8 Reactors and reactions in food processing

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Introduction

Chemical reactions are vital in food processing; for example, the development of flavour and the death of microbes during heating are all the result of reactions. To be able to design process plant efficiently, rather than by trial-and-error, it is necessary to be able to quantify the rates of reactions occurring in a food, and the ways in which they change with process variables such as temperature. The food industry tends to rely on different types of rate equation than the Arrhenius-type expressions developed by chemists; the two are, however, related, and this chapter describes both expressions and the relationship between them.

In processing, reactions are carried out in some type of vessel – the reactor. Frequently in food processing, reactions occur in process units which do other jobs, such as the sterilization reactions and changes in product taste and quality which occur within a heat exchanger. To design reactors, process engineers have developed simple mathematical models of idealized systems which will be described here. The idealized form of a tubular reactor is plug flow, where all the fluid travels at the same velocity, without any mixing, so that all parts of the flow stay in the reactor for the same amount of time. The other idealized vessel is the fully stirred vessel, in which total mixing occurs. In between lies the real world, in which some degree of intermixing and flow distribution is found in real reactors. These flows can be characterized using the residence time distribution (RTD) which measures the range of times which elements of fluid spend within the system. This concept is the basis, for example, of the design of practical sterilizers. The plant must be designed so that all the material leaving it is sterile: the RTD, once measured, allows the fastest moving part of the system to be identified. The concepts of this chapter will be used to analyse more food industry problems in Chapters 9 and 10.

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8.1 Reactor types

The word **reactor** in chemical engineering terms is the name given to a vessel in which some form of chemical reaction occurs. The use of the term in the food industry is somewhat more complicated, as reactions frequently occur in equipment primarily designed for heat exchange. Hence, in practice, reactor and heat exchanger design are inevitably going to be intimately associated. This chapter is restricted to a consideration of the gross design of a vessel based on the characteristics of the reactions occurring within it. The design of systems to achieve heat transfer is discussed in Chapters 3 and 9. Reactor types can be divided into two main categories, as follows.

- In **batch reactors**, a set amount of material is processed at a given time. Reactants (starting materials) are added, left to react and are then removed: this is not a continuous process.
- In **continuous** (or **flow**) **reactors**, material flows continuously through the reactor and is converted during its stay in the reactor. Hence there is a continuous and steady flow of reactants into and products out of the reactor. The use of continuous reactors can result in diminished labour costs and simplified automatic control, and the greater constancy in conditions allows better quality control.

8.1.1 Batch reactors

Most small- to medium-scale cooking procedures are essentially performed in a batch manner, and domestic cooking in a saucepan is a good example that illustrates the operational features. A simplified diagram of a typical batch reactor used for larger-scale operations is shown in Fig. 8.1.

The main features are as follows.

- The reactor is essentially a simple vessel in which the reaction occurs.
- Contents are well mixed, normally by stirring, so the composition is (assumed to be) the same everywhere but changes with time. Reaction rates and the amounts of heat that may be added or removed from the reactor will also change with time.
- Batch reactors tend to be cheap and versatile and can be used for other conversions.
- Filling, emptying and cleaning may be expensive in labour.

8.1.2 Tubular reactors

The tubular reactor represents one extreme case of the design of a continuous reactor, the other being the continuous stirred tank reactor described in section 8.1.3. A diagram of a typical tubular reactor is shown in Fig. 8.2.

The main features are as follows.

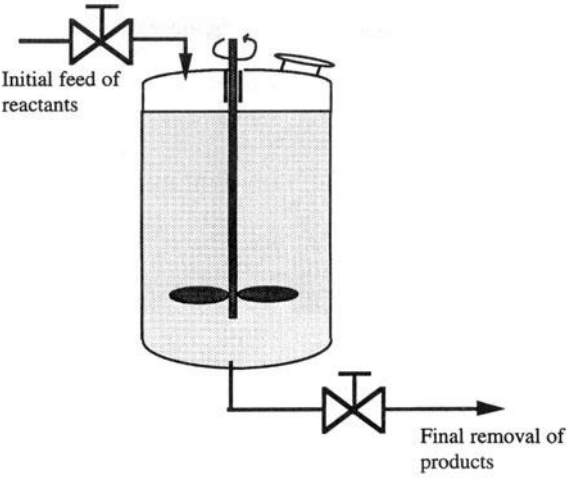

Fig. 8.1 The batch reactor.

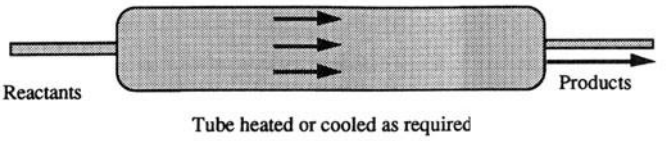

Fig. 8.2 The tubular reactor.

- The tube may be empty or packed with some form of catalyst pellets such as immobilized enzymes or immobilized metals for chemical modification of fats. If the tube contains a heterogeneous phase catalyst it is then called a **packed** (or **fixed**) **bed reactor**.
- The tube may be a single one of large diameter or a bundle of many small ones in parallel, which results in it appearing similar to a shell and tube heat exchanger, as described in Chapter 3.
- Flow through the reactor is often assumed to be plug or piston in nature: that is, there is no longitudinal (axial) mixing but there is perfect radial mixing. In this case the reactor is referred to as a **plug flow reactor** (PFR). In practice, flow may deviate significantly from idealized plug flow as a result of the design of the equipment or the properties of the material flowing through it. The nature of the actual flow through tubular reactors is described later in section 8.5.
- When the reactor is in the steady state, the local conditions (chemical composition, temperature etc.) at any point along the reactor do not vary with time, but these conditions do change along the reactor length.

- Flowrates and reactor sizes are chosen so that material resides in the reactor for an appropriate time for the reaction to proceed to the required extent. The resultant value of the Reynolds number for flow in the system will determine whether it is has a laminar or turbulent nature.
- Temperature control may be difficult, with temperature profiles building up across a radial section of the reactor if the only surface for heat transfer is the outside walls of the tube. It may be difficult to insert heating/cooling tubes within a tubular reactor.

8.1.3 Continuous stirred tank reactor (CSTR)

This type of continuous reactor is also known as a **back-mixed reactor** and represents the other extreme case of continuous reactor design. A typical diagram is shown in Fig. 8.3.

The main features are as follows.

- The tank needs to be very well mixed to prevent some material from passing too quickly through the reactor. The material emerging from the tank has the same composition as the bulk of material in the tank.
- Such reactors tend to be cheap and easy to run and a process may contain a sequence of CSTRs in series.
- Temperature control can be straightforward as cooling/steam coils can be inserted within the tank.
- The tanks are easier to clean than tubular reactors.

8.1.4 Choice of reactor type

When processing food materials, considerable attention must be given to the flow characteristics of the material in choosing the optimal reactor type.

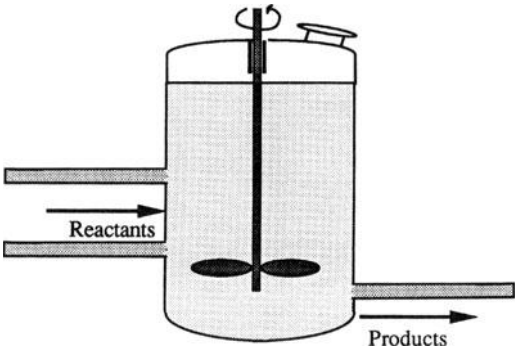

Fig. 8.3 The continuous stirred tank reactor.

The presence of complex rheologies, high viscosities and the presence of solids of different density from that of the surrounding liquid must be taken into account. For example, problems may arise if attempts are made to flow a liquid containing solids, such as a meat pie filling, through a tubular system without the chunks of meat settling out within the reactor. These problems can only be addressed for the food product of interest when its fluidic nature is known. As we shall see from what follows, a consideration of chemical reaction effects alone suggests that tubular reactors may be the preferred reactor configuration. However, such a criterion may be of minor importance compared with the problems arising from handling and pumping the material under consideration.

8.2 Physical chemistry of food reactions

In an ideal world, a prerequisite for the rational design of reactors is the availability of complete knowledge of the physical chemical characteristics of the reactions taking place. In the traditional chemical industry, this requires knowledge of the equilibrium, rate and enthalpy properties of the reactions taking place. However, reactions carried out in the food industry differ considerably from the types of reaction that form the backbone of the chemical industry, in which the identity and characteristics of the reactions are known and understood. In food processing it will almost always be necessary to make gross assumptions and simplifications about the nature of the reactions occurring in order to be able to attempt a rational design for food reactors. These simplifications are essential, as comparatively little is known about the precise physical chemical characteristics of most cooking reactions. Such studies are greatly complicated by the presence of complex reactions in which many different separate (bio)chemical reactions are taking place simultaneously, such as the multitude of reactions taking place during the heating of a food.

8.2.1 Types of reaction in the food industry

Reactions in the food industry can be segregated into a number of classes, but in many processes reactions belonging to different classes may be occurring simultaneously. Many of these reactions occur as a direct result of heating the material under consideration, but some are biologically catalysed. In addition, some reactions occur during hydration and mixing, such as the changes in structure that occur upon mixing flour with water during breadmaking. The classes of reaction include:

- sterilization reactions, in which living biological cells are killed;
- reactions in which carbohydrates, fats and proteins are modified in form as a result of thermal and other processes;

- destruction of nutrients, vitamins, enzymes and colouring compounds;
- microbial conversions (fermentations);
- enzyme-catalysed processes.

8.2.2 *Enthalpies of reaction*

In almost all reactions in the food industry it is common to assume that the amount of heat liberated or absorbed in the reaction is negligible compared with the amounts of heat needed to raise the reactants to the reaction temperature and to maintain that temperature in the presence of a variety of sources of heat loss. Such heat losses include losses from the vessel arising from conduction, convection and radiation together with the loss of water vapour during certain cooking operations and the consequent need to supply enthalpy of vaporization (latent heat) to keep liquids at their boiling point. The ability to ignore enthalpies of reaction greatly simplifies reactor analysis, but such an assumption is not possible when strongly exothermic or endothermic reactions are being considered. One example when it would be inappropriate to ignore enthalpies of reaction in food processes is in the design of biological fermentation systems. Fermenters operate at near-ambient temperatures, and heat removal has to be undertaken with only small temperature driving forces between the fermentation liquor and the cooling water. Another example occurs in breadmaking, in which the mechanical work done during the mixing process is converted into heat, which can start to cook the dough.

8.2.3 *Reaction rates*

The rates of food processes are not generally described in terms of conventional chemical kinetics, probably because the processes were first studied by biologists or biochemists rather than by chemists or engineers. A number of (rather confusing) alternative techniques have been developed instead. It is common practice in the food industry to describe the rate of a process involving some kind of reaction in terms of a parameter D, the **decimal reduction time**. Implied in this concept is the notion of some type of reaction of the form

$$\text{Reactants} \rightarrow \text{Products}$$

The decimal reduction time is the time needed for the amount of reactant to be reduced to one tenth of its original value. This time is assumed to be constant over the entire course of the reaction provided that the temperature is held constant (isothermal conditions). The value of D will, however, be a function of temperature, as described in the next section. However, it is common practice to quote D_{121}, the value of D at 121 °C, a temperature often used in canning processes. Table 8.1 contains the values of D_{121} for a

Table 8.1 Kinetic data for some reaction processes in the food industry

	D_{121} (min)	E_a (kJmol^{-1})	z (°C)
Killing of micro-organisms			
C. botulinum	0.1–0.3	265–340	8–12
B. subtilis	0.4–0.8	230–400	6.8–13
B. cereus	0.038–0.06	305	10
C. thermosaccharolyticum	3–22	1340–1780	2–10
C. sporogenes	0.15–2.6	230	9–13
Cooking value (overall quality estimation)			
Peas	12.5	80–95	17–28
Whole corn	2.4	65–80	36
Broccoli	4.4	55	44
Carrots	1.4	160	15
Green beans	1.4	90–170	14–29
Potatoes	1.2	115	21
Chemical changes			
Non-enzymatic browning	0.4–40	100–250	17–39
Hydrolysis	0.4	60–110	
Fat oxidation	–	40–100	
Denaturation of proteins	5	250–800	5–10
Vitamin destruction			
In general	100–1000	80–125	20–30
Thiamine	38–380	90–125	20–30
Ascorbic acid	245	65–160	51
Pantothenic acid	250–6400	84–160	31
Riboflavin	2800	100	28
Folic acid	2800	70	37
Enzyme inactivation			
In general	1–10	40–125	8
Peroxidase	2–3	67–85	26–37
Colour deterioration			
Chlorophyll (spinach)	14–350	30–90	38–80
Carotenoids (paprika)	0.038	140	19
Betamin (beetroot)	48	46	59

Source: adapted from Hallström *et al.* (1988)

number of different types of reaction of interest in the food industry. However, this approach to the description of reaction rates is based on empirical observation and is not necessarily consistent with a more rigourous chemical analysis of the underlying events.

The standard chemical approach to the description of reaction rates involves the concepts of **orders of reaction** and **rate constants**. The rate of reaction is expressed in terms of amount of reactant (j) converted (kilograms, moles, cell numbers etc.) per unit volume of the reactor per time, r_j. Hence for the reaction

$$aA + bB \rightarrow eE + fF \tag{8.1}$$

the rate of reaction per unit volume can be written as

$$\frac{1}{e}r_E = \frac{1}{f}r_F = -\frac{1}{a}r_A = -\frac{1}{b}r_B \tag{8.2}$$

We shall use the convention that a positive rate of reaction implies that the amount of the particular substance is increasing. Hence if the rate of reaction is being described in terms of loss of the reactant, the sign of the reaction rate will be negative. Note that the rate of reaction has not been written as dc_j/dt, as only in a batch reactor of constant volume is this term equal to the rate of reaction per unit volume. In a continuous reactor, the addition and removal of material will also affect the rate of change in the concentration of component j in addition to changes occurring as a result of reaction. Indeed, in a continuous reactor in the steady state,

$$\frac{dc_j}{dt} = 0 \qquad \text{while} \qquad r_j \neq 0 \tag{8.3}$$

as a result of the chemical reactions involving component j.

It is assumed that the rate of reaction is some function of the concentrations of the reactants (and sometimes the products). These have to be determined experimentally, but for the above reaction it may be found that

$$r_A = f\left(c_A, c_B, c_E, c_F, T, \text{pH etc.}\right) \tag{8.4}$$

In simple cases, the reaction can be classified into orders. If it is found for example that

$$-r_A = k(T)c_A^{\alpha}c_B^{\beta} \tag{8.5}$$

where $k(T)$ is a rate constant that is a function of temperature, and α and β are integers, then the reaction is said to be of $(\alpha+\beta)$th order. Hence

$-r_A = k_0$ would be a zeroth-order reaction
$-r_A = k_1c_A$ would be a first-order reaction
$-r_A = k_2c_Ac_B$ would be a second-order reaction.

But if, say,

$$-r_A = \frac{k'c_Ac_B^{1.4}}{1+k''c_A} \tag{8.6}$$

the reaction would be said to be of complex order. Reactions of complex order are produced when the reaction is a result of a series of consecutive steps.

Implicit in the above consideration is that there is knowledge of the chemical events occurring in the reaction and the factors that influence the rate of reaction. Such detailed knowledge is extremely unlikely in the food industry. However, it is often possible to reconcile the different approaches

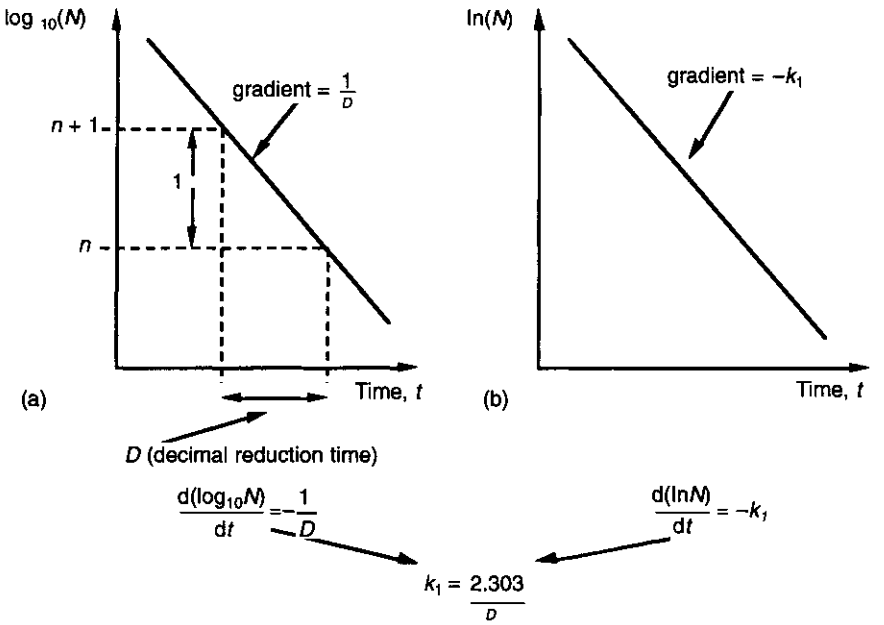

Fig. 8.4 Relationship between food and chemical approaches to reaction rates: (a) food industry reaction; (b) first-order chemical reaction.

to reaction rates used in the food and chemical industries in a straightforward manner. The ability to describe a food reaction in terms of a decimal reduction time implies, as is shown in Fig. 8.4, that the reaction is consistent with an irreversible first-order chemical reaction.

As is shown in Fig. 8.4, there is a simple relationship between D and the apparent first-order rate constant k_1, which can be obtained from a knowledge of D by using the expression

$$k_1 = \frac{2.303}{D} \tag{8.7}$$

The fact that reactions in the food industry are generally regarded as first-order leads to a conceptual problem, in that a first-order reaction implies that it is impossible to obtain complete sterilization. The time required for thermal sterilization of a food is calculated in terms of the most thermally resistant pathogen, commonly *C. botulinum*. If the concentration of this pathogen is reduced to the required level, all others will have been killed to a greater extent. Rather than total sterility, the concept of **commercial sterility** based on probabilities is used industrially; the aim of thermal

processing is to reduce the number of organisms by a very large amount (commonly by a factor of 10^{12}: the **12D cook**). This mathematical treatment theoretically implies that, in the processing of cans or other batch containers, the vast majority of units are sterile, but that there will be a very small but finite probability that a can may still contain a live organism after treatment. In practice, the presence of contaminants in food can always be traced to incorrect processing, rather than to a statistical fluke rendering the process unsuccessful.

In addition to the use of the concept of decimal reduction time, the rate of death of bacteria is often described in terms of the **thermal death time (TDT)**: the time required at a certain temperature to kill a stated number of organisms. Thermal death times are difficult to measure; they can be most easily estimated by the growth–no-growth method described by Frazier and Westhoff (1988), in which the time needed to reduce the level of organisms so that they can no longer be detected in a standard growth test is taken as the appropriate thermal death time. Thermal death time is also a function of temperature, and as the temperature increases the rate of sterilization increases.

Another term that is used is the **F-value**, which is defined as the time needed to carry out the required sterilization procedure at the common canning temperature (T_{ref}) of 121 °C. An F-value of 3 min is taken as acceptable industrially, although process design values of at least 6 min are used in practice.

8.2.4 Variation of reaction rates with temperature

It is also a well-known fact that reaction rates increase with increasing temperature. It is found that plots of $\log_{10}(D)$ or $\log_{10}(\text{TDT})$ against temperature are straight lines, and it is common to describe the variation of D (or the thermal death time) with temperature in terms of a parameter z, where z is the temperature increase that results in D being reduced to one tenth of its original value. z is also the increase in temperature necessary to achieve the same extent of reaction in one tenth of the time: that is, to reduce the TDT by a factor of 10. z is assumed to be constant over a range of temperatures close to that at which it was determined. Some values of z are shown in Table 8.1, and a value of 10 °C (that is, the value appropriate to the killing of *C. botulinum*) is often assumed for sterilization process.

The value of z can be used to estimate the effect of changing temperature on the processing time, using the equation

$$\left(\text{Time required at } T\right) = \frac{\left(\text{Time required at } T_{ref}\right)}{10^{(T-T_{ref})/z}} \tag{8.8}$$

Equation (8.8) can also be used to calculate the time at some different constant temperature that still results in the required F-value. For example, a 12D cook for *C. botulinum* ($z = 10\,°C$) requires 2.52 min at 121.1 °C: that is, it takes 2.52 min to reduce the concentration of spores to 1 in 10^{12}. This is the basis for an F-value of 3 min being commonly acceptable in industry. At 130 °C, the same F-value would be achieved by processing for

$$\frac{2.52}{10^{(130-121.1)/10}} = 0.324\,\text{min}$$

If a process is isothermal throughout its time course, equation (8.8) is adequate. However, some sterilization will occur while heating up and cooling down are occurring, and the whole temperature–time history of the food must be considered in calculating the actual degree of sterilization achieved. If the temperature–time curve for the food is known, a time known as the **integrated lethality**, defined as

$$F = \int_{\text{IN}}^{\text{OUT}} 10^{(T-T^{\text{F}}_{\text{ref}})/z_{\text{F}}}\,\text{d}t \tag{8.9}$$

can be calculated. For sterilization to be deemed successful, this time must be greater than or equal to the required F-value at temperature T_{ref}. This approach is widely used in the food industry but the major problems with it are that (a) it is algebraically complex, and (b) it is fundamentally wrong. It is argued below that sterilization probably follows Arrhenius kinetics, and the above equation is an approximation to true behaviour, but its use can underestimate the F-value achieved by up to 50% for predictions of high-temperature processes. The use of conventional chemical kinetics is easier and more accurate at high temperatures.

Analogous expressions have been written to express the degree of cooking (rather than sterilization) that a material has received. Cooking is a difficult quality to measure experimentally, but approaches that have been used as indicators of the quality of cooking include measurement of the deactivation of enzymes, the loss of vitamins and the change in the texture of the food. Thus it is possible to define the **C-value** of a process:

$$C = \int_{\text{IN}}^{\text{OUT}} 10^{(T-T_{\text{ref}})/z}\,\text{d}t \tag{8.10}$$

where again T_{ref} is the reference temperature at which the slope of the 'cooking' rate curve is z, and T is the temperature of the material being processed as a function of time t. Again, this approach approximates the true conditions.

The normal chemical approach to the variation of reaction rate constants with temperature based on kinetic theory involves the use of an **Arrhenius equation** of the form

$$k = Ae^{-E_a/RT} \tag{8.11}$$

where A is called a pre-exponential factor and E_a is the activation energy of the reaction. The temperature T must be given in kelvin, and R is the gas constant (use $R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$ when E_a is measured in $\mathrm{J\,mol^{-1}}$). This expression, unlike that for the F-value, has a sound theoretical rather than empirical basis.

At temperatures close to the value of T_{ref} at which D and z are measured (T_{ref} is usually 121.1 °C, 394.3 K in the food industry), it is possible to estimate a value of E_a from a knowledge of z using

$$E_a = \frac{2.303RT_{ref}^2}{z} \tag{8.12}$$

However, as is shown in Fig. 8.5, the form of the Arrhenius expression is not entirely consistent with a description of the system with z being a parameter that is independent of temperature.

The fact that errors in the prediction of sterilization times may occur by

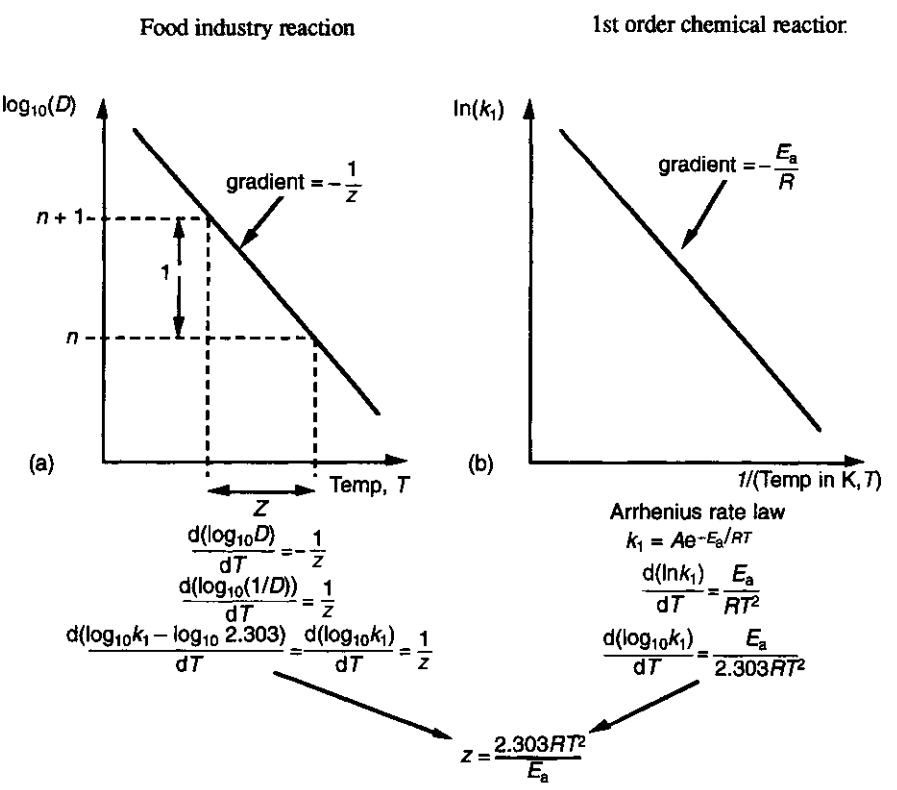

Fig. 8.5 Relationship between food and chemical approaches to the variation of reaction rates with temperature: (a) food industry reaction; (b) first-order chemical reaction.

using the z method to estimate reaction rates at temperatures far removed from T_{ref} has already been mentioned. It is suggested that the description of the variation of reaction rates with temperature by an Arrhenius expression is a more accurate approach. Table 8.1 shows a list of typical reactions occurring during food processing and values of the characteristic parameters D and z together with the derived 'chemical' rate parameter E_a. Values of k_1 appropriate to T_{ref} can be obtained from the values of D by using equation (8.7).

The design of food sterilization plant reduces, in an engineering sense, to an optimization problem: how to maximize sterilization with minimal loss in product quality. Temperature and time are the process variables, and activation energy values can be used for calculation. It can be seen from Table 8.1 that the activation energy for death of *C. botulinum* is about $300\,kJ\,mol^{-1}$ whereas that for the loss of quality in foods is in the region of $125\,kJ\,mol^{-1}$. Comparison of the rates of the two processes at 120 °C and 140 °C shows that sterilization reactions proceed about 15 times faster than loss of quality reactions at the higher temperature. This forms the basis for the design of new thermal processes, to sterilize at high temperatures and short times. This is discussed further in Chapter 9.

8.2.5 Other physical chemistry parameters

The types of reaction that occur in the food industry enable us to ignore certain other concepts that may have to be considered in the analysis of conventional chemical reactors. These factors include a consideration of equilibrium constants. Many reactions may only proceed part of the way to completion as a result of equilibrium effects. The equilibrium position of the reaction will also be a function of temperature. However, it appears that most reactions that occur in the food industry approach completion after a sufficient time and a consideration of equilibrium constants is thus inappropriate. An exception is a reaction such as carbonation, in which the solubility of carbon dioxide will depend on equilibrium effects. Certain enzyme-catalysed reactions (such as the isomerization of glucose to fructose) will also not proceed to completion, as a result of equilibrium effects.

8.2.6 Biological reactions

Rate expressions describing the reactions that occur during fermentation or enzymic processes are more complicated than those described to date, as they are not accurately described by quasi-first-order reaction rates.

Fermentations. In the most simple analysis, the rate of increase r_x in cell mass x depends on the concentration c_S of a key (growth-limiting) nutrient S in the following manner:

$$r_x = \frac{\mu_m c_S}{K_S + c_S} x \tag{8.13}$$

where K_S and μ_m are characteristic parameters for the growth of the organism on that substrate. This is the **Monod equation**. Similarly, the rate of utilization of that growth-limiting nutrient is given by

$$-r_S = \frac{\mu_m c_S}{(K_S + c_S)}\left(c_{S0} - c_S + \frac{x_0}{Y_{x/S}}\right) \tag{8.14}$$

where $Y_{x/S}$ is the growth yield coefficient on that substrate, defined as the mass of cells formed per mass of the growth-limiting nutrient consumed, and c_{S0} and x_0 are the initial concentrations of cell mass and growth-limiting nutrient respectively. However, even in brewing and other microbial fermentations used in the food industry the relationship between 'product' formation and cell production or substrate utilization is often highly complex. In these circumstances, it is not possible to describe the rates of reaction by expressions as simple as those given above. A full analysis of more accurate expressions describing the rates of fermentation reactions is given in Bailey and Ollis (1986).

Enzyme-catalysed reactions. For reactions carried out using enzymes, the simplest form of rate expression for the conversion of substrate S to product is given by

$$-r_S = \frac{V_m c_S}{K_m + c_S} \tag{8.15}$$

where V_m and K_m are characteristic parameters for enzyme catalysis under the prevailing conditions. However, if an immobilized enzyme is used where the enzyme has been immobilized to a support material, additional considerations arising from decreased rates of mass transfer to the enzymic sites may also need to be included (Bailey and Ollis, 1986).

8.3 Analysis of isothermal 'ideal' reactor systems

Our initial approach to reactor analysis will involve the assumption that the temperature is constant throughout the reactor and does not vary with time in a batch reactor or with position in a continuous reactor. This 'isothermal' assumption permits us to ignore any variations of reaction rate that will occur as a result of temperature variations in the reactor, and hence the reaction rate-constant is indeed constant throughout the reaction. The assumption of isothermal operation will be inappropriate in a wide variety of cases as reactions will inevitably start to occur in heat exchangers as process streams are being heated to the final reaction temperature. In addition, a

piece of process equipment may be specifically designed to ensure a varying temperature profile during passage of material through it (for example, a milk sterilizer/pasteurizer). However, the assumption of isothermal operation will allow the principles of reactor operation to be outlined without excessive mathematical complexity obscuring the basic concepts.

8.3.1 Concept of fractional conversion

Rather than describing extents of reaction in terms of the absolute amount of product formed or reactant utilized, it is common to use the dimensionless quantity **fractional conversion** X, defined for a component A by

$$X_A = \frac{n_{A0} - n_A}{n_{A0}} \tag{8.16}$$

where n_{A0} is the amount of reactant A at the start of the reaction and n_A is the amount left after an extent of reaction X_A has occurred. The amount of A can be expressed in any units (kilograms, moles etc.), but in this treatment the **mole** will be used as the basic unit of the amount of particular component to simplify the analysis. Obviously, the use of molar units is not well suited to most foodstuffs, where the molecular nature of the material is not well defined. Simple rearrangement of equation (8.16) yields

$$n_A = n_{A0}(1 - X_A) \tag{8.17}$$

In summary, therefore, $X_A = 0$ at the start of reaction and increases to a value of 1 when the reaction is complete.

8.3.2 Batch reactors

The following analysis of the conversion achieved in various types of reactor will be undertaken by performing a material balance on the reactor using the principles described in Chapter 2. Consider a situation in a batch reactor where a reactant A reacts irreversibly to yield products, and the reaction proceeds at a rate $-r_A$. In a batch reactor, the rates of reaction and the concentrations of reactants and products are functions of time. The simple batch reactor is shown in Fig. 8.6. A basic material balance over the system in a small time interval dt yields

Amount of component coming into the reactor
+ Amount of component made by reaction
= Amount leaving the reactor
+ Amount accumulated within the reactor

In the case of a batch reactor operating at constant volume V_r, there is no material entering or leaving the reactor. Hence:

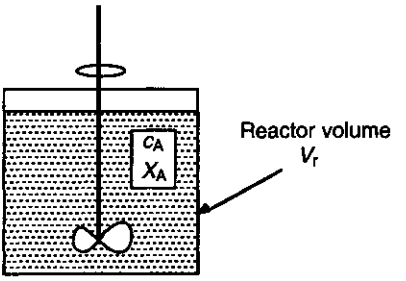

Fig. 8.6 Analysis of a batch reactor.

$$0 + V_r r_A dt = 0 + dn_A \tag{8.18}$$

The rate of conversion of reactant A to products is given by

$$r_A = \frac{1}{V_r}\frac{dn_A}{dt} = \frac{1}{V_r}\frac{d\left(n_{A0}\left(1 - X_A\right)\right)}{dt}$$
$$= -\frac{n_{A0}}{V_r}\frac{dX_A}{dt} = -c_{A0}\frac{dX_A}{dt} \tag{8.19}$$

and

$$\frac{dX_A}{dt} = \frac{-r_A}{c_{A0}} \tag{8.20}$$

This expression can then be integrated to yield the way that the extent of reaction varies with time once the rate expression r_A is known.

We have already stated that most reactions in food processing can be described in terms of pseudo-first-order chemical kinetics. Hence, for a first-order reaction where

$$r_A = -k_1 c_A = -k_1 c_{A0}\left(1 - X_A\right) \tag{8.21}$$

by combining equations (8.20) and (8.21) we find that

$$\frac{dX_A}{dt} = \frac{k_1 c_{A0}\left(1 - X_A\right)}{c_{A0}} = k_1\left(1 - X_A\right) \tag{8.22}$$

Integration of this expression (using boundary conditions that assume that $X_A = 0$ at the start of the reaction ($t = 0$) and rises to a value X_A at time t) gives

$$\int_0^{X_A} \frac{dX_A}{\left(1 - X_A\right)} = \int_0^t k_1 dt \tag{8.23}$$

$$\ln\left(1 - X_A\right) = -k_1 t \tag{8.24}$$

which on rearrangement yields

$$X_A = 1 - e^{-k_1 t} \tag{8.25}$$

Hence the fractional conversion achieved in a first-order batch reaction approaches the value of 1 asymptotically, as described by equation (8.25). The variation of extent of reaction with time as described by this expression can be seen in Fig. 8.7.

Integration of the basic equation (equation (8.20)) can be repeated in a similar manner for reactions of other orders.

EXAMPLE 8.1

A batch process is being used for cooking a food product, but the process also causes undesired breakdown of vitamin C. At present the process is carried out at 121 °C for 20 min in order to achieve satisfactory cooking. What percentage of vitamin C is destroyed in the current process, if the values of D_{121} *(min) for the cooking value and for vitamin C destruction are 12 min and 245 min respectively?*

We shall work using a pseudo-first-order rate expression. Equation (8.4) gives:

$$k = \frac{2.303}{D}$$

Hence for cooking at 121 °C:

$$k_{c121} = \frac{2.303}{12 \times 60} = 3.2 \times 10^{-3}\ s^{-1}$$

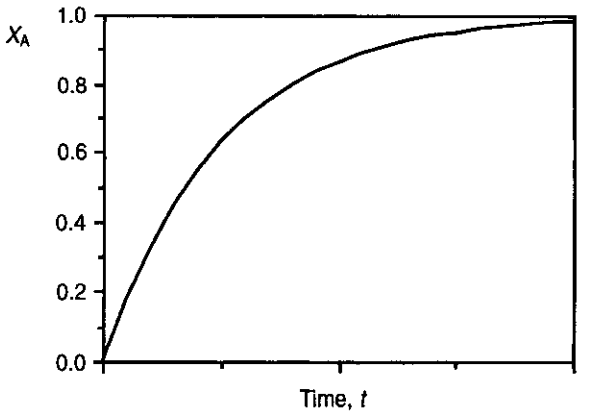

Fig. 8.7 Variation of extent of reaction with time in a first-order batch reaction.

and for vitamin C destruction at 121 °C:

$$k_{d121} = \frac{2.303}{245 \times 60} = 1.57 \times 10^{-4}\ s^{-1}$$

Equation (8.19) gives:

$$(1 - X_{c121}) = e^{-k_{c121} t_{121}} = \exp(-3.2 \times 10^{-3} \times 20 \times 60) = 0.0215$$

and

$$(1 - X_{d121}) = e^{-k_{d121} t_{121}} = \exp(-1.57 \times 10^{-4} \times 20 \times 60) = 0.828$$

Hence percentage destruction of vitamin C

$$= 100 \times (1 - 0.828) = 17.2\%$$

EXAMPLE 8.2

A modification of the process described in Example 8.1 is being considered. It is proposed to improve the process with less destruction of vitamin C by reducing the cooking time as a result of increasing the temperature to 130 °C. It is known that the values of z for the cooking process and the destruction of vitamin C are 21 °C and 51 °C respectively. What is the new cooking time and what effect do the changes have on the percentage destruction of vitamin C?

We need to estimate the values of k_c and k_d at the new temperature of 130 °C. The Arrhenius equation tells us that $k_T = Ae^{-E_a/RT}$ and $k_{T_{ref}} = Ae^{-E_a/RT_{ref}}$ Dividing these two expressions by each other, we get:

$$k_T = k_{T_{ref}} \frac{e^{-E/RT}}{e^{-E/RT_{ref}}} = k_{T_{ref}} \frac{\exp(-2.303 T_{ref}^2 / Tz)}{\exp(-2.303 T_{ref}/z)}$$

because equation (8.6) gives:

$$\rightarrow E_a = \frac{2.303 R T_{ref}^2}{z}$$

Hence

$$k_{c130} = 3.2 \times 10^{-3} \frac{\exp[(-2.303 \times 394^2)/(403 \times 21)]}{\exp(-2.303 \times 394/21)} = 8.4 \times 10^{-3}\ s^{-1}$$

$$k_{d130} = 1.57 \times 10^{-4} \frac{\exp[(-2.303 \times 394^2)/(403 \times 51)]}{\exp(-2.303 \times 394/51)} = 2.34 \times 10^{-4}\ s^{-1}$$

To calculate the new cooking time, equation (8.18) gives:

$$t_{c130} = \frac{-\ln(1-X_{c130})}{k_{c130}}$$

Assuming that the same extent of cooking reaction is achieved in each case, then

$$(1-X_{c130}) = (1-X_{c121}) = 0.0215$$

i.e. the value in Example 3.1. Therefore

$$t_{c130} = \frac{-\ln(0.0215)}{8.4\times10^{-3}} = 457\,\text{s} \equiv 7.6\,\text{min}$$

that is, the cooking time significantly reduced from the previous value of 20 min at 121 °C.

To work out the extent of vitamin C reduction at the new temperature, equation (3.19) gives:

$$(1-X_{c130}) = e^{-k_{c130}t_{130}} = \exp(-2.34\times10^{-4}\times457) = 0.899$$

Therefore percentage destruction of vitamin C $= 100\times(1-0.899) \approx 10\%$

Hence there is less destruction of vitamin C at the higher temperature.

8.3.3 Plug flow tubular reactors

In designing a tubular sterilizer, this type of reaction analysis allows the volume required to be estimated. We shall carry out an analysis of this type of flow reactor in the steady state: that is, we shall assume that local concentrations and extents of reaction have reached steady values and are not varying with time. In other words, no material accumulates or decreases within the reactor. In practice, the system will not be in a steady state during start-up (or shut-down), nor during changes in any of the operational parameters (such as flowrates and temperatures).

A balance on reactant A over the small volume element shown in Fig. 8.8 yields

$$\text{In} + \text{Made} = \text{Accumulation} + \text{Out}$$

That is,

$$F_A(1-X_A) + r_A dV_r = 0 + F_A\left[1-\left(X_A + dX_A\right)\right] \tag{8.26}$$

where F_A is the molar flow of reactant A entering the reactor. Integrating over the entire reactor (assuming no conversion at the reactor inlet) yields

$$\int_0^{X_A} F_A dX_A = \int_0^{V_r} -r_A dV_r \tag{8.27}$$

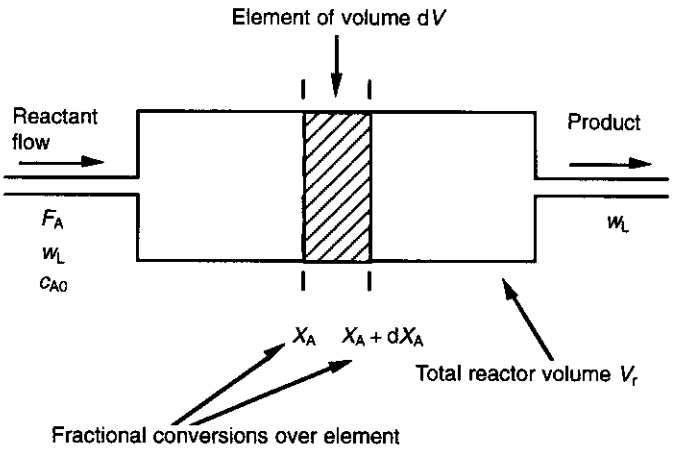

Fig. 8.8 Analysis of the plug flow reactor.

Equation (8.27) is the fundamental design equation for isothermal plug flow reactors in which reaction commences at the reactor inlet: that is, $X_A = 0$ at the inlet of the reactor.

For a flow of fluid at constant density through such a reactor at volumetric flowrate w_L:

$$F_A = w_L c_{A0} \tag{8.28}$$

That is,

$$V_r = w_L c_{A0} \int_0^{X_A} -\frac{dX_A}{r_A} \tag{8.29}$$

and for a simple first-order reaction in which $r_A = -k_1 c_A$:

$$V_r = w_L c_{A0} \int_0^{X_A} \frac{dX_A}{k_1 c_{A0}(1 - X_A)} \tag{8.30}$$

yielding

$$V_r = \frac{w_L}{k_1} \ln\left(\frac{1}{1 - X_A}\right) \tag{8.31}$$

It is convenient to introduce the concept of the **mean residence time** of material within a continuous reactor, which is simply the average length of time that material stays within the reactor as it passes through it. For a reactor devoid of catalyst particles, in which flow of material can be considered to be in plug flow, the residence time t for all material passing through the reactor is the same and is given simply by

$$t = \frac{V_r}{w_L} \tag{8.32}$$

Complications to the definition of residence time of fluid within a tubular reactor occur when the reactor contains catalyst particles. In such situations the appropriate quantity to use for the reactor volume V_r in the above expression is the void volume between the particles. Substitution of equation (8.32) into equation (8.31) followed by rearrangement yields

$$X_A = 1 - e^{-k_1 t} \tag{8.33}$$

which, on comparison with equation (8.25), shows that (as might have been anticipated intuitively) the conversion achieved in a plug flow reactor with a residence time t is the same as in a batch reactor after the reaction has proceeded for time t. Although this result has only been proved here for a first-order reaction, it is also true for any order of reaction carried out isothermally.

8.3.4 Continuous stirred tank reactors

A CSTR is a flow reactor in which a high extent of mixing of the reactor contents is achieved; this type is quite common in fermentation processes. In this analysis we shall assume 'perfect' mixing: that is, the mixing is so good that the conditions are uniform everywhere in the tank and the outlet stream also has the same properties as the contents of the tank. The situation is summarized in Fig. 8.9.

We shall again be conducting a steady-state analysis, under which circumstances the situation within the tank is not changing as a function of time. A material balance on reactant A conducted over the whole vessel requires that:

$$\text{In} + \text{Made} = \text{Out} + \text{Accumulation}$$

$$F_A + V_r r_A = F_A(1 - X_A) + 0 \tag{8.34}$$

where F_A is the molar flow of reactant A entering the stirred vessel of volume V_r. That is,

$$V_r = \frac{-X_A F_A}{r_A} \tag{8.35}$$

which is the basic design equation for a CSTR.

For our simple example involving the flow of fluid of constant density at volumetric flowrate w_L, $F_A = w_L c_{A0}$, and for a simple first-order reaction of the form $r_A = -k_1 c_A$ substitution into equation (8.35) yields

$$V_r = \frac{w_L X_A}{k_1(1 - X_A)} \tag{8.36}$$

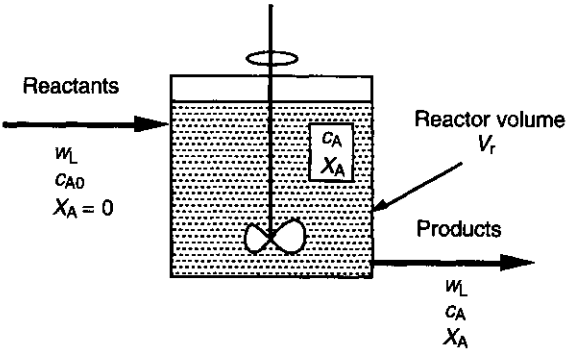

Fig. 8.9 Analysis of the continuous stirred tank reactor.

If the mean residence time of liquid in the tank is defined to be

$$t = \frac{V_r}{w_L} \tag{8.37}$$

then equation (8.36) can be rearranged to

$$X_A = \frac{k_1 t}{1 + k_1 t} \tag{8.38}$$

8.3.5 Comparison of conversions achieved in PFRs and CSTRs

Simple substitution in the above reactor conversion equations (equations (8.33) and (8.38)) enables conclusions to be drawn as to the influence of the type of continuous reactor on the conversion achieved for a given residence time. Qualitatively, the argument is based on the fact that the material within the CSTR has the same conditions as those in the outlet stream from the reactor. It can be said therefore that the CSTR 'operates at the outlet conditions from the reactor'. The concentration of reactant in the CSTR will be lower than or as low as that at any position along the length of a PFR that achieves the same overall fractional conversion. Hence the rates of reactions of simple order greater than zero will be lower in the CSTR than in the PFR, and hence longer residence times will be needed in the former to achieve the same degree of conversion. In practice this will mean that for a given volume of reactor the rate of flow through a CSTR configuration will have to be lower than for a PFR. Alternatively, to process a given stream at a constant flowrate, a larger CSTR reactor will be needed than if a PFR configuration is adopted.

The subsitution of some numbers into the design equations allows the differences between the two reactor types to be seen in a quantitative

Table 8.2 Comparison of conversions achieved in simple flow reactors

Reactor type	X_A		
	0.9	0.99	0.999
PFR	2.3	4.6	6.9
CSTR	9	99	999
Two CSTRs	4.32	18	61.2

Note: The table shows values of the dimensionless group k_1t for each circumstance.

manner. For a simple first-order reaction, equation (8.33) predicts values for the dimensionless group k_1t for a plug flow reactor for various degrees of fractional conversion. The corresponding values of this group for the same fractional conversions in a CSTR can be predicted from equation (8.38). The larger the value of this group for a given flowrate of reactant, the larger the volume of reactor needed to achieve the required conversion. Examination of Table 8.2 shows that the improvement in performance obtained by the use of a PFR rather than a CSTR gets substantially greater as the fractional conversion approaches unity: that is, as the reaction is taken to near-completion.

The following example shows that in sterilization processes, which are always characterized by the need to achieve very high extents of reaction in order to ensure sterility, the only sensible choice of continuous reactor would be one in which flow was close to plug flow. The use of reactors in which back-mixing was taking place would result in grossly impractical reactor volumes.

EXAMPLE 8.3

A continuous-flow sterilizer operating at 121 °C is being designed to treat a liquid flow of 1 l s^{-1}. Taking the value of D_{121} *for* C. botulinum *to be 0.2 min, compare the reactor volumes needed for CSTR and PFR configurations if the level of* C. botulinum *has to be reduced by six orders of magnitude. How much larger does the sterilizer have to be if the sterilization criterion is raised to 12 orders of magnitude?*

Equation (8.7) gives:

$$k = \frac{2.303}{D} = \frac{2.303}{0.2 \times 60} = 0.192\,\text{s}^{-1}$$

(a) For a 10^6 fold reduction in the level of *C. botulinum*:

$$X = 1 - 10^{-6}, \qquad \text{i.e. } (1 - X) = 10^{-6}$$

Calculation for the PFR: Equations (8.25) and (8.26) give:

$$t = \frac{1}{k} \ln\left(\frac{1}{1-X}\right) = \frac{1}{0.192} \ln(10^6) = 72\,\text{s}$$

Alternatively, we need 6 decimal reduction times and hence $t = D \times 6 = 12 \times 6 = 72\,\text{s}$. Hence the volume of the reactor, $V = w_L \times t = 10^{-3} \times 72 = 0.072\,\text{m}^3$.

Calculation for the CSTR: Equation (8.26) gives:

$$V = \frac{w_L X}{k(1-X)} = \frac{10^{-3} \times (1 - 10^{-6})}{0.192 \times 10^6} = 5208\,\text{m}^3\,!$$

(b) For a 10^{12} fold reduction in the level:

$$X = 1 - 10^{-12}, \qquad \text{i.e. } (1 - X) = 10^{-12}$$

For the PFR:

$$V = 10^{-3} \times \frac{\ln(10^{12})}{0.192} = 0.144\,\text{m}^3$$

i.e. twice as large as in part (a).

For the CSTR: $V = \dfrac{10^{-3} \times (1 - 10^{-12})}{0.192 \times 10^{-12}} = 5.2 \times 10^9\,\text{m}^3\,!!$

i.e. 10^6 times bigger than before.

Example 8.3 shows very clearly why flow sterilizers (which require very high degrees of conversion) are designed as tubular reactors in which plug flow is achieved as far as possible, and why any design based on a CSTR would be totally out of the question. The difference between the residence times needed to obtain a particular degree of conversion in each type of reactor gets yet more pronounced for reactions with orders higher than first order.

Remember that the above-stated preference for PFR-type continuous reactors is based entirely upon a consideration of the reaction kinetics. In practice, other factors associated with heat transfer, flow and mixing, together with process control and monitoring, may play important effects. In situations where a CSTR configuration has to be adopted as a result of these factors, it may be possible to achieve performance closer to that which would have been achieved by a plug flow reactor by using a sequence of CSTRs in series. For instance, a system of the same overall volume but containing two identical tanks in series can be analysed for a given fractional conversion. For a first-order reaction $k_1 t$, where t is based on the total volume of both tanks, is given by

$$k_1 t = 2\left(\sqrt{\frac{1}{1-X_A}} - 1\right) \tag{8.39}$$

The figures shown in Table 8.2 demonstrate that the dimensionless parameter characteristic of such a system would be less than for a single CSTR but is still higher than for a PFR. As the number of CSTRs is increased, the residence time gets closer to that of a PFR. In the limit, an infinite series of CSTRs would have the same residence time as a PFR.

8.4 Non-isothermal reactions

Considerable complications to the above isothermal analysis will occur when the temperature in the reactor is not constant with time or with position in the reactor. We have already stated that, in the food industry, it is likely that non-isothermal effects arise mainly from heat transfer processes rather than as a result of enthalpic processes associated with the reaction itself. However, in fermentations enthalpic processes may be significant, depending on the rate and scale of the biological reactions. To perform basic reactor analysis under non-isothermal conditions, knowledge is needed of the temperature as a function of time and position in the reactor so that a reaction rate constant appropriate to that temperature can be calculated from the Arrhenius equation (equation (8.11)). Values of the local temperature can be obtained by performing a heat balance on the system, and for reactions with negligible enthalpic effects such a heat balance with be independent of the extent of the reaction. When enthalpic effects are important, the heat balance itself will depend on the extent of reaction, leading to a coupling of the equations describing heat balance and extent of reaction.

We can discuss qualitatively an example for a simple heat exchanger in which a reaction occurs to material within the tubes. An expression showing the variation of temperature with position along a simple shell and tube heat exchanger can be derived, as has been shown in Chapter 3. This expression can be manipulated to yield the temperature at any point within the 'reactor', and an expression for the appropriate value of the local rate constant can be obtained from the Arrhenius equation (equation (8.11)) provided the activation energy of the reaction is known. Knowledge of the local rate constant enables an expression for the local value of the rate of reaction, r_A, to be constructed. Assuming that material within the tubes of the heat exchanger behaves as if it were in a plug flow reactor, equation (8.27) can now be used to describe the variation of extent of reaction with position in the heat exchanger. Integration of this expression along the length of the heat exchanger will yield the overall fractional conversion that

will be achieved. In practice, integration of the basic design equations as functions of time or position may be complicated and may require the use of numerical methods. Under these circumstances it is not possible to derive simple analytical expressions showing the variation of the extent of reaction as a function of the residence time in the reactor.

In the non-steady state regime that occurs in a batch reactor, knowledge will be needed of the rates of heat transfer to the tank in order to predict the variation of the temperature of the contents with time. This then enables expressions to be constructed describing the variation of reaction rate constants with time, which can subsequently be substituted into the basic design equations.

8.5 Non-ideal flow and mixing in continuous reactors

Up to now, we have considered two extreme approaches to continuous flow reactors: the well-mixed CSTR and the plug flow tubular reactor. In practice, neither extreme may be achieved in a real reactor because of the presence of channelling, stagnant regions or short-circuiting. Some examples of flow maldistribution are shown in Fig. 8.10.

8.5.1 Residence time distributions

Flow maldistributions within a system result in variations in the time that liquid actually resides in the reactor, and the use of simple expressions (equations (8.32) and (8.37)) for the mean residence time may be wholly inappropriate. Elements of liquid taking different routes through the reactor may take different times to pass through the reactor and may experience different profiles of temperature. Hence the conversion achieved in material taking these different routes will also be different. When a reactor exhibits channelling or short-circuiting, the residence time of material within the reactor is not as long as anticipated, resulting perhaps in less-than-satisfactory degrees of sterilization and undercooking. Conversely, the presence of stagnant regions within the reactor results in material staying within the reactor for too long a period, which may result in overcooking with concomitant loss of product quality.

Flow abnormalities are described in a quantitative manner by measurements of the distribution of residence times for liquid leaving the reactor. This distribution is called the **residence time** (or **exit age**) **distribution**, $E(t)\mathrm{d}t$. Because the distribution can be thought of as representing the probability that a given element of liquid is in the reactor for a certain length of time, it is convenient to normalize the distribution such that

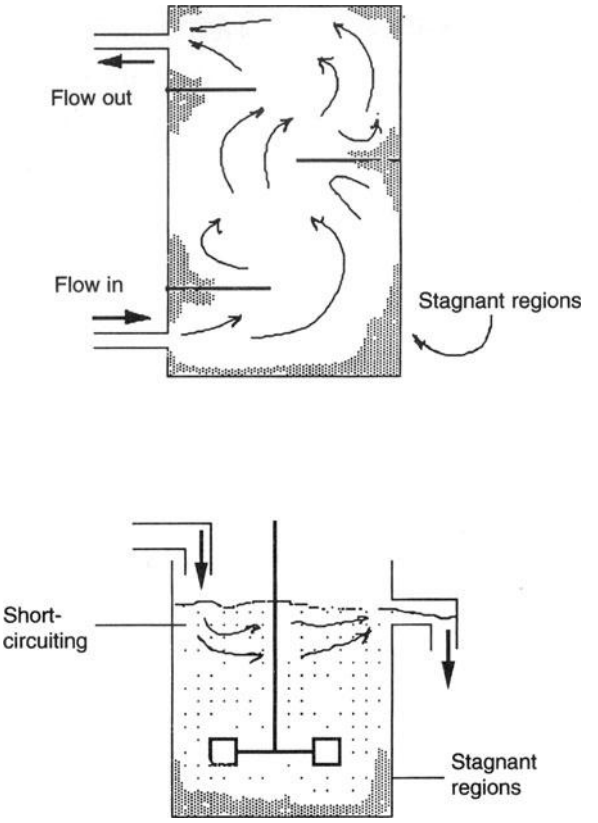

Fig. 8.10 Some examples of flow maldistribution in reactors.

$$\int_0^\infty E(t)\mathrm{d}t = 1 \tag{8.40}$$

The fraction of the exit stream that has been in the reactor for a time between t and $t + \mathrm{d}t$ (that is, of 'age' between t and $t + \mathrm{d}t$) is $E(t)\mathrm{d}t$. The normalization procedure ensures that these fractions sum up to unity. The fraction of material that is in the reactor for a time less than t_1 is

$$\int_0^{t_1} E(t)\mathrm{d}t \tag{8.41}$$

and the fraction in the reactor for longer than a time t_1 is

$$\int_{t_1}^\infty E(t)\mathrm{d}t = 1 - \int_0^{t_1} E(t)\mathrm{d}t \tag{8.42}$$

These concepts are illustrated in Fig. 8.11.

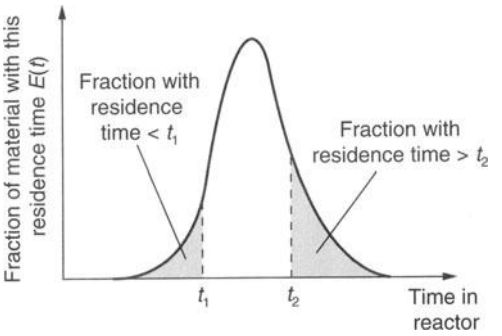

Fig. 8.11 A typical residence time distribution.

As discussed in Chapter 9, the presence of a broad residence time distribution in an item of cooking equipment can have serious consequences on the efficiency of the process. Material that emerges from the reactor with a short residence time may not have been in the reactor long enough for sterility to have been achieved, whereas material that remains in the reactor too long may be 'overcooked', with loss of quality of the product. Hence care must be taken to ensure a narrow residence time distribution, and it is important to measure the actual distribution that is achieved by a particular item of equipment (using the techniques outlined below in section 8.5.2) to confirm that such a distribution is indeed occurring.

8.5.2 Experimental characterization of non-ideal flow

Residence time distributions can be measured by the use of tracers in stimulus–response techniques. The requirements of the tracer are that it is distributed evenly in the bulk fluid flow and that its concentration can be measured conveniently in the reactor exit. The latter requires that the tracer has some physical property that can be simply measured, and such properties include radioactivity, colour and ionic strength. A discussion of the use of experimental residence time distributions to diagnose various types of poor flow in reactor systems is contained in Levenspiel (1972).

Measurement of the C-curve. In this popular method, a very short pulse of tracer is added to the liquid entering the reactor, which initially contains no tracer. The concentration of tracer in the exit stream from the reactor, c_e, is then measured as a function of time. The method is illustrated in Fig. 8.12, in which the 'reactor' could be a vessel such as a milk pasteurizer.

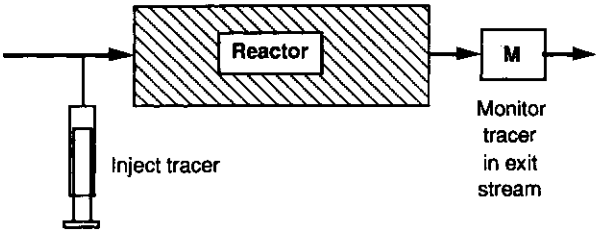

Fig. 8.12 Method for determining a C-curve.

Depending on the type of analytical equipment available, the tracer may be a coloured compound or a pulse of salt or acid/base. The concentration of tracer in the reactor exit stream can then measured by spectrophotometers, conductivity meters or pH meters fitted with flow-measuring cells. The data after normalization is called a **C-curve**. Normalization is performed by dividing the readings of c_e by A, the total area under the graph of c_e versus time. Thus

$$\int_0^\infty C(t)\mathrm{d}t = \int_0^\infty \frac{c_e}{A}\mathrm{d}t = 1 \tag{8.43}$$

where

$$A = \int_0^\infty c_e \mathrm{d}t \tag{8.44}$$

The C-curve so obtained is identical in shape to the residence time distribution $E(t)$. Typical shapes for the residence time distributions shown by CSTRs and PFRs are shown in Fig. 8.13.

For a plug flow reactor (Fig. 8.13(a)), the outlet profile has the same sharp shape as the inlet pulse except that the appearance of this pulse is delayed by a time equal to the residence time of liquid within the reactor. The RTD for a CSTR is markedly different (Fig. 8.13(b)), with the highest concentration of tracer leaving the reactor immediately after injection. This is because the tracer is mixed instantly with the contents of the reactor after injection. A typical RTD for a real reactor is shown in Fig. 8.13(c). The measurement of RTDs in real systems in operation in the food industry is discussed by Sancho and Rao (1992).

Measurement of the F-curve. This is similar to the C-curve method described above, but instead of a pulse, a step input of tracer of concentration c_{in} is added to the fluid stream entering the reactor. The concentration of tracer in the exit stream, c_e, is monitored as a function of time, and c_e/c_{in} is

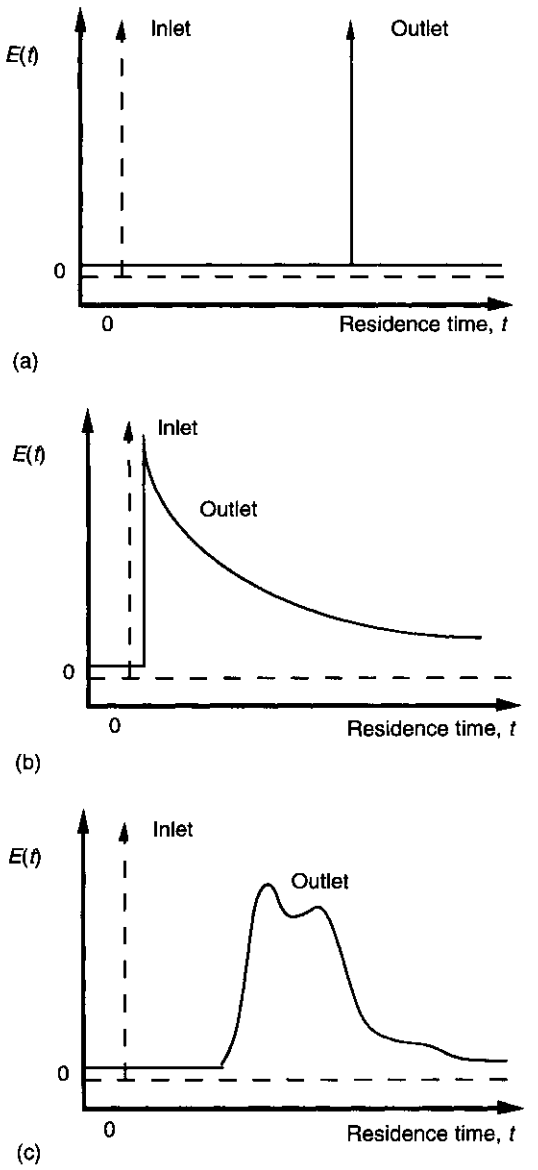

Fig. 8.13 Some residence time distributions measured with the C-curve method: (a) plug flow; (b) CSTR; (c) typical reactor.

plotted against time and is called the **F-curve**. A typical F-curve for a real reactor is shown in Fig. 8.14.

The value of F at time t_1 will be given by the fraction of tracer that has been in the reactor for a time less than t_1: that is,

$$F(t_1) = \int_0^{t_1} E(t)\mathrm{d}t \qquad \text{or} \qquad \frac{\mathrm{dF}}{\mathrm{d}t} = E(t) \tag{8.45}$$

Hence the F-curve is often called the **cumulative residence time distribution**.

8.5.3 Analysis of residence time distributions

In order to characterize the experimentally determined distribution it is often convenient to calculate its mean and variance. The mean value of the distribution is given by

$$\bar{t} = \int_0^{\infty} tE(t)\mathrm{d}t \tag{8.46}$$

and $\bar{t}$ is called the **mean residence time**. In many situations, it is convenient to show a residence time distribution as a function of dimensionless time ϑ such that

$$\vartheta = \frac{t}{\bar{t}} \tag{8.47}$$

and in such a situation the mean residence time occurs at the position where $\vartheta = 1$.

The spread of the distribution is commonly measured by the variance σ^2, defined as

$$\sigma^2 = \int_0^{\infty} t^2 E(t)\mathrm{d}t - \bar{t}^2 \tag{8.48}$$

The quantities $\bar{t}$ and σ^2 can both be easily determined by analysis of the experimental residence time distribution, using a mathematical procedure. However, reduction of the data contained in a residence time distribution to

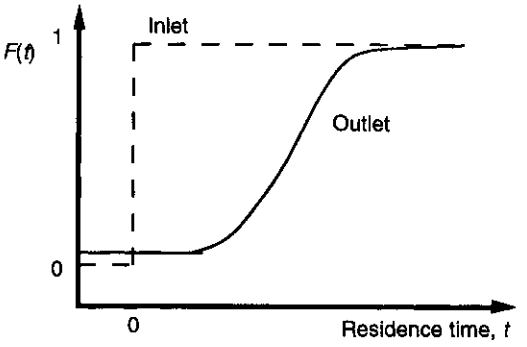

Fig. 8.14 A typical F-curve experiment.

yield the parameters $\bar{t}$ and σ^2 can result in the loss of important information contained in the distribution, particularly when the distribution is significantly asymmetrical or if it contains multiple peaks.

It is possible to characterize a non-ideal residence time distribution in certain simple situations where the distribution lies between the ideal limits of CTSR and PFR behaviour. These conditions imply that there exist no stagnant pockets and no gross by-passing or short-circuiting of liquid in the reactor. A typical shape of an RTD that can be analysed by these approaches would look like a Gaussian or Normal bell-shaped curve of the kind shown in Fig. 8.11.

Dispersion model. This model assumes that flow in the reactor is essentially plug flow on top of which is superimposed some degree of backmixing (via either slippage or eddy formation) in the axial direction, the magnitude of which is independent of position within the vessel (see Fig. 8.15(a)). This mixing results in a radial velocity distribution, and this mechanism of dispersion is analogous to molecular diffusion but is described by a parameter D_a, the **axial** (or **longitudinal**) **diffusion coefficient**. The dispersion of material flowing at a velocity v_m in the x direction is described by

$$\frac{\partial c}{\partial t} = D_a \frac{\partial^2 c}{\partial x^2} \tag{8.49}$$

It is common to introduce a dimensionless group $D_a/v_m L$, called the **vessel dispersion number** (or **inverse Peclet number**), where v_m is the mean velocity of flow through the tubular reactor of length L. Thus as:

$\frac{D_a}{v_m L} \to 0$ there is negligible dispersion, i.e. plug flow

$\frac{D_a}{v_m L} \to \infty$ there is significant dispersion, i.e. mixed flow

If an idealized pulse of tracer is applied to a reactor in which the dispersion is small, the resultant C-curve can be described by integrating equation (8.49) with appropriate boundary conditions. The result is a symmetical, Gaussian-shaped curve given by

$$C = \frac{1}{2\sqrt{\pi\left(\frac{D_a}{v_m L}\right)}} \exp\left[-\frac{\left(1-\frac{t}{\bar{t}}\right)^2}{4\left(\frac{D_a}{v_m L}\right)}\right] \tag{8.50}$$

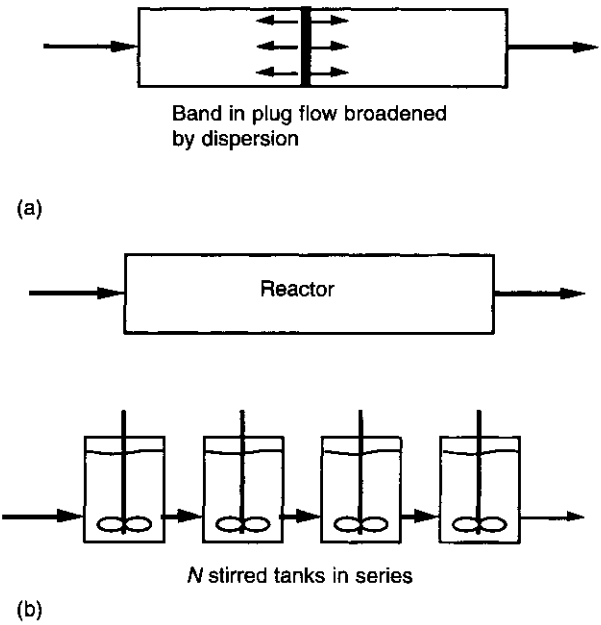

Fig. 8.15 Models for the analysis of residence time distributions: (a) the dispersion model and (b) the tanks-in-series model.

There are a number of ways of determining $D_a/v_m L$ from an experimental residence time distribution curve. Perhaps the easiest is to measure the maximum height of the normalized C-curve, which is equal to

$$\frac{1}{2\sqrt{\pi \dfrac{D_a}{v_m L}}} \tag{8.51}$$

Other methods involve calculating the variance of the experimental curve, or its width at the points of inflection, and are described in Levenspiel (1972).

The tanks-in-series model. The other main theoretical approach to a description of residence time distribution curves is the use of a tanks-in-series model. In this model, the reactor is assumed to behave as if it consisted of a number of equal-sized CSTRs placed in series one after the other (Fig. 8.15(b)). Flow through the reactor system is characterized by the parameter N, the number of tanks in the system. Again, N can be determined from the experimental data in a number of ways. The easiest is from the maximum height of the normalized curve, which is approximately equal to

$$\frac{N}{\sqrt{2\pi(N-1)}} \tag{8.52}$$

The value of N will approach infinity for an ideal plug flow system with no dispersion. Conversely, N will approach unity in a system where there is almost perfect mixing.

8.5.4 Use of RTDs to predict actual reactor conversion

As has been stated above, when a reactor has first-order reactions, a knowledge of the apparent residence time distribution of liquid within the reactor can be used to estimate unequivocally the average conversion that will be achieved in that reactor. Consider the first-order process

$$\text{A} \rightarrow \text{products} \qquad \text{with } r_{\text{A}} = -k_1 c_{\text{A}}$$

The liquid in the reactor can be considered as consisting of a large number of individual elements. Each element of liquid will have a residence time t within the reactor, and if each of these elements is considered to be a small batch reactor then the conversion achieved in that element after time t is given by equation (8.25):

$$X_{\text{A}} = 1 - \text{e}^{-k_1 t}$$

The average fractional conversion in the exit stream can then be determined from

$$\overline{X}_{\text{A}} = \int_0^\infty X_{\text{A}}(t) E(t) \text{d}t \tag{8.53}$$

This integration can be performed graphically in cases where the experimental RTD has a complex form that cannot conveniently be described by an algebraic expression. A point $(E(t), t)$ on the E curve is taken and the product

$$E(t)\left(1 - \text{e}^{-k_1 t}\right)$$

is calculated and plotted on a second graph versus the value of t. The process is repeated for a series of points over the entire range of residence times until the second graph has been built up. The integral that gives the required average fractional conversion is then simply the area under this second curve evaluated over the whole range of residence times, as shown in Fig. 8.16.

A simple computer routine can be written which performs the necessary manipulations on digitized points from the experimentally determined E-curve. This method provides therefore a useful way to predict the average conversion that will be achieved in a real reactor system.

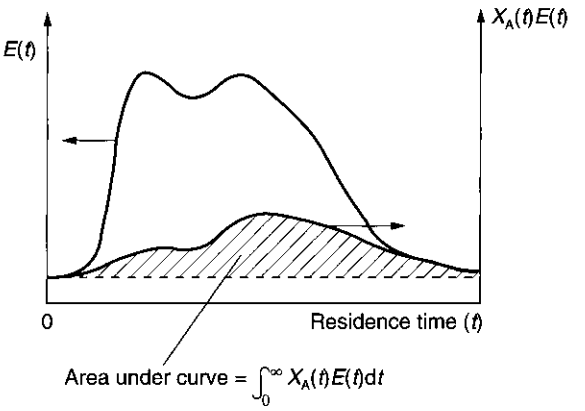

Fig. 8.16 Graphical method for estimating mean conversions for first-order reactions using residence time distributions.

Conclusions

Most food processing operations involve reactions of one type or another, most of which are thermally driven. This chapter has demonstrated how some of the techniques of chemical reaction engineering can, with profit, be used to analyse and design food processes where reactions are important. It has concentrated on a few key ideas.

You should understand how the classical descriptions of reaction kinetics can be related to food and biological operations. In particular you should understand how the physical chemist's use of reaction rate constants is related to the methods used in the food industry to describe sterilization and quality changes, that is in terms of D- and z-values, lethality measures, etc. Both methods of analysis have their merits, but it is important to know how they are related to each other.

Another theme of the chapter is to explain how the processing environment can dramatically affect process operation when reactions are involved. In particular, you should appreciate the difference between batch and continuous operations, and the significance of the mixing characteristics of the process for process efficiency and product quality. You should, then, understand the difference between a tubular or plug flow device and one which is perfectly mixed, and the significance of these ideal systems for process efficiency. Few processes are ideal in this sense, and some of the ways in which the mixing characteristics of real operations can be measured and modelled are also outlined.

References and further reading

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