated from the Sugden parachor, which can be estimated by a group contribution method (Sugden, 1924):

$$\sigma = \left[\frac{P_{ch}(\rho_L - \rho_v)}{M}\right]^4 \times 10^{-12} \tag{8.23}$$

where

σ = surface tension, mJ/m^2 (dyne/cm);
P_{ch} = Sugden's parachor;
ρ_L = liquid density, kg/m^3;
ρ_v = density of the saturated vapor, kg/m^3;
M = molecular mass;
σ, ρ_L, ρ_v evaluated at the system temperature.

The vapor density can be neglected when it is small compared with the liquid density.

The parachor can be calculated using the group contributions given in Table 8.7. The method is illustrated in Example 8.13.

8.13.1. Mixtures

The surface tension of a mixture is rarely a simple function of composition. However, for hydrocarbons a rough value can be calculated by assuming a linear relationship:

$$\sigma_m = \sigma_1 x_1 + \sigma_2 x_2 \ldots \tag{8.24}$$

Table 8.7. Contribution to Sugden's Parachor for Organic Compounds (Sugden, 1924)

Atom, Group or Bond	Contribution	Atom, Group or Bond	Contribution
C	4.8	Si	25.0
H	17.1	Al	38.6
H in (OH)	11.3	Sn	57.9
O	20.0	As	50.1
O_2 in esters, acids	60.0	Double bond: terminal	
N	12.5	2,3-position	23.2
S	48.2	3,4-position	
P	37.7	Triple bond	46.6
F	25.7	Rings	
Cl	54.3	3-membered	16.7
Br	68.0	4-membered	11.6
I	91.0	5-membered	8.5
Se	62.5	6-membered	6.1

where

σ_m = surface tension of mixture;
σ_1, σ_2 = surface tension of components;
x_1, x_2 = component mol fractions.

Example 8.13

Estimate the surface tension of pure methanol at 20°C, density 791.7 kg/m^3, molecular weight 32.04.

Solution

Calculation of parachor, CH_3OH, Table 8.7.

Group	Contribution		No.	
C	4.8	×	1	= 4.8
H—O	11.3	×	1	= 11.3
H—C	17.1	×	3	= 51.3
O	20.0	×	1	= 20.0
			Total	= 87.4

$$\sigma = \left[\frac{87.4 \times 791.7}{32.04}\right]^4 \times 10^{-12} = \underline{\underline{21.8\ \text{mJ/m}^2}} \tag{8.23}$$

Experimental value 22.5 mJ/m^2.

8.14. CRITICAL CONSTANTS

Values of the critical temperature and pressure are needed for prediction methods that correlate physical properties with the reduced conditions. It is also important to know the critical conditions when applying equation of state methods, as some of the equation of state models are unreliable close to the critical point. Experimental values for many substances can be found in various handbooks and in Appendix C. Critical reviews of the literature on critical constants and summaries of selected values have been published by Kudchadker et al. (1968), for organic compounds, and by Mathews (1972), for inorganic compounds. An earlier review was published by Kobe and Lynn (1953).

If reliable experimental values cannot be found, techniques are available for estimating the critical constants with sufficient accuracy for most design purposes. For organic compounds, Lydersen's method is normally used (Lydersen, 1955):

$$T_c = \frac{T_b}{[0.567 + \Sigma\Delta T - (\Sigma\Delta T)^2]} \tag{8.25}$$

$$P_c = \frac{M}{(0.34 + \Sigma\Delta P)^2} \tag{8.26}$$

$$V_c = 0.04 + \Sigma\Delta V \tag{8.27}$$

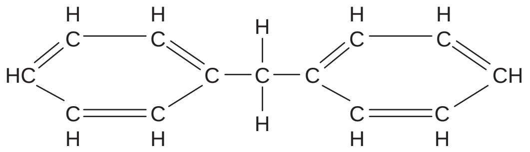
where

T_c = critical temperature, K;
P_c = critical pressure, atm (1.0133 bar);
V_c = molar volume at the critical conditions, m^3/kmol;
T_b = normal boiling point, K;
M = relative molecular mass;
ΔT = critical temperature increments, Table 8.8;
ΔP = critical pressure increments, Table 8.8;
ΔV = molar volume increments, Table 8.8;

Fedons (1982) gives a simple method for the estimation of critical temperature that does not require a knowledge of the boiling point of the compound.

Example 8.14

Estimate the critical constants for diphenylmethane using Lydersen's method; normal boiling point 537.5 K, molecular mass 168.2, structural formula:



Solution

		Total Contribution		
Group	No. of	ΔT	ΔP	ΔV
H—C—(ring)	10	0.11	1.54	0.37
—C—(ring)	2	0.022	0.308	0.072
—CH^2—	1	0.02	0.227	0.055
		Σ 0.152	2.075	0.497

$$T_c = \frac{537.5}{(0.567 + 0.152 - 0.152^2)} = \underline{\underline{772\,\text{k}}}$$

experimental value 767 K,

$$P_c = \frac{168.2}{(0.34 + 2.075)^2} = \underline{\underline{28.8\,\text{atm}}}$$

experimental value 28.2 atm,

$$V_c = 0.04 + 0.497 = \underline{\underline{0.537\,\text{m}^3/\text{kmol}}}$$

Table 8.8. Critical Constant Increments (Lydersen, 1955)

	ΔT	ΔP	ΔV		ΔT	ΔP	ΔV
Non-ring increments							
$-\mathrm{CH}_3$	0.020	0.227	0.055	$=\overset{\vert}{\mathrm{C}}-$	0.0	0.198	0.036
$-\overset{\vert}{\mathrm{C}}\mathrm{H}_2$	0.020	0.227	0.055	$=\mathrm{C}=$	0.0	0.198	0.036
$-\overset{\vert}{\underset{\vert}{\mathrm{C}}}\mathrm{H}$	0.012	0.210	0.051	$\equiv\mathrm{CH}$	0.005	0.153	0.036*
$-\overset{\vert}{\underset{\vert}{\mathrm{C}}}-$	0.00	0.210	0.041	$\equiv\mathrm{C}-$	0.005	0.153	0.036*
$=\mathrm{CH}_2$	0.018	0.198	0.045	H	0	0	0
$=\overset{\vert}{\mathrm{C}}\mathrm{H}$	0.018	0.198	0.045				
Ring increments							
$-\mathrm{CH}_2-$	0.013	0.184	0.0445	$=\overset{\vert}{\mathrm{C}}\mathrm{H}$	0.011	0.154	0.037
$-\overset{\vert}{\underset{\vert}{\mathrm{C}}}\mathrm{H}$	0.012	0.192	0.046	$=\overset{\vert}{\mathrm{C}}-$	0.011	0.154	0.036
$-\overset{\vert}{\underset{\vert}{\mathrm{C}}}-$	−0.007*	0.154*	0.031*	$=\mathrm{C}=$	0.011	0.154	0.036
Halogen increments							
$-\mathrm{F}$	0.018	0.224	0.018	$-\mathrm{Br}$	0.010	0.50*	0.070*
$-\mathrm{Cl}$	0.017	0.320	0.049	$-\mathrm{I}$	0.012	0.83*	0.095*
Oxygen increments							
$-\mathrm{OH}$ (alcohols)	0.082	0.06	0.018*	$-\overset{\vert}{\mathrm{C}}\mathrm{O}$ (ring)	0.033*	0.2*	0.050*
$-\mathrm{OH}$ (phenols)	0.031	−0.02*	0.030*	$\overset{\vert}{\mathrm{H}\mathrm{C}}=\mathrm{O}$ (aldehyde)	0.048	0.33	0.073
$-\mathrm{O}-$ (non-ring)	0.021	0.16	0.020	$-\mathrm{COOH}$ (acid)	0.085	0.4*	0.080
$-\mathrm{O}-$ (ring)	0.014*	0.12*	0.080*	$-\mathrm{COO}-$ (ester)	0.047	0.47	0.080
$-\overset{\vert}{\mathrm{C}}=\mathrm{O}$ (non-ring)	0.040	0.29	0.060	$=\mathrm{O}$ (except for combinations above)	0.02*	0.12*	0.011*
Nitrogen increments							
$-\mathrm{NH}_2$	0.031	0.095	0.028	$-\overset{\vert}{\mathrm{N}}-$ (ring)	0.007*	0.013*	0.032*
$-\overset{\vert}{\mathrm{N}}\mathrm{H}$ (non-ring)	0.031	0.135	0.037*	$-\mathrm{CN}$	0.060*	0.36*	0.080*
$-\overset{\vert}{\mathrm{N}}\mathrm{H}$ (ring)	0.024*	0.09*	0.027*	$-\mathrm{NO}_2$	0.055*	0.42*	0.078*
$-\overset{\vert}{\mathrm{N}}-$ (non-ring)	0.014	0.17	0.042*				

(*continued*)

Table 8.8. Critical Constant Increments (Lydersen, 1955)—Cont'd

	ΔT	ΔP	ΔV		ΔT	ΔP	ΔV
Sulphur increments							
—SH	0.015	0.27	0.055	—S—(ring)	0.008*	0.24*	0.045*
—S—(non-ring)	0.015	0.27	0.055	S	0.003*	0.24*	0.047*
Miscellaneous							
$-\overset{\vert}{\underset{\vert}{\mathrm{Si}}}-$	0.03	0.54*		$-\overset{\vert}{\underset{\vert}{\mathrm{B}}}-$		0.03*	

Dashes represent bonds with atoms other than hydrogen.
Values marked with an asterisk are based on too few experimental points to be reliable.

8.15. ENTHALPY OF REACTION AND ENTHALPY OF FORMATION

Enthalpies of reaction (heats of reaction) for the reactions used in the production of commercial chemicals can usually be found in the literature. Stephenson (1966) gives values for most of the production processes he describes in his book.

Heats of reaction can be calculated from the heats of formation of the reactants and products, as described in Chapter 3, Section 3.10. Values of the standard heats of formation for the more common chemicals are given in various handbooks; see also Appendix C. Care must be taken to correct the heat of reaction to the temperature and pressure of the process. A useful source of data on heats of formation and combustion is the critical review of the literature by Domalski (1972).

Benson has developed a detailed group contribution method for the estimation of heats of formation; see Benson (1976) and Benson et al. (1969). He estimates the accuracy of the method to be from ± 2.0 kJ/mol for simple compounds, to about ± 12 kJ/mol for highly substituted compounds. Benson's method and other group contribution methods for the estimation of heats of formation are described by Reid et al. (1987).

8.16. PHASE EQUILIBRIUM DATA

Phase equilibrium data are needed for the design of all separation processes that depend on differences in concentration between phases.

8.16.1. Experimental Data

Experimental data have been published for several thousand binary and many multicomponent systems. Virtually all the published experimental data has been collected together in the volumes comprising the DECHEMA vapor-liquid and liquid-liquid data collection (DECHEMA, 1977). The books by Chu et al. (1956), Hala et al. (1968, 1973), Hirata et al. (1975), and Ohe (1989, 1990) are also useful sources.

8.16.2. Phase Equilibrium

The criterion for thermodynamic equilibrium between two phases of a multicomponent mixture is that for every component, i

$$f_i^v = f_i^L \tag{8.28}$$

where f_i^v is the vapor-phase fugacity and f_i^L is the liquid-phase fugacity of component i:

$$f_i^v = P\phi_i y_i \tag{8.29}$$

and

$$f_i^L = f_i^{OL}\gamma_i x_i \tag{8.30}$$

where

P = total system pressure;
ϕ_i = vapor fugacity coefficient;
y_i = concentration of component i in the vapor phase;
f_i^{OL} = standard state fugacity of the pure liquid;
γ_i = liquid-phase activity coefficient;
x_i = concentration of component i in the liquid phase;

Substituting from equations 8.29 and 8.30 into equation 8.28 and rearranging gives

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i f_i^{OL}}{P\phi_i} \tag{8.31}$$

where

K_i is the distribution coefficient (the K value);
ϕ_i can be calculated from an appropriate equation of state (see Section 8.16.3);
f_i^{OL} can be computed from the following expression:

$$f_i^{OL} = P_i^o \phi_i^s \left\{ \exp\left\{ \frac{(P - P_i^o)}{RT} v_i^L \right\} \right\} \tag{8.32}$$

where

P_i^o = the pure component vapor pressure (which can be calculated from the Antoine equation; see Section 8.11), N/m^2;
ϕ_i^s = the fugacity coefficient of the pure component i at saturation;
v_i^L = the liquid molar volume, m^3/mol.

The exponential term in equation 8.32 is known as the *Poynting correction* and corrects for the effects of pressure on the liquid-phase fugacity.

ϕ_i^s is calculated using the same equation of state used to calculate ϕ_i.

For systems in which the vapor phase imperfections are not significant, equation 8.32 reduces to the familiar Raoult's law equation:

$$K_i = \frac{\gamma_i P_i^o}{P} \tag{8.33}$$

Relative Volatility

The relative volatility of two components can be expressed as the ratio of their K values:

$$\alpha_{ij} = \frac{K_i}{K_j} \tag{8.34}$$

For ideal mixtures (obeying Raoult's law):

$$K_i = \frac{P_i^o}{P} \tag{8.35}$$

and

$$\alpha_{ij} = \frac{K_i^o}{K_j^o} = \frac{P_i^o}{P_j^o} \tag{8.36}$$

where K_i^o and K_j^o are the ideal K values for components i and j.

8.16.3. Equations of State

An equation of state is an algebraic expression that relates temperature, pressure, and molar volume for a real fluid.

Many equations of state of varying complexity have been developed. No one equation is sufficiently accurate to represent all real gases under all conditions. The equations of state most frequently used in the design of multicomponent separation processes are given in this section. The actual equation is given for only one of the correlations, the Redlich-Kwong equation, as an illustration. Equations of state are normally solved using computer-aided design packages; see Chapter 11. For details of the other equations, consult the reference cited or the books by Reid et al. (1987), Prausnitz et al. (1998), and Walas (1985). To select the best equation to use for a particular process design, refer to Table 8.10 and Figure 8.4.

Redlich-Kwong Equation (R-K)

The Redlich-Kwong equation is an extension of the more familiar Van der Waal's equation. The Redlich-Kwong equation is

$$P = \frac{PT}{V-b} \times \frac{a}{T^{1/2}V(V+b)} \tag{8.37}$$

where

$a = 0.427\ \mathrm{R}^2 T_c^{2.5}/P_c$;
$b = 0.08664\ \mathrm{R}T_c/P_c$;

P = pressure;
V = volume.

The R-K equation is not suitable for use near the critical pressure ($P_r > 0.8$), or for liquids (Redlich and Kwong, 1949).

Redlich-Kwong-Soave Equation (R-K-S)

Soave (1972) modified the R-K equation to extend its usefulness to the critical region and for use with liquids.

Benedict-Webb-Rubin (B-W-R) Equation

The Benedict-Webb-Rubin equation has eight empirical constants and gives accurate predictions for vapor and liquid-phase hydrocarbons. It can also be used for mixtures of light hydrocarbons with carbon dioxide and water (Benedict et al., 1951).

Lee-Kesler-Plocker (L-K-P) Equation

Lee and Kesler (1975) extended the B-W-R equation to a wider variety of substances, using the principle of corresponding states. The method was modified further by Plocker et al. (1978).

Chao-Seader Equation (C-S)

The Chao-Seader equation gives accurate predictions for light hydrocarbons and hydrogen but is limited to temperatures below 530 K; see Chao and Seader (1961).

Grayson-Streed Equation (G-S)

Grayson and Streed (1963) extended the C-S equation for use with hydrogen-rich mixtures and for high-pressure and high-temperature systems. It can be used up to 200 bar and 4700 K.

Peng-Robinson Equation (P-R)

The Peng-Robinson equation is related to the R-K-S equation of state and was developed to overcome the instability in the R-K-S equation near the critical point; see Peng and Robinson (1976).

Brown K_{10} Equation (B-K_{10})

Brown (see Cajander et al., 1960), developed a method which relates the equilibrium constant K to four parameters: component, pressure, temperature, and the convergence pressure. The convergence pressure is the pressure at which all K values tend to 1. The B-K_{10} equation is limited to low pressure, and its use is generally restricted to vacuum systems.

8.16.4. Correlations for Liquid-Phase Activity Coefficients

The liquid-phase activity coefficient, γ_i, is a function of pressure, temperature, and liquid composition. At conditions remote from the critical conditions, it is virtually independent of pressure and, in the range of temperature normally encountered in distillation, can be taken as independent of temperature.

Several equations have been developed to represent the dependence of activity coefficients on liquid composition. Only those of most use in the design of separation processes will be given. For a detailed discussion of the equations for activity coefficients and their relative merits, refer to the books by Reid et al. (1987), Prausnitz et al. (1998), Walas (1985), and Null (1970).

Wilson Equation

The equation developed by Wilson (1964) is convenient to use in process design:

$$ln\gamma_k = 1.0 - ln\left[\sum_{j=1}^{n}(x_j A_{kj})\right] - \sum_{i=1}^{n}\left[\frac{x_i A_{ik}}{\sum_{j=1}^{n}(x_j A_{ij})}\right] \tag{8.38}$$

where

γ_k = activity coefficient for component k;
A_{ij}, A_{ji} = Wilson coefficients (A values) for the binary pair i, j;
n = number of components.

The Wilson equation is superior to the familiar Van-Laar and Margules equations for systems that are severely nonideal, but, like the other three suffix equations, it cannot be used to represent systems that form two liquid phases in the concentration range of interest.

A significant advantage of the Wilson equation is that it can be used to calculate the equilibrium compositions for multicomponent systems using only the Wilson coefficients obtained for the binary pairs that comprise the multicomponent mixture. The Wilson coefficients for several hundred binary systems are given in the DECHEMA vapor-liquid data collection (DECHEMA, 1977) and by Hirata (1975). Hirata gives methods for calculating the Wilson coefficients from vapor-liquid equilibrium experimental data.

Nonrandom Two Liquid (NRTL) Equation

The NRTL equation developed by Renon and Prausnitz overcomes the disadvantage of the Wilson equation in that it is applicable to immiscible systems. It can be used to predict phase compositions for vapor-liquid and liquid-liquid systems.

Universal Quasi-Chemical (UNIQUAC) Equation

The UNIQUAC equation developed by Abrams and Prausnitz is usually preferred to the NRTL equation in the computer-aided design of separation processes. It is suitable for miscible and immiscible systems, and so can be used for vapor-liquid and liquid-liquid systems. As with the Wilson and NRTL equations, the equilibrium compositions for a multicomponent mixture can be predicted from experimental data for the binary pairs that comprise the mixture. Also, in the absence of experimental data for the binary pairs, the coefficients for use in the UNIQUAC equation can be predicted by a group contribution method: UNIFAC, described in the next section.

The UNIQUAC equation is not given here, as its algebraic complexity precludes its use in manual calculations. It would normally be used as a subroutine in a design or process simulation program. For details of the equation, consult the texts by Reid et al. (1987), Prausnitz et al. (1998), or Walas (1985).

The best source of data for the UNIQUAC constants for binary pairs is the DECHEMA vapor-liquid and liquid-liquid data collection (DECHEMA, 1977).

8.16.5. Prediction of Vapor-Liquid Equilibrium

The designer will often be confronted with the problem of how to proceed with the design of a separation process without adequate experimentally determined equilibrium data. Some techniques are available for the prediction of vapor-liquid equilibrium (VLE) data and for the extrapolation of experimental values. Caution must be used in the application of these techniques in design, and the predictions should be supported with experimentally determined values whenever practicable. The same confidence cannot be placed on the prediction of equilibrium data as that for many of the prediction techniques for other physical properties given in this chapter. Some of the techniques most useful in design are given in the following paragraphs.

Estimation of Activity Coefficients from Azeotropic Data

If a binary system forms an azeotrope, the activity coefficients can be calculated from knowledge of the composition of the azeotrope and the azeotropic temperature. At the azeotropic point the composition of the liquid and vapor are the same, so from equation 8.31

$$\gamma_i = \frac{P}{P_i^{o}}$$

where P_i^{o} is determined at the azeotropic temperature.

The values of the activity coefficients determined at the azeotropic composition can be used to calculate the coefficients in the Wilson equation (or any other of the three suffix equations), and the equation can then be used to estimate the activity coefficients at other compositions.

Horsley (1973) and Gmehling (1994) give extensive collections of data on azeotropes.

Activity Coefficients at Infinite Dilution

The constants in any of the activity coefficient equations can be readily calculated from experimental values of the activity coefficients at infinite dilution. For the Wilson equation

$$\ln \gamma_1^{\infty} = -\ln \mathrm{A}_{12} - \mathrm{A}_{21} + 1 \qquad (8.39a)$$

$$\ln \gamma_2^{\infty} = -\ln \mathrm{A}_{21} - \mathrm{A}_{12} + 1 \qquad (8.39b)$$

where

γ_1^∞, γ_2^∞ = the activity coefficients at infinite dilution for components 1 and 2, respectively;

A_{12} = the Wilson A-value for component 1 in component 2;

A_{21} = the Wilson A-value for component 2 in component 1.

Relatively simple experimental techniques, using ebulliometry and chromatography, are available for the determination of the activity coefficients at infinite dilution. The methods used are described by Null (1970) and Conder and Young (1979).

Pieratti et al. (1955) have developed correlations for the prediction of the activity coefficients at infinite dilution for systems containing water, hydrocarbons, and some other organic compounds. Their method and the data needed for predictions are described by Treybal (1963) and Reid et al. (1987).

Calculation of Activity Coefficients from Mutual Solubility Data

For systems that are only partially miscible in the liquid state, the activity coefficient in the homogeneous region can be calculated from experimental values of the mutual solubility limits. The methods used are described by Reid et al. (1987), Treybal (1963), Brian (1965), and Null (1970). Treybal (1963) has shown that the Van-Laar equation should be used for predicting activity coefficients from mutual solubility limits.

Group Contribution Methods

Group contribution methods have been developed for the prediction of liquid-phase activity coefficients. The objective has been to enable the prediction of phase equilibrium data for the tens of thousands of possible mixtures of interest to the process designer to be made from the contributions of the relatively few functional groups that made up the compounds. The UNIFAC method (Fredenslund et al., 1977a) is probably the most useful for process design. Its use is described in detail in a book by Fredenslund et al. (1977b). A method was also developed to predict the parameters required for the NRTL equation: the ASOG method (Kojima and Tochigi, 1979). More extensive work has been done to develop the UNIFAC method, to include a wider range of functional groups; see Gmehling et al. (1982) and Magnussen et al. (1981).

The UNIFAC equation is the preferred equation for use in design, and it is included in all the commercial simulation and design programs.

Care must be exercised in applying the UNIFAC method. The specific limitations of the method are

1. Pressure not greater than a few bar (say, limit to 5 bar);
2. Temperature below 150°C;
3. No noncondensable components or electrolytes;
4. Components must not contain more than 10 functional groups.

8.16.6. *K*-values for Hydrocarbons

A useful source of *K*-values for light hydrocarbons is the well-known "De Priester charts" (Dabyburjor, 1978), which are reproduced as Figures 8.3a and b. These charts give the *K*-values over a wide range of temperature and pressure.

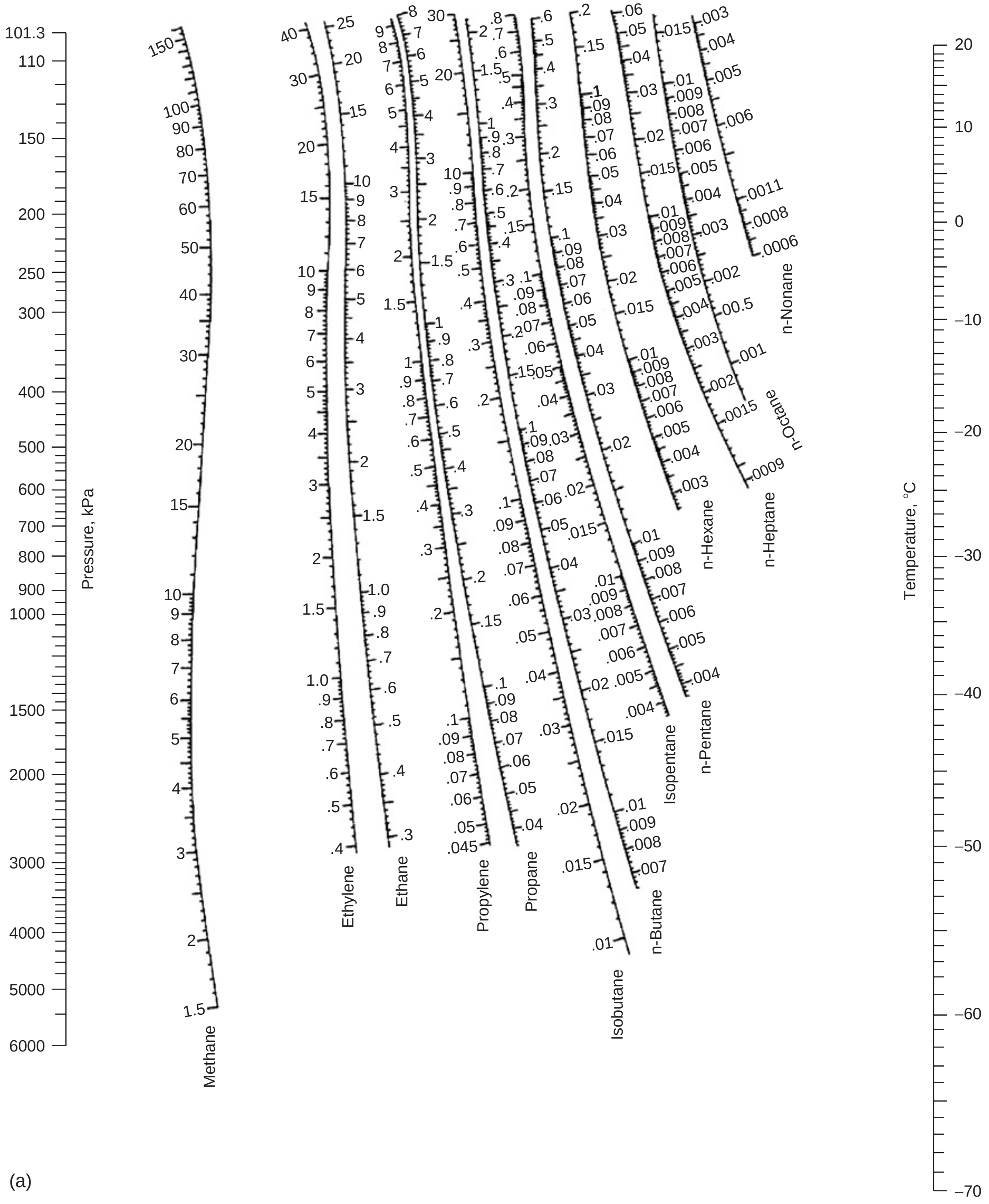
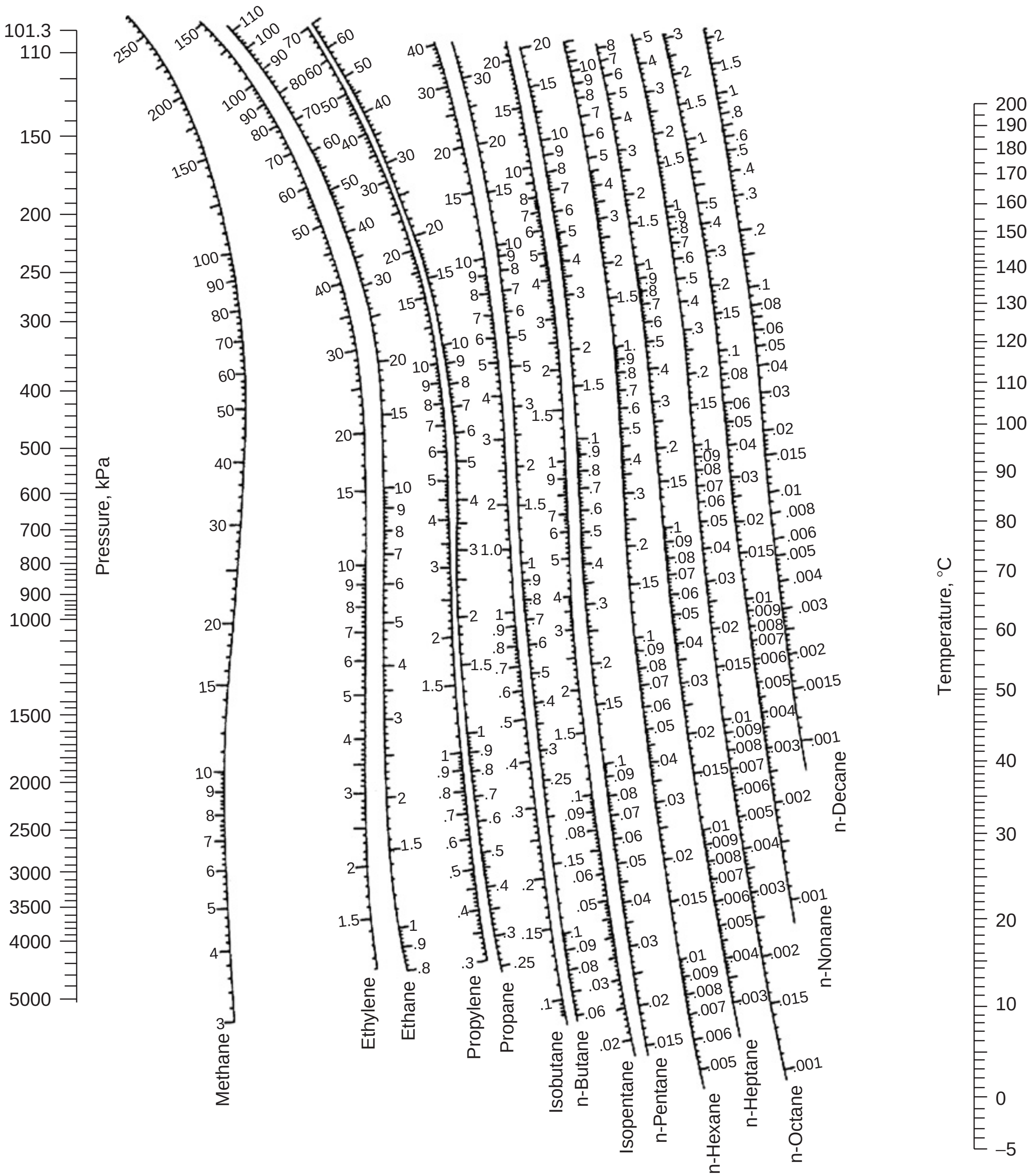


Figure 8.3. (a) De Priester chart—*K*-values for hydrocarbons, low temperature.

(*continued*)



(b)

Figure 8.3. Cont'd. (b) De Priester chart—*K*-values for hydrocarbons, high temperature.

8.16.7. Sour-Water Systems

The term *sour water* is used for water containing carbon dioxide, hydrogen sulfide, and ammonia encountered in refinery operations.

Special correlations have been developed to handle the vapor-liquid equilibrium of such systems, and these are incorporated in most design and simulation programs.

Newman (1991) gives the equilibrium data required for the design of sour water systems in chart form.

8.16.8. Vapor-Liquid Equilibrium at High Pressures

At pressures above a few atmospheres, the deviations from ideal behavior in the gas phase will be significant and must be taken into account in process design. The effect of pressure on the liquid-phase activity coefficient must also be considered. A discussion of the methods used to correlate and estimate vapor-liquid equilibrium data at high pressures is beyond the scope of this book. Refer to the texts by Null (1970), Prausnitz et al. (1998), or Prausnitz and Chueh (1968).

Prausnitz and Chueh also discuss phase equilibrium in systems containing components above their critical temperature (super-critical components).

8.16.9. Liquid-Liquid Equilibrium

Experimental data, or predictions that give the distribution of components between the two solvent phases, are needed for the design of liquid-liquid extraction processes, and mutual solubility limits are needed for the design of decanters and other liquid-liquid separators.

Perry et al. (1997) give a useful summary of solubility data. Liquid-liquid equilibrium (LLE) compositions can be predicted from vapor-liquid equilibrium data, but the predictions are seldom accurate enough for use in the design of liquid-liquid extraction processes.

Null (1970) gives a computer program for the calculation of ternary diagrams from VLE data, using the Van-Laar equation.

The DECHEMA data collection includes liquid-liquid equilibrium data for several hundred mixtures (DECHEMA, 1977).

The UNIQUAC equation can be used to estimate activity coefficients and liquid compositions for multicomponent liquid-liquid systems. The UNIFAC method can be used to estimate UNIQUAC parameters when experimental data are not available; see Section 8.16.5.

It must be emphasized that extreme caution should be exercised when using predicted values for liquid-liquid activity coefficients in design calculations.

8.16.10. Choice of Phase Equilibrium Model for Design Calculations

The choice of the best method for deducing vapor-liquid and liquid-liquid equilibria for a given system will depend on three factors:

1. The composition of the mixture (the class of system);
2. The operating pressure (low, medium, or high);
3. The experimental data available.

Classes of Mixtures

For the purpose of deciding which phase equilibrium method to use, it is convenient to classify components into the classes shown in Table 8.9.

Using the classification given in Table 8.9, we can use Table 8.10 to select the appropriate vapor-liquid or liquid-liquid phase equilibrium method.

Flowchart for Selection of Phase Equilibrium Method

The flowchart shown in Figure 8.4 has been adapted from a similar chart published by Wilcon and White (1986). The abbreviations used in the chart for the equations of state correspond to those given in Section 8.16.3.

8.16.11. Gas Solubility

At low pressures, most gases are only sparingly soluble in liquids, and at dilute concentrations the systems obey Henry's law. Markham and Kobe (1941) and Battino and Clever (1966) give comprehensive reviews of the literature on gas solubility.

Table 8.9. Classification of Mixtures

Class	Principal Interactions	Examples
I. Simple molecules	Dispersion forces	H_2, N_2, CH_4
II. Complex nonpolar molecules	Dispersion forces	CCl_4, iC_5H_{10}
III. Polarizable	Induction dipole	CO_2, C_6H_6
IV. Polar molecules	Dipole moment	dimethyl formamide, chloroethane
V. Hydrogen bonding	Hydrogen bonds	alcohols, water

Table 8.10. Selection of Phase Equilibrium Method

	Low <3 bar		Pressure Moderate <15 bar		High >15 bar	
Class of Mixture	f^L	f^V	f^L	f^V	f^L	f^V
I, II, III (none supercritical)	ES	I	ES	ES	ES	ES and K
I, II, III (supercritical)	ES	I	ES	ES	ES	ES and K
I, II, III, IV, V (vapor-liquid)	ACT	I	ACT	ES	ES	ES and K
I, II, III, IV, V (liquid-liquid)	ACT	I	ACT	ES	ES	ES
Hydrocarbons and water	ES	ES and K	ES	ES and K	ES	ES and K

I = ideal, vapor fugacity D partial pressure.
ES = appropriate equation of state.
K = equilibrium constant (K factor) derived from experimental data.
ACT = correlation for liquid-phase activity coefficient, such as Wilson, NRTL, UNIQUAC, UNIFAC. (See Section 8.16.4.) Use UNIQUAC and UNIFAC v-l-e parameters for vapor-liquid systems and l-l-e parameters for liquid-liquid systems.

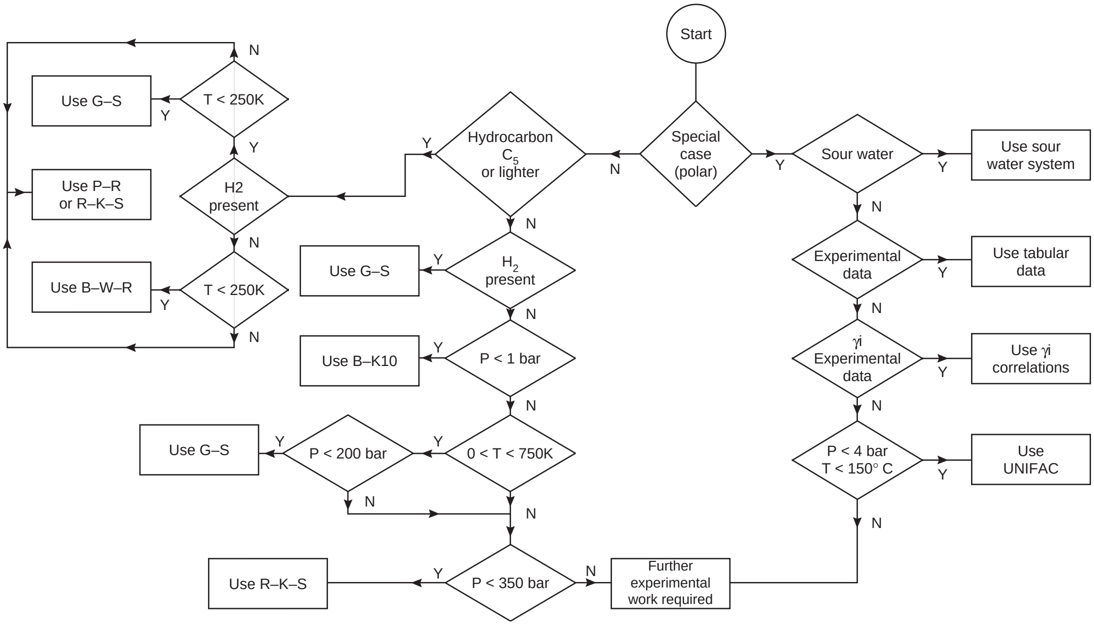


Figure 8.4. Flowchart for the selection of phase equilibrium method.

8.16.12. Use of Equations of State to Estimate Specific Enthalpy and Density

Computer-aided packages for the design and simulation of separation processes will contain subroutines for the estimation of excess enthalpy and liquid and vapor density from the appropriate equation of state.

Specific Enthalpy

For the vapor phase, the deviation of the specific enthalpy from the ideal state can be illustrated using the Redlich-Kwong equation, written in the form

$$z^3 + z^2 + z(B^2 + B - A) = 0$$

where

$z =$ the compressibility factor

$$A = \frac{a \times P}{R^2 \times T^{2.5}}$$

$$B = \frac{b \times P}{R \times T}$$

The fugacity coefficient is given by

$$\ln\ \phi = z - 1 - \ln(z - b) - \left(\frac{A}{B}\right)\ln\left(1 - \frac{B}{z}\right)$$

$$\text{and the excess enthalpy } (H - H^\circ) = RT + \int_0^v \left[T\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_v - P \right] \mathrm{d}v$$

where H is enthalpy at the system temperature and pressure and H° is enthalpy at the ideal state.

Unless liquid-phase activity coefficients have been used, it is best to use the same equation of state for excess enthalpy that was selected for the vapor-liquid equilibrium. If liquid-phase activity coefficients have been specified, then a correlation appropriate for the activity coefficient method should be used.

Density

For vapors, use the equation of state selected for predicting the vapor-liquid equilibrium. For liquids, use the same equation if it is suitable for estimating liquid density.

8.17. REFERENCES

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8.18. NOMENCLATURE

		Dimensions in **MLT$\boldsymbol{\theta}$**
A	Coefficient in the Antoine equation	—
$A_{1,2}$	Coefficients in the Wilson equation for the binary pair 1, 2	—
a	Coefficient in the Redlich-Kwong equation of state	—
B	Coefficient in the Antoine equation	θ
B_i	Second viral coefficient for component i	$\mathbf{M}^{-1}\mathbf{L}^{3}$
b	Coefficient in the Redlich-Kwong equation of state	—
C	Coefficient in the Antoine equation	θ
C_p	Specific heat capacity at constant pressure	$\mathbf{L}^{2}\mathbf{T}^{-2}\theta^{-1}$
D_L	Liquid diffusivity	$\mathbf{L}^{2}\mathbf{T}^{-1}$
D_v	Gas diffusivity	$\mathbf{L}^{2}\mathbf{T}^{-1}$
f_i	Fugacity coefficient for component i	—
f_i^{OL}	Standard state fugacity coefficient of pure liquid	—
H	Specific enthalpy	$\mathbf{L}^{2}\mathbf{T}^{-2}$
H^0	Excess specific enthalpy	$\mathbf{L}^{2}\mathbf{T}^{-2}$
I	Souders' index (equation 8.9)	$\mathbf{M}^{-1}\mathbf{L}^{3}$
K	Equilibrium constant (ratio)	—
K^0	Equilibrium constant for an ideal mixture	—
k	Thermal conductivity	$\mathbf{MLT}^{-3}\theta^{-1}$
km	Thermal conductivity of a mixture	$\mathbf{MLT}^{-3}\theta^{-1}$
L_v	Latent heat of vaporization	$\mathbf{L}^{2}\mathbf{T}^{-2}$
$L_{v,b}$	Latent heat at normal boiling point	$\mathbf{L}^{2}\mathbf{T}^{-2}$
M	Molecular mass (weight)	$\mathbf{M}$
n	Number of components	—
P	Pressure	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$ or $\mathbf{L}$
P_c	Critical pressure	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$
P_{ch}	Sugden's parachor (equation 8.23)	—
P_i^0	Vapor pressure of component i	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$ or $\mathbf{L}$
P_k	Vapor pressure of component k	$\mathbf{ML}^{-1}\mathbf{T}^{-2}$ or $\mathbf{L}$
P_r	Reduced pressure	—
ΔP_c	Critical constant increment in Lydersen equation (equation 8.26)	$\mathbf{M}^{-1/2}\mathbf{L}^{1/2}\mathbf{T}$

		Dimensions in **MLT$\boldsymbol{\theta}$**
R	Universal gas constant	$\mathbf{L}^2\mathbf{T}^{-2}\mathrm{q}^{-1}$
T	Temperature, absolute scale	θ
T_b	Normal boiling point, absolute scale	θ
T_c	Critical temperature	θ
T_r	Reduced temperature	θ
ΔT_c	Critical constant increment in Lydersen equation (equation 8.25)	—
t	Temperature, relative scale	θ
V_c	Critical volume	$\mathbf{M}^{-1}\mathbf{L}^3$
V_m	Molar volume at normal boiling point	$\mathbf{M}^{-1}\mathbf{L}^3$
ΔV_c	Critical constant increment in Lydersen equation (equation 8.27)	$\mathbf{M}^{-1}\mathbf{L}^3$
v_i	Special diffusion volume coefficient for component *i* (Table 8.5)	$\mathbf{L}^3$
v_i^0	Liquid molar volume	$\mathbf{M}^{-1}\mathbf{L}^3$
w	Mass fraction (weight fraction)	—
x	Mol fraction, liquid phase	—
y	Mol fraction, vapor phase	—
z	Compressibility factor	—
α	Relative volatility	—
β	Coefficient of thermal expansion	θ^{-1}
γ	Liquid activity coefficient	—
γ^∞	Activity coefficient at infinite dilution	—
μ	Dynamic viscosity	$\mathbf{ML}^{-1}\mathbf{T}^{-1}$
μ_b	Viscosity at boiling point	$\mathbf{ML}^{-1}\mathbf{T}^{-1}$
μ_m	Viscosity of a mixture	$\mathbf{ML}^{-1}\mathbf{T}^{-1}$
ρ	Density	$\mathbf{ML}^{-3}$
ρ_L	Liquid density	$\mathbf{ML}^{-3}$
ρ_v	Vapor (gas) density	$\mathbf{ML}^{-3}$
ρ_b	Density at normal boiling point	$\mathbf{ML}^{-3}$
σ	Surface tension	$\mathbf{MT}^{-2}$
σ_m	Surface tension of a mixture	$\mathbf{MT}^{-2}$
ϕ	Fugacity coefficient	—
ϕ^s	Fugacity coefficient of pure component	—
ϕ^L	Fugacity coefficient of pure liquid	—
ϕ^V	Fugacity coefficient of pure vapor	—
Suffixes		
a, b i, j, k $1, 2$	Components	
L	Liquid	—
V	Vapor	—

8.19. PROBLEMS

8.1. Estimate the liquid density at their boiling points for the following:

1. 2-butanol;
2. Methyl chloride;
3. Methyl ethyl ketone;
4. Aniline;
5. Nitrobenzene.

8.2. Estimate the density of the following gases at the conditions given:

1. Hydrogen at 20 bara and 230°C;
2. Ammonia at 1 bara and 50°C and at 100 bara and 300°C;
3. Nitrobenzene at 20 bara and 230°C;
4. Water at 100 bara and 500°C. Check your answer using steam tables;
5. Benzene at 2 barg and 250°C;
6. Synthesis gas ($N_2 + 3H_2$) at 5 barg and 25°C.

8.3. Make a rough estimate of the viscosity of 2-butanol and aniline at their boiling points, using the modified Arrhenius equation. Compare your values with those given using the equation for viscosity in Appendix C.

8.4. Make a rough estimate of the thermal conductivity of n-butane both as a liquid at 20°C and as a gas at 5 bara and 200°C. Take the viscosity of the gaseous n-butane as $0.012\,\text{mN m}^{-2}\text{s}$.

8.5. Estimate the specific heat capacity of liquid 1,4 pentadiene and aniline at 20°C.

8.6. For the following compounds, estimate the constants in the equation for ideal gas heat capacity, equation 3.19, using the method given in Section 8.9.2.

1. 3-methyl thiophene;
2. Nitrobenzene;
3. 2-methyl-2-butanethiol;
4. Methyl-t-butyl ether.

8.7. Estimate the heat of vaporization of methyl-t-butyl ether, at 100°C.

8.8. Estimate the gaseous phase diffusion coefficient for the following systems, at 1 atmosphere and the temperatures given:

1. Carbon dioxide in air at 20°C;
2. Ethane in hydrogen at 0°C;
3. Oxygen in hydrogen at 0°C;
4. Water vapor in air at 450°C;
5. Phosgene in air at 0°C.

8.9. Estimate the liquid-phase diffusion coefficient for the following systems at 25°C:

1. Toluene in n-heptane;
2. Nitrobenzene in carbon tetrachloride;
3. Chloroform in benzene;
4. Hydrogen chloride in water;
5. Sulfur dioxide in water.

8.10. Estimate the surface tension of pure acetone and ethanol at 20°C, and benzene at 16°C, all at 1 atmosphere pressure.

8.11. Using Lydersen's method, estimate the critical constants for isobutanol. Compare your values with those given in Appendix C.

8.12. The composition of the feed to a debutanizer is as follows. The column will operate at 14 bar and below 750 K. The process is to be modeled using a commercial simulation program. Suggest a suitable phase equilibrium method to use in the simulation.

Feed composition:

		kg/h
propane	C_3	910
isobutane	i-C_4	180
n-butane	n-C_4	270
isopentane	i-C_5	70
normal pentane	n-C_5	90
normal hexane	n-C_6	20

8.13. In the manufacture of methyl ethyl ketone from butanol, the product is separated from unreacted butanol by distillation. The feed to the column consists of a mixture of methyl ethyl ketone, 2-butanol, and trichloroethane. What would be a suitable phase equilibrium correlation to use in modeling this process?