INSTRUMENTATION IN THE CHEMICAL AND PETROLEUM INDUSTRIES-Vol. 9

PETROCHEMICAL UNIT PROCESSES
PART 2:
KINETIC REACTORS

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KINETIC REACTORS

Programmed by
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INSTRUMENTATION IN THE CHEMICAL AND PETROLEUM INDUSTRIES-Vol. 9

Petrochemical Unit Processes
Part 2: Kinetic Reactors

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FOREWORD

These proceedings result from the 1973 ISA Joint Spring Conference held at Stouffer's Riverfront Inn in St. Louis, Missouri on April 23, 24, 25 and 26, 1973.

This is the second of the projected series of tutorial symposia. These tutorials are aimed at presenting in symposium format a planned sequence of papers which will develop a single area or single type of operation from introduction and definition through the latest applications. Such a presentation offers a unique opportunity for those participating to organize and refresh their expertise if they are already familiar with the area or to learn the operations and techniques involved if they have no previous experience in this area.

The tutorial symposium also offers the various divisions of ISA a unique way to cooperate in making their specialized knowledge available to the members. By concentrating joint sessions on a single topic the viewpoints of the process engineers, measurement and control personnel, educators and maintenance people can all be considered. It is hoped that in this way an integrated view of the operation will be obtained. With an understanding of how the various parts fit together and interact with each other, the whole operation will be better understood and in the long run made more profitable.

We would like to acknowledge with appreciation the total cooperation of the education committee, the process measurement and control division (PMCD), the chemical and petroleum industries division (CHEMPID), and the analytical instrument division (AID). The various joint sessions would not have been possible without their help.

The proceedings contain 11 papers and the papers were capped with a panel discussion. These sessions represent an enormous amount of time and effort on the part of the twenty authors and five sessions developers. There is no adequate way to express our thanks for the effort of these people to make this symposium a success.

Finally, the host committee and R. Q. Brown, the general program chairman, deserve our thanks for a job well done.

B. S. Swanson
Education Program Chairman

CONTENTS

FUNDAMENTALS OF REACTOR ENGINEERING

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ABSTRACT

In this presentation, the fundmanetal reactor design calculations for ideal reactors are discussed. Single phase, non-catalytic reactions are studied for single and multiple reaction systems. We will review calculation procedures for single reactors, multiple-reactors, and plug flow reactor systems.

INTRODUCTION

Chemical reactor engineering is the procedure involved in chosing the type of equipment for carrying out a chemical reaction, specifying the size of this equipment, and recommending the mode of operation of the equipment.

The equipment in which the reaction is performed is called a chemical reactor. The reactor may be a vessel, tank, pipe, column, or any type of container which enhances the environment of the system in which the chemical reaction occurs. Thus depending upon the type of chemical reaction system, the reactor might be designed (1) to either maximize or minimize the mixing of the reactants and product, (2) to operate at the optimum residence time for the reactant mixture, (3) to enhance the reaction and control the reactor temperature by either adding or removing heat, (4) to introduce recycling inorder to improve the yields obtained on a single pass through the reactor, (5) to use a series of reactors, (6) if necessary, to disperse, contact and coalesce multiphase reactant mixtures and possibly catalysts, (7) to safely contain the reaction under potentially hazardous temperatures, pressure, and corrosive conditions, (8) to enable control in upsets of any reactor variables, and (9) to allow for ease in the physical maintanance of the chemical reactor system.

Following the design of a chemical reactor, two important objectives of chemical reaction engineering are (1) to appraise the operating performance of the existing reactor system in terms of the overall, long-term economics of the process and, (2) to develop the ability to control relatively short-term changes in operating conditions in an optimal sense.

In this tutorial paper, some of the fundamental principles and relationships involved in choosing the type of reactor and calculating its size are developed and reviewed. We will be concerned with concepts related to the steady-state operation of ideal reactors such as the batch reactor, the mixed flow reactor, and the plug flow reactor. In ideal reactors we assume that the fluid within the reactor is either perfectly mixed throughout or not mixed at all as it moves through the reactor. The general advantages and disadvantages of each type of reactor will be reviewed. Design calculational procedures are discussed for single reactors, multiple-reactor systems, and plug flow reactors with recycle. The design procedure and conclusions are strongly dependent upon the type of reaction system, and we will consider single reaction and multiple reaction systems. We will consider only single phase, non-catalytic reactions in this introductory paper. In the papers to follow, such topics as reactor design for multiphase systems with or without catalysts, effects of non-ideal patterns in reactors, and the consideration of heat effects will be discussed.

Even though we will not discuss reactor dynamics or stability problems relating to changes of input variables with time, many of the mathematical relations and fundamental principles developed here will lay the groundwork for the later papers in this symposium.

This tutorial paper is a condensation of the material presented by Levenspiel[1] and also summarizes material from a number of other excellent sources (2,3,4,5). For more details, the reader is urged to obtain and review these original sources. In order to clarify the fundamentals of chemical reaction engineering, a number of figures and numerical examples from the above sources are presented in this paper.

TYPES OF REACTORS

Equipment in which single phase reactions can be carried out can be classified into three general types: the batch, the steady-state flow, and the unsteady-state flow or semi-batch reactor. See Figure 1. It is assumed that the batch and semi-batch reactors are perfectly mixed reactors. In

this introductory paper, for brevity we will not consider the variable volume semibatch reactors or any other less frequently used types of reactors.

3.1 BATCH REACTORS (Figure 1a)

In ideal batch reactors, the reactnats are initially fed into a vessel or tank, kept well agitated, and left to react for a certain time. The resultant mixture is then discharged. This is an unsteady-state operation where composition (and possibly temperature) varies with time in the reactor; however, at any instant in time the composition and temperature throughout the reactor is uniform. The final composition (or conversion or yield) is dependent upon the time of reaction. For a so-called non-ideal batch reactor, the compositions in the reactor at any time may vary with position. Non-ideal mixing complicates reactor design calculations.

Batch reactors are simple and find applications in small-scale or complicated processes that manufacture expensive products. These reactors are also frequently used in laboratory studies of the chemical reaction kinetics of the process in order to determine a kinetic rate expression. Batch reactors have the advantage of general versatility, requiring little supporting equipment (instrumentation), combined with a potentiality of high yield of the desired product. However, these reactors have the disadvantage of being generally more expensive to operate than other types of reactors at the same production rate -- labor costs are high and one is generally restricted to small scale operations.

These reactors are generally constructed in the form of a tank where all three dimensions are roughly of the same order of magnitude, in order to enhance internal mixing. The reader is referred elsewhere for a description of the mechanical features of some batch reactors (Smith, p. 105-108).

3.2 PLUG FLOW (Figure 1b)

This type of steady-state flow reactor is sometimes also called plug flow, piston flow, ideal tubular, and unmixed flow reactor. The pattern of flow of fluid through the reactor is termed plug flow. It is characterized by the fact that flow of fluid through the reactor is orderly with no element of fluid overtaking or mixing with any other element ahead or behind. (Actually, there may be lateral mixing of the fluid in an ideal plug flow reactor; however, there must be no mixing or diffusion along the flow path. The necessary and sufficient condition for plug flow is for the "residence time" in the reactor to be the same for all elements of fluid.) In this type of reactor, the reactants are fed continuously into a tube (or other device with a high L/D ratio); and the mixture reacts as it flows through the tube. The compositions and possibly the temperature vary along the length of the reactor; however, for steady-state conditions, the compositions and temperature do not change with time at any particular point along the length of the reactor.

Plug flow reactors are generally used for large scale continuous processes. These reactors have the advantage of ease of control, generally unvarying product quality, mechanical simplicity, and high throughput. High pressure reactions are usually best performed in tubular type reactors.

The high ratio of surface area (available for heat transfer) to reactor volume for plug flow reactors and the high heat transfer coefficients make it possible for high heat transfer rates between the reaction mixture and the surroundings. This is desirable when the heat of reaction is high, and endothermic, for example, in the thermal cracking of hydrocarbons.

It is also advantageous to use plug flow reactors for laboratory chemical kinetic studies of very fast reactions.

There are significant advantages in using plug flow reactors compared to reactors with mixing in terms of the reactor size required, but this will be discussed later. The plug flow reactor has the disadvantage of having a fixed "holding time" for a given throughput; and hence, these reactors are very expensive for reactions that require high holding times. On the other hand for a series type of reaction where the intermediate product is desired, a tubular reactor is often more suitable because of the lack of spread of residence times of the fluid elements in the reactor. Flow in a plug flow reactor may be accompanied by appreciable pressure drop, especially when gases are involved or when mixtures of liquids and gases occur, as in liquid hydrocarbon cracking.

The plug flow reactor can also be used for heterogeneous, catalytic fixed-bed systems. In this case, the reactor is packed with a solid catalyst. A disadvantage of this arrangement is that there is a possibility of "hot spots" within the bed. With catalyst aging, these hot spots may slowly move down the plug flow reactor. It can be difficult to replace the catalyst in such reactors.

3.3 MIXED FLOW REACTOR (Figure 1e)

This type of ideal steady-state flow reactor is also called the mixed reactor, the backmix reactor, the ideal stirred tank reactor, well stirred reactor, or the CFSTR (constant flow stirred tank reactor). As these names suggest, this is a reactor in which the reactants are fed at a constant rate into a vessel or tank in which the contents are well stirred and uniform throughout with respect to time and location. The contents of the reactor continuously exit from the reactor and the composition and temperature of the exiting stream is the same as that in the mixed flow reactor.

When a flow reactor consists of a vessel whose diameter is of the same order of magnitude as its length and when the flow rate (ft/sec) is low, considerable mixing (but not complete) may occur in the reactor. The design of a reactor under these circumstances of partial mixing is difficult because the extent of mixing cannot be accurately predicted at present. However, with properly

designed mechanical stirring equipment, essentially perfect mixing can be obtained. Under this condition, the reactor-design calculations are greatly simplified because the rate of reaction is a constant. This will be discussed later.

There are certain situations in which a design engineer would consider it advantageous to use a mixed flow reactor. These are:

(1) It is possible to operate such a reactor under nearly isothermal conditions even when the heat of reaction is high -- an impossibility in a long, plug flow reactor. Operation at nearly isothermal conditions is desired, for example, in order to minimize undesirable side reactions, avoid temperatures which might have unfavorable rates (the rate is related to the temperature and magnitude of the activation energy), and minimize damage to temperature sensitive products.

(2) Mixed flow reactors, by virtue of their generally large volumes can represent an economical method of providing a long residence time. This can be very useful if the reaction rate is low.

(3) If one of the reactants is of an explosive nature at high concentrations, a mixed flow reactor would be preferred because the reactant concentration in the feed would be reduced immediately to that of the reactor effluent.

(4) In kinetic studies to determine the reaction rate, the reaction rate is determined directly from design equations without integration. The ease of interpretation of data from a mixed reactor makes its use very attractive in kinetic studies, in particular with messy reactions (e.g., multiple reactions and solid catalyzed reactions.)

There are certain disadvantages to the use of mixed flow reactors which can perhaps be deduced from the previous discussion -- particularly of plug flow reactors. One point which has not been mentioned previously is the relative difficulty of constructing a mixed flow reactor to handle gaseous systems. The problem is insuring complete mixing of the gaseous mixtures, which is generally less of a problem with liquid systems.

4. KINETICS OF CHEMICAL REACTIONS

In this section, we will consider homogeneous reactions. In this type of reaction, all of the reacting materials are within a single phase. Thus, the rate of reaction of any reaction component $\underline{A}$ is defined as

$$r_A = \frac{1}{V} \left(\frac{dN_A}{dt}\right)_{\text{by reaction}}$$

$$= \frac{(\text{moles of } \underline{A} \text{ which appear by reaction})}{(\text{unit volume}) (\text{unit time})} \qquad (1)$$

Consider the reaction

$$a'\underline{A} + b'\underline{B} \rightarrow c'\underline{C} \qquad (2a)$$

In this case, the reaction component $\underline{A}$ is being consumed; and the rate is negative. Thus, $-r_A$ is the rate of disappearance of the reactant $\underline{A}$.
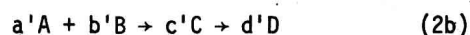
For most chemical reactions, the rate of reaction is a function of the conditions of the materials in the phase. Thus

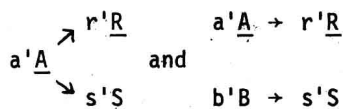$$r_A = f(\text{temperature, pressure, composition})$$

$$= f(\text{temperature, composition})$$

For the moment, we will assume that the temperature of the system is constant. In order to determine the functional relationship between the rate and composition, we must know something about the stoichiometry of the reaction(s), i.e., is more than one reaction occurring? And which reaction(s) are the rate determining step(s)? And finally what mathematical expression(s) determine the kinetics of the reaction(s)?

One may encounter single reactions such as that expressed by Equation (2a) above. One may also encounter multiple reaction systems such as series reactions

$$a'\underline{A} + b'\underline{B} \rightarrow c'\underline{C} \rightarrow d'\underline{D} \qquad (2b)$$

or parallel reactions

$$a'\underline{A} \nearrow^{r'\underline{R}}_{\searrow s'\underline{S}} \qquad \text{and} \qquad \begin{array}{l} a'\underline{A} \rightarrow r'\underline{R} \\ b'\underline{B} \rightarrow s'\underline{S} \end{array}$$

or even more complicated stoichiometry resulting from combinations of the above reactions. The above are irreversible reactions. In some cases, the chemical reaction may be reversible, for example

$$a'\underline{A} + b'\underline{B} \leftrightarrows c'\underline{C} + d'\underline{D}$$
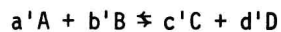
Although we will not discuss reversible reaction in this introductory paper, they are important; and for these reaction, there is a maximum possible yield (equilibrium yield) that can be obtained in a reactor.

4.1 REPRESENTATION OF A REACTION RATE

Although there has been considerable progress in determining rate expression from theoretical considerations (1,2,3), these attempts have generally not been too successful. Thus, one usually obtains or is given an empirically determined rate expression for the concentration dependency. For example, the rate of reaction for Equation (2a) might be approximated by an expression of the following type

3

$$r_A = k c_A^a c_B^b \qquad (3)$$

where a and b are <u>not necessarily</u> equal to the stoichiometric coefficients a' and b'. It is important to note that Equation (3) is not the only form of rate expression which describes all single, irreversible reactions. The search for an adequate rate expression and mechanism to fit experimental data is an important topic and is described in detail elsewhere (1,2,3).

4.1.1 <u>Reaction Order</u>.

The powers to which the concentrations in the rate expression are raised are related to the reaction order. Thus for the reaction described by Equation (3):

<u>a</u>th - order with respect to <u>A</u>

<u>b</u>th - order with respect to <u>B</u>

(<u>a</u> + <u>b</u>) = <u>n</u>th - order <u>overall</u>

Since the order refers to an empirically found rate expression, it can have a fractional power and need not be an integer. The order of a reaction can vary with concentration level in liquid phase reactions and with absolute pressure in gas phase reactions.

4.1.2 <u>Reaction Constant k</u>.

When the rate expression for a homogeneous chemical reaction is written in the form of Equation (3) the <u>dimensions</u> of the rate constant k for the nth-order reaction are

$$(\text{time})^{-1} (\text{concentration})^{1-n}$$

4.2 TEMPERATURE DEPENDENCY OF A RATE EQUATION

For many reactions, the temperature dependency of a rate expression is manifested by changes in the reaction constant, k, with temperature. This temperature dependency can be closely approximated in many cases by the Arrhenius' law

$$k = k_o e^{-E/RT} \qquad (4)$$

where k_o is called the frequency factor and E is called the activation energy of the reaction (See reference (1), page 22). Certain theories suggest that $k_o = k' T^m$, but in most cases one can neglect any temperature variations of k_o.

From Arrhenius' law a plot of ln (k) vs. T^{-1} gives a straight line, with large slope for large E and small slope for small E. Thus, reactions with large activation energies have rates of reaction which are very temperature-sensitive.

It is important to note that for some reaction systems a large change in temperature may not only change the rate constant but may even change the mechanism of the reaction and, hence, alter the entire rate expression.

4.3 OTHER TERMS DESCRIBING CHEMICAL REACTIONS

4.3.1 <u>Limiting Reactant</u>.

If in a reacting system, the reactants are not present in the proportions required by the stoichiometric equation, then the reactant which is <u>not</u> in excess is the limiting reactant. The other reactant is in excess of that which is required.

4.3.2 <u>Fractional Conversion</u>.

The fraction of reactant converted into product is defined as the fractional conversion, X_A

$$X_A = \frac{N_{A_0} - N_A}{N_{A_0}} \qquad (5)$$

where N_{A_0} and N_A equal the initial and final moles of reactant A. It is usually of practical importance to consider the fractional conversion of the limiting reactant. Occasionally, we refer to fractional conversion as simply the conversion. The fractional conversion is sometimes used as a variable in reaction engineering analysis in place of concentration C_A. These two terms are related as follows:

(1) For a constant density system where V does not change

$$C_A = C_{A_0} (1 - X_A) \qquad (6a)$$

or

$$X_A = 1 - C_A / C_{A_0} \qquad (6b)$$

where C_{A_0} is the inital concentration of <u>A</u> in the system.

(2) For a <u>variable volume</u> (gas system)

$$V = V_o (1 + \varepsilon X_A) \qquad (7)$$

where ε is the fractional change in volume of the system between no conversion and complete conversion of reactant <u>A</u>

$$\varepsilon = \frac{V\big|_{X_A=1} - V\big|_{X_A=0}}{V\big|_{X_A=0}} \qquad (8)$$

As an example of the calculation of ε, consider the following isothermal gas-phase reaction

$$\underline{A} \rightarrow 3\underline{R}$$

(a) Starting with pure reactant <u>A</u>

$$\varepsilon = (3 - 1)/1 = 2$$

(b) Starting with 75% inerts

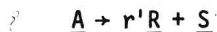$$\varepsilon = \frac{(0.75 + 0.75) - (0.25)}{1} = 1.25$$

This approach can be extended to ideal liquids if the reaction results in a linear volume expansion. Thus

$$C_A/C_{A_0} = (1 - X_A)/(1 + \varepsilon X_A) \qquad (9a)$$

or

$$X_A = \frac{1 - C_A/C_{A_0}}{1 + \varepsilon C_A/C_{A_0}} \qquad (9b)$$

4.3.3 Yield.

Consider the following reaction

$$\underline{A} \rightarrow r'\underline{R} + \underline{S}$$

Let N_{A_0} moles of $\underline{A}$ be fed to the reactor of which a total of $m_A (= N_{A_0} - N_A)$ moles react to give m_R $(= r'm_A)$ moles of $\underline{R}$. The total conversion (X_A) of $\underline{A}$ is m_A/N_{A_0} $(= r'X_A)$. In this paper, the yield of product $\underline{R}$ is m_R/N_{A_0} $(= r'X_A)$.

The concept of "yield" is very useful for the description of the frequent situation in which only part of a reactant is converted to the desired product, while some is unavoidably converted to unwanted side products. For example, consider the reaction

$$\underline{A} \nearrow^{\underline{B} + \underline{C}}_{\searrow \underline{D} + \underline{E}} \qquad \text{competitive reaction}$$

where only $\underline{B}$ is the desired product. In this case, suppose one obtains m_B moles of $\underline{B}$. The yield is either m_B/N_{A_0} or m_B/m_A depending upon one's definition. The calculation of yield for competitive reactions in different reaction systems is difficult and will be discussed later.

5. INTRODUCTION TO REACTOR DESIGN (Single Ideal Reactors)

The general types of ideal reactor systems were qualitatively discussed in Section 2. In chemical reactor engineering, we generally want to know for a given reaction what size and type of reactor and method of operation are best for a given job. It will be shown in this section that for the ideal reactors described earlier, the four key reactor design variables are fractional conversion X_A, rate of reaction r_A, reactor volume V, and input reactant flow rate F_{A_0}.

We can relate the above four key variables by means of a material balance for any reactant in an element of volume of the reactor (See Figure 1f). Thus for any component

$$\begin{pmatrix} \text{rate of reactant} \\ \text{flow into element} \\ \text{of volume} \end{pmatrix} - \begin{pmatrix} \text{rate of reactant} \\ \text{flow out of} \\ \text{element of volume} \end{pmatrix}$$

$$- \begin{pmatrix} \text{rate of reactant} \\ \text{loss due to chemical} \\ \text{reaction within the} \\ \text{element of volume} \end{pmatrix}$$

$$= \begin{pmatrix} \text{rate of} \\ \text{accumulation of} \\ \text{reactant in element} \\ \text{of volume} \end{pmatrix} \qquad (10)$$

Depending on the type of reactor, one or more terms in Equation (10) may be zero. Equation (10) is used repeatedly in this paper.

For non-isothermal operation, an energy balance must be used in conjunction with material balances. The starting equation is identical to Equation (10) except energy is the conserved quantity. The use of the energy balance will be explained in detail in a later paper.

In this section we will consider homogeneous, isothermal systems. We will derive performance equations for ideal types of reactors. These performance equations will in some cases involve integrals of rate expressions, which will be integrated for a few special types of rate expressions.

5.1 IDEAL BATCH REACTORS (see figure 1a)

Applying Equation (10), a material balance for reactant A we obtain the following differential material balance

$$0 - 0 - (-r_A V) = \frac{dN_A}{dt} = \frac{d}{dt}[N_{A_0}(1 - X_A] = -N_{A_0}\frac{dX_A}{dt}$$

or

$$(-r_A)V = N_{A_0}\frac{dX_A}{dt} \qquad (11)$$

Rearranging and integrating, we obtain

$$t = N_{A_0} \int_{X_{A_0}}^{X_{A_f}} \frac{dX_A}{(-r_A)V} \qquad (12)$$

If the density of the fluid remains constant, we obtain

$$t = C_{A_0} \int_{X_{A_0}}^{X_{A_f}} \frac{dX_A}{(-r_A)} = -\int_{C_{A_0}}^{C_{A_f}} \frac{dC_A}{(-r_A)} \qquad (13)$$

For all reactions in which the volume of the reacting mixture changes proportionately with conversion (such as single gas-phase reactions with significant density changes), Equation (12) becomes

$$t = C_{A_0} \int_{X_{A_0}}^{X_{A_f}} \frac{dX_A}{(-r_A)(1 + \varepsilon X_A)} \qquad (14)$$

Equations (11)-(14) apply for isothermal and non-isothermal conditions.

5.2 FLOW REACTORS

4.2.1 <u>Space-time and Space-velocity</u>. Just as the reaction time t is the natural measure of the processing rate in a batch reactor, so are the space-time and space-velocity the proper performance measure of flow reactors.

Space-time, τ:

$$\tau = \left(\begin{array}{l} \text{time required to process one} \\ \text{reactor volume of feed measured} \\ \text{at } \underline{\text{specified}} \text{ conditions} \end{array} \right) = [\text{time}]$$

(15)

Space-velocity, s:

$$s = \left(\begin{array}{l} \text{number of reactor volumes of feed} \\ \text{at specified conditions which can} \\ \text{be treated in unit time} \end{array} \right)$$

$$= [\text{time}^{-1}]$$

(16)

These two variables are the reciprocal of each other, i.e.,

$$\tau = 1/s$$

Generally the specified conditions are the temperature, pressure, and state of the material being feed into the reactor. If so, then

$$\tau = \frac{V}{v_0} = \frac{(\text{reactor volume})}{(\text{volumetric feed rate})}$$

(18)

where

$$v = (F_{A_0}/C_{A_0})$$

$$= (\text{moles of A entering/time/} [\frac{(\text{moles of A in})}{(\text{volume of feed})}])$$

The specified conditions need not always be the feed conditions; and, hence, the calculated volumes of s would be different depending upon the definition. These definitions were first proposed by Hougen and Watson (1947) as a more rational criteria than time for the design of any type of continuous flow reactor.

5.2.2 <u>Steady-State Plug Flow Reactor</u>. This type of reactor was described in Section 2. Since the concentration of reactant changes continuously as the reactant mixture flows through the reactor, we must write the material balance [Equation (10)] over a differential volume element of the reactor Thus,

$$F_A\big|_Z - F_A\big|_{Z+\Delta Z} - [-r_A A_c \Delta Z] = 0$$

(19)

Dividing by ΔZ, rearranging, and taking the limit as $\Delta Z \to 0$, we obtain

$$\frac{dF_A}{dZ} = r_A A_c$$

(20)

Since

$$F_A = F_{A_0}(1 - X_A)$$

(21)

and

$$dV = A_c d_Z$$

(22)

then

$$F_{A_0} dX_A = (-r_A)dV$$

(23)

Integrating Equation (23) over the entire reactor volume

$$\frac{V}{F_{A_0}} = \frac{\tau}{C_{A_0}} = \int_{X_{A_0}}^{X_{A_f}} \frac{dX_A}{(-r_A)}$$

(24)

$$\tau = \frac{V}{v_0} = C_{A_0} \int_{X_{A_0}}^{X_{A_f}} \frac{dX_A}{(-r_A)}$$

(25)

Note that r_A is a function of conversion.

If the <u>density</u> of the fluid remains constant,

$$X_A = 1 - C_A/C_{A_0}$$

(6b)

and we obtain

$$\tau_p = -\int_{C_{A_0}}^{C_{A_f}} \frac{dC_A}{(-r_A)}$$

(26)

Comparison of Equations (13) and (26) indicates that for systems of <u>constant density</u> (constant-volume batch and constant-density plug flow), the performance equations are identical. In this case, τ for plug flow is equivalent to t for the batch reactors. However, for systems of variable density there is no exact correspondence between t and τ; and one must use either Equation (12) or (14) for batch systems and Equation (25) for plug flow systems.

5.2.3 <u>Steady State Mixed Flow Reactor</u>. Since the composition in this type of ideal reactor is uniform throughout, we apply the material balance, Equation (10), to the <u>entire</u> reactor.

$$F_{A_0}(1 - X_{A_i}) - F_{A_0}(1 - X_A) - [-r_A V] = 0$$

(27)

Rearranging

$$\tau_m = \frac{V}{v_0} = \frac{C_{A_0}(X_{A_f} - X_{A_i})}{(-r_A)_f} \qquad (28)$$

If the system is constant density

$$\tau_m = \frac{V}{v_0} = \frac{C_{A_0} - C_{A_f}}{(-r_A)_f} \qquad (29)$$

Notice that integration is not required to determine τ_m.

5.2.4 Graphical Evaluation of Performance Equation. The performance equations developed in Section 4.2.1-3 interrelate the rate of reaction, the extent of reaction, the reactor volume, and the feed rate. Thus if any of the above three quantities are known, then the fourth can be determined assuming the input composition of the feed is known.

It is helpful when comparing the size required for different reactor systems to accomplish the same extent of reaction to prepare the type of figure illustrated in Figure E1. The ratio of shaded areas gives the ratio of space-times of the mixed and plug flow reactors. The rate curve drawn is typical of the large class of single reactions whose rate decreases continuously on approach to equilibrium. For such reactions, it can be seen that mixed flow always needs a larger volume than does plug flow, all other conditions being equal.

If the rate relationship is known, the integral in the performance equations developed earlier can be determined from the graphical integration of the above type of figure. The integrals in the performance equations can also be evaluated by finite difference numerical techniques such as Simpson's rule or if the kinetic rate expressions are very simple may even be integrated analytically. See the following example.

EXAMPLE 1.   Plug Flow Reactor Performance (1)

A homogeneous gas reaction $\underline{A} \rightarrow 3\underline{R}$ has a reported rate at $215^\circ C$

$$-r_A = 10^{-2} C_A^{1/2}, \text{ [mol/liter·sec]}$$

Find the space-time needed for 80% conversion of a 50% $\underline{A}$ - 50% inert feed to a plug flow reactor operating at $215^\circ C$ and 5 atm (C_{A_0} = 0.0625 mol/liter).

Solution

For this stoichiometry and with 50% inerts, two volumes of feed gas would give four volumes of completely converted product gas, thus

$$\varepsilon = \frac{4 - 2}{2} = 1$$

in which case the plug flow performance equation, Equation (25), becomes

$$\tau = C_{A_0} \int_0^{X_{A_f}} \frac{dX_A}{-r_A} = C_{A_0} \int_0^{X_{A_f}} \frac{dX_A}{kC_{A_0}^{1/2} (\frac{1 - X_A}{1 + X_A})^{1/2}}$$

$$= \frac{C_{A_0}^{1/2}}{k} \int_0^{0.8} (\frac{1 + X_A}{1 - X_A})^{1/2} dX_A \qquad (i)$$

The integral can be evaluated in any one of three ways: graphically, numerically, or analytically. Let us illustrate these methods. Graphical Integration. First evaluate the function to be integrated at selected values (see Table E1), and plot this function (see Figure E1).

Counting squares or estimating by eye we find

$$\text{Area} = \int_0^{0.8} (\frac{1 + X_A}{1 - X_A})^{1/2} dX_A = (1.70)(0.8) = 1.36$$

Numerical Integration. Using Simpson's rule, applicable to an even number of uniformly spaced intervals on the X_A axis, we find for the data of Table E1

$$\int_0^{0.8} (\frac{1 + X_A}{1 - X_A})^{1/2} dX_A = \text{(average height)(total width)}$$

$$= [\frac{1(1) + 4(1.227) + 2(1.528) + 4(2) + 1(3)}{12}](0.8)$$

$$= 1.331$$

Analytical Integration. From a table of integrals

$$\int_0^{0.8} (\frac{1 + X_A}{1 - X_A})^{1/2} dX_A = \int_0^{0.8} \frac{1 + X_A}{\sqrt{1 - X_A^2}} dX_A$$

$$= \text{arc sin}(X_A - \sqrt{1 - X_A^2}) \Big|_0^{0.8} = 1.328$$

(See Figure E2)

The method of integration recommended depends on the situation. In this problem probably the

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numerical method is the quickest and simplest and gives a good enough answer for most purposes.

So with the integral evaluated, Eq. (i) becomes

$$\tau = \frac{(0.0625 \text{ mol/liter})^{1/2}}{(10^{-2} \text{ mol}^{1/2}/\text{liter}^{1/2} \cdot \text{sec})} \quad (1.33) = 33.2 \text{ sec}$$

5.3 DESIGN FOR SINGLE REACTIONS

Single reactions are chemical reactions whose progress can be described and followed adequately by using one and only one rate expression coupled with the necessary stoichiometric anc equilibrium expressions. For such reactions, product distribution is fixed; hence, the important factor in comparing designs is the reactor size.

In a latter section we will briefly discuss how the pattern of flow in a reactor affects the product distribution (between desired and undesirable products) for multiple reaction systems.

5.3.1 Size Comparison of Single Ideal Reactors.
For systems of constant density or volume ($\epsilon = 0$), the required volume for a given conversion and production rate of an ideal batch reactor is the same as for an ideal plug flow reactor. Thus · except for special cases, we can focus our attention on a comparison between mixed flow and plug flow reactors.

The comparison of size requirements for different types of reactors depends upon the type of chemical rate expression.

Simple nth-order rate law

$$-r_A = k \, c_A^n$$

For an ideal mixed flow reactor when $X_{A_0} = 0$,

$$\tau_m = \left[\frac{C_{A_0} V}{F_{A_0}}\right]_m = \frac{1}{kC_{A_0}^{n-1}} \left[\frac{X_A(1 + \epsilon X_A)^n}{(1-X_A)^n}\right] \quad (30)$$

For plug flow

$$\tau_p = \left[\frac{C_{A_0} V}{F_{A_0}}\right]_p = \frac{1}{kC_{A_0}^{n-1}} \left[\int_0^{X_A} \frac{(1 + \epsilon X_A)^n}{(1-X_A)^n} \, dX_A\right] \quad (31)$$

A convenient way of comparing the mixed and plug flow reactors is to consider the ratio of residence times of the two types of reactors:

$$\lambda = \tau_m/\tau_p$$

$$\lambda = \frac{\left[X_A \dfrac{(1 + X_A)^n}{X_A(1 - X_A)}\right]_m}{\left[\displaystyle\int_0^{X_A} \dfrac{(1 + X_A)^n}{(1 - X_A)^n} \, dX_A\right]_p} \quad (32)$$

The above relations assume that C_{A_0} and F_{A_0} are the same for each reactor. For ideal reactors, $\lambda \geq 1$.

When either the density of the system is constant or there is no expansion ($\epsilon = 0$), Equation (32) can be integrated to give:

$$\lambda = \tau_m/\tau_p = \frac{\left[\dfrac{X_A}{(1 - X_A)^n}\right]_m}{\left[\dfrac{(1 - X_A)^{1-n} - 1}{n-1}\right]_p} \quad n \neq 1 \quad (33a)$$

$$\lambda = \tau_m/\tau_p = \frac{\left[\dfrac{X_A}{1 - X_A}\right]_m}{[-\ln (1-X_A)]_p} \quad n = 1 \quad (33b)$$

Levenspiel (1) has prepared a figure which represents Equations (32) and (33) and is reproduced here as Figure 2. Note that the ordinate essentially gives the volume ratio of reactor volume, i.e.,

$$\lambda = \tau_m/\tau_p = V_m/V_p$$

Levenspiel observes the following:

1. For any particular conversion duty and for all positive reaction orders the mixed reactor is always larger than the plug flow reactor. The ratio of volumes increases with reaction order. For zero-order reactions, reactor size is independent of the type of flow.

2. When conversion is small, the reactor performance is only slightly affected by flow type, the volume ratio approaching unity as conversion approaches zero. The ratio increases very rapidly at high conversion; consequently a proper representation of the flow becomes very important in this range of conversion.

3. Density variation during reaction affects design; however, it is normally of secondary importance compared to the difference in flow type. Expansion (or density decrease) during reaction increases the volume ratio, in other words, expansion further decreases the effectiveness of the mixed reactor with respect to the plug flow reactor; density increase during reaction has the opposite effect.

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Levenspiel (1) presents Figures 3 and 4 which show the same first- and second-order curves for $\varepsilon = 0$ but also include dashed lines which represent fixed values of the dimensionless reaction rate group, defined as

k for first-order reaction

kC_{A_0} for second-order reaction

$kC_{A_0}^{n-1}$ for nth-order reaction

With these dashed curves, one can compare different reactor types, reactor sizes, and conversion levels. Example 2 illustrates the usefulness of these figures.

5.3.2 Variation of Reactant Ratio for Second-Order Reactions. Second-order reactions of two components and of the type

$$A + b'B \quad Products$$

$$M = \frac{C_{B_0}}{b'C_{A_0}} = Reactant\ Ratio$$

$$-r_A = -r_B/b' = kC_A C_B \qquad (34)$$

behave as second-order reactions of one component when the reaction ratio M is unity. Thus

$$-r_A = kC_A C_B = kC_A^2 \quad when\ M = 1 \qquad (35)$$

On the other hand, when a large excess of reactant B is used, then its concentration does not change appreciably ($C_B \cong C_{B_0}$); and the reaction approaches first-order behavior with respect to the limiting component A, or

$$-r_A = kC_A C_B = (kC_{B_0})C_A = k'C_A \quad when\ M \gg 1$$
$$(36)$$

Thus in Figure 2 and in terms of the limiting component (defined to be component A), the size ratio of mixed to plug flow reactors is represented by the region between the first-order and the second-order curves -- depending on the value of the molar feed ratio, M.

EXAMPLE 2 (1) Reactor performance from design charts.

The aqueous reaction $A + B \rightarrow$ products with known kinetics

$$-r_A = (500\ liter/mol \cdot min)C_A C_B$$

is to take place in an experimental tubular reactor (assume plug flow) under the following

conditions:

volume or reactor V = 0.1 liter
volumetric feed rate v = 0.05 liter/min
concentration of reactants in feed, $C_{A_0} = C_{B_0}$
= 0.01 mol/liter

(a) What fractional conversion of reactants can be expected?

(b) For the same conversion as in part (a), what size of stirred tank reactor (assume mixed flow is needed?

(c) What conversion can be expected in a mixed reactor equal in size to the plug flow reactor?

Solution

For an equimolar feed we may treat this as a second-order reaction of the type

$$\underline{A} \rightarrow products, \quad -r_A = kC_A^2$$
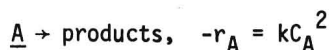
in which the performance charts, Figures 2 and 4 apply. The sketch of Figure E3 shows how these charts are used.

(a) Conversion in plug flow. The space-time is

$$\tau = \frac{VC_{A_0}}{F_{A_0}} = \frac{V}{v} = \frac{0.1\ liter}{0.05\ liter/min} = 2\ min$$

Therefore, the value of the second-order reaction rate group is

$kC_{A_0}\tau = (500\ liter/mol \cdot min)(2\ min)(0.01\ mol/liter)=10$

From the plug flow line of Figure 4 and the calculated value of $kC_{A_0}\tau$ we find (see Figure E3) that the conversions are:

$$X_A = X_B = 0.91$$

(b) Size of mixed reactor for identical treatment rate of feed. For identical C_{A_0} and F_{A_0}, the ordinate of Figure 2 and 4 reduces to the volume ratio of the two reactors, V_m/V_p. Thus for the same X_A we find

$$\frac{V_m}{V_p} = 11$$

in which case

$$V_m = (11)(0.1\ liter) = 1.1\ liter$$

(c) Conversion in a mixed reactor of the same size. For the same size reactor we must remain on the same $kC_{A_0}\tau$ line. Thus moving along this line from plug to mixed flow in Figure 4 we find

Conversion: $X_A = 0.73$

The graphical method was used in this example to illustrate the use of these charts. Analytic solution is also possible. The following examples illustrate the latter approach in searching for optimum operating conditions.

EXAMPLE 3. Finding the optimum reactor size (1)

One hundred gram moles of R are to be produced hourly from a feed consisting of a saturated solution of A (C_{A_0} = 0.1 mol/liter) in a mixed flow reactor. The reaction is

$$\underline{A} \rightarrow \underline{R}, \quad r_R = (0.2 \text{ hr}^{-1})C_A$$
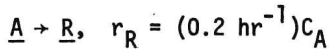
Cost of reactant at C_{A_0} = 0.1 mol/liter is

$$\$_A = \$0.50/\text{mol } \underline{A}$$

Cost of reactor including installation, auxiliary equipment, instrumentation, overhead, labor, depreciation, etc., is

$$\$_m = \$0.01/\text{hr}\cdot\text{liter}$$

What reactor size, feed rate, and conversion should be used for optimum operations? What is the unit cost of R for these conditions if unreacted $\underline{A}$ is discarded?

Solution

This is an optimization problem which balances high fractional conversion (low reactant cost) in a large reactor (high equipment cost) on the one hand versus low fractional conversion in a small reactor on the other. The solution involves finding an expression for the total cost of the operation and minimizing it. On an hourly basis the total cost is

$$\$_t = \binom{\text{volume of}}{\text{reactor}}\left(\frac{\text{cost}}{(\text{hr})(\text{volume of reactor})}\right)$$

$$+ \binom{\text{feed rate}}{\text{of reactant}}\binom{\text{unit cost}}{\text{of reactant}}$$

$$= V\$_m + F_{A_0}\$_A$$

Let us evaluate the terms in this cost equation. For a first-order reaction, Equation (28) gives

$$V = \frac{F_{A_0}X_A}{kC_{A_0}(1 - X_A)}$$

Noting that the rate of production of R is

$$F_R = F_{A_0}X_A = 100 \text{ mol/hr}$$

We can eliminate F_{A_0} and can write the total cost expression in terms of one variable alone, X_A. Thus

$$\$_t = \frac{F_R}{kC_{A_0}(1 - X_A)}\$_m + \frac{F_R}{X_A}\$_A$$

$$= \frac{100}{(0.2)(0.1)(1 - X_A)}(0.01) + \frac{100}{X_A}(0.5)$$

$$\$_t = \frac{50}{1 - X_A} + \frac{50}{X_A}$$

To find the condition for minimum cost, differentiate this expression and set to zero. Thus

$$\frac{d(\$_t)}{dt} = 0 = \frac{50}{(1 - X_A)^2} - \frac{50}{X_A^2}$$

or

$$X_A = 0.5$$

Hence the optimum conditions are

Conversion:

$$X_A = 0.5$$

Feed rate:

$$F_{A_0} = \frac{F_R}{X_A} = \frac{100}{0.5} = 200 \text{ mol } \underline{A}/\text{hr} \text{ or}$$

$$v = \frac{F_{A_0}}{C_{A_0}} = 2000 \text{ liter/hr}$$

Reactor size:

$$V = \frac{F_{A_0}X_A}{kC_{A_0}(1-X_A)} = \frac{100}{(0.2)(0.1)(0.5)} = 10,000 \text{ liter}$$

Cost of production:

$$\frac{\$_t}{F_R} = \frac{V\$_m + F_{A_0}\$_A}{F_R} = \frac{10,000 \ (0.01) + 200(0.5)}{100}$$

$$= \$2.00/\text{mol } R$$

5.4 MULTIPLE-REACTOR SYSTEMS

5.5.1 Plug Flow Reactors in Series. Consider N plug flow reactors connected in series and let X_i equal the fractional conversion of the stream leaving the ith reactor. For the ith reactor:

$$V_i = F_{A_0} \int_{X_{A_{i-1}}}^{X_{A_i}} \frac{dX_A}{-r_A} \qquad (37a)$$

$$V = \sum_{i=1}^{N} V_i = F_{A_0} \int_{X_{A_0}}^{X_{A_N}} \frac{dX_A}{-r_A} \qquad (37b)$$

Hence, N plug flow reactors in series with a total volume V gives the same conversion as a single plug flow reactor of volume V.

5.5.2 Equal-size Mixed Flow Reactors in Series.
In plug flow the concentration of reactant decreases progressively through the system; in mixed flow the concentration drops immediately to a low value. Because of this fact, a plug flow reactor is more efficient than a mixed reactor for reactions whose rates increase with reactant concentration. It can be shown that as the number of mixed flow reactors in series is increased, the overall volume required for a given conversion approaches that for a plug flow system.

First-Order Reactions. Applying a material balance about the ith reactor for $\varepsilon = 0$

$$vC_i - vC_{i-1} - (-kC_i)V_i = 0$$

$$v(C_{i-1} - C_i) = kC_i V_i$$

$$\therefore \quad \tau_i = \frac{V_i}{v} = \frac{C_{i-1} - C_i}{kC_i} \qquad (38a)$$

$$\frac{C_{i-1}}{C_i} = 1 + k\tau_i \qquad (38b)$$

The space-time τ (or the mean residence time t) is the same for all equal-size reactors, and hence

$$\frac{C_0}{C_N} = \frac{1}{1 - X_{A_N}} = (1 + k\tau_i)^N \qquad (39a)$$

The residence time for the entire system is

$$\tau_N = N\tau_i = \frac{N}{k} \left[\left(\frac{C_0}{C_N}\right)^{1/N} - 1 \right] \qquad (39b)$$

The above equation can be shown to equal the relation for plug flow [Equation (31) with $\varepsilon = 0$] when $N \to \infty$ by an application of L'Hopital's rule

$$\tau_p = \frac{1}{k} \ln \frac{C_0}{C_f} \qquad (40)$$

Levenspiel plots the ratio of Equation (39b) and (40), τ_N/τ_p in Figures 3 and 4. This ratio is basically the ratio of reactor volumes for N equal-sized reactors to that for a plug flow reactor.

EXAMPLE 4. Mixed flow reactors in series (1)

At present 90% of reactant A is converted into product by a second-order reaction in a single mixed flow reactor. We plan to place a second reactor similar to the one being used in series with it.

(a) For the same treatment rate as that used at present, how will this addition affect the conversion of reactant?

(b) For the same 90% conversion, by how much can the treatment rate be increased?

Solution

The sketch of Figure E4 shows how the performance chart of Figure 4 can be used to help solve this problem.

(a) Find the conversion for same treatment rate. For the single reactor at 90% conversion we have from Figure 4

$$kC_0\tau = 90$$

For the two reactors the space-time or holding time is doubled; hence the operation will be represented by the dashed line where

$$kC_0\tau = 180$$

This line cuts the N=2 line at a conversion X = 97.4%

(b) Find the treatment rate for the same conversion. Staying on the 90% conversion line we find for N=2 that

$$kC_0\tau = 27.5$$

(See Figure E4). Comparing the value of the reaction rate group for N = 1 and N = 2 we find

$$\frac{(kC_0\tau)_{N=2}}{(kC_0\tau)_{N=1}} = \frac{\tau_{N=2}}{\tau_{N=1}} = \frac{(V/v)_{N=2}}{(V/v)_{N=1}} = \frac{27.5}{90}$$

Since $V_{N=2} = 2V_{N=1}$ the ratio of flow rates becomes

$$\frac{v_{N=2}}{v_{N=1}} = \frac{90}{27.5} (2) = 6.6$$

Thus the treatment rate can be raised to 6.6 times the original. NOTE. If the second reactor had been operated in parallel with the original unit then the treatment rate could only be doubled. Thus

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