

Nuffield Advanced Chemistry

CHEMICAL ENGINEERING

A Special Study

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This students' book consists of the text of the Special Study
but not the experiments, which will be given on separate sheets.

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The content of the comment and case study boxes in the students' text does *not* have to be learnt.

Re:act provides study guides for each chapter, web-links, answers to frequently asked questions, and revision questions.

1.1 What is chemical engineering?

In our modern industrial society there is an enormous demand for substances which do not occur naturally, but have to be made from raw materials found in the earth, sea, and air. Such substances include petrol, paint, plastics, fertilizers, steel, glass, paper, cement, and pharmaceuticals, and are produced by a wide variety of different manufacturing processes. The technology underlying such processes is known as **chemical engineering**. This is the applied science concerned with changes in the composition or physical state of materials in bulk, and is both an academic discipline and a vitally important profession.

Chemical engineers at work

The chemist demonstrates the feasibility of a chemical reaction in the laboratory and specifies the conditions under which it will take place. The chemical engineer designs and supervises the construction and operation of the large-scale plant required to convert a laboratory synthesis into an industrial process producing hundreds or even thousands of tonnes of material a year. This calls for a thorough understanding of the chemistry of the process. Other skills are required too. The chemical engineer must understand the physics and mathematics underlying the problems of heat and mass flow which arise when large quantities of material have to be heated or moved about. He or she must also know the properties of the materials used to build the plant itself, such as how they will stand up to high pressures and temperatures, and how they will withstand corrosion and wear.

Chemical engineers are employed in a wide variety of process industries from brewing and baking to petrochemicals and plastics. Within these industries, the type of activity with which they are involved may vary considerably.

Some chemical engineers may spend much of their working lives in the field of research and development (R&D), either in the large research laboratories operated by industrial companies or in universities. Their job is to investigate and develop new processes and products, and to try to modify existing processes to make them more efficient. Others are engaged in plant design and construction, perhaps working for a contracting firm which specializes in the design and construction of plant for chemical manufacturers. Once a plant is built and successfully in operation, chemical engineers are responsible for keeping it running at maximum efficiency, while maintaining product quality specifications, and for making arrangements for maintenance and modifications to be carried out as necessary.

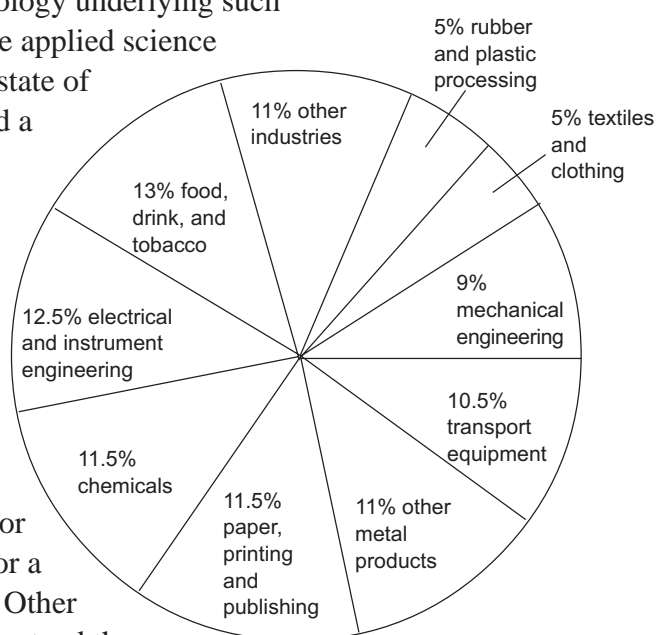


Figure 1.1 The chemical industry is one of the UK's largest and most successful industries. (from *The essential chemical industry*)

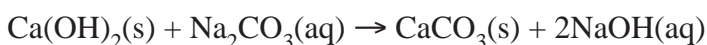
Wherever they work, chemical engineers are usually members of a team. They are often required to co-ordinate the activities of members of other specialist disciplines involved in the construction and maintenance of chemical plant. These include chemists, mechanical engineers, civil engineers, control engineers, electrical engineers, plant operators, and so on. To get the best from such a team requires considerable management skill, and such experience often leads eventually to senior positions in industry.

Chemical engineering is a career for people who can accept challenge and responsibility extending far beyond the confines of the laboratory. It is founded upon a thorough knowledge and understanding of the fundamental sciences of chemistry, physics, and mathematics.

1.2 Working on the large scale

Imagine that you have been asked to prepare a 1-gram sample of sodium hydroxide in the laboratory, starting from other chemicals of your choice. You might begin by thinking of all the chemical reactions you have met which produce sodium hydroxide and choosing the one which seems most convenient. Try to list some of the possible reactions, and note the advantages and disadvantages of each.

A student's plan for a preparation might read as follows. 'Sodium hydroxide can be made in the laboratory by pouring some sodium carbonate solution into a test-tube and adding some solid calcium hydroxide. The test-tube is shaken to mix the reactants and heated over a Bunsen burner.



A precipitate of calcium carbonate is formed which is filtered off to leave a clear solution of sodium hydroxide. Solid sodium hydroxide may be obtained from this solution by careful evaporation to dryness.'

This sounds quite reasonable for a 1-gram laboratory preparation, but the world demand for sodium hydroxide is about 30 million tonnes per year.

Now imagine that you are a chemical engineer and have been asked to report on a possible process to produce just a small proportion of this total world demand, say 10 000 tonnes per year. You will note that 10 000 tonnes is 10^{10} grams or if you like, ten thousand million times as much as your 1-gram laboratory sample.

In order to appreciate the extra problems which this enormous scale of operations presents to a chemical engineer, let's break down the simple laboratory preparation into stages.



Figure 1.2 The main chemical industry manufacturing sites in Great Britain (Chemical Industries Association)

Storage

In the laboratory report, it is simply assumed that the sodium carbonate solution and calcium hydroxide are first collected from their storage places, usually bottles on shelves. Such details cannot be left unmentioned when hundreds of tonnes of materials are needed every day.

It is important to make planned decisions about the amounts of the raw materials to be stored. The following factors must be considered.

- The cost of the storage tanks, especially if the materials are corrosive, highly flammable, or toxic.
- The value of the land required for storage.
- The value of the materials stored and the working capital tied up with them.
- Economies of scale when buying in bulk.
- The desirability of using of fresh raw materials, which then require less storage.
- Materials requiring special storage conditions, such as refrigeration, or storage out of contact with the air.
- Additional safety concerns where materials are stored in bulk.
- The cost to the company should stocks run out and production be brought to a halt (if this occurs, materials may have to be bought expensively from a competitor in order to honour marketing contracts).

Transport of materials

The next stage in the laboratory preparation is to carry the sodium carbonate solution across the laboratory and pour some of it into a test-tube. Energy must be supplied to do this, and on an industrial scale this may well involve using an electrically driven pump to move the liquid from the storage tank to the reactor vessel through a series of pipes.

In an industrial plant, materials have to be moved between different stages: reactor vessels, distillation columns, and so on. This is particularly important in **continuous processes** where there must be a steady flow of raw materials into the plant and finished products out of the plant. This continual flow of materials is called the **process stream**. Because fluids (of which gases are a special case) are easier to meter and to control than solids, most continuous processes involve material in the liquid or gaseous state. A detailed knowledge of fluid flow is therefore essential in designing an industrial plant, and this important topic is considered in Chapter 3.

Mixing

In the laboratory we often mix reactants together by shaking them up in a test-tube, another process which requires the supply of energy. It is clearly not practical to have large reaction vessels bouncing up and down in a chemical plant.

The energy required for mixing must be supplied in other ways. Reactants may be mechanically stirred using large rotary agitators driven by electric motors, rather like scaled-up laboratory stirrers. Another common method of mixing makes use

of a phenomenon of fluid flow – **turbulence** – which is particularly relevant to continuous processes. The conditions under which turbulence occurs are discussed in Chapter 3. This is important because in a large-scale process the rate of mixing may control the rate of reaction to a greater extent than changes in concentration.

Transfer of heat

In our laboratory process, heat energy is supplied in a very inefficient manner by holding the test-tube containing the reactants in a Bunsen flame. An industrial process may involve thousands of times as much heat energy, since large amounts of materials are heated up or cooled down during the various stages of manufacture. Heat energy is expensive and so energy transfer must be carried out as efficiently as possible.

One of the first stages in designing a chemical plant is to draw up an **energy balance** showing clearly how much energy must be given to and taken from each process stage. This, with an estimate of the materials involved (the **mass balance**), allows the first rough calculations of the cost of running the plant to be made.

The ways in which heat may be supplied to the process include: the combustion of a fuel, the use of an electric current, superheated steam, and energy from a chemical reaction.

Heat may be transferred to the process stream by **direct transfer**. This happens when a fuel is burned in direct contact with the material to be heated, as in a blast furnace or cement kiln.

Alternatively, **indirect transfer** may occur when there is a physical barrier between the source of heat and the material to be heated, for example in steam boilers and heat exchangers. Such indirect transfer is normally more significant, and heat exchangers are considered further in Chapter 4.

Separation

Going back to our laboratory preparation: after heating, the precipitate of calcium carbonate is filtered off using a filter paper and funnel, leaving a solution of sodium hydroxide. On the industrial scale, this corresponds to the end of the **synthesis stage** of the process and the beginning of the **separation stage**.

Most separation techniques used in the laboratory, such as filtration, centrifuging, distillation, and solvent extraction, have their industrial equivalents. In addition, chemical engineers have developed other separation techniques which are not suitable for laboratory use.

However, all separation techniques, whether on a laboratory or industrial scale, have one thing in common: they rely for their success on a difference in properties between the materials to be separated.

Waste products

It is becoming increasingly expensive for the chemical industry to dispose of waste products. This, combined with growing public concern about the impact of chemicals on the environment, means that the industry can no longer be satisfied by

high yields from established processes but has to look for new routes to the same products. The new routes convert a very high proportion of the chemicals in the starting materials into useful products.

Laboratory chemists calculate the percentage yield relative to the theoretical yield based on the balanced chemical equation. But even a 100% yield, in these terms, may involve a substantial amount of unwanted by-products. An older process for making phenol from benzene created 1 mol of sodium sulphite (126g), for every mole of phenol (88g) produced.

This might be acceptable if there is sufficient demand for the sodium sulphite, but if not, it presents a serious waste management problem, and adds significantly to costs.

It is much better to reduce the amount of waste generated in the first place, rather than treat it at a later date. Calculating the yield does not show how efficiently the reactants have been used in generating the desired product, and so does not indicate how effectively waste is being reduced.

A new measure being used by chemists to measure the efficiency of chemical routes to products is the **atom economy**.

$$\text{Atom economy} = \frac{\text{mass of atoms in the desired product}}{\text{mass of atoms in the reactants}} \times 100$$

This is a much tougher test of the efficiency of a process than the yield. It is a way of showing how efficiently a particular reaction makes use of the reactant atoms.

In the 1980s the analgesic ibuprofen was manufactured by a six-stage process with an overall atom economy of just 40.1%. In the 1990s a new three-stage process was developed with an atom economy of 77.4%. This shows how innovative thinking can improve the route to a commercial product.

Process control

In a laboratory we normally rely on our senses to tell us when things are not going according to plan, so that we can quickly decide what adjustments are necessary and carry them out. For instance, our eyes enable us to see when the contents of a test-tube are being overheated and our brain responds by instructing our hand to move the test-tube out of the flame.

With a large-scale continuous process it is neither practical nor desirable to use this kind of manual control, and one of the characteristics of a modern chemical plant is a sophisticated automatic control system.

Sensors are used around the plant to measure variables such as temperature, pressure, and flow rate. This information is transmitted to an automatic controller (often an on-line computer) which is programmed to adjust control valves in order to maintain the desired operating conditions and to ensure a consistent quality of product.

For maximum efficiency, automatic process control has become increasingly important. A major design consideration on any plant is how and where to incorporate instruments such as flow meters, thermometers, pressure gauges, and automatic analysers into the plant equipment.

Summary

We have seen that the same chemical and physical principles underlie both large-scale and small-scale operations but that, in industry, the use of large quantities of materials may introduce factors which are unimportant or even non-existent on a laboratory scale. Amongst the problems which the chemical engineer must consider are:

- methods of storage
- methods of transferring materials
- vessel design and materials of construction
- method of operation (batch or continuous)
- methods of heating and cooling
- optimum economic conditions (not necessarily the same as optimum chemical conditions)
- toxicity and fire hazards
- instrumentation and control
- reduction and disposal of waste products.

1.3 The chemical industry

The chemical industry converts raw materials found in the earth, sea, and air into new substances of greater value to humankind. Such operations are often carried out on a vast scale which can be difficult to comprehend fully; for instance, the annual world production of nitrogenous fertilizers is in excess of 50 million tonnes. The continuing availability of such materials at reasonable cost is essential for the survival of our society, few aspects of which are untouched by the products of the chemical industry.

The basic **raw materials** of the chemical industry are

- petroleum, coal,
- air,
- water,
- vegetable materials,
- minerals such as metal ores, salt, limestone, and gypsum.

Many products are made from these raw materials via important intermediate chemicals. Examples are ethene, ammonia, chlorine, sulphuric acid, sodium hydroxide, and sodium carbonate. These materials, although rarely seen by the average citizen, are made in very large quantities and are known as **bulk chemicals**.

Most bulk chemicals are used to make many different products. Each manufacturing process forms part of a complex network of processes which are inter-related chemically and economically, connecting raw materials to final products.

It is important to realize that the route by which a particular chemical is manufactured may change over the years for a variety of reasons such as availability of raw materials, new technology, energy costs, the changing demand for by-products, the need to reduce wastes and cut pollution, and so on.

For instance, considerable quantities of sodium hydroxide were once manufactured using the 'lime-soda' process which involved reacting sodium carbonate with calcium hydroxide in a manner similar to that described in the laboratory process earlier in this chapter. However, the growth in demand for chlorine manufactured by the electrolysis of brine produced abundant supplies of cheap sodium hydroxide as a by-product. A consequence of this was that by 1970 virtually all the lime-soda plants throughout the world had been closed down.

Significant changes in the structure of the chemical industry are likely to occur as raw materials such as petroleum and certain minerals become scarcer.

Considerable research is being directed into ways of producing many organic chemicals from coal or plant material (biomass), opening up exciting possibilities for the chemical engineers of the future.

1.4 Products from the chemical industry

The chemical industry produces five categories of product ranging from bulk chemicals to high-value chemicals produced in small amounts.

Basic inorganics and fertilizers

Basic inorganic chemicals include sulphuric and nitric acid, sodium hydroxide, chlorine and ammonia. These bulk chemicals are manufactured in millions of tonnes per year.

Dyestuffs, paints and pigments

Manufacturing and innovation in the field of dyestuffs, paints and pigments has been an area of strength for the UK chemical industry.

Petrochemicals and polymers

The UK has a petrochemical industry which benefits from oil and gas from the North Sea. One of the building blocks is ethene, made by cracking ethane in natural gas, or the naphtha fraction from oil distillation.

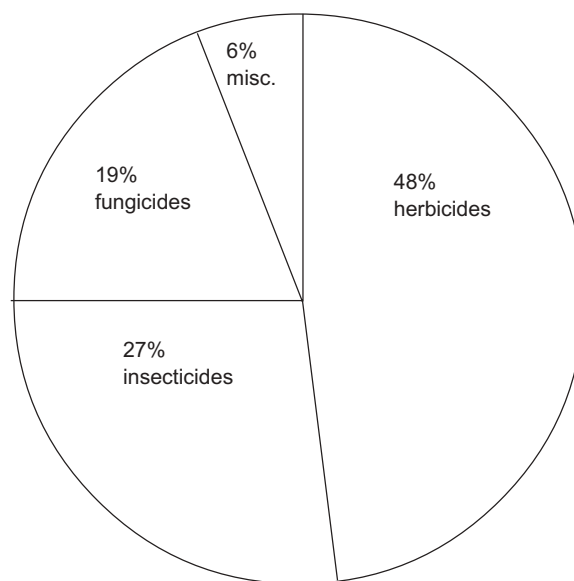


Figure 1.3 Uses of nitric acid. Annual production of nitric acid is 60 million tonnes per year worldwide of which about 20 million tonnes is made in Europe
(from *The Essential Chemical Industry*)



Figure 1.4 Ethene pipelines connect refineries and chemicals plants in the UK . Annual production of ethene is 2.1 million tonnes in the UK and over 80 million tonnes in the rest of the World. (from *The Essential Chemical Industry*)

Pharmaceuticals

This sector of the industry invests heavily in research. Today the industry is heavily influenced by genomics and biotechnology.

Specialities

Speciality chemicals are the intermediates and end products required for the production of a wide range of goods including food flavourings, liquid crystals, printing inks, and agricultural chemicals, as well as formulations for personal care and cleaning.

2.1 What are unit operations?

In most manufacturing plants the chemicals flow from one part of the plant to another. Along the way there are pieces of equipment, each of which is designed to carry out a particular function. Each of these functions is called a 'unit operation'.

Hundreds of operations may be involved in a complex process such as nylon manufacture, and each one requires the design, construction, and maintenance of a separate item of equipment. Chemical engineering places great emphasis on the study of these unit operations, because the same theory is applicable to a particular operation (such as distillation) whether on a butanone plant or a hydrogen cyanide plant. Thus the concept of unit operations provides a framework for the study of the technology of chemical processes which spreads across the boundaries of different manufacturing industries.

Unit operations may be classified into three main groups:

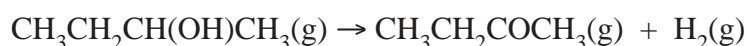
- transport of materials
- energy transfer
- separation

In this Special Study there is a chapter on each of the main groups of unit operations, and there is at least one experiment associated with each.

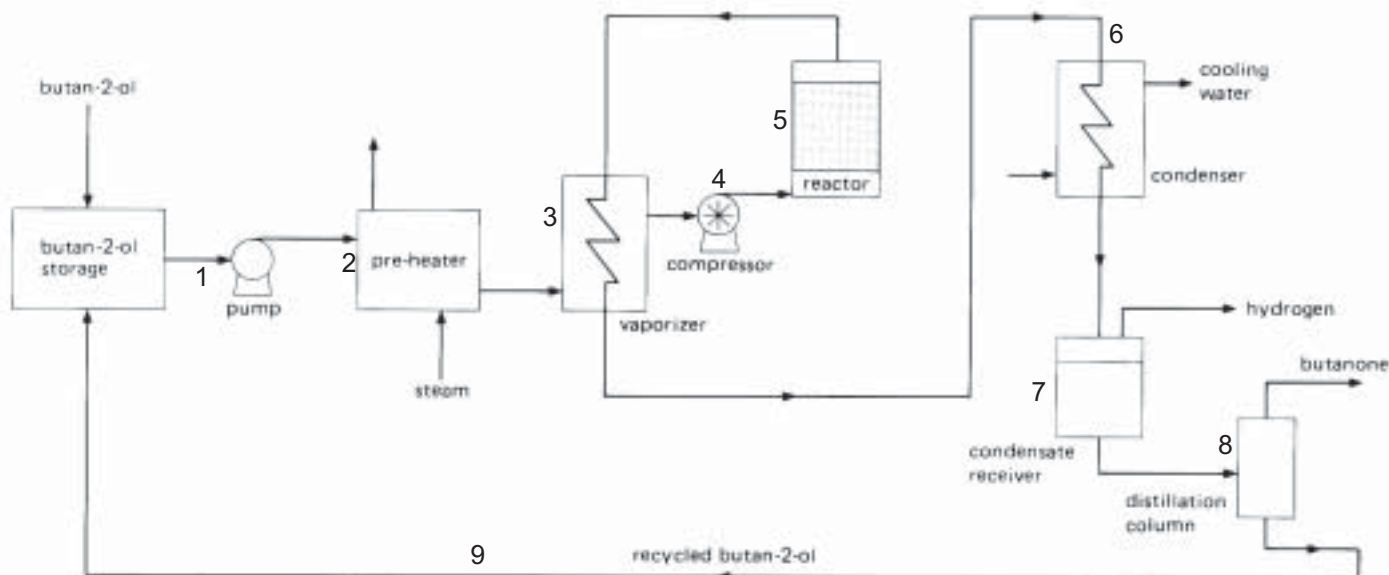
2.2 Flowsheets

The various unit operations in a process can be linked together on a flowsheet. This is a diagram of the process, with lines to indicate the flow of materials. Conventional symbols are used to represent the reactor and the unit operations. The following flowsheet is for a process for making butanone from butan-2-ol.

Butanone (commonly known as methyl ethyl ketone or M.E.K.) is an important industrial solvent with an annual worldwide production figure in the region of 100 000 tonnes. The process described involves the catalytic dehydrogenation of butan-2-ol for which the overall equation is:



This is a vapour-phase reaction in which the butan-2-ol vapour is passed over a zinc oxide catalyst.



1 Feed

The butan-2-ol is pumped at a carefully controlled flow rate from storage tanks. This is classified as transport of materials. Flow along pipes is a very important part of most processes. See Chapter 3 for ways in which this flow takes place.

2 Pre-heat

The reaction is to take place in the vapour phase. The butan-2-ol is first heated to its boiling point of 100 °C using superheated steam. This is achieved using a heat exchanger. This particular heat exchanger is called a 'pre-heater' because of the job it does. See Chapter 4 for heat exchangers.

3 Vaporize

The hot gases leaving the reactor are used to vaporize the boiling butan-2-ol before it enters the reactor. The vaporiser is designed to achieve the desired reactor inlet temperature. The vaporiser is another kind of heat exchanger.

4 Compress

The hot vapour is compressed to force it through the plant at optimum pressure. A pump designed to pump gases is called a compressor.

5 React

Butan-2-ol vapour is passed over a zinc oxide catalyst at 400 to 500 °C and undergoes dehydrogenation to butanone with a typical yield of about 90 %. Reactors are of various different kinds. See Chapter 6 for the performance characteristics of several of them.

3 Cool

The hot gases leaving the reactor are cooled in the heat exchanger used to vaporize the butan-2-ol feed.

6 Condense

On further cooling in a water-cooled condenser – yet another heat exchanger – most of the butanone and unreacted butan-2-ol condense to liquids. The other reaction product, hydrogen, remains as a gas.

7 Separate

A condensate receiver is used to separate the liquid and gas in the process stream. Some of the butanone and unreacted butan-2-ol remain in the vapour phase and are carried off with the hydrogen gas.

8 Distil

The butanone product is separated from unreacted butan-2-ol by distillation. Heat energy must be supplied to boil the mixture of the two liquids, and the butanone vapour emerging from the top of the distillation column must be cooled and condensed. The butanone product is run to storage tanks and any recovered butan-2-ol is recycled – process stream 9.

9 Recycle

Unreacted butan-2-ol is recycled.

You should notice several things from the flowsheet on the previous page.

Energy-saving is of very great importance to the economic success of the plant. Wide use is made of heat exchangers, so that hot fluids from one part of the plant are used to heat up fluids in other parts.

Reactions seldom go to completion. When reactant concentrations are low, reactions are too slow to be economically viable. It is usually better to separate unreacted material and re-cycle it.

The reactor itself may be a relatively small part of the plant, apparently much less impressive than the equipment for the pre-treatment and separation parts of the process.

This chapter is about how materials are moved about in a chemical plant. Whenever possible, materials are moved about as fluids.

We shall look first at the theory which explains some aspects of the behaviour of fluids: how fluids flow through pipes, around particles, and through loosely packed solids. This theory can be used in the design of equipment for moving fluids about, measuring flow rates, separating products as in filtering, mixing immiscible fluids, and so on.

Physicists refer to this as **fluid dynamics**; civil and marine engineers who are concerned with movement of, or through, water refer to it as **hydraulics**; and aeronautical engineers interested in the same sort of problems in air talk about **aerodynamics**.

The chemical engineer has borrowed from all these sources, but there are many problems which are peculiar to chemical processes. These problems include novel features such as the flow of reacting liquids, the physical properties of which are changing as the reaction proceeds.

3.1 How fluids flow through pipes

Fluids are generally moved about in pipes. A chemical reactor may be nothing more than a pipe or an enlarged section of a pipe. A heat exchanger in which fluids are heated and cooled is usually a complicated system of pipes.

The force of gravity may be enough to cause a liquid to flow from one vessel to another, but generally it is necessary to supply energy by means of a pump at some stage. The chemical engineer must be able to calculate the resistance to flow through a pipe in order to specify the size and type of pump required, and the power of the motor needed to drive it.

The total resistance is made up of two parts: the resistance arising from viscous friction within the pipe, and the height through which the fluid is to be lifted. Further resistance occurs, of course, if the fluid is to be pumped into a vessel at a higher pressure.

The viscosity factor is frequently the more important. Viscosity results from the intermolecular forces within the liquid. Problems often arise with very viscous liquids such as heavy oils. Pumping may also be difficult when a fluid has to flow through obstructions in the pipe – examples are a bed of catalyst pellets or a heat exchanger made of small bore pipes with many bends.

The frictional forces arising from the viscosity of a liquid can act in two different ways.

1 Sometimes the flow velocity is small, and the fluid is viscous and nowhere very far from the pipe walls. Then the fluid flows as if it were in layers sliding

over one another. The fluid velocity is at a maximum in the centre of the pipe and decreases in a fairly uniform manner to zero in contact with the pipe walls. This is known as **streamline** (or **laminar**) flow, because all elements of fluid move in orderly lines along the pipe, with a velocity distribution as shown in figure 3.1a.

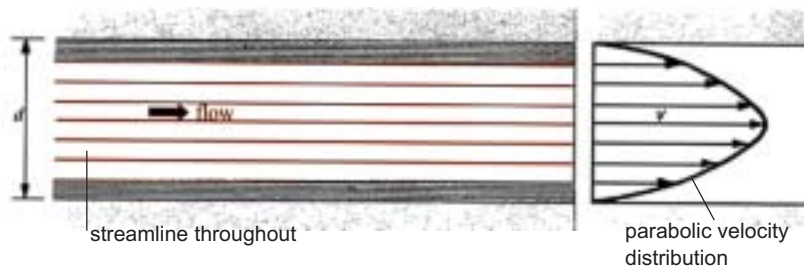


Figure 3.1a Streamline flow at low Reynolds Number

2 Sometimes the flow velocity is high, the fluid viscosity low, and the stabilizing pipe walls are far distant. Then small disturbances upset the streamline path of the fluid, adjacent elements interfere with one another, and swirling eddies develop. This is known as **turbulent** flow.

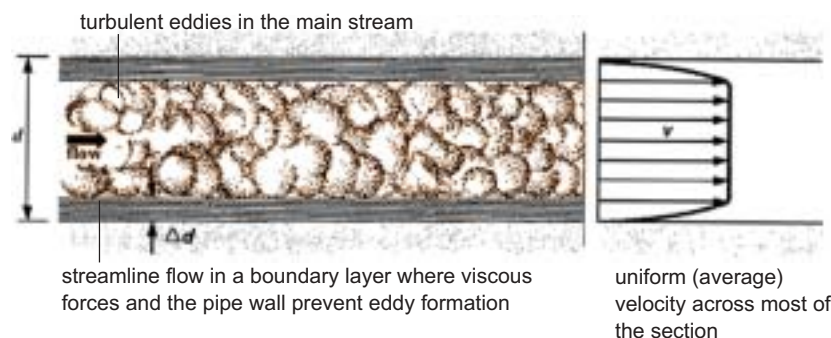


Figure 3.1b Turbulent flow at high Reynolds Number

The velocity distribution in figure 3.1b shows a fairly uniform fluid velocity across most of the pipe diameter but, no matter how vigorous the turbulence, there is always a narrow but important **boundary layer** next to the wall where viscous forces and the rigid wall successfully preserve streamline flow.

Turbulence only occurs as a result of viscosity. Whether flow is streamline or turbulent largely depends on the ratio of inertial to viscous forces. This important ratio is given by the Reynolds Number. For flow in a pipe the Reynolds Number (Re) is given by:

$$Re = \frac{4m}{\pi d\mu}$$

m = mass flow rate d = diameter of pipe μ = fluid viscosity

Since the Reynolds Number is a ratio of forces, it is dimensionless. (Clearly, m , d and μ must be expressed in consistent units.) In general, when the value of the Reynolds Number exceeds a certain critical value, the nature of the fluid flow in the pipe will change from streamline to turbulent.

Other things being equal, it requires less power to pump a fluid in streamline than in turbulent flow. This is because much energy is wasted creating turbulent eddies.

Why chemical engineers generally prefer turbulent flow

a It is often necessary to mix fluids in a pipe. This is done effectively by turbulent eddies. Mixing in streamline flow is largely a result of diffusion – a slow process. Turbulent flow along a few metres of pipe is equivalent to shaking reagents together in a laboratory test-tube.

b It is much easier to heat or cool fluids flowing through pipes when the flow is turbulent. This is because, in streamline flow, heat can only pass into the liquid

by conduction. This is slow through most fluids. In turbulent flow, bulk movement occurs. Hot fluid at the walls is moved into the main stream and mixed. This forced convection is very effective in transferring heat throughout the fluid.

c A length of pipework is normally designed to carry a specified mass flow rate of fluid, m , say 2000 kg hr^{-1} . The expression given above for Reynolds Number shows that for a fixed mass flow rate, a low Reynolds Number (and hence streamline flow) calls for a large pipe diameter. However, the cost of increasing the pipe diameter quickly outstrips the cost of pumping. Even if the other advantages of turbulent flow are not important, the minimum overall cost is often obtained using fairly small diameter pipes with turbulent flow.

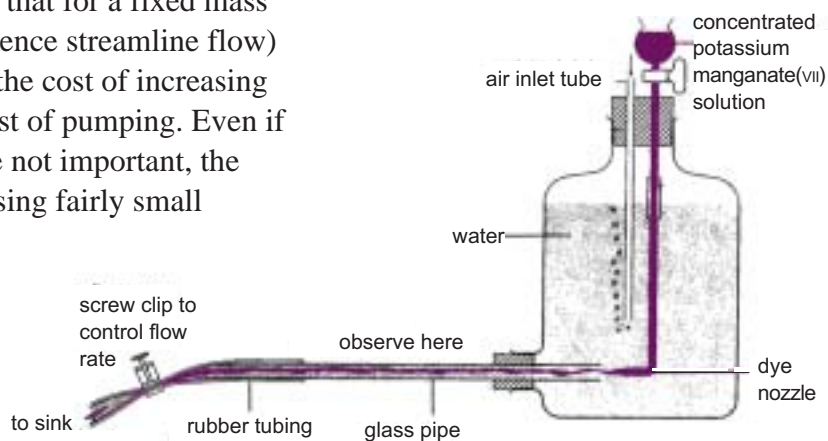


Figure 3.2 This apparatus can be used to investigate the relationship between pipe diameter, flow rate and flow pattern.

3.2 How fluid flow is measured

It is necessary to measure flow rates in order to monitor the operation of a chemical plant. Generally the overall process is controlled by adjusting flow rates using automatic control valves. For example, the temperature in a reactor may be lowered by increasing the flow of cooling water.

Many flow-measuring instruments used in large-scale continuous processes depend upon the application of Bernoulli's Law. This is a special case of the Law of Conservation of Energy. It states that, if friction losses are ignored, the energy per unit volume is constant along any streamline in a liquid. Hence for the flow of fluids along a horizontal pipe:

Gain in kinetic energy per unit volume = Loss in potential energy per unit volume

If there is a constriction in the pipe, the fluid flows faster and its kinetic energy increases. The loss in potential energy is shown by a related drop in pressure. If the fluid slows down, the pressure is observed to increase. A **venturi flow meter** is shown in figure 3.3.

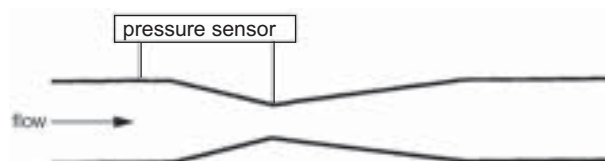


Figure 3.3 Venturi flow meter

A venturi flow meter consists of a smooth contraction within the pipe, followed by a smooth expansion to the original diameter. The reduced section or 'throat' causes an increase in fluid velocity with a corresponding decrease in pressure, in accordance with Bernoulli's principle. This pressure difference between the throat and the up-stream pipe gives a measure of the fluid velocity and hence flow rate.

A cruder variation of this type of instrument is the **orifice meter**, which consists simply of a plate containing a machined hole (or orifice) placed across the pipe (figure 3.4). The pressure drop across the orifice is also a measure of the flow rate within the pipe.

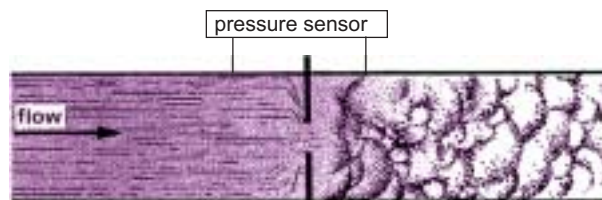


Figure 3.4 Orifice flow meter

The *overall* pressure loss across a venturi meter may be as low as 1 %. However, a typical orifice plate might give a 5 to 6 % pressure loss. This is because of the much larger frictional losses due to turbulence. Despite this disadvantage, orifice meters are frequently used. They are easier and cheaper to install and need less space. For instance, they may be incorporated in pipe joints.

If flow in an open channel is to be measured, Bernoulli's principle may again be used, by making the liquid flow over a weir, as in figure 3.5. The height of liquid standing over the weir is a measure of the pressure drop and so the liquid flow rate.

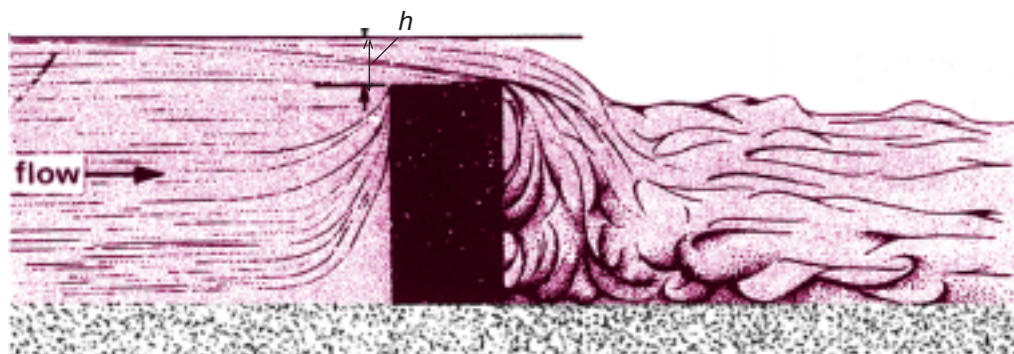


Figure 3.5 Weir meter in an open channel. The height, h , is a measure of the flow rate.

Finally a very convenient meter commonly used on a chemical plant is the **variable area meter** or **rotameter**. This consists of a vertical transparent tube, the diameter of which increases slightly with height. There is a bullet-shaped bob in the tube. Upward-flowing fluid lifts the bob until the gap around it is wide enough for the pressure drop just to support it. The tube is graduated, and so the instrument can be calibrated. The bob can be made of any suitable material, so the meter can be used with corrosive fluids. This arrangement is suitable for gases or liquids and can be used for small flow-rates (see figure 3.6).

This isn't a complete list of all the methods of measuring flow. Many ingenious devices, such as ultra-sonic and electromagnetic flow meters, are used for special purposes.

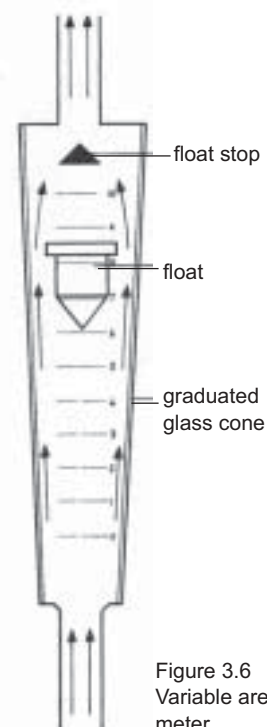


Figure 3.6 Variable area meter

3.3 Other applications of fluid flow

An understanding of the behaviour of fluids in motion is also important to the chemical engineer when considering the flow of fluids around particles – particularly in a ‘packed bed’ consisting of many solid particles touching each other. Flow through packed beds is very common in the chemical industry. Most catalytic reactors involve a bed of catalyst pellets or powder. Gases are dried by blowing them through beds of silica gel or activated alumina. Filtration often involves the flow of liquid through a bed of loosely-packed solid particles.

Fluid which finds its way through the spaces within a packed bed of particles is rather like fluid flowing through a narrow tortuous pipe with rough walls and, as we might expect, the laws of fluid flow are similar. Flow through a ‘pipe’, and flow around a particle are at the two ends of a continuous ‘spectrum’ of conditions. They are sufficiently related for much of the mathematics to be common to both.

3.4 Transport of solids

Solids may vary in many ways: in particle size and range, density, moisture content, free-flowing tendency, and so on. They are commonly moved by conveyor belt, though it can be difficult to achieve the accurate control of flow rate needed for continuous processes.

An alternative way of transporting solids for short distances is by a screw feeder. These are frequently used to feed polymer granules to moulding machines, or coal to furnaces. They can give very accurate control of flow rates.

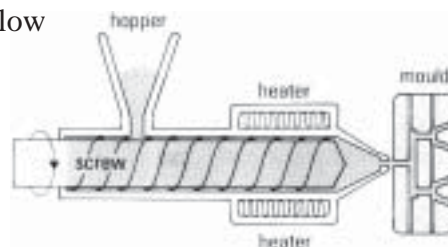


Figure 3.7 A screw feeder forces the polymer granules into the hot zone where they melt and flow into a mould

Another useful way of moving solids is in suspension in a fluid. For example, coal and china clay may be transported in pipes over considerable distances as fine particles suspended in a fast-moving stream of water. This is called hydraulic conveying. Transporting granular or powdered solids in a fast-moving air-stream is called pneumatic conveying. It has long been used for loading and unloading grain ships. It is extensively used in the chemical industry, for example in transferring catalyst particles between reactor and regenerator in fluidised catalytic cracking units.

4.1 Heat exchangers

Many chemical reactions and separation operations rely for their success on the accurate control of temperature. Heating and cooling the process stream at various stages is very important. On a chemical plant, this is brought about by using **heat exchangers** to transfer heat energy from one fluid to another.

One of the simplest heat exchangers is the Liebig water-cooled condenser, commonly used in laboratories. This consists of a 'tube' through which the fluid to be cooled is passed, surrounded by a 'shell' through which the cooling fluid, usually water, flows.

This type of 'shell and tube' heat exchanger is much used in industry, though in a considerably modified form. To appreciate the design of industrial heat exchangers, we shall first develop the theory of heat transfer for a simple laboratory device.

4.2 The theory of heat transfer

Consider a stream to be cooled in a simple shell and tube heat exchanger. There are two basic ways of carrying out this operation

A Parallel-current flow where both the hot fluid and the cooling water flow through the exchanger in the same direction.

B Counter-current flow where the hot fluid and the cooling water flow through the exchanger in opposite directions.

Figure 4.1 shows these two modes of operation, together with typical temperature profiles for the fluids within the exchanger. In practice, counter-current flow is generally preferred. Greater cooling can be achieved. The following theory applies to this method.

The basic equation which describes the performance of a heat exchanger is:

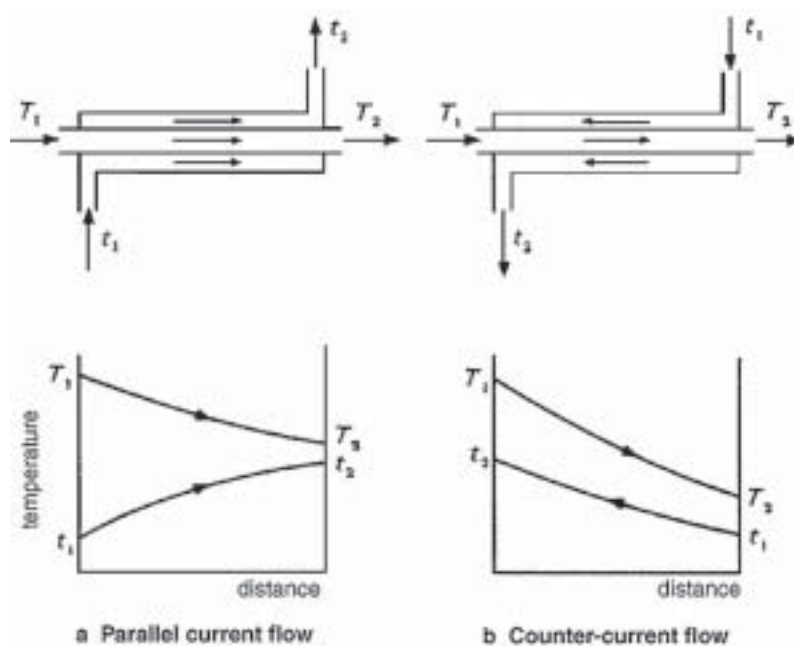
$$Q = UA \Delta t$$

Where

Q = the **duty** of the exchanger; i.e. the amount of heat to be transferred in kJ hr^{-1}

U = the **heat transfer coefficient**; this is a measure of the efficiency of the process; its units are $\text{kJ hr}^{-1} \text{m}^{-2} \text{K}^{-1}$

Figure 4.1 Temperature variation in a heat exchanger



A = the **area of surface** over which the heat transfer takes place in m^2 .

Δt = the **temperature difference** in K

This temperature difference varies in different parts of the heat exchanger whichever type of flow is being used. Some sort of mean value must be used. In the experiment which goes with this chapter, the value which is most appropriate is called the **log mean temperature difference**. It is calculated from the inlet and outlet temperatures, according to the expression:

$$\Delta t_m = \frac{(T_1 - t_2) - (T_2 - t_1)}{\ln [(T_1 - t_2) / (T_2 - t_1)]}$$

T_1 , T_2 , t_1 and t_2 are as shown in figure 4.1b on the previous page.

4.3 Industrial heat exchangers

The duty of a heat exchanger depends on

- A the heat transfer coefficient
- B the surface area across which heat is transferred
- C the temperature difference

In the design of heat exchangers, chemical engineers attempt to achieve optimum values for each of these variables.

Heat transfer coefficient, U

High operating values for the heat transfer coefficient are obtained by the following means.

- a Ensuring that the fluid flow is turbulent. This keeps to a minimum the thickness of the film at both surfaces of the tube. Here the fluid is in streamline flow, or even stationary, and heat transfer can be by conduction only as shown in figure 4.2.
- b Constructing the tubes of a material with a high thermal conductivity.
- c Keeping the walls of the tubes clean and free from coatings of 'scale' or other solids. Where fouling of this type is likely, the exchanger must be designed for ease of cleaning and maintenance.

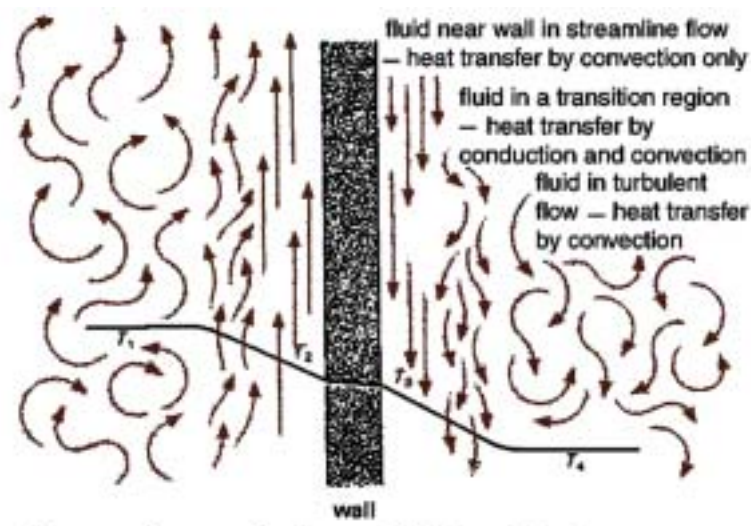


Figure 4.2 Heat transfer between fluids in turbulent flow

Surface area, A

A large surface area of tube is desirable. To achieve this many small tubes are used rather than a single large one. However, the larger the number of tubes, the greater the capital cost of the exchanger and the pumping costs to operate it. In practice, an optimum value of the area is chosen so as to give minimum overall costs. Some tubes have special 'fins' attached to increase the effective surface area for heat transfer.

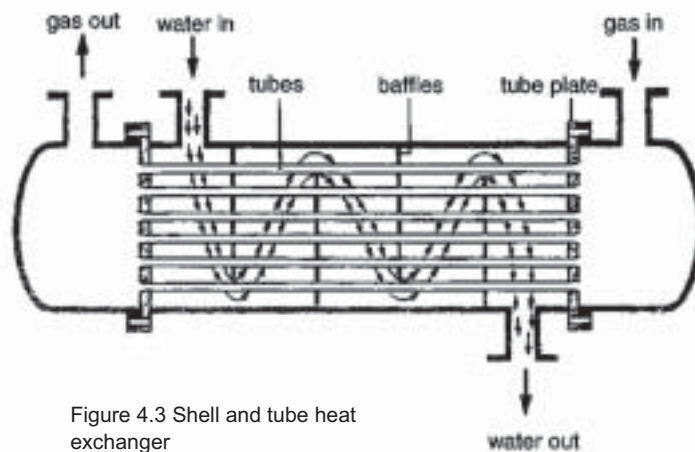


Figure 4.3 Shell and tube heat exchanger

Temperature difference, Δt

The higher the temperature difference between the two fluids, the greater the heat transfer. However, the value of this variable is often dictated by the heating or cooling agent available.

River water at 5 to 15 °C is often used as a cooling agent, with a maximum discharge temperature of 50 °C or less. In some locations, suitable cooling water is not available, and air-cooled heat exchangers must be used.

The most common heating agent on chemical plant is high pressure steam at about 150 °C. Sometimes the steam is produced in a central place and piped to each of several heat exchangers in different locations around the plant.

A typical industrial shell and tube exchanger is shown in figure 4.3. It consists of dozens or even hundreds of small-bore tubes (the tube bundle) through which the process stream passes. A second fluid, perhaps cold water for cooling or steam for heating, passes over the outside of the tubes within the shell. Its path is directed backwards and forwards over the tubes by means of baffles.

Heat exchangers perform a wide variety of functions in different situations, and are often given names to indicate their function. Thus preheater, reboiler, condenser, cooler, vaporiser, and economiser are all names for heat exchangers used for different applications.

Figure 4.4 shows a distillation column with four associated heat exchangers. The chemical and economic viability of a process may well depend on the efficient use and recovery of energy.

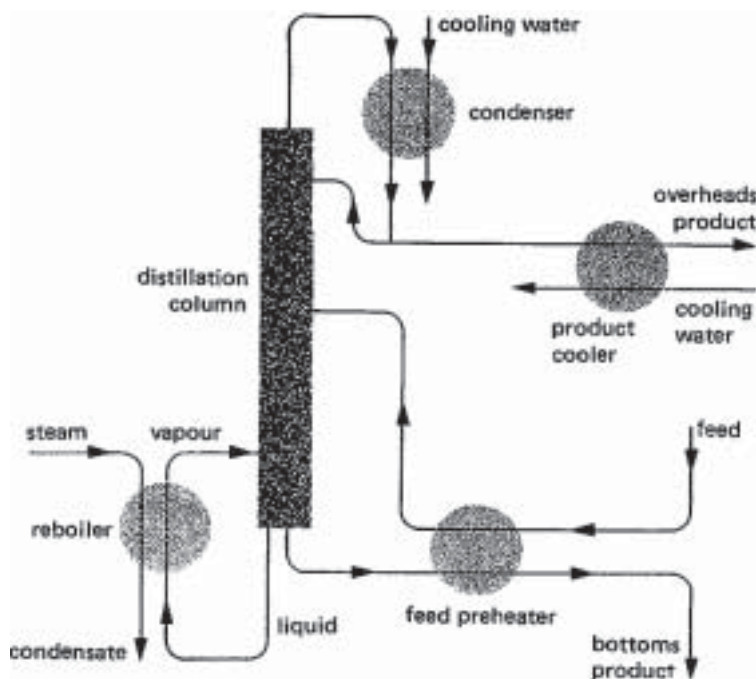


Figure 4.4 Distillation column with ancillary heat exchange equipment

Most chemical processes may be divided into two main stages:

- the **synthesis** stage in which the required product is formed from reactant materials;
- the **separation** stage in which the required product is separated from the rest of the reaction mixture.

The synthesis stage is carried out in a vessel called the **reactor**. On a chemical plant, this may often appear small and unimpressive compared with some of the other equipment present. However, the performance of the reactor influences the design and operation of almost every other part of the plant. The reactor lies at the heart of any chemical process. Its design must be undertaken early in the development stage, and will often dictate the capital cost and economic viability of the overall plant.

5.1 Types of reactor

The function of the reactor is to produce a certain product from given reactants at the required rate. There are three main types of chemical reactor commonly used to achieve these objectives. These are:

- a the batch reactor
- b the continuous stirred tank reactor
- c the continuous tubular reactor.

The batch reactor

In this type of reactor, all of the reactants are placed together in a vessel, and the mixture is stirred and heated as appropriate until the reaction is sufficiently complete.

In a batch reactor the rate of reaction falls as the reactants are used up. At any particular instant all the material present has reached the same stage of reaction.

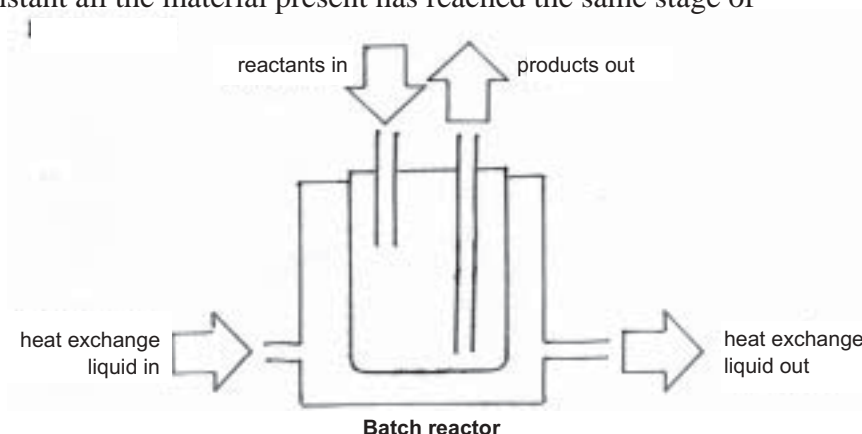


Figure 5.1
Batch reactor

The continuous stirred tank reactor (CSTR)

An alternative to batch operation is to feed reactants continuously into the reactor at one point, and withdraw products at an equal flow rate elsewhere. The chemicals react as they flow through the system.

A typical continuous stirred tank reactor is shown in figure 5.2. Reactants flow continuously into a vigorously stirred vessel. Products are withdrawn at the same rate, so a steady state is maintained. The contents are thoroughly mixed to give a uniform composition throughout. The composition of the outlet stream will be the same as in the bulk of the vessel.

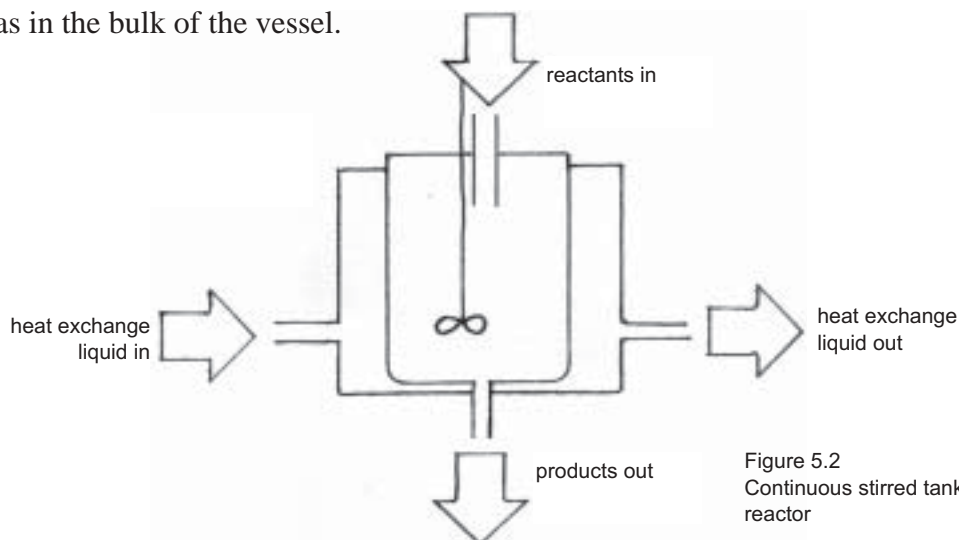


Figure 5.2
Continuous stirred tank reactor

The continuous tubular reactor

In this type of reactor, the reactants are fed continuously into one end of a tubular vessel and products flow out at the other end (figure 4.3). This is a steady rate operation. With constant flow rates, the conditions at any particular point remain constant with time.

At a distance x downstream from the inlet, reactants have spent a time x/v in contact, where v is the flow velocity through the reactor. Changes in time in a batch reactor become identical with changes in position (x) in a tubular reactor. The significant characteristic of tubular reactors is that no attempt is made to mix together materials which are at different stages of reaction. The overall length of the reactor is determined by the contact time needed to achieve the desired concentration of product.

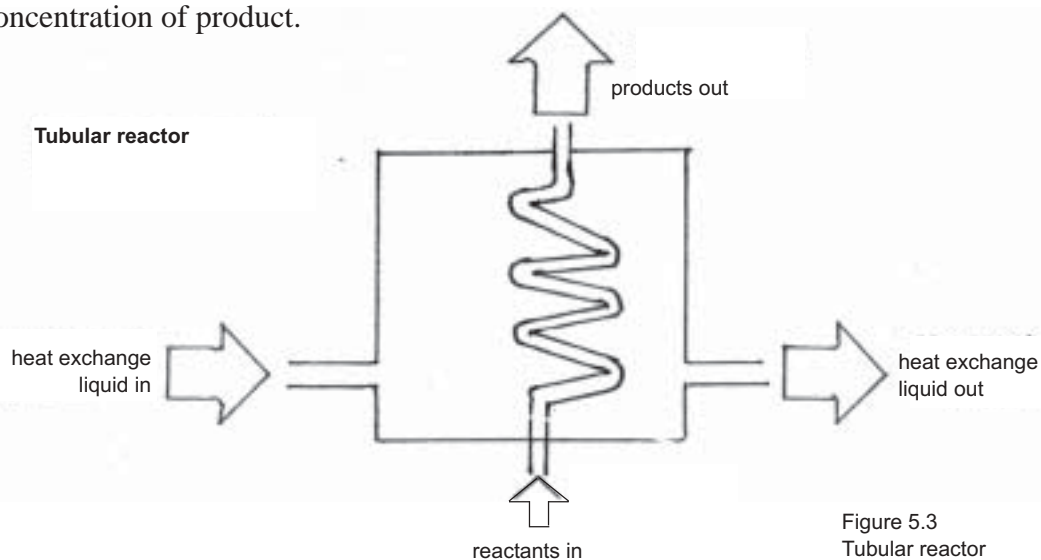


Figure 5.3
Tubular reactor

5.2 Design equations

For each type of chemical reactor, it is possible to derive a general design equation. This enables the user to calculate the length of time reactants must remain in the reactor to achieve a certain percentage conversion of reactants into products. All design equations will involve the rate constant for the reaction. In this study we will confine our attention to first order reactions for which the rate equation is

$r_A = k[A]$ where r_A is the rate of the reaction, k is the rate constant and $[A]$ is the concentration of reactant A.

Design equation for a batch reactor

The form of the rate equation shown above is not quite what we need. It is possible to convert it into a form which relates the time, t , to the rate constant, k , to the initial concentration, $[A]_0$, and to the desired concentration of $[A]$.

This form of the equation is known as its 'integrated form' and is:

$$t = \frac{1}{k} \ln \frac{[A]_0}{[A]}$$

The mathematical argument by which this conversion is done is not something which you need to learn, but if you would like to know, it is given on page 46.

We are not going to do an experiment on batch reactors here because in all probability all the reactions you have done on reaction kinetics have been conducted in batch reactors and you did several of these in Topic 11.

Design equation for a continuous stirred tank reactor (CSTR)

For a continuous process, the reactants are being added and the products removed continuously so flow data needs to be incorporated. It is important to realise that we are talking about a **stirred** tank. The mixing in this is assumed to be so effective that the material flowing **out of** the tank has the same concentration as the material **in** the tank. The equivalent of the time of the reaction is the **mean residence time**, the average time which a molecule spends in the tank. The symbol used for mean residence time is the Greek letter 'tau', τ .

The design equation for a CSTR is:

$$\frac{V}{u} = \tau = \frac{[A]_0 - [A]}{k[A]}$$

where V is the volume of the tank and u is the volume flow rate through the reactor.

Again, the mathematical argument by which this is derived does not have to be learned for this Study, but see page 46 if you are interested.

5.3 Which is better, a batch reactor or a continuous stirred tank reactor?

In the design of any chemical reactor, two factors are normally fixed from the outset: the kinetics of the reaction and the required output of product. The chemical engineer uses all available information to make decisions about the type of reactor to be used, its physical dimensions, and the optimum conditions under which it is to operate.

The design equations described earlier in this chapter enable comparisons to be made between theoretical yields of product from a continuous stirred tank reactor and a batch reactor during the same time interval.

For a first-order reaction in a continuous stirred tank reactor, the design equation is

$$\frac{V}{u} = \tau = \frac{[A]_0 - [A]}{k[A]}$$

If:

$$\text{Volume (V)} = 22 \text{ m}^3$$

$$\text{Flow rate (u)} = 1.65 \text{ m}^3 \text{ min}^{-1}$$

$$\text{Rate constant (k)} = 0.122 \text{ min}^{-1}$$

$$[A]_0 = 1 \text{ mol dm}^{-3}$$

Then, using the design equation $[A] = 0.38 \text{ mol dm}^{-3}$

This represents a 62 % yield of products.

The mean residence time works out as 13.3 minutes.

For a first order reaction in a batch reactor, the design equation is

$$t = \frac{1}{k} \ln \frac{[A]_0}{[A]}$$

If we use the same initial concentration and rate constant as before, we can calculate what conversion can be achieved in the same time as the mean residence time of the continuous stirred tank reactor, 13.3 minutes.

Perhaps a little surprisingly we find that an 80 % yield results.

The batch reactor gives a larger percentage conversion than the continuous stirred tank reactor, using the same size vessel over the same period of time. We can put these results in a rather different way. A batch reactor will achieve a particular percentage conversion in a shorter time than a continuous stirred tank reactor.

The major disadvantage of batch reactors is that many ancillary operations are necessary both before and after the reaction takes place. The reactor vessel must be filled with measured quantities of reactants, the batch must be tested to ensure that it has reached the desired percentage conversion, and the vessel must then be emptied completely. The time spent on these operations is called 'shut-down' time. The manufacture of a large quantity of product requires very many batches, and it is the overall time of the cycle of all operations which

must be considered when comparing batch and continuous processes. (See figure 5.4 below.) For most processes, the shut-down time would be so large that a greater throughput can be obtained from a continuous reactor.

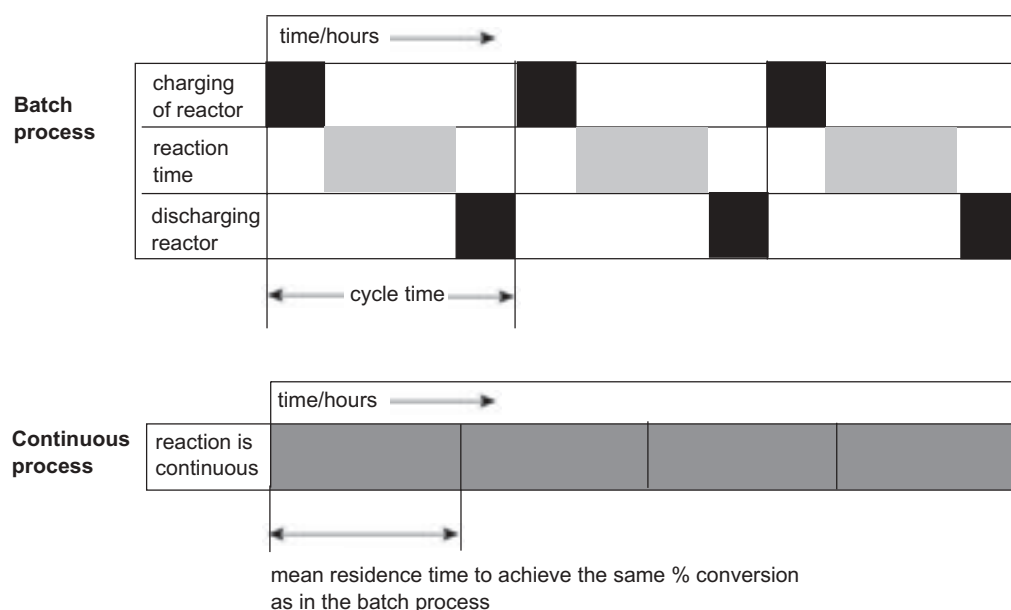


Figure 5.4 Comparative performances of batch and continuous processes.

The decision whether to operate on a batch or continuous basis is also influenced by factors such as the following.

Staffing

The staff required to operate a process is related to the number of times an operating condition has to be changed. Which type of processing requires the greater number of people to operate it?

Automation

This relies on instruments, and instruments require conditions which are as steady as possible. Which type of process is more easily automated?

Degree of control

Control over a process, whether manual or by instruments, is the result of a series of adjustments. The effect of an adjustment is noted, and subsequently a finer adjustment is made. The longer the time available under steady conditions, the more refined the adjustment. Which type of process allows the greater control?

Cost of plant

In a continuous process, conditions at any point in the system are constant, and the equipment is 'tailor-made' for those conditions. In batch processing, multi-purpose units are frequently used. These are large-scale equivalents of laboratory apparatus, and are obtainable 'off the shelf' from chemical plant manufacturers. Which type of process is likely to have the higher capital costs?

Generally speaking, batch operation is used for processes which produce relatively small quantities of material such as in the pharmaceutical, fine chemicals, or dyestuffs industry. A well-equipped batch reactor (or autoclave)

allows great flexibility of operation, as it may be used to produce a different product each day. Batch reactors are also frequently used for polymerization, paint manufacture, and fermentation processes where the shut-down time allows thorough cleaning of the reaction vessels. This avoids build-up of unwanted by-products or harmful bacteria. However, for most other large-scale processes continuous operation is generally favoured.

Zinc chelate, a real case of reactor choice

A major manufacturer makes a product called zinc chelate for agriculture and horticulture. This is used to provide the trace element zinc for crops. The problem is that simple zinc compounds react with other chemicals with which plants are treated and the zinc is precipitated. This makes spraying impossible. The answer is to make a soluble zinc complex which will not precipitate. To do this, zinc sulphate is reacted with edta and sodium hydroxide.

The reactants are combined in a batch reactor. This consists of a stainless steel cylinder about 3 metres high and 2.5 metres in diameter. It is about the size of a room in a house. Water is piped into the reactor by opening a valve. The operatives then tip in 40 bags of solid edta followed by 29 bags of zinc sulphate. Each bag contains 25 kg. A large paddle-stirrer agitates the mixture, and sodium hydroxide solution is then piped in via a valve.

The firm uses a batch process, because the demand for the product is seasonal and insufficient to keep the plant operating throughout the year. Batch production has the advantage that the reactor tank can be used to make other products when it is not required for zinc chelate.

The firm says that if demand were to increase, continuous operation would be considered. A continuous process is technically more complicated and more costly to install, but once in place it involves lower labour costs and gives a higher annual production. More product is not an advantage, however, if the demand for it is not there.

5.4 Design equation for a tubular reactor

In an 'ideal' tubular reactor, all elements of the reaction mixture are assumed to take the same time to pass along the reactor tube, This situation is known as 'plug flow', and no 'back-mixing' occurs between materials at different stages of reaction. The chemicals react as they proceed along the reactor tube. The reactant concentration falls steadily from its initial value $[A]_0$ at the inlet to its final value $[A]$ at the exit. Consequently the design equation for a tubular reactor is similar to that for a batch reactor. In fact, the situation can be thought of as a continuous series of batch reactors moving along the tube.

If V is the reactor volume and u is the flow rate through the reactor, then the residence time τ is given by:

$$\tau = V/u$$

and the design equation is

$$\frac{V}{u} = \tau = \frac{1}{k} \ln \frac{[A]_0}{[A]}$$

There is an experiment in which this design equation is used.

For a given flow rate and percentage conversion, a tubular reactor has a smaller volume than the equivalent stirred tank reactor. This is likely to make the tubular reactor cheaper to manufacture.

5.5 More about which type of reactor to choose

We have already seen why continuous stirred tank reactors are generally preferred to batch reactors. Tubular reactors seem to give the advantages of batch reactors – faster reaction or smaller volume – without the need to spend time on filling and emptying. Why are tubular reactors not the automatic choice?

It is not uncommon for by-products to be formed in a reaction mixture, due to undesired chemical reactions. For example, suppose a reactant A produces the desired product B, but this undergoes further reaction to form the undesired product C. In order to suppress the conversion of B to C, the concentration of B must be kept as low as possible within the reaction mixture. Where B is the desired product, a tubular reactor will give the best performance, because the concentration of B is lower in a tubular reactor. A stirred tank reactor will tend to favour the formation of C.

5.6 Temperature control

Most chemical reactions involve a significant energy change, either exothermic or endothermic. This will tend to alter the temperature of the reaction mixture as reaction proceeds. If no attempt is made to compensate for this by heating or cooling the reaction mixture, the reactor is said to be operating **adiabatically**. This may be used to advantage for moderately exothermic reactions, where the increase in temperature will maintain the reaction rate as the reactant concentration falls.

However, with highly exothermic reactions, a significant rise in temperature will occur unless heat is removed from the mixture during the reaction. For many chemical systems, the rate of reaction doubles for every 10 °C rise in temperature. This can quickly lead to a ‘runaway’ situation, with disastrous consequences.

With most chemical reactions, an optimum temperature range needs to be maintained. The reactor design must incorporate provision for heat transfer. In the extreme case where the temperature of the reaction mixture is held constant throughout, the reactor is said to be operating **isothermally**.

Accurate temperature control is readily obtainable in a continuous stirred tank reactor where the contents are thoroughly mixed and uniform throughout, but such control is less easy to obtain in tubular reactors where concentrations are varying as the liquid moves.

One of several possible ways of achieving temperature control in a continuous stirred tank reactor is to have a coiled tube carrying a heating or cooling agent within the tank.

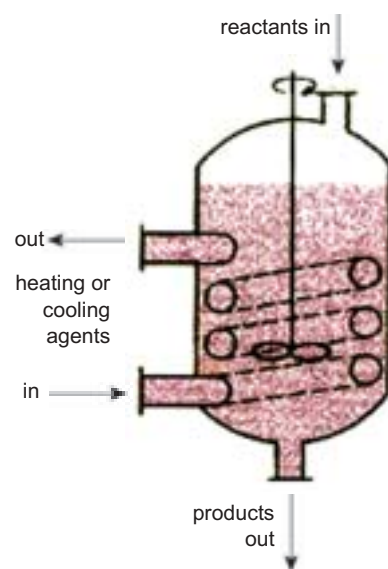


Figure 5.5 Heat transfer in stirred tank reactor

It is not usually too difficult to separate the products of a chemical reaction on a laboratory scale unless you want a very high degree of purity. Solids can be separated from liquids by filtering or centrifuging. You can isolate a single component from liquid mixtures by distillation or solvent extraction. All such techniques take advantage of differences in properties of the substances to be separated.

The chemical engineer uses these same principles to design equipment which can perform the task on a large scale, frequently on a continuous basis, at rates of hundreds of tonnes of product per day. Much of the equipment on a typical chemical plant may well be concerned with such separation operations.

6.1 Separation operations

Separation operations may be divided into two main categories: **mechanical separation** and **mass transfer operations**.

Mechanical separation

Mechanical separation operations depend on differences in bulk properties, such as density or particle size, to bring about the separation of different components of a mixture. Typical examples include the following.

Screening or sieving

Screening is based on size differences between the components of a solid-solid mixture, and is the simplest operation (figure 6.1).

The continuous vacuum filter

This is the industrial equivalent of a laboratory suction filter. In figure 6.2 the mixture of liquid and solid ('slurry') is fed into a trough. A large hollow drum is suspended in the trough as shown. The outside of the drum is perforated metal or woven wire string, and is covered with a filter cloth, on top of which are closely spaced strings. The pressure inside the drum is reduced by suction so that the liquid ('mother liquor') is sucked inwards, and the solid forms a cake on the outside. When the filter is running, the drum rotates and a 'cake' of solid is formed. As this comes out of the slurry it is washed. Both washings and mother liquor are sucked inside the drum and run off.

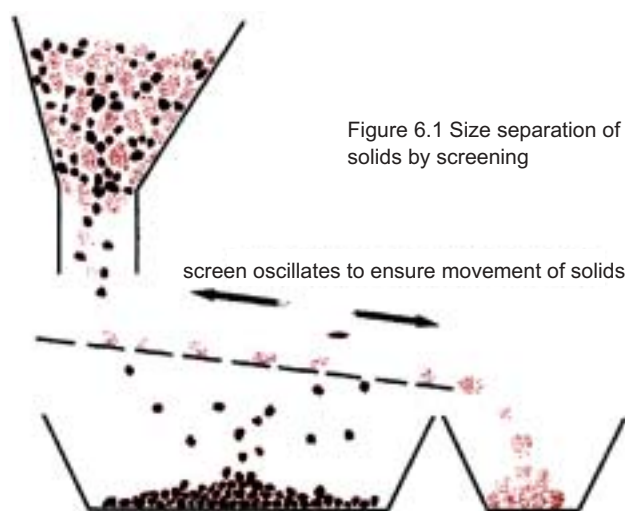


Figure 6.1 Size separation of solids by screening

The filter cake has to be removed before the next cycle. In figure 6.2 this is done by leading the strings around an external roller, so that the cake falls off into a container. This diagram also shows a valve ensuring that suction is applied selectively to only two-thirds of the circumference of the drum.

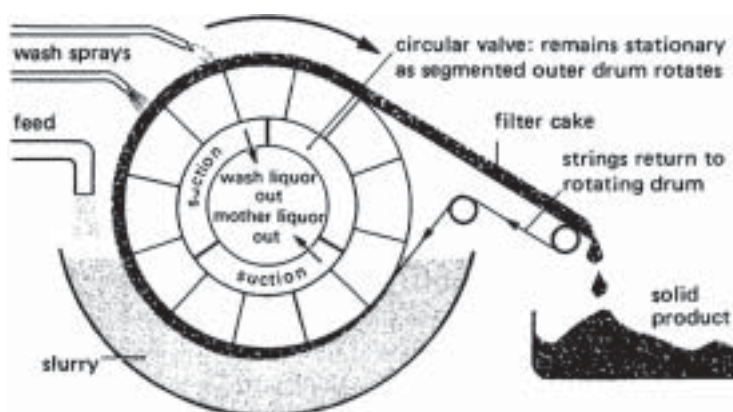


Figure 6.2 Filtration using a continuous vacuum cleaner. The 'mother liquor' is the solution which 'gave birth' to the crystals now being separated by filtration.

The centrifuge

The centrifuge is used for solid–liquid separation, on the same principle as a laboratory centrifuge.

Figure 6.3 shows a continuous centrifuge.

As it rotates, the solid collects on the lining of the cylindrical basket. The mother liquor and washing water pass through the perforated basket into collecting boxes.

A pusher blade gradually moves the solid layer through the washing zone and out to a discharge point.

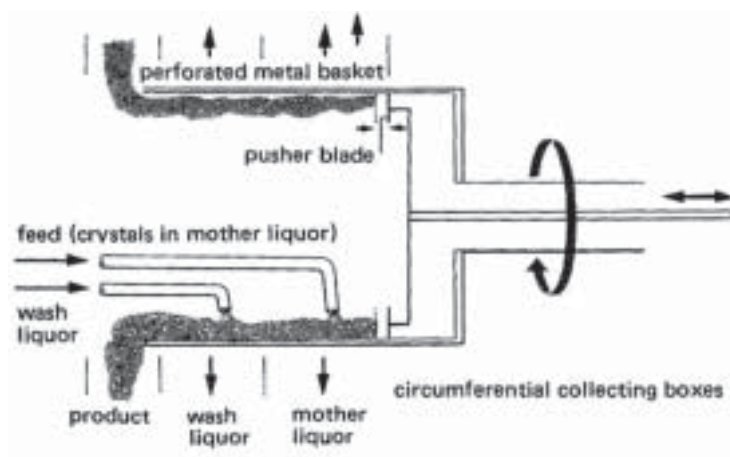


Figure 6.3 Solids separation in a centrifuge

Mass transfer operations

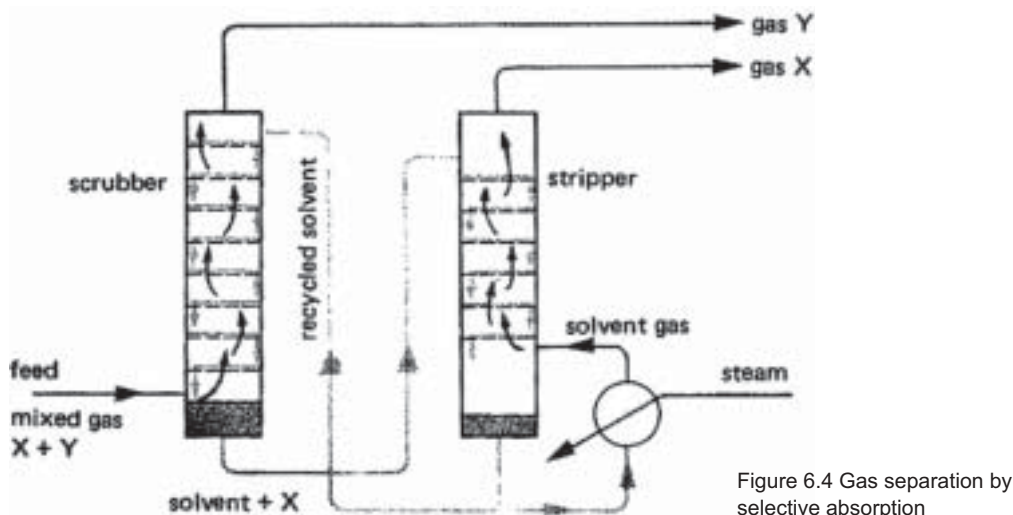
Mass transfer operations are characterized by the movement of one substance through another on a molecular scale. Such separation techniques are based on the principle that substances tend to distribute themselves in different concentrations in different phases. Important mass transfer operations include the following examples.

- gas absorption
- solvent extraction
- distillation.

Of these, **distillation** is the most important of the mass transfer separation operations – see page 34. **Distillation** takes advantage of the difference in composition usually found between a liquid mixture and the vapour with which it is in equilibrium.

Gas absorption

Gas absorption is used to separate a mixture of gases using a selective solvent in an absorption tower or 'scrubber'. For instance, a mixture of two gases X and Y might be separated in this way. A packed tower brings the gas mixture into contact with a solvent in which gas X is soluble but gas Y is not. Gas absorption (or 'scrubbing') is characterized by mass transfer in one direction only – from the gas to the liquid phase. The reverse process, where mass transfer occurs from the liquid to the gas phase, is called 'stripping', and is frequently used to recover the absorbed gas from a solvent. Figure 6.4 shows an **absorber/stripper** system which might be used to bring about complete separation of gases such as nitrogen and ammonia, using water as the solvent.



The gas mixture and solvent are passed through the absorber in opposite directions (counter-current flow) to maintain the maximum 'driving force' for mass transfer between phases. A large surface area of contact between phases is achieved by using trays or packings similar to those used in distillation columns. The stripping works by raising the temperature, which reduces the solubility of the gas.

Solvent extraction

Solvent extraction is used for liquid–liquid separation, and depends on the partition effect of a solute between two immiscible liquids.

For instance, if a mixture of butan-2-ol and water is agitated with a suitable solvent such as 1,1,2-trichloroethane, most of the butan-2-ol but virtually none of the water enters the trichloroethane layer. To increase mass transfer, and hence approach equilibrium conditions more rapidly, the interfacial area between the two phases is made as large as possible by mechanical agitation.

Because they are immiscible and have different densities, the water and trichloroethane separate into two layers when agitation ceases. Most of the butan-2-ol is now in the trichloroethane layer, from which it may be separated by distillation. You may have carried out this kind of separation operation in the laboratory using a tap funnel.

Solvent extraction may be carried out on a continuous basis using mixer–settler units. These consist of two tanks. One is agitated to bring the two liquid phases into contact, and the other is calm to allow them to settle out (figure 6.5). The solvent phase now contains the dissolved solute. This is called the **extract**. The residual phase from which solute has been removed is called the raffinate.

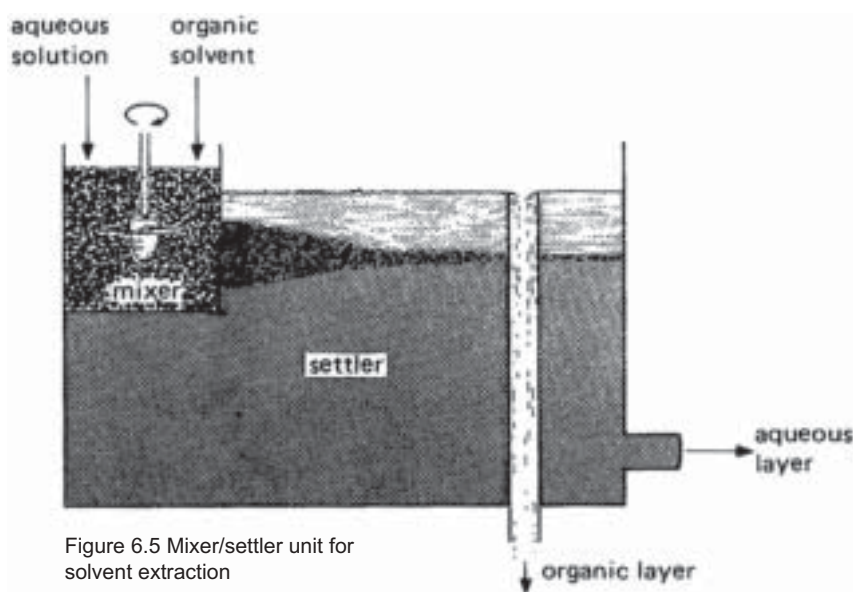


Figure 6.5 Mixer/settler unit for solvent extraction

Distillation

Distillation is the most important separation technique used in the chemical industry. It has a firm quantitative basis and can be very closely controlled. In this chapter some important factors in distillation are described in a semi-quantitative manner, to determine the conditions for efficient separation.

6.2 Liquid/vapour equilibrium

Most mixtures of liquids can be separated by distillation. This is possible if the liquid mixture, and the vapour with which it is in equilibrium at its boiling point, have different compositions.

At a fixed pressure, the boiling point of a liquid mixture depends on its composition. The liquid line in figure 6.6 relates boiling point and composition for a mixture of two liquids, A and B. The composition of the vapour in equilibrium with each liquid mixture may also be shown on the same diagram, and produces a corresponding vapour line.

A liquid of composition X_1 boils at a temperature T_1 to give a vapour of composition X_2 . Notice that the vapour produced is richer in the more volatile component than the original liquid mixture. Such temperature/composition diagrams can be obtained by measuring the boiling point of various liquid mixtures, and finding the boiling points of the condensates from them.

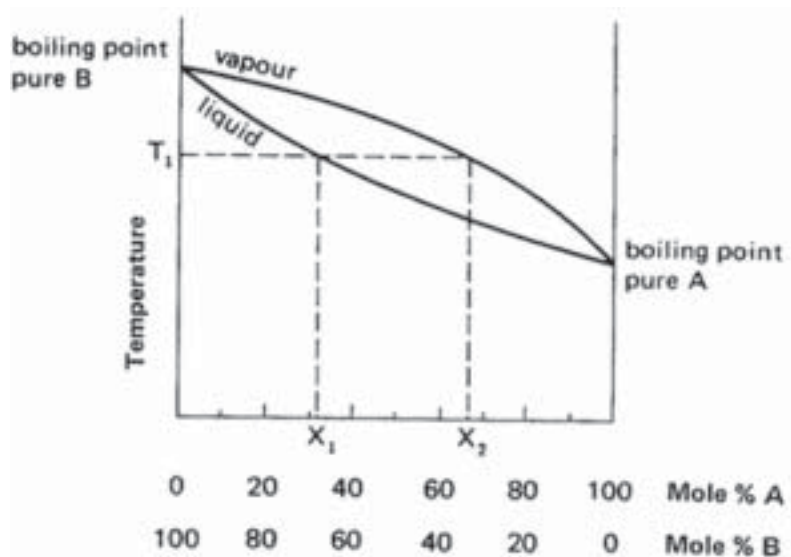


Figure 6.6 Temperature/composition diagram for a mixture of liquids A and B

6.3 Fractionating columns

Simple distillation produces a distillate which is richer in the more volatile component than the original mixture. Successive simple distillations bring about further separation, but such a procedure would be very inefficient to operate. A fractionating column is a device which accomplishes in one operation the equivalent of many successive simple distillations.

The easiest fractionating column to understand is probably a bubble-cap column, as used in some large-scale distillations (see figure 6.7).

Vapour boiled off from the liquid in the kettle (the industrial equivalent of a flask) passes up the column and condenses on the first plate. This condensate is of the same composition as the rising vapour, and thus one distillation stage has been completed.

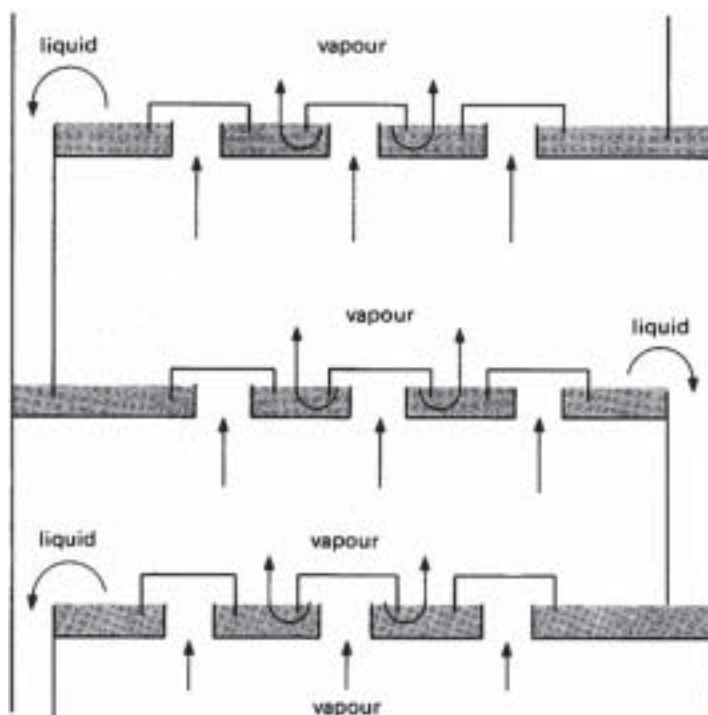


Figure 6.7 Plate and bubble column

The bubble caps force following vapour to bubble through the condensed liquid on the plate, and the heat from this vapour causes the liquid to boil.

This gives off a new vapour of a composition even richer in the more volatile component which condenses on the second plate, completing a second distillation stage.

In this simple treatment, each distillation stage or 'step' on the temperature/composition diagram corresponds to one **theoretical plate** in a fractionating column.

In practice, no plate performs as efficiently as this. Each plate receives liquid from the plate above by means of an overflow weir, so the composition of liquid on a plate is not identical to the vapour rising from the plate below. Nevertheless, the interchange of components (mass transfer) between the vapour rising up the column and the liquid flowing down means that a fractionating column gives the same overall effect as several successive simple distillations.

Bubble caps are expensive on the laboratory scale, and the same effect can be obtained by using a column packed with glass beads or rings. This provides a large area of wet surface for vapour and liquid to approach equilibrium at all heights in the column.

6.4 Reflux ratio

In most fractional distillations carried out in the laboratory, virtually all the vapour which reaches the top of a fractionating column has been removed via a side-arm tube, condensed to liquid, and leaves the system. It is normal industrial practice to return some of the condensed vapour back down the column – to **reflux** it. The ratio of reflux flow rate to distillate flow rate is known as the **reflux ratio**.

$$\text{Reflux ratio} = \frac{\text{reflux rate}}{\text{distillate rate}}$$

The greater the value of the reflux ratio, the more effective is the separation, giving a distillate of greater purity. This advantage is countered by a slower production of distillate. You can have high purity or you can have product quickly, but not both!

6.5 The conditions for continuous distillation

A fractional distillation column designed for continuous operation is shown in figure 6.8.

The mixture to be distilled is fed into the system at a steady rate, and product is continuously removed both at the top and bottom of the column. Heat input is either by pre-heating the feed or re-boiling the bottom residue, using a suitable heat exchanger.

The less volatile component is removed as liquid from below the bottom plate, and the more volatile component is removed as vapour from the top plate.

The boiling liquid on each intermediate plate becomes progressively richer in the more volatile component as the column is ascended. There is a corresponding temperature gradient within the column.

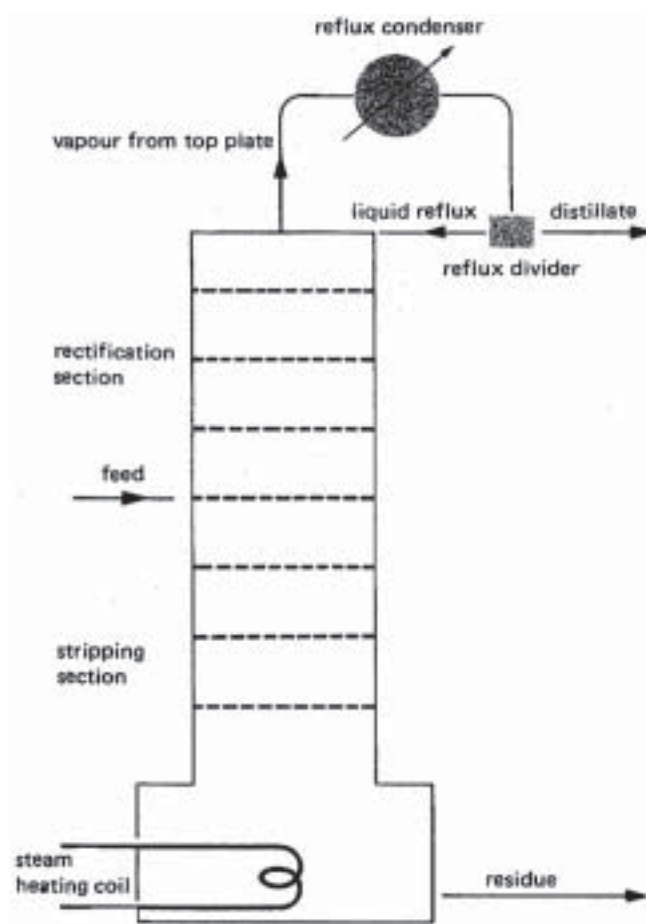


Figure 6.8 Arrangement for continuous fractional distillation

The feed must be introduced into the side of the column at a height where its composition corresponds to the composition of the liquid on the plate. In this way, the steady state within the column is not disturbed.

The part of the column above the feed point is called the **rectification** section. In this section the feed is concentrated to the desired distillate quality. Below the feed point is the **stripping** section where the more volatile component is progressively stripped out until an acceptable lower limit of concentration is obtained.

The residue is removed as a liquid. In many processes, the liquid residue is as saleable as the distillate, and sufficient plates are present in the stripping section to bring the residue liquid up to the customers' product specification for purity.

Batch and continuous fractionating columns operate by the same mechanism but have one major difference. In a batch still, the conditions gradually change with time because material is being removed as distillate from a fixed quantity of liquid being distilled. This change of composition can be countered by progressively increasing the reflux ratio. In a continuous still, the conditions remain steady because a steady feed of uniform composition compensates for the removal of distillate and residue.

6.6 Column efficiency

The internal structure of a fractionating column must be designed to bring ascending vapour and descending liquid into intimate contact, so that mass transfer of the components may readily occur. Both packed columns and plate columns are used in industry.

Packed columns

Packed columns consist of a hollow shell filled with a large number of specially-shaped rings made from ceramic, glass, metal, or plastic.

Plate columns

Plate columns contain trays on which liquid rests and through which ascending vapour rises. Traditionally, these have been constructed with bubble caps, but the high cost of these has resulted in their replacement, for many applications, by modern devices such as valve trays and sieve trays.

In their simplest form, sieve trays consist of steel plates drilled with holes. The liquid on each plate is prevented from flowing down through these holes only by the upward flow of vapour from below. Consequently, precise control of conditions within the column is essential. With valve trays these holes are closed off if the vapour flow rate falls.

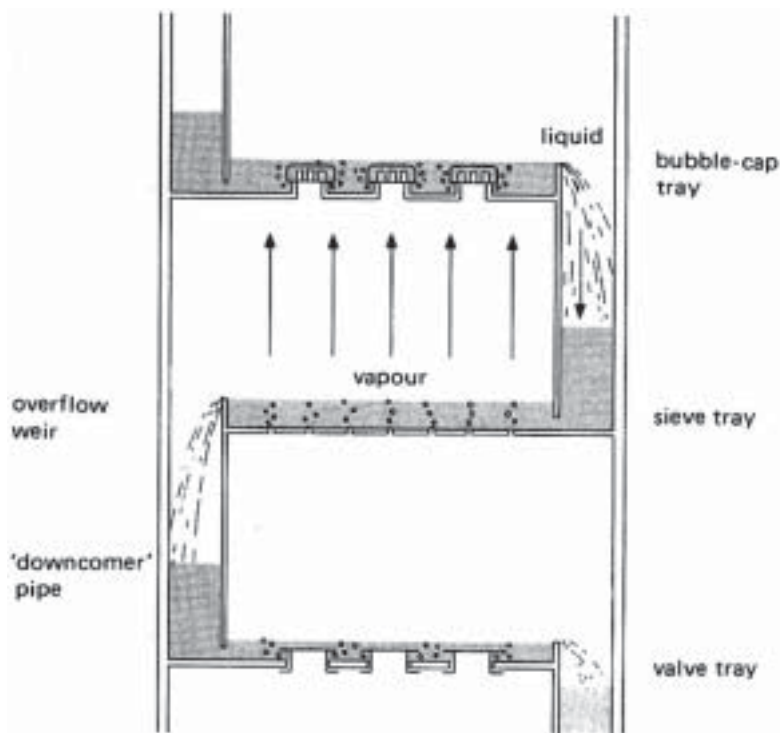


Figure 5.9 Three types of tray commonly used in distillation columns. All the trays in one column are normally of one type

Plate columns have the main advantages that they can cope with a wide range of conditions, including foaming liquids. They are easily cleaned, and enable side-streams to be removed at intermediate points in the column if desired. Packed columns are generally cheaper to construct for small diameters (less than 1 m) and have superior corrosion resistance since inert ceramic packing materials may be used.

The main disadvantages of packed columns are that liquid tends to flow down the walls of the tower instead of through the packing, and for large columns the sheer weight of packing may impose severe structural loads.

6.7 Economics and optimisation

The cost of operating a distillation column can be broken down into two principal parts:

- the capital cost of building the column, and
- the cost of running it once it has started to function.

These costs depend upon the number of plates, and upon the reflux ratio.

The capital cost is high for very low reflux ratios, since a large number of plates would be required. The capital cost is also high for very high reflux ratios, since a large plate area would be needed to produce the desired flow rate of product.

The running costs increase with increasing reflux ratio, since a higher proportion of liquid is flowing back down the column and the distillation is slower. At total reflux the running costs are infinitely large, since no product at all is obtained. This is shown in figure 6.10.

The sum of these two curves gives the total cost, and the value of the reflux ratio which corresponds to the minimum total cost is the optimum reflux ratio.

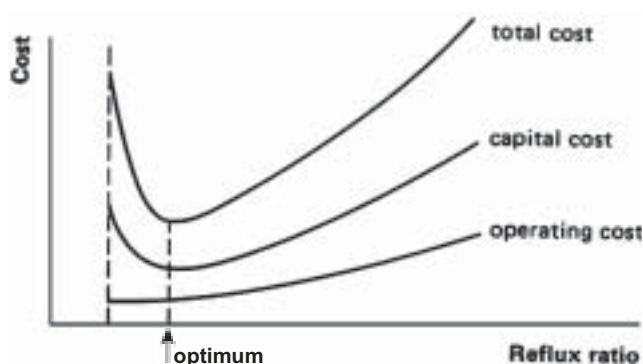


Figure 6.10 The cost of operating a distillation column

How does a large, complex, expensive industrial plant come into being? In this chapter we shall consider how a company develops a new idea, from preliminary work in the laboratory, to a pilot plant producing small amounts of product, and finally to the design and construction of a full-scale plant.

7.1 Examining a new project

All new industrial processes begin with an 'idea'. This may involve an entirely new product or a better way of making an existing product. Many ideas originate from pure research carried out in the laboratories of chemical companies, universities, and government establishments. Others stem from experience gained during industrial production and marketing. These can lead to an awareness of the need for a new or modified product.

Once a production idea has been established, it is usually carefully examined in three stages:

- a preliminary investigation
- b laboratory tests
- c pilot plant trials.

The preliminary investigation involves examining the scientific and economic soundness of each of the possible routes by which the product can be manufactured. The requirements of each process, such as raw materials, equipment, heat and electricity are listed, together with the predicted yields of products and by-products. This information is used to prepare a mass balance for the material flow, and an energy balance for the energy flow within the proposed plant. An estimate of the capital and running costs of a process emerges; this usually enables the best production route to be selected.

If the preliminary investigation establishes the existence of a viable production route, laboratory tests are carried out to gather as much information as possible about the chemistry of the process. Kinetic and equilibrium data for the reactions will be established, possible by-products will be identified, and the effects of scaling up will be investigated.

The consequences of scaling up are of critical importance in process development. Consider the simple case of a cubic stirred tank reactor 1 m wide, in which an exothermic reaction is carried out (figure 7.1). The volume of the reactor contents is 1 m³ and the surface area of the reactor through which heat may be lost is 6 m².

Now suppose a similar reactor 2 m wide is to be constructed. The volume of the reactor contents will now be 2 m × 2 m × 2 m = 8 m³, with a surface area of 24 m². Scale-up has increased the volume of the reaction mixture producing

heat by a factor of eight. However, the surface area of the reactor through which this heat can escape has only increased by a factor of four. Clearly, the scaled-up reactor will operate at a higher temperature and, since this will increase the rate of reaction and hence the rate of heat evolution, a temperature 'runaway' becomes a real possibility.

A small item of equipment may operate in a satisfactory manner. The effect of doubling its size may be disastrous unless the consequences of scaling up are anticipated and compensated for. How would you solve the problem in the above example?

If a process still appears viable after laboratory tests, the next step is generally the construction and running of a small-scale pilot plant. Proceeding to the pilot plant stage involves a considerable increase in expenditure on the project. This important decision is often taken by a project committee formed from representatives of all the company departments concerned. The pilot plant is operated on a continuous basis, and usually gives much valuable information on the effects of scale-up, engineering design of equipment, materials of construction and corrosion problems. The small amounts of material produced may be used by the sales department for a preliminary market evaluation of the product.

The information gathered during pilot plant operation enables a pictorial flowsheet to be drawn up for the full-scale plant. This shows the major items of the plant, and gives the principal technical information from which detailed engineering drawings are prepared and capital costs are estimated.

The pictorial flowsheet also enables an estimate to be made of the day-to-day running costs of the plant, including consumption of steam, electricity, and water, maintenance costs, cost of labour, and so on. The sum of the capital and running costs gives the amount of money needed to make the product.

Considerable thought must be given to the materials of construction. Excessive corrosion causes the plant to wear out rapidly and may contaminate or discolour the product. The uses and limitations of some common fabrication materials are given on the next page.

A predicted value of sales is made by the sales department and this, minus the cost of making and marketing the product, represents the potential profit. If the project proves to be a borderline case, the flowsheet can be used to identify the main items of cost, and further work can be concentrated on trying to reduce these.

Ultimately, the decision whether or not to build the plant is made by the company directors who sift the evidence for and against a particular project. They obtain this evidence firstly from the various departments within the company, secondly from their inside information concerning the company's financial position, and thirdly from their knowledge of industry in general, developments in world trade, and political and economic trends at home.

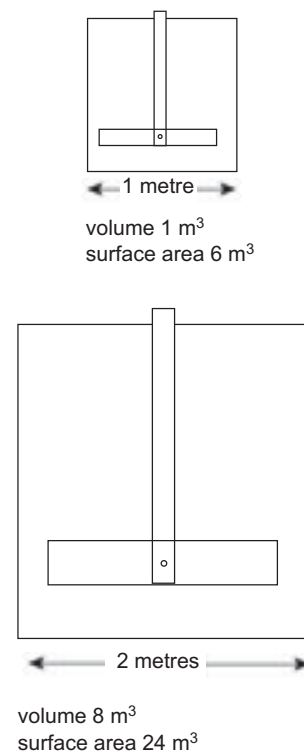


Figure 7.1

Uses and limitations of some common fabrication materials

Material	Advantages	Disadvantages
Mild steel	<p>cheap</p> <p>good mechanical strength</p> <p>easily fabricated</p> <p>resistant to most organic liquids and dilute alkalis</p> <p>widely used for most general purpose construction</p>	<p>readily corroded by dilute acids and moisture in atmosphere</p>
Stainless steel	<p>good corrosion resistance under oxidising conditions</p> <p>withstands nitric and organic acids</p>	<p>several times more expensive than mild steel;</p> <p>corroded by acids under reducing conditions, and by solutions containing chloride ions</p>
Aluminium	<p>significantly lighter than steel</p> <p>easily fabricated</p> <p>good corrosion resistance to organic acids, nitric acid, and nitrates</p>	<p>relatively expensive</p> <p>corroded by alkalis and halogen acids</p>
Copper	<p>easily fabricated</p> <p>resistant to acids and alkalis</p>	<p>very expensive</p> <p>corroded by ammonia and amines</p> <p>may discolour certain products</p>
Glass	<p>relatively cheap</p> <p>transparent</p> <p>resists corrosion by almost all chemicals including bromine</p> <p>may be used to line vessels and pipes</p>	<p>susceptible to mechanical and thermal shock</p> <p>corroded by hydrofluoric acid</p>
Synthetic polymers	<p>very light</p> <p>good resistance to corrosion by inorganic chemicals</p> <p>may be used to line steel vessels</p>	<p>may soften and melt at moderate temperatures</p> <p>often corroded by organic chemicals</p>

7.2 Building a plant

A decision to go ahead is made. The building programme is planned in great detail so that items of equipment are available when required, and costly delays are avoided. It is usual to prepare a schedule for each section of the plant, showing the times of ordering, the expected delivery date, and the dates when erection will be started and completed. This enables the whole work to be coordinated. Progress is constantly monitored, and any delays minimized by the rescheduling of other operations. The work must proceed as smoothly as possible: first the site work and drainage, then the foundations, then the steelwork, buildings, vessels, machines, and pipes, and finally the motors and instruments. A few months' delay in production may cost hundreds of thousands of pounds – while a plant is under construction, interest charges are paid on the capital investment without any return being made.

Once construction is complete, the plant is ready for 'start-up'. Whenever possible, items of equipment are first run under minimum load conditions. The pumps and tanks are tested with water, and the blowers and fans are tested with air. This is to ensure that the plant is correctly assembled and will run as intended when the chemical materials, which may be poisonous or corrosive, are introduced.

Serious problems during start-up are not uncommon. There are few operations which are not affected in one way or another by scaling up, and it may take weeks or even months to commission a complex new plant.

Even when the plant is running continuously it will be kept under constant review, both to improve the efficiency of the process, and to make any product modification necessary to suit customer requirements.

Meanwhile, research continues to develop new products and processes in order to ensure the future survival of the company.

7.3 Mass balance

The preparation of mass and energy balances is an essential feature of almost all chemical engineering design where flows of material are involved.

Mass balances are based on the principle that during physical and chemical changes matter is neither created nor destroyed.

Some operations carried out within the system do not involve a chemical reaction. They are of a physical nature only, such as distillation or solvent extraction. A simple mass balance can be drawn up for each of the components separately.

An example of this is provided by the final separation stage in a plant designed to convert butan-2-ol into butanone. Figure 7.3 shows the flow diagram and its associated mass balance. The mass balance is incomplete, but the missing figures may easily be filled in by applying the ideas described above.

There is no reaction in this part of the process, so the mass of butanone remains constant, as does the mass of butan-2-ol.

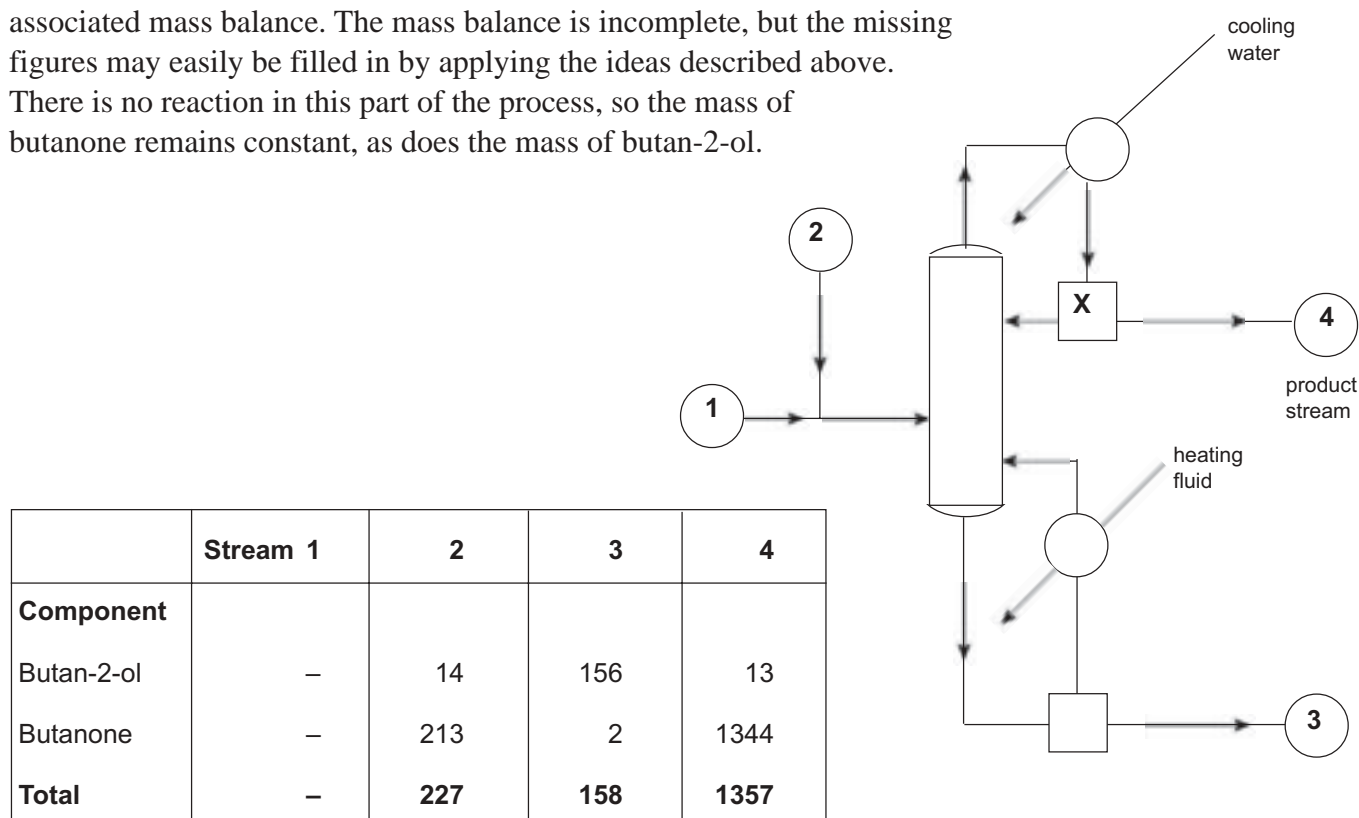


Figure 7.3

Butan-2-ol: all the butan-2-ol which goes in via streams 1 and 2 must come out in streams 3 and 4. Streams 3 and 4 together have a combined flow rate of $156 + 13 = 169 \text{ kg hr}^{-1}$, so stream 1 must have a flow rate of $169 - 14 = 155 \text{ kg hr}^{-1}$.

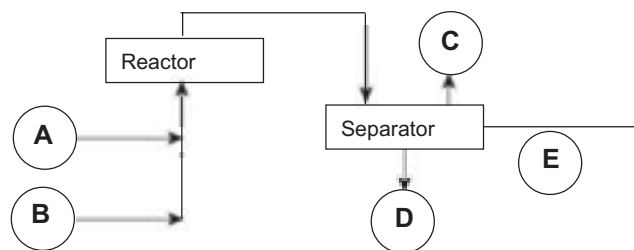
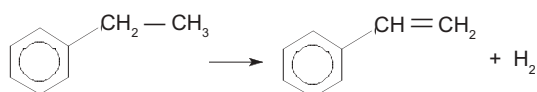
Butanone: streams 3 and 4 have a combined flow rate of $2 + 1344 = 1346 \text{ kg hr}^{-1}$.

The butanone in stream 1 must flow at $1346 - 213 = 1133 \text{ kg hr}^{-1}$.

The total flow rate in stream 1 is $155 + 1133 = 1288 \text{ kg hr}^{-1}$.

If there is a reaction the mass balance for the whole system can still be applied since there will still be no change in the *total* mass of material.

Consider, for example, part of a plant for making phenylethene. The main reaction involved is represented by the equation:



There are, however, side-reactions resulting in other products such as methane and methylbenzene.

All the figures in the table below are flow rates in kg hr^{-1} .

	A	B	C	D	E
Water	156780			156780	
Ethane			402		
Hydrogen			?		
Methane			300		
Benzene					1045
Ethylbenzene		71020			38848
Methylbenzene					1726
Phenylethene					27872
Tars					355
Temperature / °C	720	530	105	95	95

Flow rates in kg per hour.

The question is: how much hydrogen will there be in stream C?

There is obviously a reaction in this sequence, but it everything which goes in via stream B comes out via streams C and E. (We can ignore A and D for this purpose, because these evidently contain water for a heat exchanger.)

So the hydrogen stream flow rate is given by

$$71020 - 402 - 300 - 1045 - 38848 - 1726 - 27872 - 355 = 472 \text{ kg hr}^{-1}.$$

The temperatures of the various streams are also given in the table. Comparison of stream A with stream D suggests that the butan-2-ol must be heated to a suitable temperature since the temperature of the water in the heat exchanger goes down. The temperature of 720°C for stream A suggests that the water is in the form of steam as it goes into the heat exchanger.

7.4 Energy balances

Mass balances provide an accounting system for the flow rate of material through a chemical plant. Energy balances enable chemical engineers to predict the energy transfer requirements at each stage. The high cost of energy demands great efficiency in this area, and every effort must be made to ensure that surplus energy from one section of the plant will be used elsewhere with a minimum of waste.

If there is no chemical reaction, the total energy entering the system is equal to the total energy leaving it. An energy balance for a heat exchanger is a fairly simple task to complete.

Consider a heat exchanger designed to cool 2600 kg hr⁻¹ of ethanoic anhydride, initially at 140 °C. It is common practice to calculate the heat content of a process stream relative to an arbitrary reference temperature at which the materials are said to possess zero heat content. (273 K is often used by chemical engineers.) The heat content of a stream above this temperature may be calculated using the expression:

Heat content = mass flow × specific heat capacity × temperature above datum

For example, if the specific heat capacity of ethanoic anhydride is taken as 2.0 kJ kg⁻¹ K⁻¹, then the heat content of the input stream is

$$2600 \times 2.0 \times 140 = 728\,000 \text{ kJ hr}^{-1}.$$

This ethanoic anhydride is to be cooled using river water at 15 °C, with a maximum discharge temperature of 30 °C. Suppose the optimum water flow rate through the heat exchanger is 8000 kg hr⁻¹.

Specific heat capacity of water = 4.2 kJ kg⁻¹ K⁻¹

Heat content of input cooling water = 8000 × 4.2 × 15 = 504000 kJ hr⁻¹

Heat content of output cooling water = 8000 × 4.2 × 30
= 1 008 000 kJ hr⁻¹

IN		Anhydride product cooler			OUT			
Material	Flow /kg hr ⁻¹	Temperature / °C	Heat content /kJ hr ⁻¹		Material	Flow /kg hr ⁻¹	Temperature / °C	Heat content /kJ hr ⁻¹
Cooling water	8000	15	504 000		Ethanoic anhydride	2600	?	?
Ethanoic anhydride	2600	140	728 000		Cooling water	8000	30	1 008 000
Input			1 232 000	Total	Output			1 232 000

By applying a heat balance over the heat exchanger, it is possible to calculate the exit temperature of the ethanoic anhydride.

Total heat input = total heat output
 728 000 + 504 000 = 1 008 000 + heat content of anhydride exit stream

Let the temperature of the anhydride exit stream be t °C

$$224\,000 = 2600 \times 2.0 \times t$$

$$t = 43 \text{ °C}$$

GLOSSARY

ADIABATIC. A system is adiabatic if heat energy is not allowed to pass into or out of the system.

BATCH REACTOR. Reactor in which the contents are admitted, allowed to react and then pumped out.

BERNOULLI PRINCIPLE. Energy per unit volume is constant along any streamline in a liquid

BOUNDARY LAYER. The thin streamline layer next to the pipe wall when the bulk of the liquid is in turbulent flow.

CENTRIFUGE. Separation method involving the rapid rotation of a container so that suspended solid is forced to the outer end of the container.

CHEMICAL ENGINEERING. The technology involved in the production of substances with specific uses from raw materials.

CONTINUOUS REACTOR. A reactor into which reactants are continuously fed and from which products are continuously removed.

COUNTER CURRENT FLOW. Situation in a heat exchanger where the hot and cold fluids move in opposite directions.

CSTR. Continuous stirred tank reactor. A reactor in which the reactants are continuously admitted and the products removed at the same rate. Mixing needs to be as near perfect as possible.

DESIGN EQUATION. Mathematical equation which relates time to extent of reaction

DIRECT TRANSFER. A process where there is direct contact between the heat source and the material to be heated.

DUTY. The quantity of heat to be transferred in one hour (usually) from the hotter to the cooler fluid in a heat exchanger.

ENERGY BALANCE. Statement which equates the energy entering a process to the energy leaving it, taking into account any energy

produced or absorbed by chemical reactions.

HEAT TRANSFER COEFFICIENT. A measure of the efficiency of a heat transfer process; the constant in the heat transfer equation defining the duty of a heat exchanger.

HEAVY CHEMICALS. Compounds intermediate between raw materials and final products. These are made in large quantities and each may be used in a variety of different manufacturing processes.

INDIRECT TRANSFER. A process where heat is transferred without direct contact between the heat source and the material to be heated.

ISOTHERMAL. A system is isothermal if it is maintained at constant temperature

MASS BALANCE. Statement which equates the mass of material entering a process and the mass of material leaving it.

MEAN RESIDENCE TIME. The average time which a molecule spends in a reactor.

OPTIMISATION. Economically, the most advantageous compromise between the capital cost of a plant and the cost of operating it.

ORIFICE METER. Flow-measuring device which depends on allowing the fluid through a small hole and measuring the resulting change of pressure.

PARALLEL CURRENT FLOW. Situation in a heat exchanger where the hot and cold fluids move in the same direction.

PILOT PLANT. Small scale working model of a process intended to give information about scale-up problems, engineering design, construction materials and corrosion problems.

PNEUMATIC CONVEYING. Transport of finely-divided solids in a fast-moving air stream.

PROCESS STREAM. A part of a process where materials pass from one unit operation to the next, usually along a pipe.

RAW MATERIALS. Basic substances available from the earth, air or sea which can be converted into useful materials.

RECTIFICATION SECTION. The part of a continuous distillation column above the feed point

REFLUX RATIO. The rate of reflux onto a fractionating column divided by the rate of removal of distillate from it.

RESEARCH AND DEVELOPMENT. Section of a company's operation which investigates and develops new processes and devises methods of making existing ones more efficient

REYNOLDS NUMBER. Ratio of inertial to viscous forces in a flowing fluid.

SCREW FEEDER Method of conveying solids using a rotating Archimedean screw.

SCRUBBING. Method of removing a component of a gas mixture by using a solvent sprayed down a tower whilst the gas mixture passes up.

SENSORS. Devices for measuring some property (such as flow-rate) in a specific part of a process.

SHELL AND TUBE. Popular design of heat exchanger consisting of an outer container fitted with internal baffles and an internal bundle of tubes made from a heat-conducting material.

SOLVENT EXTRACTION. Process of removing a solute from a solution by using a second solvent which is immiscible with the original one. This familiar laboratory process can be made continuous in chemical industry.

STREAMLINE FLOW. Kind of flow pattern in which a fluid behaves as if it were in layers sliding over each other.

STRIPPING SECTION. The part of a continuous distillation column below the feed point.

THEORETICAL PLATE. One of a sequence of distillation processes which make up the fractional distillation of a liquid mixture. It consists of one boiling-condensation-reboiling operation.

TUBULAR REACTOR. Reactor consisting of a length of tube, sometimes arranged in a spiral shape, in which a reaction occurs as the reactants pass along it.

TURBULENT FLOW. Kind of flow pattern containing swirling eddies. There is always a streamline layer next to the pipe wall (see boundary layer).

UNIT OPERATION. Individual operation performing a distinct function in a chemical plant. There are three main types: transport of materials, energy transfer and separation.

VACUUM FILTER. Adaptation for continuous operation of the kind of filtration under reduced pressure familiar in laboratory practice.

VARIABLE AREA METER. Flow-measuring device using a floating 'bob' in a vertical, graduated, tapered tube.

VENTURI EFFECT. Decrease in pressure caused by a constriction in a tube through which a fluid is passing.

VISCOSITY. Resistance to fluid flow caused by intermolecular forces within the fluid.

A design equation describes how the time taken for a reaction is related to the concentration of a reactant when that time has elapsed. The design equations derived here are for a first order reaction of a reactant identified as A.

Batch reactor

The rate equation for a first order reaction is

$$\frac{-d[A]}{dt} = k[A] \quad \text{where } \frac{-d[A]}{dt} \text{ is the rate of the reaction and } k \text{ is the rate constant}$$

$$\text{rearranging this } \frac{-d[A]}{[A]} = k dt$$

on integration

$$-\ln[A] = kt + C \quad \text{where } C \text{ is the constant of integration}$$

at the start of the reaction, when $[A]$ is $[A]_0$, $t = 0$

so the constant C is given by $C = -\ln[A]_0$

Substituting this in the previous equation and rearranging gives

$$kt = \ln[A]_0 - \ln[A]$$

$$\text{Rearranging again gives } t = \frac{1}{k} \cdot \ln \frac{[A]_0}{[A]}$$

Continuous stirred tank reactor

For a continuous process, the reactants are being continuously added and the reaction mixture, including the product, is being continuously removed. Flow data must therefore be incorporated in the design equation. Let the volume of the reactor be $V \text{ dm}^3$ and the volume flow rate through the reactor be $u \text{ dm}^3 \text{ min}^{-1}$. The mean residence time, τ , which is the equivalent of the time, t , used for a batch reactor, is given by

$$\tau = V/u \text{ min}$$

If the concentration of A entering the tank is $[A]_0$ then the number of moles of A entering the tank in time τ is $[A]_0 u \tau$

If the concentration of A leaving the reactor is $[A]$ then the number of moles of A leaving the tank in time τ is $[A] u \tau$

The number of moles of A reacting in time τ is $rV\tau$ where r is the rate of the reaction.

Applying a mole balance,

Moles entering = moles reacting + moles leaving

$$\text{So } [A]_0 u \tau = rV\tau + [A] u \tau$$

Dividing through this equation by $u \tau$ and rearranging gives

$$V/u = \tau = \frac{[A]_0 - [A]}{r}$$

For a first order reaction $r = k[A]$

$$\text{So } V/u = \tau = \frac{[A]_0 - [A]}{k[A]}$$