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Chemical Engineering: Basics & Applications

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First Edition

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Authored by

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Al-Saeed University, Taiz (2026)

Abstract

This text, **"Chemical Engineering: Basics & Applications"** provides a comprehensive foundation in Chemical Reaction Engineering (CRE), focusing on the rational design and performance analysis of chemical reactors. It distinguishes CRE from chemical kinetics by positioning the latter as a tool for determining reaction rates and mechanisms, while the former applies this kinetic data to specify reactor size, configuration, and operating conditions.

The core analytical framework is built upon the **general balance equation**, which accounts for mass or energy across finite or differential control volumes through the summation of input, output, generation, and accumulation rates. The text systematically explores the three primary ideal reactor models: **Batch Reactors (BR)** for small-volume, high-value production; **Continuous Stirred-Tank Reactors (CSTR)**, characterized by perfect mixing and backmix flow; and **Plug-Flow Reactors (PFR)**, which model tubular flow without axial mixing.

Special emphasis is placed on **catalysis**, detailing how catalysts enhance reaction rates and selectivity without altering thermodynamic equilibrium. The book addresses practical engineering challenges, including catalyst deactivation, mass transfer gradients in porous particles, and non-isothermal operation requiring simultaneous energy balances. Finally, the text bridges theory and practice through the integration of modern simulation tools—**CHEMCAD and COCO**—to solve complex industrial problems such as biomass-to-methanol conversion, natural gas liquefaction, and distillation column sizing.

Preface

The field of Chemical Engineering stands at the vital intersection of fundamental science and industrial application. At its heart lies the chemical reactor—a sophisticated environment where molecular transformations are harnessed to meet the needs of modern society. Writing **"Chemical Engineering: Basics & Applications"** was driven by a singular mission: to bridge the gap between theoretical chemical kinetics and the practical, often complex, realities of reactor design and process simulation.

As an engineer, one quickly realizes that designing a reactor is perhaps the most demanding task in the profession. It requires more than just an understanding of how fast a reaction occurs; it demands a holistic command of thermodynamics, mass and energy balances, and economic viability. This book is structured to guide the reader through this multidisciplinary landscape. We begin with the "microscopic" world of molecular collisions and rate laws, and systematically scale up to the "macroscopic" world of industrial-scale Batch, CSTR, and Plug-Flow reactors.

In today's industrial environment, the "tools in our workshop" have evolved. Therefore, a significant focus of this work is dedicated to the integration of modern computational tools. By incorporating worked problems using **CHEMCAD** and **COCO** simulations, this book aims to equip students and researchers with the digital proficiency required to model real-world processes—from biomass-to-methanol conversion to complex distillation and refrigeration systems.

This book is intended to be both a foundational map for those new to the field and a practical reference for those looking to apply advanced simulation techniques to contemporary engineering challenges. It is my hope that these pages provide not only the technical knowledge required for rigorous design but also the inspiration to solve the pressing industrial and environmental problems of our time.

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Key Contents

CHEMICAL ENGINEERING: BASICS & APPLICATIONS

1- INTRODUCTION

Chemical reaction engineering (CRE) is concerned with the rational design and/or analysis of performance of chemical reactors.

Chemical kinetics is concerned with the rates of chemical reactions, that is, with the quantitative description of how fast chemical reactions occur, and the factors affecting these rates.

A chemical reactor is a device in which change in composition of matter occurs by chemical reaction. The chemical reaction is normally the most important change, and the device is designed to accomplish that change. Design includes determining the type, size, configuration, cost, and operating conditions of the device.

CORRELATION BETWEEN KINETICS AND CHEMICAL REACTION ENGINEERING

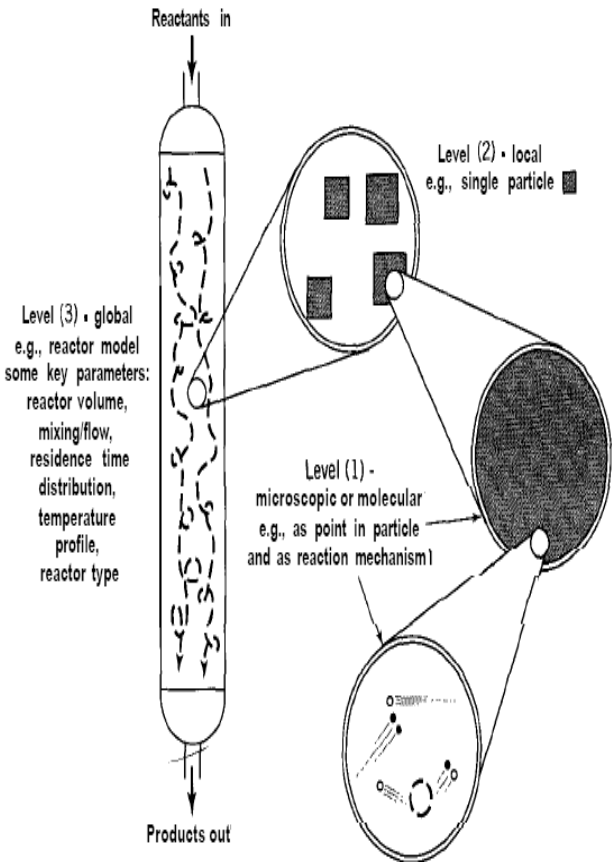
In chemical kinetics, the chemical reactor used to carry out the reaction is a tool for determining something about the reacting system: rate of reaction and dependence of rate on various factors, such as concentration of species i (c_i) and temperature (T). **In chemical reaction engineering (CRE)**, the information obtained from kinetics is a means to determine something about the reactor: size, flow and thermal configuration, product distribution, etc. **There are three levels of system size to compare the nature of kinetics and of CRE which are as follows:**

(1) ***Microscopic or molecular system:*** a collection of reacting molecules is sufficiently large to constitute a point in space, characterized, at any given instant, by a single value for each of concentration c_i ,temperature *T,* pressure (P), and density (ρ).

(2) ***Local macroscopic system:*** for example, one solid particle reacting with a fluid, in which there may be gradients of c_i, *T,* etc. within the particle.

(3) ***Global macroscopic system:*** for example, a collection or bed of solid particles reacting with a fluid, in which, in addition to local gradients within each particle, there may be global gradients throughout a containing vessel, from particle to particle and from point to point within the fluid.

These levels are illustrated in the right-side figure.



ASPECTS OF KINETICS

Rate of Reaction-Definition

We define the rate of reaction verbally for a species involved in a reacting system either as a reactant or as a product. The system may be single-phase or multiphase, may have fixed density or variable density as reaction proceeds, and may have uniform or varying properties (e.g., ρ, c_A, T, P) with respect to position at any given time. ***The extensive rate of reaction*** with respect to a species A, R_A, is the observed rate of formation of A:

$$R_A = \frac{\text{moles A formed}}{\text{unit time}}, \text{ e.g., } \frac{\text{mol}}{\text{s}} \qquad (1)$$

The intensive rate of reaction, r_A, is the rate referred to a specified normalizing quantity (NQ), or rate basis, such as volume of reacting system or mass of catalyst:

$$r_A = \frac{\text{moles A formed}}{(\text{unit time})(\text{unit NQ})}, \text{ e.g., } \frac{\text{mol}}{(\text{s})(\text{m}^3)} \qquad (2)$$

The rate, R_A or r_A, as defined is negative if A is consumed, and is positive if A is produced. One may also define a species-independent rate of reaction for a single reaction or step in a mechanism, but this requires further consideration of stoichiometry.

The rate r_A is independent of the size of the reacting system and of the physical circumstances of the system, whereas A is not. Thus, r_A may be considered to be the **"point"** or **"intrinsic" rate** at the molecular level and is the more useful quantity. The two rates are related as follows, with volume V as NQ: For a uniform system, as in a well-stirred tank,

$$R_A = r_A V \qquad (3)$$

For a nonuniform system,

$$R_A = r_A \int_{V_i}^{V_f} dV \qquad (4)$$

Parameters Affecting Rate of Reaction: The Rate Law

Rate of reaction depends on a number of parameters, the most important of which are usually

(1) ***The nature of the species involved in the reaction;*** Many examples of types of very fast reactions involve ions in solution, such as the neutralization of a strong acid by a strong base, and explosions. In the former case, the rate of change may be dictated by the rate at which the reactants can be brought into intimate contact. At the other extreme, very slow reactions may involve heterogeneous reactions, such as the oxidation of carbon at room temperature. The reaction between hydrogen and oxygen to form water can be used to illustrate both extremes. Subjected to a spark, a mixture of hydrogen and oxygen can produce an explosion, but in the absence of this, or of a catalyst such as finely divided platinum, the reaction is extremely slow. In such a case, it may be wrongly supposed that the system is at equilibrium, since there may be no detectable change even after a very long time.

(2) ***Concentrations of species;*** **Rate of reaction usually depends on concentration of reactants (and sometimes of products), and usually increases as concentration of reactants increases. Thus, many combustion reactions occur faster in pure oxygen than in air at the same total pressure.**

(3) ***Temperature;*** **Rate of reaction depends on temperature and usually increases nearly exponentially as temperature increases. An important exception is the oxidation of nitric oxide (NO), which is involved in the manufacture of nitric acid; in this case, the rate decreases as T increases.**

(4) ***Catalytic activity;*** **Many reactions proceed much faster in the presence of a substance which is itself not a product of the reaction. This is the phenomenon of catalysis, and many life processes and industrial processes depend on it. Thus, the oxidation of SO_2 to SO_3 is greatly accelerated in the presence of V_2O_5 as a catalyst, and the commercial manufacture of sulfuric acid depends on this fact.**

(5) ***Nature of contact of reactants;*** **The nature or intimacy of contact of reactants can greatly affect the rate of reaction. Thus, finely divided coal burns much faster than lump coal. The titration of an acid with a base occurs much faster if the acid and base are stirred together than if the base is simply allowed to "dribble" into the acid solution. For a heterogeneous, catalytic reaction, the effect may show up in a more subtle way as the dependence of rate on the size of catalyst particle used**

(6) ***Wavelength of incident radiation;*** **Some reactions occur much faster if the reacting system is exposed to incident radiation of an appropriate frequency. Thus, a mixture of hydrogen and chlorine can be kept in the dark, and the reaction to form hydrogen chloride is very slow; however, if the mixture is exposed to ordinary light, reaction occurs with explosive rapidity. Such reactions are generally called photochemical reactions.**

The way in which the rate of reaction depends on these parameters is expressed mathematically in the form of a rate law; that is, for species A in a given reaction, the rate law takes the general form

$$r_A = r_A(conc.,\ temp.,\ cat.\ activity,\ \text{etc.}) \qquad (5)$$

The form of the rate law must be established by experiment, and the complete expression may be very complex and, in many cases, very difficult, if not impossible, to formulate explicitly.

Kinetics and Chemical Reaction Stoichiometry

All chemical change is subject to the law of conservation of mass, including the conservation of the chemical elements making up the species involved, which is called chemical stoichiometry (from Greek relating to measurement (-metry) of an element (stoichion)).

The conservation of atomic species is commonly expressed in the form of chemical equations, corresponding to chemical reactions. We refer to the stoichiometric constraints expressed this way as chemical reaction stoichiometry. A simple system is represented by one chemical equation, and a complex system by a set of chemical equations. Determining the number and a proper set of chemical equations for a specified list of species (reactants and products) is the role of chemical reaction stoichiometry.

Worked problem 1.1

The oxidation of sulfur dioxide to sulfur trioxide in the manufacture of sulfuric acid is an example of a simple system. It involves 3 species (SO_2, O_2 and SO_3) with 2 elements (S and O). The stoichiometry of the reaction can be represented by one, and only one, chemical equation (apart from a multiplicative factor):

$2\,SO_2 + O_2 = 2\,SO_3$ **(A)**

$-2\,SO_2 - O_2 + 2\,SO_3 = 0$ **(B)**

Using Mathematica, determine/ construct a set of chemical equations to represent a reacting system involving these 3 species.

Solution 1.1

Equation (A) or (B) stems from the fact that the two element balances involve three quantities related to amounts of the species. These balances may be written as follows:

For S: $1\Delta n_{SO2} + 0\,\Delta n_{O2} + 1\,\Delta n_{SO3} = 0$ **(C)**

For O: $2\,\Delta n_{SO2} + 2\,\Delta n_{O2} + 3\,\Delta n_{SO3} = 0$ **(D)**

where Δn_{SO2} = the change in moles of SO_2 by reaction, and similarly for Δn_{O2}, and Δn_{SO3}.

The coefficients in equations (C) and (D) form a matrix A in which each column represents a species and each row an element:

$$A=\begin{pmatrix}1 & 0 & 1\\ 2 & 2 & 3\end{pmatrix} \qquad \textbf{(E)}$$

The entries in A are the subscripts to the elements in the molecular formulas of the substances (in an arbitrary order). Each column is a vector of the subscripts for a substance, and A is called a *formula matrix*.

In this case, A can be transformed by elementary row operations (multiply the second row by 1/2 and subtract the first row from the result) to the unit matrix or reduced row-echelon form:

$$A^*=\begin{pmatrix}1 & 0 & 1\\ 2/2 & 2/2 & 3/2\end{pmatrix}=\begin{pmatrix}1 & 0 & 1\\ 1 & 1 & 1.5\end{pmatrix}\rightarrow\begin{pmatrix}1 & 0 & 1\\ 1-1 & 1-0 & 1.5-1\end{pmatrix}$$

$$A^*=\begin{pmatrix}1 & 0 & 1\\ 0 & 1 & 1/2\end{pmatrix} \qquad \textbf{(F)}$$

The form in (F) provides a solution for Δn_{SO2} and Δn_{O2} in equations (C) and (D) in terms of Δn_{SO3}. This is

$$\Delta n_{SO_2} = -\Delta n_{SO_3};\quad \text{and } \Delta n_{O_2} = -(1/2)\Delta n_{SO_3} \qquad \textbf{(G)}$$

which may be written as

$$\frac{\Delta n_{SO_2}}{-1} = \frac{\Delta n_{O_2}}{-1/2} = \frac{\Delta n_{SO_3}}{1} \qquad \text{(G')}$$

The numbers - 1, - 1/2, and 1 in (G') are in proportion to the stoichiometric coefficients in equation (B), which provides the same interpretation as in (G) or (G'). The last column in (F) gives the values of the stoichiometric coefficients of SO_2 and O_2 (on the left side) in a chemical equation involving one mole of SO_3 (on the right side):

$$+1\ SO_2 + 1/2\ O_2 = 1\ SO_3 \qquad \text{(H)}$$

or, in conventional form, on elimination of the fraction:

$$2SO_2 + O_2 = 2SO_3 \qquad \text{(H')}$$

SO_2 and O_2 are said to be component species, and SO_3 is a noncomponent species. The number of components C is the rank of the matrix A (in this case, 2):

$$\text{rank (A)} = C$$

Usually, but not always, C is the same as the number of elements, M. In this sense, C is the smallest number of chemical "building blocks" (ultimately the elements) required to form a system of specified species.

More generally, a simple system is represented by

$$\sum_{i=1}^{N} \nu_i A_i = 0 \qquad (1)$$

where N is the number of reacting species in the system, ν_i is the stoichiometric coefficient for species i [negative (-) for a species written on the left side of = and positive (+) for a species written on the right side], and A_i is the molecular formula for species i.

For a simple system, if we know the rate of reaction (r) for one species, then we know the rate for any other species from the chemical equation, which gives the ratios in which species are reacted and formed:

$$r = \frac{r_{SO_2}}{-2} = \frac{r_{O_2}}{-1} = \frac{r_{SO_3}}{2} \qquad (2)$$

where the signs correspond to consumption (-) and formation (+); r is positive. More generally, for a simple system, the rates r and r_i are related by

$$r = r_i/\nu_i; \qquad i = 1, 2, \ldots, N \qquad (3)$$

Exercise 1.1

The dehydrogenation of ethane (C_2H_6) is used to produce ethylene (C_2H_4), along with H_2, but other species, such as methane (CH_4) and acetylene (C_2H_2), may also be present in the product stream. Using Muthematica, determine C and a permissible set of components, and construct a set of chemical equations to represent a reacting system involving these five species.

Kinetics and Thermodynamics/Equilibrium

Kinetics and thermodynamics address different kinds of questions about a reacting system. The methods of thermodynamics, together with certain experimental information, are used to answer questions such as (1) what is the maximum possible conversion of a reactant, and the resulting equilibrium composition of the reacting system at given conditions of T and P, and (2) at given T and P, how "far" is a particular reacting system from equilibrium, in terms of the "distance" or affinity measured by the Gibbs energy driving force (ΔG)? Another type of question, which cannot be answered by thermodynamic methods, is: If a given reacting system is not at equilibrium, at what rate, with respect to time, is it approaching equilibrium? This is the domain of kinetics.

These questions point up the main differences between chemical kinetics and chemical thermodynamics, as follows:

(1) Time is a variable in kinetics but not in thermodynamics; rates dealt with in the latter are with respect to temperature, pressure, etc., but not with respect to time; equilibrium is a time-independent state.

(2) We may be able to infer information about the mechanism of chemical change from kinetics but not from thermodynamics; the rate of chemical change is dependent on the path of reaction, as exemplified by the existence of catalysis; thermodynamics, on the other hand, is not concerned with the path of chemical change, but only with "state" and change of state of a system.

(3) The AG of reaction is a measure of the affinity or tendency for reaction to occur, but it tells us nothing about how fast reaction occurs; a very large, negative ΔG, as for the reaction $C + O_2 \rightarrow CO_2$, at ambient conditions, although favorable for high equilibrium conversion, does not mean that the reaction is necessarily fast, and in fact this reaction is very slow; we need not be concerned about the disappearance of diamonds at ambient conditions.

(4) Chemical kinetics is concerned with the rate of reaction and factors affecting the rate, and chemical thermodynamics is concerned with the position of equilibrium and factors affecting equilibrium.

Kinetics and Transport Processes

At the molecular or microscopic level, chemical change involves only chemical reaction. At the local and global macroscopic levels, other processes may be involved in change of composition. These are diffusion and mass transfer of species as a result of differences in chemical potential between points or regions, either within a phase or between phases. The term "chemical engineering kinetics" includes all of these processes, as may be required for the purpose of describing the overall rate of reaction. Yet another process that may lead to change in composition at the global level is the mixing of fluid elements as a consequence of irregularities of flow (nonideal flow) or forced convection.

Still other rate processes occur that are not necessarily associated with change in composition: heat transfer and fluid flow. Consideration of heat transfer introduces contributions to the energy of a system that are not associated with material flow, and helps to determine T. Consideration of fluid flow for our purpose is mainly confined to the need to take frictional pressure drop into account in reactor performance. Further details for quantitative descriptions of these processes are introduced as required.

ASPECTS OF CHEMICAL REACTION ENGINEERING

Reactor Design and Analysis of Performance

Reactor design embodies many different facets and disciplines, the details of some of which are outside our scope. Here, we focus on process design as opposed to mechanical design of equipment. Other aspects are implicit, but are not treated explicitly: instrumentation and process control, economic, and socioeconomic (environmental and safe-operation). Reactor design is a term we may apply to a new installation or modification; otherwise, we may speak of the analysis of performance of an existing reactor.

Parameters Affecting Reactor Performance

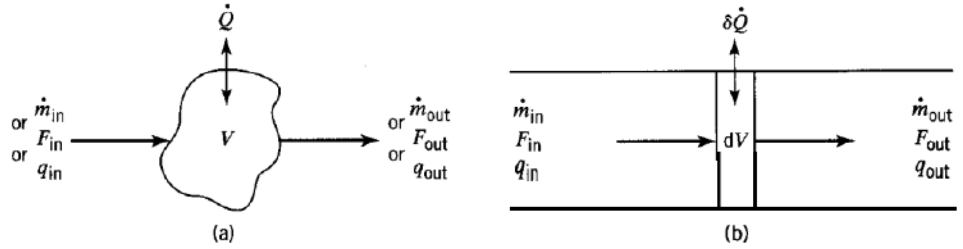
The term "reactor performance" usually refers to the operating results achieved by a reactor, particularly with respect to fraction of reactant converted or product distribution for a given size and configuration; alternatively, it may refer to size and configuration for a given conversion or distribution. In any case, it depends on two main types of behavior: (1) rates of processes involved, including reaction and heat and mass transfer, sometimes influenced by equilibrium limitations; and (2) motion and relative-motion of elements of fluid (both single-phase and multiphase situations) and solid particles (where involved), whether in a flow system or not.

At this stage, type (1) is more apparent than type (2) and we provide some preliminary discussion of (2) here. Flow characteristics include relative times taken by elements of fluid to pass through the reactor (residence-time distribution), and mixing characteristics for elements of fluid of different ages: point(s) in the reactor at which mixing takes place, and the level of segregation at which it takes place (as a molecular dispersion or on a macroscopic scale). Lack of sufficient information on one or both of these types is a major impediment to a completely rational reactor design.

Balance Equations

One of the most useful tools for design and analysis of performance is the balance equation. This type of equation is used to account for a conserved quantity, such as mass or energy, as changes occur in a specified system; element balances and stoichiometry.

The balance is made with respect to a "control volume" which may be of finite (V) or of differential (dV) size, as illustrated in Figure (a) and (b).



The "dot" in $\dot{m}$ is used to distinguish flow rate of mass from static mass, *m*. It is not required for *F* and q, since these symbols are not used for corresponding static quantities.

Control volumes of finite (V) size (a) and of differential (dV) size (b) with material inlet and outlet streams and heat transfer ($\dot{Q}$, $\delta\dot{Q}$)

The balance equation, whether for mass or energy (the two most common uses for our purpose), is of the form:

$$\begin{pmatrix}\text{rate of input of mass (or energy) to control volume}\end{pmatrix} - \begin{pmatrix}\text{rate of output of mass (or energy) from control volume}\end{pmatrix} = \begin{pmatrix}\text{rate of accumulation of mass (or energy) within control volume}\end{pmatrix}$$

This Equation used as a mass balance is normally applied to a chemical species. For a simple system only one equation is required, and it is a matter of convenience which substance is chosen. For a complex system, the maximum number of independent mass balance equations is equal to *R*, the number of chemical equations or noncomponent species.

The input and output terms of equation may each have more than one contribution. The input of a species may be by convective (bulk) flow, by diffusion of some kind across the entry point(s), and by formation by chemical reaction(s) within the control volume. The output of a species may include consumption by reaction(s) within the control volume. There are also corresponding terms in the energy balance (e.g., generation or consumption of enthalpy by reaction), and in addition there is heat transfer (Q), which does not involve material flow. The accumulation term on the right side of equation is the net result of the inputs and outputs; for steady-state operation, it is zero, and for unsteady-state operation, it is nonzero.

The control volume depicted in Figures (a) and (b) is for one fixed in position (i.e., fixed observation point) and of fixed size but allowing for variable mass within it; this is often referred to as the Eulerian point of view. The alternative is the Lagrangian point of view, which focuses on a specified mass of fluid moving at the average velocity of the system; the volume of this mass may change.

In further considering the implications and uses of these two points of view, we may find it useful to distinguish between the control volume as a region of space and the system of interest within that control volume. In doing this, we consider two ways of describing a system. The first way is with respect to flow of material:

(Fl) Continuous-flow system: There is at least one input stream and one output stream of material; the mass inside the control volume may vary.

(F2) Semicontinuous-flow or semibatch system: There is at least one input stream or one output stream of material; the mass inside the control volume does vary for the latter.

(F3) Nonflow or static system: There are no input or output streams of material; the mass inside the control volume does not vary.

A second way of describing a system is with respect to both material and energy flows:

(Sl) An open system can exchange both material and energy with its surroundings.

(S2) A closed system can exchange energy but not material with its surroundings.

(S3) An isolated system can exchange neither material nor energy with its surroundings.

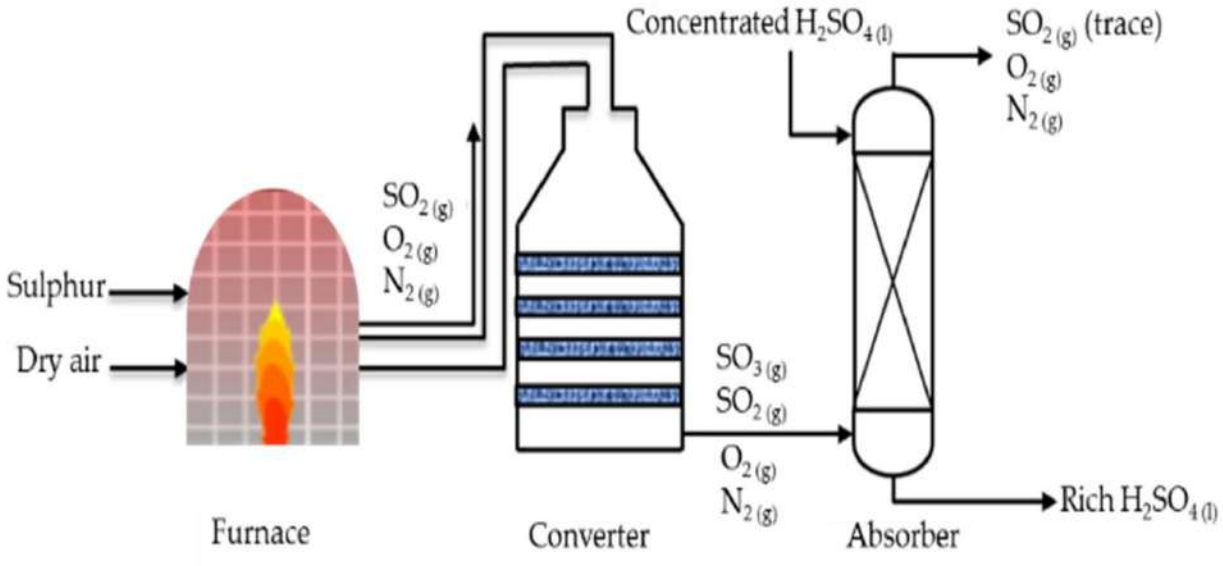
(S4) An adiabatic system is one for which Q = 0.

An Example of an Industrial Reactor

One of the most important industrial chemical processes is the manufacture of sulfuric acid. A major step in this process is the oxidation of SO_2 with air or oxygen-enriched air in the reversible, exothermic reaction corresponding to equation (A).

$$2\ SO_2 + O_2 = 2\ SO_3 \qquad \text{(A)}$$

This is carried out in a continuous-flow reactor ("SO_3 converter") in several stages, each stage containing a bed of particles of catalyst (promoted V_2O_5).



2- Kinetics and Ideal Reactor Models

Reactor Models

Based on the mode of operation

Batch Reactors
(Equipped with stirrer
Complete mixing of reactants)

Continuous Reactors

Based on Ideal Flow Patterns

Tubular Flow (TF) Reactors

In tubular flow, there is no mixing in the direction of flow; it is most closely approached by flow through an open tube.

Plug Flow Reactors (PFR)

Flat velocity profile at relatively high Reynolds number (Re)

Laminar Flow Reactors (LFR)

parabolic velocity profile at relatively low Re

Backmix Flow (BMF) Reactors

There is complete mixing; it is most closely approached by flow through a vessel equipped with an efficient stirrer.

we thus focus on four types of ideal reactors:

(1) Batch reactor (BR), based on complete mixing;
(2) Continuous-flow stirred tank reactor (CSTR), based on backmix flow;
(3) Plug-flow reactor (PFR), based on plug flow; and
(4) Laminar-flow reactor (LFR), based on laminar flow.

We describe each of these in more detail in turn, with particular emphasis on the material-balance equation in each of the first three cases, since this provides an interpretation of rate of reaction; for the last case, LFR, we consider only the general features at this stage.

TIME QUANTITIES

(1) Residence time (t) **of an element of fluid is the time spent by the element of fluid in a vessel. In some situations, it is the same for all elements of fluid, and in others there is a spread or distribution of residence times.**

(2) Mean residence time **($\bar{t}$) is the average residence time of all elements of fluid in a vessel.**

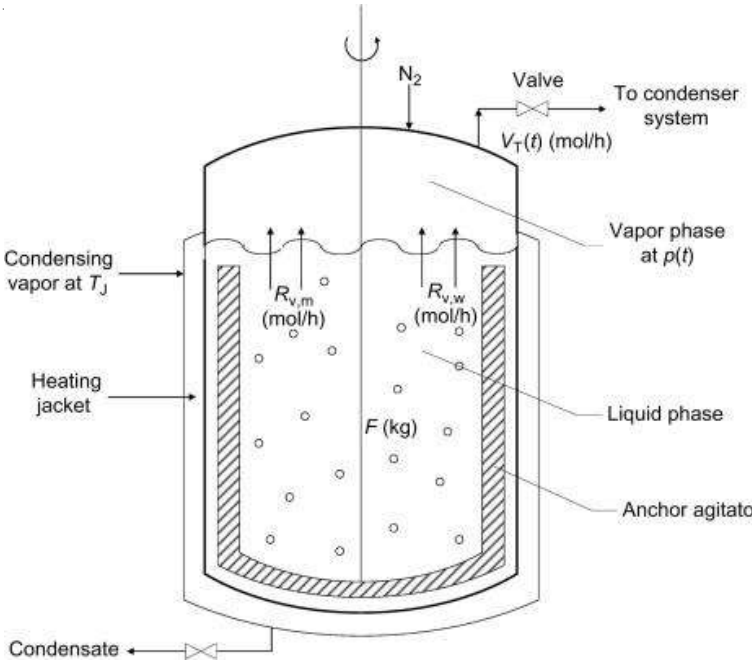
(3) Space time **(τ) is usually applied only to flow situations, and is the time required to process one reactor volume of inlet material (feed) measured at inlet conditions. That is, τ is the time required for a volume of feed equal to the volume of the vessel (V) to flow through the vessel. The volume V is the volume of the vessel accessible to the fluid. τ can be used as a scaling quantity for reactor performance, but the reaction conditions must be the same, point-by-point, in the scaling.**

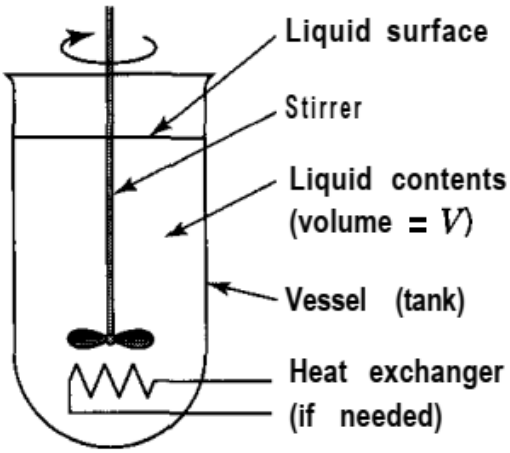
(4) Space velocity **(S_v) is the reciprocal of space time, and as such is a frequency (time^{-1}): the number of reactor volumes of feed, measured at inlet conditions, processed per unit time.**

BATCH REACTOR (BR)

General Features

A batch reactor (BR) is sometimes used for investigation of the kinetics of a chemical reaction in the laboratory, and also for larger-scale (commercial) operations in which a number of different products are made by different reactions on an intermittent





A batch reactor has the following characteristics:

(1) Each batch is a closed system.
(2) The total mass of each batch is fixed.
(3) The volume or density of each batch may vary (as reaction proceeds).
(4) The energy of each batch may vary (as reaction proceeds); for example, a heat exchanger may be provided to control temperature, as indicated in Figure.
(5) The reaction (residence) time t for all elements of fluid is the same.
(6) The operation of the reactor is inherently unsteady-state; for example, batch composition changes with respect to time.
(7) Point (6) notwithstanding, it is assumed that, at any time, the batch is uniform (e.g., in composition, temperature, etc.), because of efficient stirring.

Material Balance; Interpretation of r_i

Consider a reaction represented by A + . . . → products taking place in a batch reactor, and focus on reactant A.

$$\begin{pmatrix} rate\ of\ input \\ of\ A\ into \\ cotrol\ volume \end{pmatrix} - \begin{pmatrix} rate\ of\ output \\ of\ A\ from \\ control\ volume \end{pmatrix} = \begin{pmatrix} rate\ of\ accumulation \\ of\ A\ within \\ control\ volume \end{pmatrix} \qquad (1)$$

For a batch reactor, the only possible input and output terms are by reaction, since there is no flow in or out. For the reactant A in this case, there is output but not input. Equation (1) then reduces to

$$-\begin{pmatrix}\textit{rate of reaction}\\ \textit{of A in}\\ \textit{control volume}\end{pmatrix}=\begin{pmatrix}\textit{rate of accumulation}\\ \textit{of A within}\\ \textit{control volume}\end{pmatrix} \qquad (2)$$

or

$$(-r_A)V = -\mathrm{d}n_A/\mathrm{d}t, \qquad (3)$$

where V is the volume of the reacting system (not necessarily constant), and n_A is the number of moles of A at time t. Hence the interpretation of r_A, for a batch reactor in terms of amount n_A is

$$(-r_A) = -(1/V)(\mathrm{d}n_A/\mathrm{d}t) \qquad (4)$$

If A is the limiting reactant, it may be convenient to normalize n_A in terms of f_A, the fractional conversion of A, defined by

$$f_A = (n_{Ao} - n_A)/n_{Ao} \qquad \text{(BR)} \qquad (5)$$

where n_{Ao}, is the initial amount of A; f_A may vary between 0 and 1.

or

$$f_A = \frac{n_{Ao}}{n_{Ao}} - \frac{n_A}{n_{Ao}} = 1 - \frac{n_A}{n_{Ao}} \qquad (6)$$

Differentiating Equation (6) and rearranging,

$$df_A = -\frac{dn_A}{n_{Ao}} \qquad or \quad dn_A = -n_{Ao}\,df_A \qquad (7)$$

Substituting Equation (7) into Equation (4),

$$(-rA) = \left(\frac{n_{Ao}}{V}\right)\frac{df_A}{dt} \qquad (8)$$

Whether A is the limiting reactant or not, it may be convenient to normalize by means of the extent of reaction, ξ, defined for any species involved in the reaction by

$$\mathrm{d}\xi = \mathrm{d}n_i/\nu_i; \qquad i = 1, 2, \ldots, \mathrm{N} \qquad (9)$$

Substituting Equation (9) into Equation (4),

$$(-r_A) = -(\nu_A/V)(\mathrm{d}\xi/\mathrm{d}t) \qquad (10)$$

Normalization may be by means of the system volume V. This converts n_A into a volumetric molar concentration (molarity) of A, c_A, defined by

$$c_A = n_A/V \qquad or \quad n_A = c_A V$$
$$or \quad dn_A = c_A dV + V dc_A \qquad (11)$$

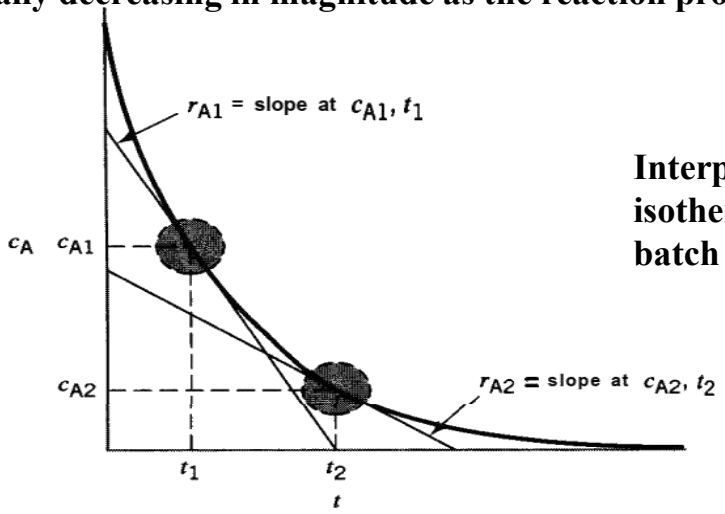
Substituting Equation (11) into Equation (4),

$$(-r_A) = -\frac{dc_A}{dt} \quad -\frac{c_A}{V}.\frac{dV}{dt} \qquad (12)$$

For a constant-density reaction, $dV/dt=0$ and equation (12) reduces to

$$(-r_A) = -\frac{dc_A}{dt} \qquad (13)$$

Thus, for a constant-density reaction in a BR, r_A, may be interpreted as the slope of the c_A-t relation. This is illustrated in Figure below, which also shows that r_A itself depends on t, usually decreasing in magnitude as the reaction proceeds, with increasing t



Interpretation of r_A for an isothermal, constant-density batch system.

Worked problem 2.1

For a reaction represented by A → products, in which the rate, ($-r_A$), is proportional to c_A, with a proportionality constant k_A, show that the time (t) required to achieve a specified fractional conversion of A (f_A) is independent of the initial concentration of reactant c_{A_0}. Assume reaction occurs in a constant-volume batch reactor.

Solution 2.1

The rate law can be written as,

$$(-r_A) = k_A c_A \qquad (1)$$

From the material- balance equation for a constant- density reaction in BR,

$$(-r_A) = -\frac{dc_A}{dt} \qquad (2)$$

Equating Equations (1) and (2),

$$k_A c_A = -\frac{dc_A}{dt}$$

On integration between c_{A_0} at $t=0$ to c_A at $t= t$,

$$\int_0^t dt = -\frac{1}{k_A}\int_{c_{A0}}^{c_A}\frac{dc_A}{c_A} = -\frac{1}{k_A}[-\ln c_A]_{c_{Ao}}^{c_A}$$

$$t = \frac{1}{k_A} ln\left(\frac{c_{Ao}}{c_A}\right) \qquad (3)$$

$$f_A = (n_{Ao} - n_A)/n_{Ao} \qquad (BR)$$

$$f_A = \frac{n_{Ao}}{n_{Ao}} - \frac{n_A}{n_{Ao}} = 1 - \frac{n_A}{n_{Ao}}$$

$$f_A = 1 - \frac{n_A/V}{n_{Ao}/V} = 1 - \frac{c_A}{c_{Ao}}$$

$$\frac{c_A}{c_{Ao}} = 1 - f_A \qquad \text{or} \qquad \frac{c_{Ao}}{c_A} = \frac{1}{1-f_A} \qquad (4)$$

Substituting Equation (4) into Equation (3),

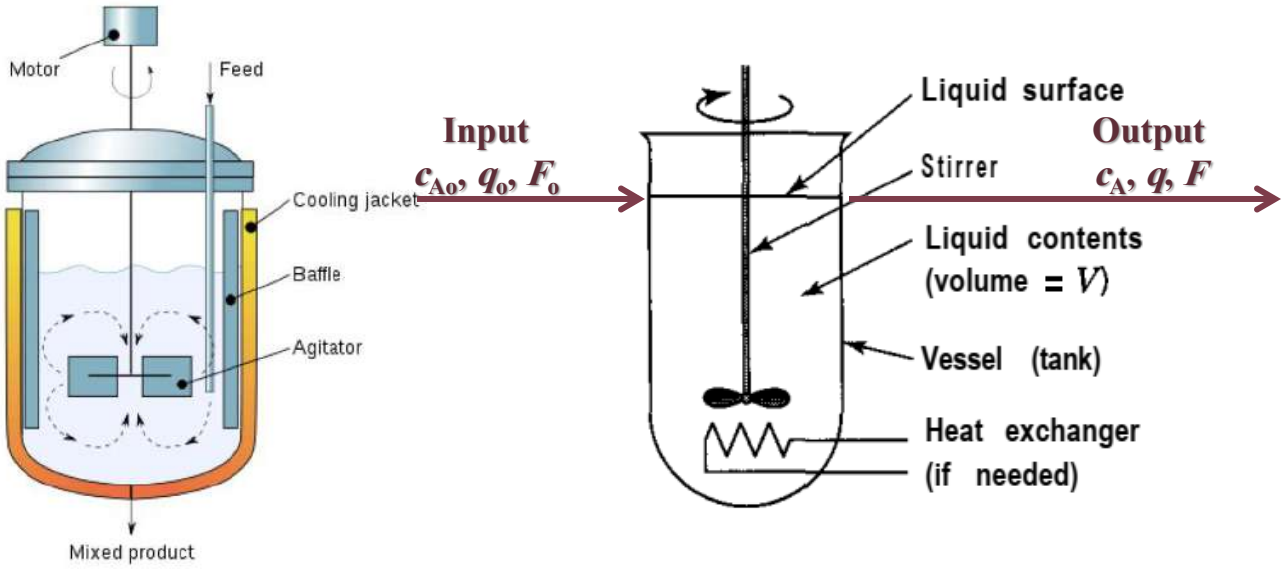
$$t = \frac{1}{k_A} ln\left(\frac{1}{1 - f_A}\right) \qquad (5)$$

So, Equation (5) shows that the time t is independent of c_{Ao}

CONTINUOUS STIRRED-TANK REACTOR (CSTR)

General Features

A continuous stirred-tank reactor (CSTR) is normally used for liquid-phase reactions, both in a laboratory and on a large scale. It may also be used, however, for the laboratory investigation of gas-phase reactions, particularly when solid catalysts are involved, in which case the operation is batchwise for the catalyst (see Figures below). Stirred tanks may also be used in a series arrangement (e.g., for the continuous copolymerization of styrene and butadiene to make synthetic rubber).



The CSTR has the following characteristics:

(1) The flow through the vessel(s), both input and output streams, is continuous but not necessarily at a constant rate.
(2) The system mass inside each vessel is not necessarily fixed.
(3) The fluid inside each vessel is perfectly mixed (backmix flow, BMF), and hence its properties are uniform at any time, because of efficient stirring.
(4) The density of the flowing system is not necessarily constant; that is, the density of the output stream may differ from that of the input stream.
(5) The system may operate at steady-state or at unsteady-state.
(6) A heat exchanger may be provided in each vessel to control temperature.

There are several important consequences of the model described in the six points above, as shown partly in the property profiles:

[l] Since the fluid inside the vessel is uniformly mixed (and hence elements of fluid are uniformly distributed), all fluid elements have equal probability of leaving the vessel in the output stream at any time.
[2] As a consequence of [l], the output stream has the same properties as the fluid inside the vessel.
[3] As a consequence of [2], there is a step-change across the inlet in any property of the system that changes from inlet to outlet; this is illustrated in the Figure for c_A.

[4] There is a continuous distribution (spread) of residence times (t) of fluid elements; the spread can be appreciated intuitively by considering two extremes: (i) fluid moving directly from inlet to outlet (short t), and (ii) fluid being caught up in a recycling motion by the stirring action (long t); this distribution can be expressed exactly mathematically.

[5] The mean residence time, $\bar{t}$; of fluid inside the vessel for steady-state flow is

$$\bar{t} = V/q \qquad \text{(CSTR)} \tag{1}$$

where q is the steady-state flow rate (e.g., $m^3\ s^{-1}$) of fluid leaving the reactor; this is a consequence of [2] above.

[6] The space time, τ for steady-state flow is

$$\tau = V/q_o \tag{2}$$

where q_0 is the steady-state flow rate of feed at inlet conditions; note that for constant-density flow, $q_0 = q$, and $\tau = \bar{t}$: Equation (2) applies whether or not density is constant, since the definition of τ takes no account of this.

[7] In steady-state operation, each stage of a CSTR is in a stationary state (uniform c_A, T, etc.), which is independent of time.

It is important to understand the distinction between the implications of points [3] and [5]. Point [3] implies that there is instantaneous mixing at the point of entry between the input stream and the contents of the vessel; that is, *the input stream instantaneously blends with what is already in the vessel. This does not mean that any reaction taking place in the fluid inside the vessel occurs instantaneously.* The time required for the change in composition from input to output stream is $\bar{t}$; point [5], which may be small or large.

Material Balance; Interpretation of r_i

Consider again a reaction represented by A + . . . → products taking place in a single-stage CSTR. The general balance equation, written for A with a control volume defined by the volume of fluid in the reactor, becomes

$$\begin{pmatrix}\text{rate of input}\\ \text{of A into}\\ \text{cotrol volume}\end{pmatrix} - \begin{pmatrix}\text{rate of output}\\ \text{of A into}\\ \text{cotrol volume}\end{pmatrix} + \begin{pmatrix}\text{rate of reaction}\\ \text{of A in}\\ \text{control volume}\end{pmatrix} = \begin{pmatrix}\text{rate of accumulation}\\ \text{of A within}\\ \text{control volume}\end{pmatrix} \tag{3}$$

or, on a molar basis, $F_{Ao} - F_A + r_A V = dn_A/dt$ **(4)**

(for unsteady- state operation)

$$F_{Ao} - F_A + r_A V = 0 \quad (5)$$

(for steady- state operation)

where F_{Ao} and F_A are the molar flow rates, mol s^{-1}, say, of A entering and leaving the vessel, respectively, and V is the volume occupied by the fluid inside the vessel. Since a CSTR is normally only operated at steady-state for kinetics investigations, we focus on equation (5)

$$(-r_A) = (F_{Ao} - F_A)/V \quad (6)$$

For a flow system, the fractional conversion of A (f_A), extent of reaction (ξ), and molarity of A (c_A) are defined in terms of F_A rather than n_A:

$$f_A = (F_{Ao} - F_A)/F_{Ao} \quad (7)$$

$$\xi = \Delta F_A/\nu_A = (F_A - F_{Ao})/\nu_A \quad (8)$$

$$c_A = F_A/q \quad (9)$$

} Flow system

Substituting equations (7), (8), and (9) into equation (6)

$$(-r_A) = (F_{Ao} - F_A)/V = -\Delta F_A/V = -\Delta F_A/q\bar{t} \quad (10)$$

$$= F_{Ao} f_A/V \quad (11)$$

$$= -\nu_A \xi/V \quad (12)$$

$$= (c_{Ao} q_o - c_A q)/V \quad (13)$$

If density is constant, which is usually assumed for a liquid-phase reaction (but is usually not the case for a gas-phase reaction), equation (13) takes a simpler form, since $q_o = q$ and $\tau = \bar{t}$. Then,

$$(-r_A) = (c_{Ao} - c_A)/(V/q) = -\Delta c_A/\bar{t} \quad \textit{(constant density)} \quad (14)$$

In a BR, r_A changes with t as reaction proceeds, but for steady-state operation of a CSTR, r_A is constant for the *stationary-State conditions* (c_A, T, etc.) prevailing in the vessel.

Worked problem 2.2

For a liquid-phase reaction of the type A + . . . → products, an experimental CSTR of volume 1.5 L is used to measure the rate of reaction at a given temperature. If the steady- state feed rate is 0.015 L s^{-1}, the feed concentration (c_{Ao}) is 0.8 mol L^{-1}, and A is 15% converted on flow through the reactor, what is the value of ($-r_A$)?

Solution 2.2

$$F_{Ao} = \frac{n_{Ao}}{\tau} = \frac{n_{Ao}}{V} \times \frac{V}{\tau} \quad \text{or} \quad F_{Ao} = c_{Ao} q_o$$

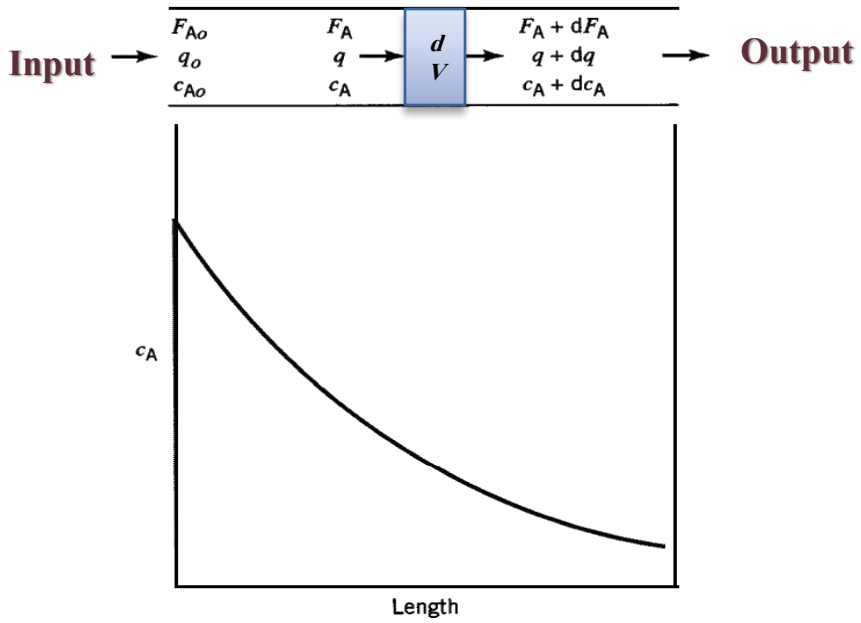
Also, $(-r_A) = F_{Ao} f_A/V$

Therefore, $(-r_A) = F_{Ao} f_A/V = c_{Ao} q_o f_A/V = 0.8(0.015)0.15/1.5 = 1.2 \times 10^{-3}$ mol $L^{-1} s^{-1}$

PLUG-FLOW REACTOR (PFR)

General Features

A plug-flow reactor (PFR) may be used for both liquid-phase and gas-phase reactions, and for both laboratory-scale investigations of kinetics and large-scale production. The reactor itself may consist of an empty tube or vessel, or it may contain packing or a tied bed of particles (e.g., catalyst particles). The former is illustrated in Figure below, in which concentration profiles are also shown with respect to position in the vessel.



The characteristics of a PFR are as follows:

(1) The flow through the vessel, both input and output streams, is continuous, but not necessarily at constant rate; the flow in the vessel is PF.
(2) The system mass inside the vessel is not necessarily fixed.
(3) There is no axial mixing of fluid inside the vessel (i.e., in the direction of flow).
(4) There is complete radial mixing of fluid inside the vessel (i.e., in the plane perpendicular to the direction of flow); thus, the properties of the fluid, including its velocity, are uniform in this plane.
(5) The density of the flowing system may vary in the direction of flow.
(6) The system may operate at steady-state or at unsteady-state.
(7) There may be heat transfer through the walls of the vessel between the system and the surroundings.

Some consequences of the model described in the seven points above are as follows:

[l] Each element of fluid has the same residence time t as any other; that is, there is no spread in t.
[2] Properties may change continuously in the direction of flow, as illustrated for c_A in the Figure above.
[3] In the axial direction, each portion of fluid, no matter how large, acts as a closed system in motion, not exchanging material with the portion ahead of it or behind it.
[4] The volume of an element of fluid does not necessarily remain constant through the vessel; it may change because of changes in T, P and n_t, the total number of moles.

Material Balance; Interpretation of r_i

Consider again a reaction represented by A + . . . → products taking place in a PFR. The general balance equation,

$$\begin{pmatrix}\text{rate of input}\\ \text{of A into}\\ \text{cotrol volume}\end{pmatrix}-\begin{pmatrix}\text{rate of output}\\ \text{of A into}\\ \text{cotrol volume}\end{pmatrix}+\begin{pmatrix}\text{rate of reaction}\\ \text{of A in}\\ \text{control volume}\end{pmatrix}=\begin{pmatrix}\text{rate of accumulation}\\ \text{of A within}\\ \text{control volume}\end{pmatrix} \quad (1)$$

$$F_{Ao} - (F_A + dF_A) + r_A V = dn_A/dt \quad (2)$$

(for unsteady- state operation)

$$F_{Ao} - (F_A + dF_A) + r_A V = 0 \quad (3)$$

(for steady- state operation)

At steady-state for kinetics investigations, we focus on equation (3)

$$(-r_A) = [F_{Ao} - (F_A - dF_A)]/V \quad (4)$$

The interpretations of r_A in terms of F_A, f_A, ξ, and c_A

$$(-r_A) = -dF_A/dV = -dF_A/q dt \quad (5)$$

$$= F_{Ao}\, d f_A/dV \quad (6)$$

$$= -\nu_A d\xi/dV \quad (7)$$

$$= -d(c_A q)/dV \quad (8)$$

If density is constant, equation (8) takes the form of

$$(-r_A) = -dc_A/(dV/q) = -dc_A/dt \ (\textit{constant density}) \quad (9)$$

$$t = V/q_o \quad (\textit{constant density}) \quad (10)$$

whether V represents the total volume of the vessel, in which case t is the residence time of fluid in the vessel (≡ $\bar{t}$ for a CSTR), or part of the volume from the inlet ($V = 0$).

Worked problem 2.3

Calculate (a) the residence time, t, and (b) the space time, τ, and (c) explain any difference between the two, for the gas-phase production of C_2H_4 from C_2H_6 in a cylindrical PFR of constant diameter, based on the following data and assumptions:

(1) The feed is pure C_2H_6 (A) at 1 kg s^{-1}, 1000 K and 2 bar.

(2) The reaction rate is proportional to c_A at any point, with a proportionality constant of k_A = 0.254 s^{-1} at 1000 K; that is, the rate law is $(-r_A) = k_A c_A$.

(3) The reactor operates isothermally and at constant pressure.

(4) $f_A = 0.20$ at the outlet.

(5) Only C_2H_4 and H_2 are formed as products.

(6) The flowing system behaves as an ideal-gas mixture.

Solution 2.3

(a) The gas flowing at a volumetric rate q at any point generates the control volume dV in time dt. That is.

$$dV = qdt \qquad or\ dt = \frac{dV}{q} \qquad (1)$$

The total residence time, t, is obtained by integrating equation (1) from inlet to outlet.

$$t = \int dt = \int \frac{dV}{q} \qquad (2)$$

$$Since, \qquad (-r_A) = \frac{F_{Ao} df_A}{dV}$$

$$or \qquad dV = \frac{F_{Ao} df_A}{(-r_A)} \qquad (3)$$

Substituting equation (3) into equation (2) gives,

$$t = \int \frac{F_{Ao} df_A}{(-r_A) q} \qquad (4)$$

Also, the rate law is

$$(-r_A) = k_A c_A \qquad (5)$$

So, equation (4) can be written as

$$t = \int \frac{F_{Ao} df_A}{k_A c_A q} = \frac{F_{Ao}}{k_A} \int \frac{df_A}{c_A q} \qquad (6)$$

or

$$t = \frac{F_{Ao}}{k_A} \int \frac{df_A}{F_A} \qquad (7)$$

$$Since\ F_A = F_{Ao}(1 - f_A) \qquad (8)$$

Substituting equation (8) into equation (7) and integration from inlet condition, f_A=0 to outlet condition, f_A=0.2,

$$t = \frac{F_{Ao}}{k_A} \int \frac{df_A}{F_{Ao}(1 - f_A)} = \frac{F_{Ao}}{k_A F_{Ao}} \int \frac{df_A}{(1 - f_A)} = \frac{1}{k_A} \int_0^{0.2} \frac{df_A}{(1 - f_A)}$$

$$\therefore t = \frac{1}{k_A} [-ln\,(1 - f_A)]_0^{0.2}$$

$$t = \frac{1}{0.254\ s^{-1}} [-ln(0.8)] = 0.89\ s$$

(b) From the definition of space time

$$\tau = \frac{V}{q_o} \qquad (9)$$

$$Since, \qquad dV = \frac{F_{Ao} df_A}{(-r_A)}$$

$$or, \qquad V = \int \frac{F_{Ao} df_A}{(-r_A)} \qquad (10)$$

Substituting equation (10) into equation (9)

$$or, \qquad V = \frac{1}{q_o}\int \frac{F_{Ao}df_A}{(-r_A)} \qquad (11)$$

Substituting equation (5) into equation (11)

$$\tau = \frac{1}{q_o}\int \frac{F_{Ao}df_A}{k_A c_A} = \frac{F_{Ao}}{q_o k_A}\int \frac{df_A}{c_A} \qquad (12)$$

$$c_A = \frac{n_A}{V} = \frac{n_A P}{n_A RT} = \frac{P}{RT} \qquad since\ PV = n_A RT \qquad (13)$$

$$F_A = c_A \times q = \frac{P}{RT} \times q$$

$$\therefore q = \frac{F_A RT}{P} = \frac{F_t RT}{P} \qquad since\ F_t = total\ molar\ flow\ rate \qquad (14)$$

$$Also, q_o = \frac{F_o RT}{P} = \frac{F_t RT}{P} \qquad (14')$$

The total molar flow rate, F_t is obtained as follows:

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

F_A	F_{C2H4}	F_{H2}
$F_{Ao}(1-f_A)$	$F_{Ao}f_A$	$F_{Ao}f_A$

$$F_t = F_{Ao}(1-f_A) + F_{Ao}f_A + F_{Ao}f_A = F_{Ao}(1+f_A) \qquad (15)$$

Substituting equation (13), (14), (14') and (15) into equation (12)

$$\tau = \frac{1}{k_A}\int_0^{0.2} \frac{(1+f_A)df_A}{(1-f_A)} = \frac{1}{k_A}[-2ln(1-f_A) - (f_A)]_0^{0.2}$$

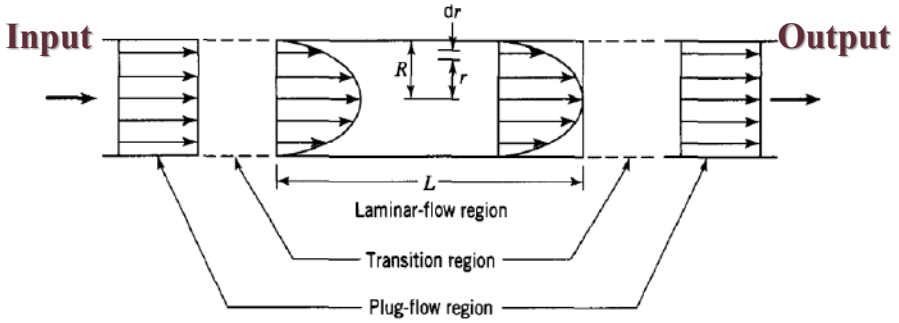
$$\tau = \frac{1}{0.254\ s^{-1}}[-2\ ln(0.8) - (0.2)] = 0.99\ s$$

(c) $\tau > t$, because τ, based on inlet conditions, does not take the acceleration of the flowing gas stream into account. The acceleration, which affects t, is due to the continuous increase in moles on reaction.

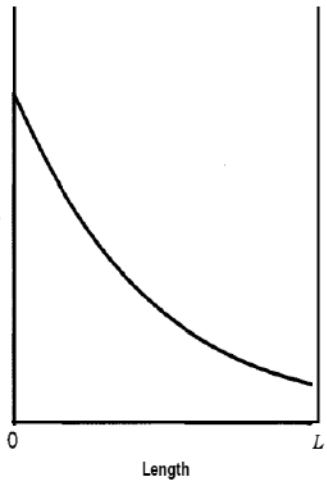
LAMINAR-FLOW REACTOR (LFR)

General Features

A laminar-flow reactor (LFR) is rarely used for kinetic studies, since it involves a flow pattern that is relatively difficult to attain experimentally. However, the model based on laminar flow, a type of tubular flow, may be useful in certain situations, both in the laboratory and on a large scale, in which flow approaches this extreme (at low Re). Such a situation would involve low fluid flow rate, small tube size, and high fluid viscosity, either separately or in combination, as, for example, in the extrusion of high-molecular-weight polymers. Nevertheless, we consider the general features of an LFR at this stage for comparison with features of the other models introduced above.



Consider, the laminar-flow region of length *L* and radius *R* ; fluid is shown entering at left by PF and leaving at right by PF, with a transition region between PF and LF; in other words, regardless of how fluid enters and leaves, we assume that there is a region in which LF is fully established and maintained; *r* is the (variable) radius between the center line (*r* = 0) and the wall (*r* = *R*).



The general characteristics of the simplest model of a continuous LFR, illustrated schematically in the Figure above,

(1) The flow through the vessel is laminar (LF) and continuous, but not necessarily at constant rate.
(2) The system mass inside the vessel is not necessarily fixed.
(3) There is no axial mixing of fluid inside the vessel.
(4) There is no radial mixing of fluid inside the vessel.
(5) The density of the flowing system is not necessarily constant.
(6) The system may operate at steady-state or at unsteady-state.
(7) There may be heat transfer through the walls of the vessel between the system and the surroundings.

Some consequences of the model described in the seven points above are as follows:

[l] From point (l), the velocity profile is parabolic; that is, the linear (axial) velocity *u* depends quadratically on radial position *r* , as described by fluid mechanics:

$$u(r) = u_o[1 - (r/R)^2] \qquad (1)$$

where u_o is the (maximum) velocity at the center of the vessel, and the mean velocity $\bar{u}$ is

$$\bar{u} = u_o/2 \qquad (2)$$

[2] Points (3) and (4) above imply no molecular diffusion in the axial and radial directions, respectively.

[3] A cylindrical LFR can be pictured physically as consisting of a large number of thin cylindrical shells (each of thickness *dr*) of increasing radius (from center to wall) moving or slipping past each other with decreasing velocity (from center to wall); the residence time of a thin cylindrical shell at radius *r* is

$$t(r) = L/u(r) \qquad (3)$$

and the mean residence time of all fluid in the vessel is

$$\begin{aligned} i &= L/\bar{u} \\ &= 2t(r)[1 - (r/R)^2] \end{aligned} \qquad (4)$$

SUMMARY OF RESULTS FOR IDEAL REACTOR MODELS

Item	BR	CSTR	PFR
(1) Definitions f_A c_A	$(n_{Ao} - n_A)/n_{Ao}$ n_A/V	$(F_{Ao} - F_A)/F_{Ao}$ F_A/q	
(2) Reaction rate $(-r_A)$	$(n_{Ao}/V)\, df_A/dt$	$F_{Ao}\, f_A/V$	$F_{Ao}\, df_A/dV$
(3) Time quantities τ t $\bar{t}$	(N/A) $t = \bar{t}$ $= n_{Ao} \int df_A/V(-r_A)$	V/q_o $t = \bar{t}$ V/q	V/q_o $t = \bar{t}$ $= \int dV/q$
(4) Special case of constant- density system f_A $(-r_A)$ t $\bar{t}$	$(n_{Ao} - n_A)/n_{Ao}$ $-dc_A/dt$ $= -\int dc_A/(-r_A)$ $t = \bar{t}$	$(c_{Ao} - c_A)/c_{Ao}$ $(c_{Ao} - c_A)q_o/V$ $V/q_o = \tau$	$(F_{Ao} - F_A)/F_{Ao}$ $-dc_A/dt$ $t = \bar{t}$ $V/q_o = \tau$

Exercises 2.1

1- The half-life ($t_{1/2}$) of a reactant is the time required for its concentration to decrease to one-half its initial value. The rate of hydration of ethylene oxide (A) to ethylene glycol ($C_2H_4O + H_2O \rightarrow C_2H_6O_2$) in dilute aqueous solution is proportional to the concentration of A, with a proportionality constant $k_A = 4.11 \times 10^{-5}$ s^{-1} at 20 °C for a certain catalyst ($HC1O_4$) concentration (constant). Determine the half-life ($t_{1/2}$, or equivalent space-time ($\tau_{1/2}$), in s, of the oxide (A) at 20 °C if the reaction is carried out

(a) In a batch reactor,

(b)In a CSTR operating at steady-state.

(c) Explain briefly any difference between the two time quantities in (a) and (b).

2- Calculate the mean residence time ($\bar{t}$) and space time (τ) for reaction in a CSTR for each of the following cases, and explain any difference between (t) and τ: (a)Homogeneous liquid-phase reaction, volume of CSTR (V) = 100 L, feed flow rate (q_o) = 10 L min^{-1}; (b)Homogeneous gas-phase reaction, V = 100 L, q_o = 200 L min^{-1} at 300 K (T_o); stoichiometry: A(g) = B(g) + C(g); reactor outlet temperature (T) = 350 K; reactor inlet and outlet pressures essentially the same and relatively low; conversion of A, 40%.

3- The decomposition of phosphine (PH_3) to phosphorus vapor (P_4) and hydrogen is to take place in a plug-flow reactor at a constant temperature of 925 K. The feed rate of PHs and the pressure are constant. For a conversion of 50% of the phosphine, calculate the residence time (t) in the reactor and the space time (τ); briefly explain any difference. Assume the rate of decomposition is proportional to the concentration of PH_3 at any point, with a proportionality constant $k = 3.6 \times 10^{-3}$ s^{-1} at 925 K.

4- An experimental "gradientless" reactor, which acts as a CSTR operating adiabatically, was used to measure the rate of oxidation of SO_2, to SO_3 with a V_2O_5 catalyst. The catalyst is present as a fixed bed (200 g) of solid particles within the reactor, with a bulk density (mass of catalyst/volume of bed) of 500 g L^{-1} and a bed voidage (m^3 void space m^{-3} bed) of 0.40; a rotor within the reactor serves to promote BMF of gas. Based on this information and that given below for a particular run at steady-state, calculate the following:

(a)The fraction of SO_2 converted (f_{SO_2}) in the exit stream;

(b)The rate of reaction, $-r_{SO_2}$, mol SO_2 reacted (g cat)$^{-1}$ s^{-1}; at what T does this apply?

(c) The mean residence time of gas ($\bar{t}$) in the catalyst bed, s;

(d)The space time, τ, for the gas in the catalyst bed, if the feed temperature T_o is 548 K.

Additional information:

Feed rate (total F_{to}): 1.2 mol min^{-1}.

Feed composition: 25 mole % SO_2,25% O_2, 50% N_2 (inert)

T (in reactor): 800 K, P (inlet and outlet): 1.013 bar

Concentration of SO_3 in exit stream: 10.5 mole %.

5- An aqueous solution of ethyl acetate (A), with a concentration of 0.3 mol L^{-1} and flowing at 0.5 L s^{-1}, mixes with an aqueous solution of sodium hydroxide (B), of concentration 0.45 mol L^{-1} and flowing at 1.0 L s^{-1}, and the combined stream enters a CSTR of volume 500 L. If the reactor operates at steady-state, and the fractional conversion of ethyl acetate in the exit stream is 0.807, what is the rate of reaction ($-r_A$)?

3- DESIGN EQUATIONS FOR A BATCH REACTOR

We first consider uses of batch reactors, and their advantages and disadvantages compared with continuous-flow reactors. After considering what the essential features of process design are, we then develop design or performance equations for both isothermal and nonisothermal operation. The latter requires the energy balance, in addition to the material balance. We continue with an example of optimal performance of a batch reactor, and conclude with a discussion of semibatch and semicontinuous operation.

USES OF BATCH REACTORS

The use of batch reactors in commercial processes is usually most suitable for small-volume production, particularly for situations in which switching from one process or product to another is required, as in the manufacture of pharmaceuticals. Typically, in such processes, the value of the products is relatively large compared with the cost of production. However, batch reactors may also be used for large-volume production. Examples are the production of "vinyl" (polyvinyl chloride or PVC) involving suspension polymerization, and of emulsion-polymerized latex.

If products of different purity are required, portions of the batch may be removed at different times. In this type of operation, referred to as a semibatch process the system is no longer closed, since some mass is added to, or removed from, the system during the process. If addition of reactants and removal of products occur continuously, the process is classified as continuous, and specific flow rates at the inlet and outlet of the reactor may be identified.

Comparison of batch and continuous operation

	Batch operation	Continuous operation
(1)	Usually better for small- volume production (A)	Better for indefinitely long production runs of one product or set of products (A)
(2)	More flexible for multiproduct (multiprocess) operation (A)	(N/A)
(3)	Capital cost usually relatively low (A)	Capital cost usually relatively high (D)
(4)	Easy to shut down and clean for fouling service (A)	(N/A)
(5)	Inherent down-time between batches (D)	No down-time except for scheduled and emergency maintenance (A); but loss of production in lengthy stoppages can be costly (D)
(5)	Operating cost may be relatively high (D)	Operating cost relatively low (A)
(7)	Unsteady-state operation means process control and obtaining uniformity of product more difficult (D)	Steady-state operation means process control and obtaining uniformity of product less difficult (A)

(A) advantageous, (D) disadvantageous, (N/A) not applicable.

General Considerations

The process design of a batch reactor may involve determining the time (t) required to achieve a specified fractional conversion (f_A, for limiting reactant A, say) in a single batch, or the volume (V) of reacting system required to achieve a specified rate of production on a continual basis. The phrase "continual basis" means an ongoing operation, that is, operation "around the clock" with successive batches. This includes allowance for the down-time (t_d) during operation for loading, unloading, and cleaning. The operation may involve constant or varying density (ρ), and constant or varying temperature (T). The former requires an equation of state to determine V, and latter requires the energy balance to determine T.

1- Time of Reaction

Consider the reaction

$$A + \ldots \rightarrow \nu_C C + \ldots$$

Interpretation of the mass balance in BR gives the time of reaction,

$$t = n_{Ao} \int_{f_{A1}}^{f_{A2}} \frac{df_A}{(-r_A)V} \qquad (1)$$

where t is the time required for reaction in an uninterrupted batch from fractional conversion f_{Al} to f_{A2}, and n_{Ao} is the initial number of moles of A. Equation (1) is a general form and t depends on ($-r_A$) and V.

2- Rate of Production; Volume of Reactor

Suppose aforementioned reaction is carried out in a batch reactor of volume V on a continual basis. To determine the rate of production, we must take into account the time of reaction (t in equation (1)) and the down-time (t_d) between batches. The total time per batch, or cycle time, is

$$t_c = t + t_d \qquad (2)$$

The rate of production (formation) of C on a continual basis is then

$$Pr(C) = \frac{moles\ of\ C\ formed}{Batch\ time}$$

$$Pr(C) = \frac{\nu_C(nC_2 - n_{C1})}{t_c} = \frac{\nu_C \Delta n_C}{t + t_d} = -\frac{\nu_C \Delta n_A}{t + t_d} \qquad (3)$$

If $f_{A1} = \frac{n_{Ao} - n_{A1}}{n_{Ao}}$ $\qquad n_{Ao} f_{A1} = n_{Ao} - n_{A1}$

and $f_{A2} = \frac{n_{Ao} - n_{A2}}{n_{Ao}}$ $\qquad n_{Ao} f_{A2} = n_{Ao} - n_{A2}$

Therefore, $n_{A2} - n_{A1} = -(n_{Ao} f_{A2} - n_{Ao} f_{A1})$

$$\therefore -\Delta n_A = n_{Ao}(f_{A2} - f_{A1}) \qquad (4)$$

Substituting equation (4) into equation (3)

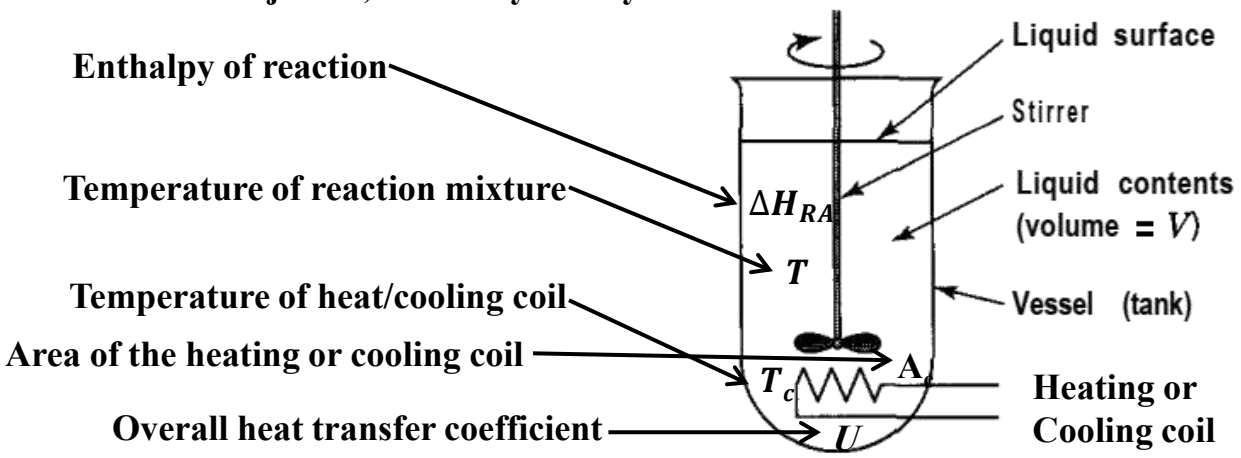
$$Pr(C) = \frac{\nu_C n_{Ao}(f_{A2} - f_{A1})}{t + t_d} \qquad (5)$$

3- Energy Balance; Temperature Change

The energy balance in general, from equation

$$\begin{pmatrix}\text{rate of}\\ \text{input of}\\ \text{energy}\end{pmatrix} - \begin{pmatrix}\text{rate of}\\ \text{output of}\\ \text{energy}\end{pmatrix} = \begin{pmatrix}\text{rate of}\\ \text{accumulation}\\ \text{of energy}\end{pmatrix} \qquad (6)$$

Each term refers to a control volume, which for a BR is the volume of the reacting system. The input of energy may be by heat transfer from a heating coil or jacket, and/or by generation by reaction. Similarly, the output of energy may be by loss by reaction.



The rate of heat transfer, $\dot{Q}$ whether it is an input or output, may be expressed as:

$$\dot{Q} = UA_c(T_c - T)_m \qquad (7)$$

Where U = the overall heat transfer coefficient, J m^{-2} s^{-1} K^{-1} or $Wm^{-2}K^{-1}$, obtained experimentally or from an appropriate correlation;

A_c = the area of the heating or cooling coil, m^2;

T_c = the temperature of the coil, K (not necessarily constant with respect to position or time);

$(T_c - T)_m$ = the appropriate mean temperature difference, ΔT_m.

If $\dot{Q} > 0$ ($T_c > T$), the heat transfer is an input (to the reacting system), and the converse applies if $\dot{Q} < 0$.

$$\text{rate of generation or loss of energy by reaction} = (-\Delta H_{RA})(-r_A)V \qquad (8)$$

$$\begin{aligned}\text{rate of accumulation} &= dH/dt\\ &= n_t C_P dT/dt\\ &= m_t c_P dT/dt\end{aligned} \qquad (9)$$

where n_t is the total number of moles, C_P is the (total) molar heat capacity of the system at constant pressure, c_p is the specific heat capacity as a pure species at constant pressure, m_t is the total (specific) mass of the system.

Substituting equations (7), (8) and (9) into energy- balance equation (6)

$$UA_c(T_c - T)_m + (-\Delta H_{RA})(-r_A)V = n_t C_P \frac{dT}{dt} \quad (10)$$

Equation (10) is valid whether heat is transferred to or from the system, and whether the reaction is exothermic or endothermic. Note that each term on the left side of equation (10) may be an input or an output.

In the energy balance, for isothermal operation of the reaction A + . . .→ product(s), dT/dt = 0, so that equation (10) becomes

$$\dot{Q} = UA_c(T_c - T)_m = -(-\Delta H_{RA})(-r_A)V \text{ (isothermal operation)} \quad (11)$$

From the material balance in terms of f_A,

$$(-r_A) = (n_{Ao}/V)(df_A/dt) \quad (12)$$

Substituting equation (12) into equation (11)

$$\dot{Q} = UA_c(T_c - T)_m = -(-\Delta H_{RA})n_{Ao}(df_A/dt) \quad (13)$$

For simplicity, if we assume that T_c is constant throughout the coil at a given instant, then T_c depends on t,

$$T_c = T - \frac{(-\Delta H_{RA})n_{Ao}}{UA_c}\frac{df_A}{dt} \quad (14)$$

Worked problem 3.1

Determine the time required for 80% conversion of 7.5 mol A in a 15-L constant-volume batch reactor operating isothermally at 300 K. The reaction is first-order with respect to A, with $k_A = 0.05\ min^{-1}$ at 300 K.

Solution 3.1

$$t = n_{Ao}\int_{f_{A1}}^{f_{A2}} \frac{df_A}{(-r_A)V}$$

$$or\ t = n_{Ao}\int_0^{f_A} \frac{df_A}{(-r_A)V} \quad (1)$$

$$(-r_A) = k_A c_A = k_A c_{Ao}(1 - f_A) \quad (2)$$

$$c_{Ao} = \frac{n_{Ao}}{V} \quad (3)$$

Substituting equations (2) and (3) into equation (1)

$$t = \frac{1}{k_A}\int_0^{f_A} \frac{df_A}{(1 - f_A)} = \frac{1}{k_A}[-ln(1 - f_A)]_0^{f_A}$$

$$t = \frac{1}{0.05\ min^{-1}}[-ln(0.20)] \quad = 32.2 \text{ min}$$

Worked problem 3.2

A liquid-phase reaction between cyclopentadiene (A) and benzoquinone (B) is conducted in an isothermal batch reactor, producing an adduct (C). The reaction is first-order with respect to each reactant, with $k_A = 9.92 \times 10^{-3}$ L mol^{-1} s^{-1} at 25°C. Determine the reactor volume required to produce 175 mol C h^{-1}, if $f_A = 0.90$, $c_{Ao} = c_{Bo} = 0.15$ mol L^{-1}, and the down-time t_d between batches is 30 min. The reaction is A + B → C.

Solution 3.2

This example illustrates the use of the design equations to determine the volume of a batch reactor (V) for a specified rate of production *Pr(C)*, and fractional conversion (f_A) in each batch. The time for reaction (t) each batch is initially unknown, and must first be determined from equation

$$t = n_{Ao} \int_{f_{A1}}^{f_{A2}} \frac{df_A}{(-r_A)V} \qquad (1)$$

Since $c_{Ao} = c_{Bo}$,

$$(-r_A) = k_A c_A c_B = k_A c_A^2 = k_A c_{Ao}^2 (1 - f_A)^2 \qquad (2)$$

Substituting equation (2) into equation (1) and integrating from f_{A1}=0 to f_{A2}=f_A

$$t = c_{Ao} \int_0^{f_A} \frac{df_A}{k_A c_{Ao}^2 (1 - f_A)^2} = \frac{1}{k_A c_{Ao}} \int_0^{f_A} \frac{df_A}{(1 - f_A)^2} = \frac{1}{k_A c_{Ao}} \frac{f_A}{(1 - f_A)}$$

$$t = \frac{1}{9.92 \times 10^{-3} L\, mol^{-1} s^{-1} \times 0.15\, mol\, L^{-1}} \times \frac{0.9}{0.1} = 6050\, s = 1.68\, h$$

The volume of a batch reactor (V) can now be calculated

$$V = \frac{(t + t_d) Pr(C)}{\nu_C c_{Ao} f_A} = \frac{(1.68 + 0.5)175}{1(0.15)0.9} = 2830 \text{ L or } 2.83 \text{ m}^3$$

Exercise 3.1

A gas-phase reaction A + B → C is to be conducted in a l0-L (initially) isothermal batch reactor at 25'C at constant P. The reaction is second-order with respect to A, with $k_A = 0.023$ L mol^{-1} s^{-1}. Determine the time required for 75% conversion of 5 mol A.

Worked problem 3.3

Determine $\dot{Q}$ and T_c (as functions of time, t) required to maintain isothermal conditions in the reactor in Worked problem 3.1, if ΔH_{RA} = -47,500 J mol^{-1}, UA_c = 25.0 W K^{-1}, and T=300 K.
Does $\dot{Q}$ represent a rate of heat removal or heat addition?

Solution 3.3

$$\dot{Q} = UA_c(T_c - T)_{lm} = -(-\Delta H_{RA})n_{Ao}(df_A/dt) \qquad (1)$$

We first obtain df_A/dt for a first-order reaction, and use this to eliminate f_A in terms of t.

$$t = n_{Ao}\int_{f_{A1}}^{f_{A2}} \frac{df_A}{(-r_A)V}$$

Removing the integral and rearranging,

$$\frac{df_A}{dt} = \frac{V}{n_{Ao}}(-r_A) \qquad (2)$$

$$(-r_A) = k_A c_A = k_A(1 - f_A)c_{Ao} \qquad (3)$$

$$c_{Ao} = \frac{n_{Ao}}{V} \qquad (4)$$

Substituting equation (4) into equation (3),

$$(-r_A) = \frac{k_A n_{Ao}}{V}(1 - f_A) \qquad (5)$$

Substituting equation (5) into equation (2),

$$\frac{df_A}{dt} = \frac{V}{n_{Ao}}(-r_A) = \frac{V}{n_{Ao}}k_A\frac{n_{Ao}}{V}(1 - f_A) = k_A(1 - f_A) \qquad (6)$$

From equation (6),

$$k_A dt = \frac{df_A}{(1 - f_A)}$$

On integration,

$$k_A t = k_A\int dt = \int \frac{df_A}{(1 - f_A)} = -ln\,(1 - f_A)$$

Removing ln,

$$(1 - f_A) = e^{-kt}$$

$$\therefore \quad f_A = 1 - e^{-k_A t} \qquad (7)$$

Substituting equations (6) and (7) into equation (1)

$$\dot{Q} = -(-\Delta H_{RA})n_{Ao}k_A e^{-k_A t} = -(47{,}500)7.5(0.05/60)e^{-0.05t} = -297e^{-0.05t} \text{ J s}^{-1} \text{ or W}$$

Since $\dot{Q} < 0$, it represents heat removal from the system, which is undergoing an exothermic reaction.

Similarly, from the following equation, we obtain for the coolant temperature T_c in the coil

$$T_c = T - \frac{(-\Delta H_{RA})n_{Ao}k_A e^{-k_A t}}{UA_c}$$

$$T_c = 300 - \frac{47{,}500(7.5)}{25.0}\frac{0.05}{60}e^{-0.05t} = 300 - 119e^{-0.05t}$$

with T_c in K and t in min.

SEMIBATCH AND SEMICONTINUOUS REACTORS

A semibatch reactor is a variation of a batch reactor in which one reactant may be added intermittently or continuously to another contained as a batch in a vessel, or a product may be removed intermittently or continuously from the vessel as reaction proceeds. The reaction may be single-phase or multiphase. As in a batch reactor, the operation is inherently unsteady-state and usually characterized by a cycle of operation, although in a more complex manner.

A semicontinuous reactor is a reactor for a multiphase reaction in which one phase flows continuously through a vessel containing a batch of another phase. The operation is thus unsteady-state with respect to the batch phase, and may be steady-state or unsteady-state with respect to the flowing phase, as in a fixed-bed catalytic reactor or a fixed-bed gas-solid reactor, respectively.

we consider various modes of operation of these types of reactors, their advantages and disadvantages, and some design aspects. Since there are many variations of these reactors, it is difficult to generalize their design or analysis, and consequently we use an example for illustration.

Modes of Operation: Semibatch and Semicontinuous Reactors

Semibatch Reactors

(1) In Figure (A), depicting a homogeneous liquid-phase reaction of the type A + B → products, reactant B is initially charged to the vessel, and reactant A is added at a prescribed rate, as reaction proceeds.

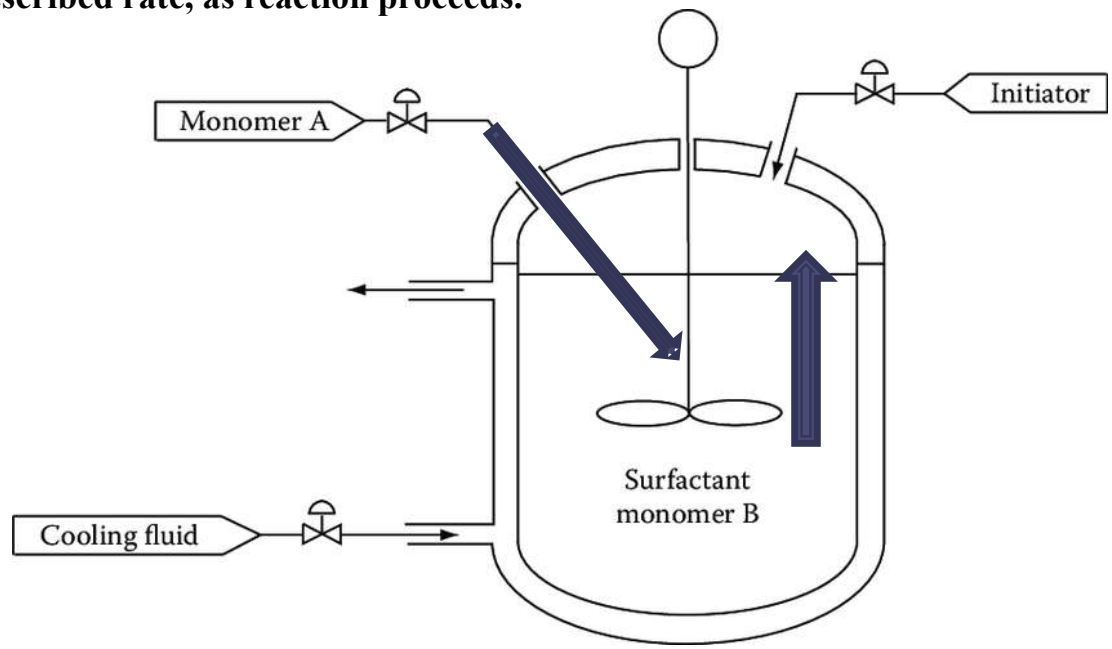


Figure (A)

(2) In Figure (B), depicting a "liquid-phase" reaction in which a gaseous product is formed, gas is removed as reaction proceeds; an example is the removal of $H_2O(g)$ in an esterification reaction.

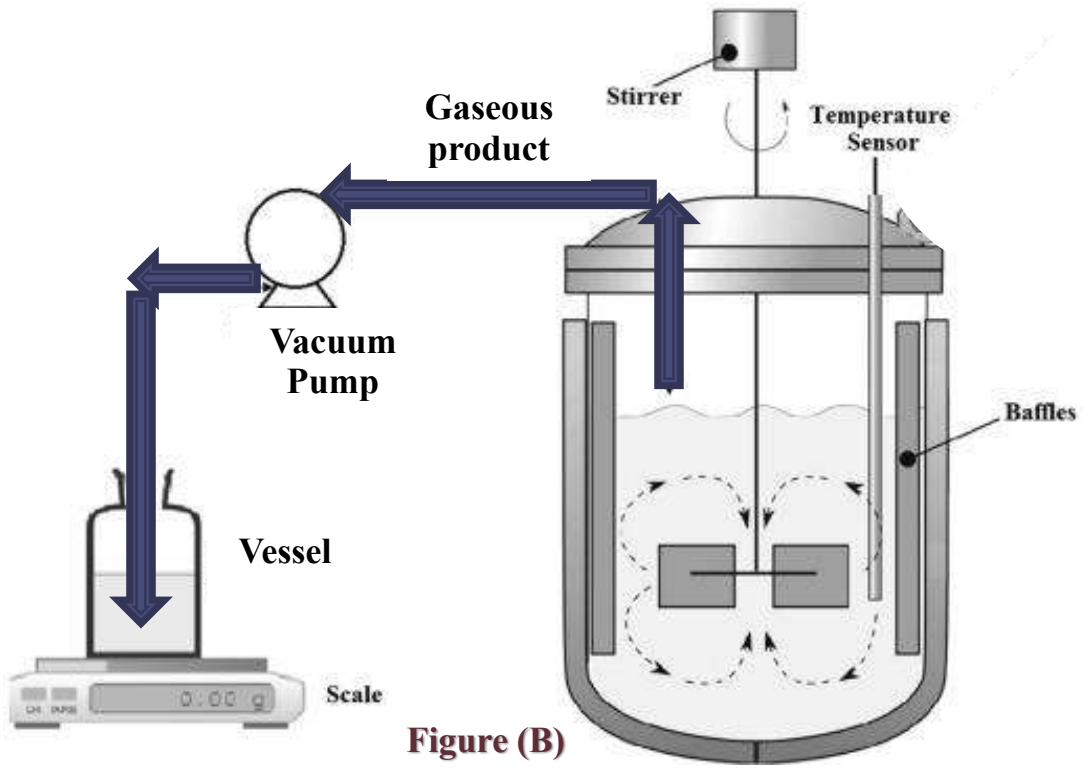


Figure (B)

(3) In Figure (C), a combination of these two modes of operation is shown.

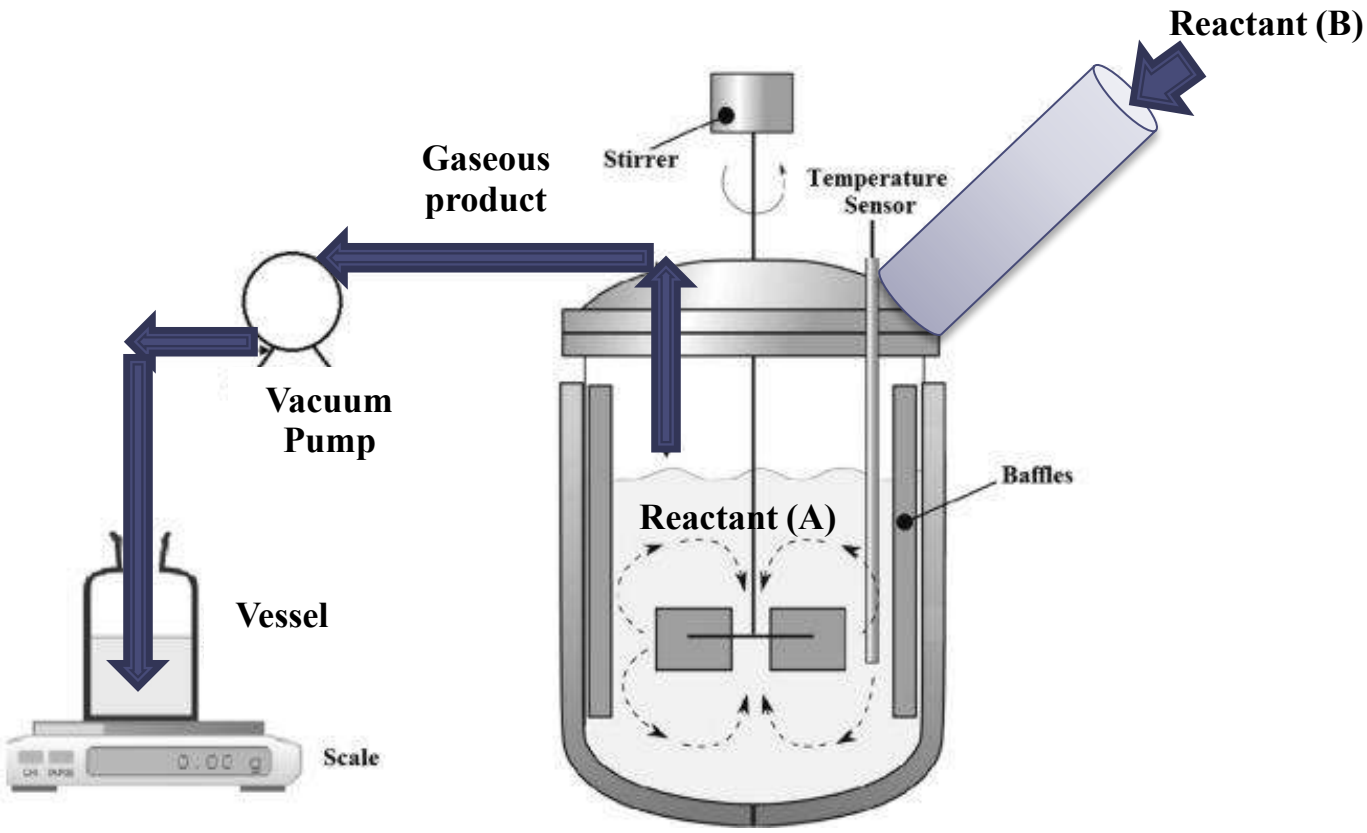


Figure (C)

Semicontinuous Reactors

In Figure (D), depicting a gas-liquid reaction of the type A(*g*) + B(*l*) → products, reactant A is dispersed (bubbled) continuously through a batch of reactant B; an important example is an aerobic fermentation in which air (or O_2) is supplied continuously to a liquid substrate (e.g., a batch of culture, as in penicillin production).

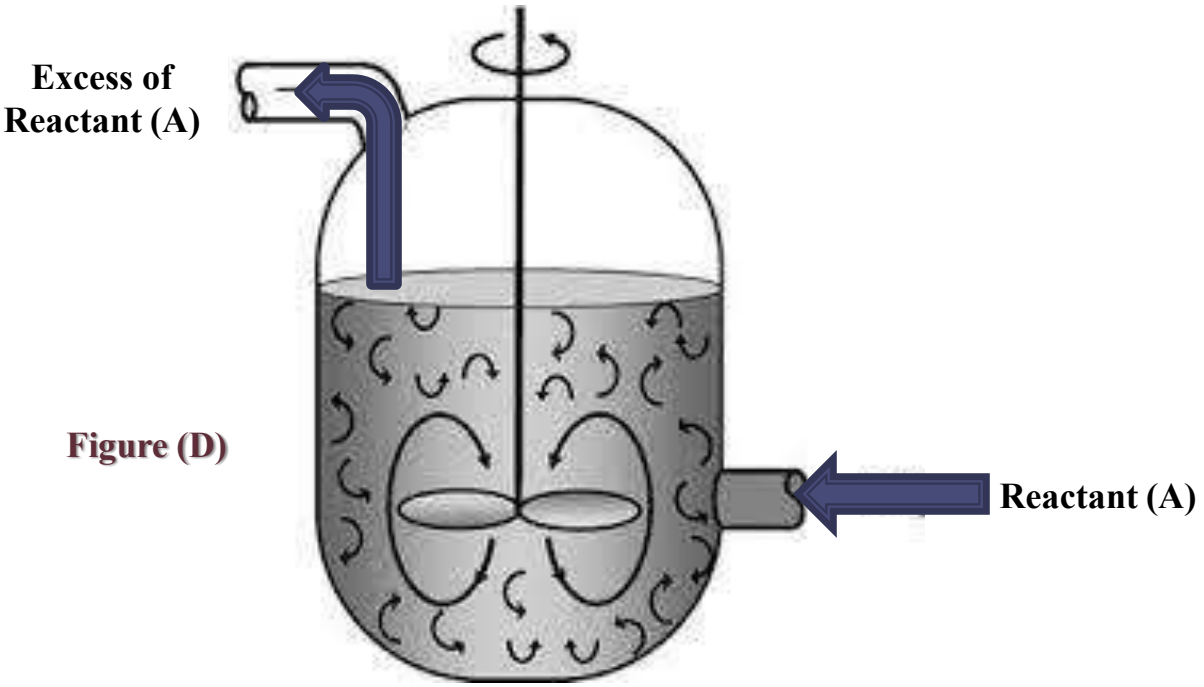


Figure (D)

In Figure (E) depicting a fixed-bed catalytic reactor for a gas-solid (catalyst) reaction, the bed of catalyst is a batch phase, and the reacting gas phase flows continuously through the bed. A fluidized-bed reactor may be operated in a similar manner. A reactor for chemical vapor deposition (CVD) is also operated in this manner, although gas flows continuously over a solid substrate in the form of a surface, rather than through a bed of particles. Semicontinuous operation is appropriate for a catalyst that does not deactivate over time or deactivates slowly.

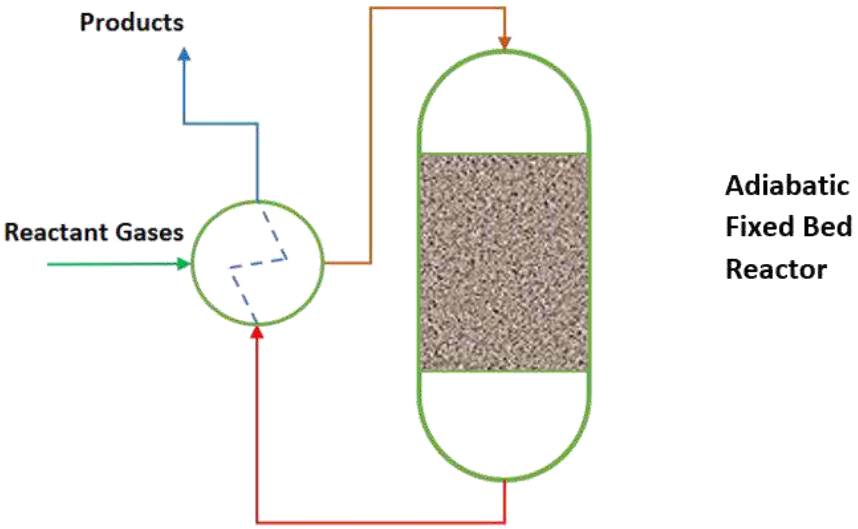


Figure (E)

If the catalyst deactivates rapidly, the reactor configuration shown in Figure (F) may be used. This consists of two identical fixed-bed reactors operating in parallel, with each alternating, in a prescribed cyclic manner, between reaction and regeneration. This is a rather complex mode of operation, requiring intricate piping and valving, and timing devices for overall continual operation. Wherever feasible, it should be replaced by inherently continuous operation for both reaction and regeneration, as in a fluidized-bed reactor.

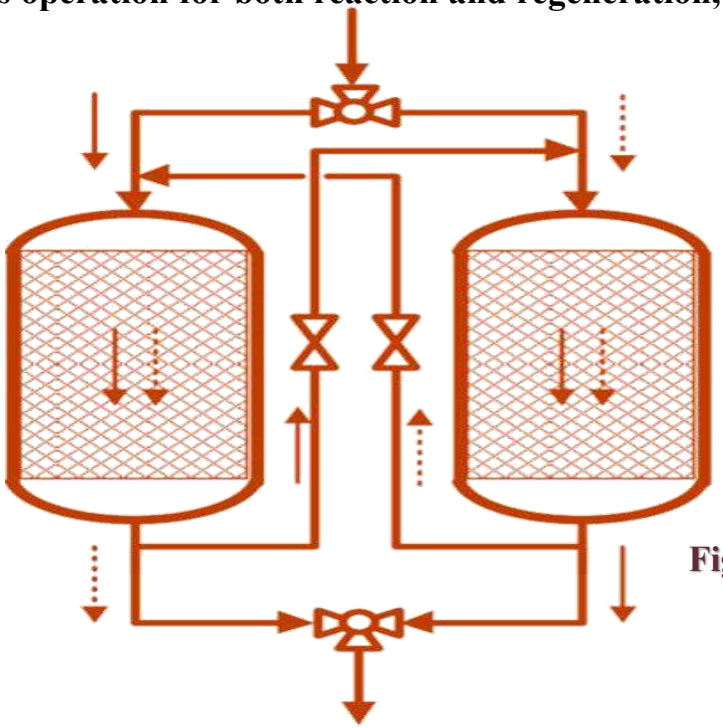


Figure (F)

Advantages and Disadvantages (Semibatch Reactor)

Advantages:

(1) In comparison with a batch reactor, the gradual or intermittent addition of a reactant (say, B in A + B → products, Figure (A) in semibatch operation can result in improved control of T, particularly for a reaction with a large ΔH .

(2) Similarly, the concentration of a reactant can be kept relatively low (B in point (1)) or high (A in point (1)) if either is advantageous for suppressing undesired side reactions.

(3) The withdrawal of a product (continuously, as in Figure (B), or intermittently) can result in higher conversion of a reactant, particularly if the reaction is equilibrium-limited.

Disadvantages:

(1) As in the case of a batch reactor, the production rate may be limited because of the cyclic nature of the operation.

(2) Also, as in the case of a batch reactor, the operating cost may be relatively high.

(3) The design or performance analysis is complicated because of the unsteady-state operation.

(4) Semicontinuous operation shown in Figure (F) requires intricate piping and valving.

Exercises 3.2

1- At elevated temperatures, NO_2 (A) decomposes into NO and O_2. The reaction is second-order with respect to NO_2, and at 400 °C the rate constant is $k_A = 5.36 \times 10^{-4}$ kPa^{-1} s^{-1}. If a sample of NO_2 is placed in a constant-volume batch reactor maintained at 673 K, and the initial pressure is 50 kPa, calculate the time required (in seconds) for the total pressure P to change by 10 kPa.

2- A liquid-phase reaction A + B → C is conducted in a 50-L batch reactor. The reaction is first-order with respect to each reactant.

(a) Determine the time required for 90% conversion of A, if the reaction occurs isothermally at T_o.

(b) Determine $\dot{Q}$ and T_c (as functions of time), if a cooling coil is placed in the tank to maintain the isothermal conditions.

(c) For (a), sketch the conversion-versus-time and temperature-versus-time profiles.

Data: c_{Ao} and c_{Bo} are 0.50 mol L^{-1} and 0.75 mol L^{-1}, respectively. The initial temperature (T_o) is 400 K, The fluid density is 0.75 g cm^{-3}, and the heat transfer parameter (UA_c) for part (b) is 100 W K-l. The reaction is exothermic (- 145 kJ (mol A)$^{-1}$), and $k_A = 1.4 \times 10^7 e^{-7700/T}$ L mol^{-1} min^{-1}.

3- The liquid-phase reaction A + 2B + C takes place isothermally in a batch reactor of volume V = 7500 L. The batch-cycle time ($t_c = t + t_d$) is considered to be fixed by a shift period of 8 h. If the down-time (td) between batches is 45 min, calculate the rate of production of B (mol h^{-1}) on a continual basis, with 1 batch per shift, if the feed concentration (c_{Ao}) is 3.0 mol L^{-1}. The rate of reaction is given by $(-r_A) = k_A c_A^{0.5}$, where $k_A = 0.0025$ L$^{0.5}$ mol$^{-0.5}$ min^{-1}.

4- DESIGN EQUATIONS FOR CONTINUOUS STIRRED-TANK REACTORS (CSTR)

here, we will develop the basis for design and performance analysis for a CSTR (continuous stirred-tank reactor). The general features of a CSTR are outlined previously. The essential features, as applied to complete dispersion at the microscopic level, i.e., nonsegregated flow, are recapitulated as follows:

(1) The flow pattern is BMF, and the CSTR is a "closed" vessel.
(2) Although flow through the CSTR is continuous, the volumetric flow rates at the inlet and exit may differ because of a change in density.
(3) BMF involves perfect mixing within the reactor volume, which, in turn, implies that all system properties are uniform throughout the reactor.
(4) Perfect mixing also implies that, at any instant, each element of fluid within the reactor has an equal probability of leaving the vessel.
(5) As a result of (4) there is a continuous distribution of residence times.
(6) As a result of (4) the outlet stream has the same properties as the fluid inside the vessel.
(7) As a result of (6), there is a step-change across the inlet in any property that changes from inlet to outlet.
(8) Although there is a distribution of residence times, the complete mixing of fluid at the microscopic and macroscopic levels leads to an averaging of properties across all fluid elements. Thus, the exit stream has a concentration (average) equivalent to that obtained as if the fluid existed as a single, large fluid element with a residence time of $\bar{t}$ = V/q

ADVANTAGES AND DISADVANTAGES OF A CSTR

Advantages

(1) Relatively cheap to construct;
(2) Ease of control of temperature in each stage, since each operates in a stationary state; heat transfer surface for this can be easily provided;
(3) Can be readily adapted for automatic control in general, allowing fast response to changes in operating conditions (e.g., feed rate and concentration);
(4) Relatively easy to clean and maintain;
(5) With efficient stirring and viscosity that is not too high, the model behavior can be closely approached in practice to obtain predictable performance.

Disadvantages

The most obvious disadvantage in principle stems from the fact that the outlet stream is the same as the contents of the vessel. This implies that all reaction takes place at the lowest concentration (of reactant A, say, c_A) between inlet and outlet. For normal kinetics, in which rate of reaction ($-r_A$) decreases as c_A decreases, this means that a greater volume of reactor is needed to obtain a desired conversion. (For abnormal kinetics, the opposite would be true, but this is unusual-what is an example of one such situation?)

DESIGN EQUATIONS FOR A SINGLE-STAGE CSTR

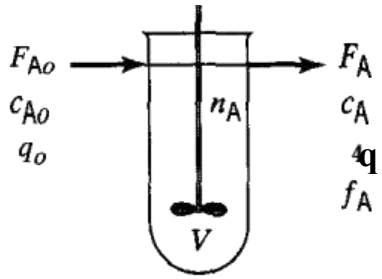
General Considerations; Material and Energy Balances

The process design of a CSTR typically involves determining the volume of a vessel required to achieve a specified rate of production. Parameters to investigate include the number of stages to use for optimal operation, and the fractional conversion and temperature within each stage. We begin, however, by considering the material and energy balances for a single stage CSTR.

1- Material Balance; Volume of Reactor; Rate of Production

For continuous operation of a CSTR as a "closed" vessel, the general material balance equation for reactant A (in the reaction A + . . .→ ν_c C + . . .), with a control volume defined as the volume of fluid in the reactor, is written as

Quantities in material balance equation for CSTR



$$\left(\begin{array}{c}\text{rate of}\\ \text{input of}\\ \text{A by flow}\end{array}\right)-\left(\begin{array}{c}\text{rate of}\\ \text{output of}\\ \text{A by flow}\end{array}\right)-\left(\begin{array}{c}\text{rate of}\\ \text{disappearance}\\ \text{of A by}\\ \text{reaction}\end{array}\right)=\left(\begin{array}{c}\text{rate of}\\ \text{accumulation}\\ \text{of A within}\\ \text{the control}\\ \text{volume}\end{array}\right) \qquad (1)$$

Thus, in terms of molar flow rates, with only unreacted A in the feed (f_{Ao} =0)

$$F_{A0} - F_A - (-r_A)V = dn_A/dt \qquad (2)$$

or, in terms of volumetric flow rates,

$$c_{Ao}q_o - c_A q - (-r_A)V = dn_A/dt \qquad (3)$$

and, in terms of fractional conversion of A,

$$F_{Ao}f_A - (-r_A)V = dn_A/dt \qquad (4)$$

For steady-state operation, with $dn_A/dt = 0$, from equations (3) and (4)

$$\begin{aligned} V &= (c_{Ao}q_o - c_A q)/(-r_A) \\ &= F_{Ao}f_A/(-r_A) \end{aligned} \qquad (5)$$

The mean residence time is given by

$$\bar{t} = V/q \qquad (6)$$

and the space time by

$$\tau = V/q_o \qquad (7)$$

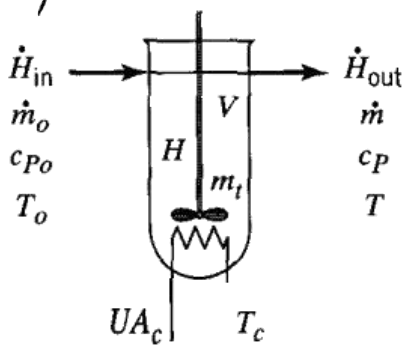
The rate of production in terms of the product C is the molar rate of flow of C from the reactor. That is,

$$Pr(C) = F_C = \nu_C F_{Ao} f_A = c_C q \qquad (8)$$

2- Energy Balance

For a continuous-flow reactor, such as a CSTR, the energy balance is an enthalpy (*H*) balance, if we neglect any differences in kinetic and potential energy of the flowing stream, and any shaft work between inlet and outlet. Then the energy (enthalpy) equation in words is

$$\left(\begin{array}{c}\text{rate of}\\ \text{input of}\\ \text{enthalpy by}\\ \text{flow, heat}\\ \text{transfer or}\\ \text{reaction}\end{array}\right) - \left(\begin{array}{c}\text{rate of}\\ \text{output}\\ \text{of enthalpy by}\\ \text{flow, heat}\\ \text{transfer or}\\ \text{reaction}\end{array}\right) = \left(\begin{array}{c}\text{rate of}\\ \text{accumulation}\\ \text{of enthalpy}\\ \text{within control}\\ \text{volume}\end{array}\right) \qquad (9)$$



Quantities in energy-balance equation for CSTR

To translate this into operational form, we use the total specific mass flow rate, $\dot{m}$, rather than molar flow rate, to show an alternative treatment to that used for a BR. An advantage to this treatment is that in steady-state operation, $\dot{m}$ is constant, whereas the molar flow rate need not be. Thus, using T_{ref} as a reference temperature to evaluate the enthalpy for the inlet and outlet streams, we have

$$\int_{T_{ref}}^{T_o} \dot{m}_o c_{Po} dT - \int_{T_{ref}}^{T} \dot{m} c_P dT + UA_c(T_c - T), + (-\Delta H_{RA})(-r_A)V = dH/dt = d(m_t c_P T)/dt \qquad (10)$$

For steady-state operation, $\dot{m} = \dot{m}_o$, and the right side vanishes; furthermore, if c_P and T_c are constant, and if we choose $T_{ref} = T_o$, so that the enthalpy input by flow is zero, then

$$\dot{m} c_P(T_o - T) + UA_c(T_c - T) + (-\Delta H_{RA})(-r_A)V = 0 \qquad (11)$$

or, on substitution of $F_{Ao} f_A$ for $(-r_A)V$ from equation (5)

$$\dot{m} c_p(T_o - T) + UA_c(T_c - T) + (-\Delta H_{RA})F_{Ao} f_A = 0 \qquad (12)$$

Equation (12) relates f_A and T for steady-state operation; solving for f_A, we have:

$$f_A = \frac{\dot{m} c_P T_o + UA_c T_c}{(-\Delta H_{RA})F_{Ao}} + \left[\frac{\dot{m} c_p + UA_c}{(-\Delta H_{RA})F_{Ao}}\right] T \qquad (13)$$

The use of the energy balance in the design of a CSTR depends on what is specified initially. If T is specified, the energy balance is uncoupled from the material balance, and is used primarily to design the heat exchanger required to control T; V is given by the performance equation (5). If T is not specified, as in adiabatic operation, the material and energy balances are coupled (through T), and must be solved simultaneously.

Worked problem 4.1

For the liquid-phase reaction A + B → products at 20°C suppose 40% conversion of A is desired in steady-state operation. The reaction is pseudo-first-order with respect to A, with $k_A = 0.0257$ h^{-1} at 20 °C. The total volumetric flow rate is 1.8 m^3 h^{-1}, and the inlet molar flow rates of A and B are F_{Ao} and F_{Bo} mol h^{-1} , respectively. Determine the vessel volume required, if, for safety, it can only be filled to 75% capacity.

Solution 4.1

Since this is a liquid-phase reaction, we assume density is constant. The quantity V in the material-balance equation (5) is the volume of the system (liquid) in the reactor. The reactor (vessel) volume is greater than this because of the 75%-capacity requirement. From the specified rate law,

$$(-r_A) = k_A c_A = k_A c_{Ao}(1 - f_A) \qquad (1)$$

The material- balance equation is

$$V = (c_{Ao} - c_A)q/(-r_A) \qquad \text{(constant density)} \qquad (2)$$

Substituting equation (1) into equation (2)

$$V = F_{Ao} f_A / k_A c_{Ao}(1 - f_A) \qquad (3)$$

Since, $F_{Ao} = q_o c_{Ao}$ (4)

Equation (4) becomes,

$$V = q_o f_A / k_A (1 - f_A) \qquad (5)$$

$$= 1.8(0.4)/0.0257(0.6) = 46.7 \text{ m}^3$$

and the actual volume of the vessel V_{act} is

$$V_{act} = \frac{V}{Capacity\%} \times 100 \quad = \frac{46.7\ m^3}{75} \times 100 = 62.3\ m^3$$

Worked problem 4.2

A liquid-phase reaction A → B is to be conducted in a CSTR at steady-state at 163°C. The temperature of the feed is 20 °C and 90% conversion of A is required. Determine the volume of a CSTR to produce 130 kg B h^{-1}, and calculate the heat load ($\dot{Q}$) for the process. Does this represent addition or removal of heat from the system?

Data:

$c_P = 2.0$ J g^{-1} K^{-1} $\quad M_A = M_B = 200$ g mol^{-1}

$\rho = 0.95$ g cm^{-3} $\quad \Delta H_{RA} = -87$ kJ mol^{-1}

$k_A = 0.80$ h^{-1} at 163°C

Solution 4.2

V may be determined from the material-balance equation, together with the given rate law:

$$V = F_{Ao} f_A / (-r_A)$$

$$(-r_A) = k_A c_A$$

$$V = F_{Ao} f_A / (-r_A) = F_{Ao} f_A / k_A c_A$$

$$= F_{Ao} f_A / k_A c_{Ao}(1 - f_A) = f_A q / k_A (1 - f_A) \qquad (1)$$

$$q = \frac{Pr(B)_{kg}}{f_A \rho} = \left(\frac{130 kg B}{h}\right)\left(\frac{1}{0.90}\right)\left(\frac{cm^3}{0.95\ g}\right)\left(\frac{1\ L}{1000\ cm^3}\right)\left(\frac{1000\ g}{1\ kg}\right)$$

$$= 152 \text{ Lh}^{-1}$$

$$\therefore \quad V = \frac{(0.90)(152\ Lh^{-1})}{(0.89\ h^{-1})(0.1)} = 1710\ L$$

The heat load, $\dot{Q}$ is obtained from the energy-balance equation for steady- state operation with constant values for the various parameters:

$$\dot{Q} = UA_c(T_c - T) = -\dot{m} c_P (T_o - T) - (-\Delta H_{RA}) F_{Ao} f_A$$

$$\dot{m} = \frac{Pr(B)g}{f_A} = \frac{130000 kg}{0.90} \qquad c_P = 0.002 \text{ kJ g}^{-1}\text{K}^{-1}$$

$$-\Delta H_{RA} = 87 \text{ kJ/mol} \qquad F_{Ao} = \frac{Pr(B)_g}{f_A M_A} = \frac{130000}{(0.90)\ (200)}$$

$$\dot{Q} = \frac{130000\ g}{0.90}\ (0.002)(20 - 163) - (87)\frac{130000}{(0.9)(200)}(0.90)$$

$$\dot{Q} = 41311 - 56550 = -15239 \text{ kJ h}^{-1}$$

Since $\dot{Q}$ is negative, heat is removed from the system

Exercises 4.1

1- Suppose the liquid-phase hydration of ethylene oxide (A) to ethylene glycol, $C_2H_4O + O_2(A) \rightarrow C_2H_6O_2$, takes place in a CSTR of volume (V) 10,000 L; the rate constant is k_A 2.464×10^{-3} min^{-1}.

(a) Calculate the steady-state fractional conversion of A (f_A), if the feed rate (q_o) is 0.30 L

s^{-1} and the feed concentration (c_{Ao}) is 0.120 mol L^{-1}.

(b) If the feed rate suddenly drops to 70% of its original value, and is maintained at this new value, (i) what is the value of f_A after 60 min, and (ii) how close (%) is this value to the new steady-state value?

(c) What is the ratio of the steady- state production rate in (b) to that in (a)?

2- For the reaction between hydrocyanic acid (HCN) and acetaldehyde (CH_3CHO) in aqueous solution,

$$HCN\ (A) + CH_3CHO\ (B) \rightarrow CH_3CH(OH)CN$$

the rate law at 25 °C and a certain pH is $(-r_A) = k_A c_A c_B$, where k_A = 0.210 L mol^{-1} min^{-1}. If the reaction is carried out at steady-state at 25 °C in a CSTR, how large a reactor (V/L) is required for 75% conversion of HCN, if the feed concentration is 0.04 mol L^{-1} for each reactant, and the feed rate is 2 L min^{-1}?

3- The liquid-phase reaction A + B → C takes place in a single-stage CSTR. The rate law for the reaction is $(-r_A) = k_A c_A c_B$.

(a) Calculate the feed rate, q_o, that maximizes the rate of production of C.

(b) For the feed rate in (a), calculate the outlet values of c_A, c_B, c_C, and f_A.

Data: k_A = 0.005 L mol^{-1} s^{-1}; c_{Ao} = 0.2 mol L^{-1}; c_{Bo}, = 0.01 mol L^{-1}; V = 10,000 L.

5- Effect of Temperature on Reaction Rate: Arrhenius Equation; Activation Energy

A rate of reaction usually depends more strongly on temperature than on concentration. Thus, in a first-order ($n = 1$) reaction, the rate doubles if the concentration is doubled. However, a rate may double if the temperature is raised by only 10 K, in the range, say, from 290 to 300 K. This essentially exponential behavior is analogous to the temperature-dependence of the vapor pressure of a liquid, p^*, or the equilibrium constant of a reaction, K_{eq}. In the former case, this is represented approximately by the Clausius-Clapeyron equation,

$$\frac{d\ln p^*}{dT} = \frac{\Delta H^{vap}(T)}{RT^2} \qquad (1)$$

where ΔH_{vap} is the enthalpy of vaporization. The behavior of K_{eq} is represented (exactly) by the van't Hoff equation

$$\frac{d\ln K_{eq}}{dT} = \frac{\Delta H^{\circ}(T)}{RT^2} \qquad (2)$$

where ΔH^o is the standard enthalpy of reaction.

Influenced by the form of the van't Hoff equation, Arrhenius (1889) proposed a similar expression for the rate constant k_A to represent the dependence of $(-r_A)$ on T.

$$\frac{d\ln k_A}{dT} = \frac{E_A}{RT^2} \qquad (3)$$

where E_A is a characteristic (molar) energy, called the energy of activation. Since $(-r_A)$ (hence k_A increases with increasing T) almost every case, E_A is a positive quantity

Integration of equation (3) on the assumption that E_A is independent of T leads to

$$\ln k_A = \ln A - E_A/RT \qquad (4)$$

$$k_A = A \exp(-E_A/RT) \qquad (5)$$

where A is a constant referred to as the pre-exponential factor. Together, E_A and A are called the Arrhenius parameters. Equations (3), (4) and (5) are all forms of the Arrhenius equation.

Worked problem 5.1

It is sometimes stated as a rule of thumb that the rate of a chemical reaction doubles for a 10 K increase in T. Is this in accordance with the Arrhenius equation? Determine the value of the energy of activation, E_A, if this rule is applied for an increase from (a) 300 to 310 K, and (b) 800 to 810 K.

Solution 5.1

For two different temperatures (T_1 and T_2) correspond two different rate constants (k_{A1} and k_{A2})

$$lnk_{A1} = lnA - \frac{E_A}{RT_1} \quad (1)$$

$$lnk_{A2} = lnA - \frac{E_A}{RT_2} \quad (2)$$

Subtracting equation (1) from equation (2)

$$lnk_{A2} - lnk_{A1} = \frac{E_A}{RT_1} + \frac{E_A}{RT_2}$$

$$ln\frac{k_{A2}}{k_{A1}} = \frac{E_A}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (3)$$

$$E_A = \frac{Rln(k_{A2}/k_{A1})}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$(a)\ E_A = \frac{(8.314)ln(2)}{\left(\frac{1}{300} - \frac{1}{310}\right)} = 53600\ J/mol$$

$$(b)\ E_A = \frac{(8.314)ln(2)}{\left(\frac{1}{800} - \frac{1}{810}\right)} = 373400\ J/mol$$

These are very different values, which shows that the rule is valid for a given reaction only over a limited temperature range.

Exercise 5.1

Suppose the liquid-phase reaction A + B → products was studied in a batch reactor at two temperatures and the following results were obtained:

T/°C	f_A	t/min
20	0.75	20
30	0.62	9

Stating all assumptions made, calculate E_A, the Arrhenius energy of activation, for the reaction. Note that the order of reaction is not known.

6- Catalysis and Catalytic Reactions

Many reactions proceed much faster in the presence of a substance that is not a product (or reactant) in the usual sense. The substance is called a catalyst, and the process whereby the rate is increased is catalysis. Some industrially important catalytic reactions (with their catalysts) which are the bases for such large-scale operations as the production of sulfuric acid, agricultural fertilizers, plastics, and fuels are:

$$SO_2 + \frac{1}{2}O_2 \rightleftarrows SO_3 \qquad \text{(promoted } V_2O_5 \text{ catalyst)}$$

$$N_2 + 3H_2 \rightleftarrows 2NH_3 \qquad \text{(promoted Fe catalyst)}$$

$$C_8H_{10} \rightleftarrows C_8H_8 + H_2 \qquad (K_2CO_3, \text{ Fe oxide catalyst})$$

$$CO + 2H_2 \rightleftarrows CH_3OH \qquad \text{(Cu, Zn oxide catalyst)}$$

Nature and Concept

The following points set out more clearly the qualitative nature and concept of catalysis and catalysts:

(1) The primary characteristic is that a catalyst increases the rate of a reaction, relative to that of the uncatalyzed reaction.

(2) A catalyst does not appear in the stoichiometric description of the reaction, although it appears directly or indirectly in the rate law and in the mechanism. It is not a reactant or a product of the reaction in the stoichiometric sense.

(3) The amount of catalyst is unchanged by the reaction occurring, although it may undergo changes in some of its properties.

(4) The catalyst does not affect the chemical nature of the products. This must be qualified if more than one reaction (set of products) is possible, because the catalyst usually affects the selectivity of reaction.

(5) Corresponding to (4), the catalyst does not affect the thermodynamic affinity of a given reaction. That is, it affects the rate but not the tendency for reaction to occur. It does not affect the free energy change (ΔG) or equilibrium constant (K_{eq}) of a given reaction. If a catalyst did alter the position of equilibrium in a reaction, this would be contrary to the first law of thermodynamics, as pointed out by Ostwald many years ago, since we would then be able to create a perpetual motion machine by fitting a piston and cylinder to a gas-phase reaction in which a change in moles occurred, and by periodically exposing the reacting system to the catalyst.

(6) Since a catalyst hastens the attainment of equilibrium, it must act to accelerate both forward and reverse reactions. For example, metals are good hydrogenation and dehydrogenation catalysts.

(7) Although it may be correct to say that a catalyst is not involved in the stoichiometry or thermodynamics of a reaction, it is involved in the mechanism of the reaction. In increasing the rate of a reaction, a catalyst acts by providing an easier path, which can generally be represented by the formation of an intermediate between catalyst and reactant, followed by the appearance of product(s) and regeneration of the catalyst. The easier path is usually associated with a lower energy barrier, that is, a lower E_A.

Types of Catalysis

(1) Molecular catalysis. **The term molecular catalysis is used for catalytic systems where identical molecular species are the catalytic entity, like the molybdenum complex**

(2) Surface catalysis. **As the name implies, surface catalysis takes place on the surface atoms of an extended solid. This often involves different properties for the surface atoms and hence different types of sites. Because the catalyst is a solid, surface catalysis is by nature heterogeneous.**

(3) Enzyme catalysis. **Enzymes are proteins, polymers of amino acids, which catalyze reactions in living organisms-biochemical and biological reactions. The systems involved may be colloidal-that is, between homogeneous and heterogeneous.**

(4) Autocatalysis. **In some reactions, one of the products acts as a catalyst, and the rate of reaction is experimentally observed to increase and go through a maximum as reactant is used up. This is autocatalysis. Some biochemical reactions are autocatalytic.**

(5) Homogeneous catalysis. **The reactants and the catalyst are in the same phase. Examples include the gas-phase decomposition of many substances, including diethyl ether and acetaldehyde, catalyzed by iodine, and liquid-phase esterification reactions, catalyzed by mineral acids**

(6) Heterogeneous catalysis. **The catalyst and the reactants are in different phases. Examples include the many gas-phase reactions catalyzed by solids (e.g., oxidation of SO_2 in presence of V_2O_5). Others involve two liquid phases (e.g., emulsion copolymerization of styrene and butadiene, with the hydrocarbons forming one phase and an aqueous solution of organic peroxides as catalysts forming the other phase).**

General Aspects of Catalysis

1- Catalytic Sites

For catalytic reactions which take place on surfaces, the term "catalytic site" is used to describe a location on the surface which bonds with reaction intermediates. This involves a somewhat arbitrary division of the continuous surface into smaller ensembles of atoms. two important aspects of surface catalysis that distinguish it from molecular catalysis:

(1) A distribution of "sites" exists on surfaces.

(2) Intermediates on adjacent sites can interact because of the extended nature of the surface.

2- Catalytic Effect on Reaction Rate

Catalysts increase the reaction rate by lowering the energy requirements for the reaction. This, in turn, results from the ability of the catalyst to form bonds to reaction intermediates to offset the energy required to break reactant bonds. An example of a catalyst providing energetically easier routes to products is found in the multistep reaction for the methanol-synthesis reaction, $CO + 2H_2 + CH_3OH$. In general, the reaction rate is proportional to the amount of catalyst. This is true if the catalytic sites function independently. The number of turnovers per catalytic site per unit time is called the *turnover frequency*.

3- Catalytic Control of Reaction Selectivity

In addition to accelerating the rates of reactions, catalysts control reaction selectivity by accelerating the rate of one (desired) reaction much more than others. Nickel surfaces catalyze the formation of methane from CO and H_2 but methanol is the major product on palladium surfaces.

4- Catalyst Effect on Extent of Reaction

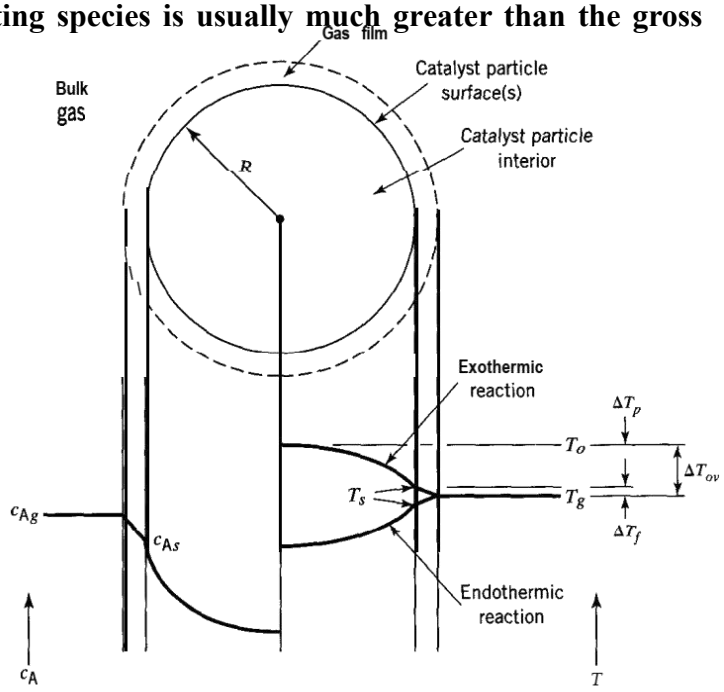
A catalyst increases only the rate of a reaction, not the thermodynamic affinity. Since the presence of the catalyst does not affect the Gibbs energy of reactants or products, it does not therefore affect the equilibrium constant for the reaction. It follows from this that a catalyst must accelerate the rates of both the forward and reverse reactions, since the rates of the two reactions must be equal once equilibrium is reached.

HETEROGENEOUS CATALYSIS: KINETICS IN POROUS CATALYST PARTICLES

General Considerations

For a solid-catalyzed gas-phase reaction, the catalyst is commonly in the form of particles or pellets of various possible shapes and sizes, and formed in various ways. Such particles are usually porous, and the interior surface accessible to the reacting species is usually much greater than the gross exterior surface.

The porous nature of the catalyst particle gives rise to the possible development of significant gradients of both concentration and temperature across the particle, because of the resistance to diffusion of material and heat transfer, respectively. The situation is illustrated schematically in the Figure for a spherical or cylindrical (viewed end-on) particle of radius R. The gradients on the left represent those of c_A, say, for A(g) + . . . → product(s), and those on the right are for temperature T; the gradients in each case, however, are symmetrical with respect to the centerline axis of the particle. there is a spontaneous tendency for A to move from the bulk gas (c_{Ag}) to the interior of the particle, first by mass transfer to the exterior surface (c_{As}) across a supposed film, and then by some mode of diffusion through the pore structure of the particle.



Concentration (c_A) and temperature (Z') gradients (schematic) in a porous catalyst particle (spherical or end-on cylindrical); ΔT_p is the temperature drop across the particle itself, and ΔT_f is that across the gas film.

Next, consider the gradients of temperature. If the reaction is exothermic, the center of the particle tends to be hotter, and conversely for an endothermic reaction. Two sets of gradients are thus indicated in the above Figure. Heat transfer through the particle is primarily by conduction, and between exterior particle surface (T_s) and bulk gas (T_g) by combined convection-conduction across a thermal boundary layer, shown for convenience in the Figure to coincide with the gas film for mass transfer.

Particle Density and Voidage (Porosity)

Particle density, ρ_P, is defined by

$$\rho_p = m_p/v_p \qquad (1)$$

where m_p and v_p are the mass and volume of the particle, respectively. Particle voidage, ϵ_p, is the ratio of the volume of void space (pores) in the particle, v_V to the volume of the particle, v_p:

$$\epsilon_p = v_V/v_p \qquad (2)$$

Because of the voidage, the particle density is less than the intrinsic density of the solid catalyst material, $\rho_s = m_p/ v_s$,where v_s is the volume of solid in the particle, but is related to it by

$$\rho_p = \rho_S(1 - \epsilon_p) \qquad (3)$$

since $v_p = v_V + v_S$.

Modes of Diffusion; Effective Diffusivity

Diffusion is the spontaneous migration of a species in space, relative to other species, as a result of a variation in its chemical potential, in the direction of decreasing potential. The variation of chemical potential may arise as a result of variation of concentration or temperature or by other means, but we consider only the effect of concentration here

From a molecular point of view inside a catalyst particle, diffusion may be considered to occur by three different modes: molecular, Knudsen, and surface. Molecular diffusion is the result of molecular encounters (collisions) in the void space (pores) of the particle. Knudsen diffusion is the result of molecular collisions with the walls of the pores. Molecular diffusion tends to dominate in relatively large pores at high P, and Knudsen diffusion tends to dominate in small pores at low P. Surface diffusion results from the migration of adsorbed species along the surface of the pore because of a gradient in surface concentration.

The phenomenological description of the rate of diffusion in terms of Fick's (first) law. According to this, for steady- state diffusion in one dimension (coordinate x) of species A, the molar flux, N_A, in, say, mol m^{-2} (cross-sectional area of diffusion medium) s^{-1}, through a particle is

$$N_A = -D_e dc_A/dx \qquad (1)$$

where D_e is the effective diffusivity for A.

The effective diffusivity D_e is a characteristic of the particle that must be measured for greatest accuracy. However, in the absence of experimental data, D_e may be estimated in terms of molecular diffusivity, D_{AB} (for diffusion of A in the binary system A + B), Knudsen diffusivity, D_K, particle voidage, ϵ_p, and a measure of the pore structure called the particle tortuosity, τ_p.

An estimate for D_{AB} is

$$D_{AB} = \frac{0.00188T^{3/2}[(M_A + M_B)/M_A M_B]^{1/2}}{P\Omega_D d_{AB}^2} \qquad (2)$$

where D_{AB} is in $cm^2\ s^{-1}$, T is in K, M_A and M_B are the molar masses of A and B, respectively, in g mol^{-1}, P is pressure in kPa, d_{AB} is the collision diameter, $(d_A + d_B)/2$, in nm, and Ω_D is the so-called collision integral.

The Knudsen diffusivity may be estimated from

$$D_K = 9700 r_e (T/M)^{1/2} \qquad (3)$$

where D_K is in $cm^2\ s^{-1}$, r_e is the average pore radius in cm, and M is molar mass. Equation (3) applies rigorously to straight, cylindrical pores, and is an approximation for other geometries.

The overall diffusivity, D^*, is obtained from D_{AB} and D_K by means of the conventional expression for resistances in series:

$$\frac{1}{D^*} = \frac{1}{D_{AB}} + \frac{1}{D_K} \qquad (4)$$

The effective diffusivity is obtained from D^*, but must also take into account the two features that (1) only a portion of the catalyst particle is permeable, and (2) the diffusion path through the particle is random and tortuous. These are allowed for by the particle voidage or porosity, ϵ_p, and the tortuosity, τ_p, respectively. The former must also be measured, and is usually provided by the manufacturer for a commercial catalyst. For a straight cylinder, $\tau_p = 1$, but for most catalysts, the value lies between 3 and 7; typical values are given by Satterfield.

The final expression for estimating D_e is

$$D_e = D^* \epsilon_p / \tau_p \qquad (5)$$

Equation (5) reveals the "true" units of D_e, m^3 (void space) m^{-1} (particle) s^{-1}, as opposed to the "apparent" units in equation (1), $m^2\ s^{-1}$.

Particle Effectiveness Factor η

Definition of η

Since c_A and T may vary from point to point within a catalyst particle, the rate of reaction also varies. This may be translated to say that the effectiveness of the catalyst varies within the particle, and this must be taken into account in the rate law. For this purpose, we introduce the particle effectiveness factor η, the ratio of the observed rate of reaction for the particle as a whole to the intrinsic rate at the surface conditions, c_{As} and T_s. In terms of a reactant A,

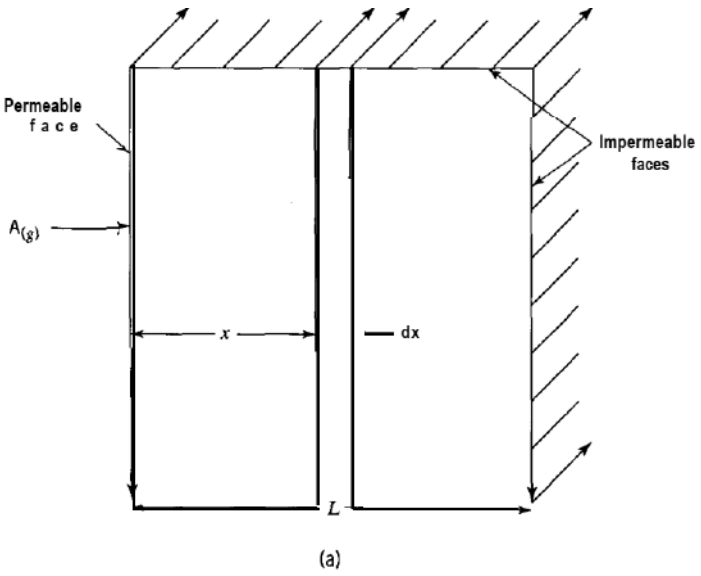
$$\eta = r_A\,(observed)/r_A(c_{As}, T_s) \qquad (1)$$

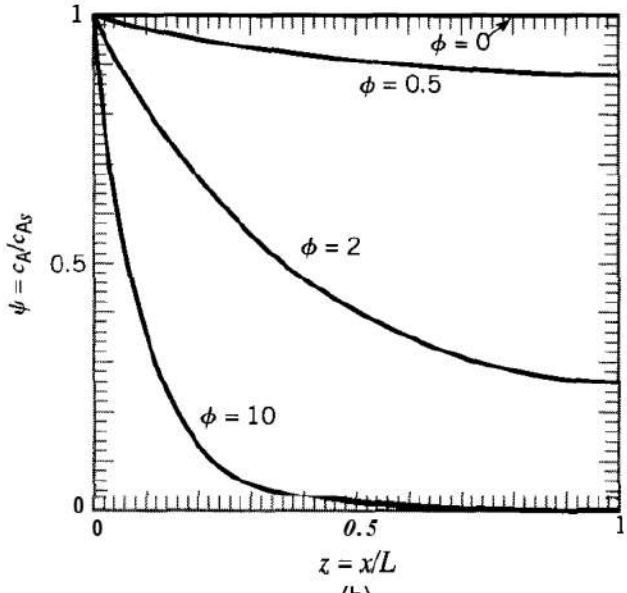
We wish to discover how η depends on reaction and particle characteristics in order to use equation (1) as a rate law in operational terms. To do this, we first consider the relatively simple particle shape of a rectangular parallelepiped (flat plate) and simple kinetics.

η for Flat-Plate Geometry

For a flat-plate porous particle of diffusion-path length *L* (and infinite extent in other directions), and with only one face permeable to diffusing reactant gas A, obtain an expression for η, the particle effectiveness factor defined by equation (1), based on the following assumptions:

(1) The reaction A(g) → product(s) occurs within the particle.
(2) The surface reaction is first order.
(3) The reaction is irreversible.
(4) The particle is isothermal.
(5) The gas is of constant density.
(6) The overall process is in steady-state.
(7) The diffusion of A in the particle is characterized by the effective diffusivity D_e, which is constant.
(8) There is equimolar counterdiffusion (reactants and products).





(a) Representation of flat-plate geometry; (b) concentration profile *Ψ*(*Φ*, z) (dimensionless) for various values of Thiele modulus *Φ*.

$$z = x/L \qquad (2)$$

$$\phi = L(k_A/D_e)^{1/2} \qquad (n = 1) \qquad (3)$$

$$\eta = (\tanh\phi)/\phi \qquad \text{(flat plate)} \qquad (4)$$

$$\text{where } \tanh\phi = \sinh\phi/\cosh\phi = (e^{\phi} - e^{-\phi})/(e^{\phi} + e^{-\phi}). \qquad (5)$$

Substitution of the result given by equation (4) into the definition of η given by equation (1) yields the modified first-order rate law for an isothermal particle of this geometry:

$$(-r_A)_{obs} = \eta k_A c_{As} = \frac{\tanh \phi}{\phi} k_A c_{As} \qquad (6)$$

where Φ is given by equation (3). Equation (6) is in terms of η and c_{As}. The form in terms of the observable concentration of A(c_{Ag}) requires consideration of the (additional) resistance to mass transfer exterior to the particle.

1- Effect of Particle Geometry (Shape) on η

The results for spherical and cylindrical shapes are approximately in the limit of $\Phi \rightarrow$ large, become the same, if the Thiele modulus is normalized in terms of a common effective diffusion-path-length parameter, L_e defined by

$$L_e = \frac{\text{volume of particle}}{\text{exterior permeable surface area}} \qquad (7)$$

$$\phi' = L_e (k_A/D_e)^{1/2} \qquad (n = 1) \qquad (8)$$

The consequences of this normalization are summarized for the various shapes in Tables A and B.

Table (A) Effectiveness factor (η) for various particle shapes

Shape	ϕ	Ψ	η
flat plate[a]	$L(k_A/D_e)^{1/2}$	$\cosh[\phi(1-z)]/\cosh\phi$	$(\tanh\phi)/\phi$
flat plate[b]	$L(k_A/D_e)^{1/2}$	$\cosh[\phi(\frac{1}{2}-z)]/\cosh(\phi/2)$	$\tanh(\phi/2)/(\phi/2)$
sphere[c]	$R(k_A/D_e)^{1/2}$	$\frac{R}{r}\frac{\sinh(\phi r/R)}{\sinh\phi}$	$\frac{3}{\phi}\left(\frac{1}{\tanh\phi}-\frac{1}{\phi}\right)$
cylinder'	$R(k_A/D_e)^{1/2}$	(in terms of Bessel functions (BF))	$\frac{2}{\phi}$ (ratio of BF)

[a] One face permeable
[b] Two faces permeable.
[c] R is particle radius; r is radial coordinate ($r = 0$ at center of particle).

Table (B) Thiele modulus (Φ') normalized with respect to shape and asymptotic value of η

Shape	L_e	ϕ'	Asymptotic value of η	
			$\phi \rightarrow \infty$	$\phi' \rightarrow \infty$
flat plate (1)	L	ϕ_{FP1}	$1/\phi_{FP1}$	$1/\phi'$
flat plate (2)	$L/2$	$\phi_{FP2}/2$	$2/\phi_{FP2}$	$1/\phi'$
sphere	$R/3$	$\phi_s/3$	$3/\phi_s$	$1/\phi'$
cylinder	$R/2$	$\phi_c/2$	$2/\phi_c$	$1/\phi'$

2- Effect of Order of Reaction on η

The order of reaction affect the value of η according to these relation and Table (C):

$$\phi'' = \left(\frac{n+1}{2}\right)^{1/2} \phi' \qquad (9)$$

$$= \left(\frac{n+1}{2}\right)^{1/2} \frac{L_e}{L}\phi \qquad (10)$$

$$= L_e \left(\frac{n+1}{2} \frac{k_A c_{As}^{n-1}}{D_e}\right)^{1/2} \qquad (11)$$

$$\eta \to 1/\phi'' \text{ as } \phi'' \to \text{large}$$

Table (C) Thiele modulus (Φ") normalized with respect to order of reaction (n) and asymptotic value of η

			Asymptotic value of η	
n	ϕ'	ϕ''	$\phi' \to cc$	$\phi'' \to \infty$
0	$L_e(k_A/c_{As}D_e)^{1/2}$	$\phi'/2^{1/2}$	$2^{1/2}/\phi'$	$1/\phi''$
1	$L_e(k_A/D_e)^{1/2}$	ϕ'	$1/\phi'$	$1/\phi''$
2	$L_e(k_A c_{As}/D_e)^{1/2}$	$\phi'/(2/3)^{1/2}$	$(2/3)^{1/2}/\phi'$	$1/\phi''$

3- Dependence of η on Temperature

The definition of the particle effectiveness factor η involves the intrinsic rate of reaction, ($-r_A)_{int}$, for reaction A → products, at the exterior surface conditions of gas-phase concentration (c_{As}) and temperature (T_s). Thus, from equation (1)

$$(-r_A)_{obs} = \eta(-r_A)_{int,c_{As},T_s} \qquad (12)$$

So far, we have assumed that the particle is isothermal and have focused only on the diffusional characteristics and concentration gradient within the particle, and their effect on η.

The overall drop in temperature ΔT_{ov} from the center of the particle to bulk gas may be divided into two parts:

$$\Delta T_{ov} = \Delta T_p + \Delta T_f \qquad (13)$$

where ΔT_p is the drop across the particle itself, and ΔT_f is that across the gas film or the thermal boundary layer. It is the gradient across the particle, corresponding to ΔT_{ov} that influences the particle effectiveness factor, η. The gradient across the film influences the overall effectiveness factor, η_o.

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CATALYST DEACTIVATION AND REGENERATION

Despite advances in catalyst design, all catalysts are subject to a reduction in activity with time (deactivation). The rate at which the catalyst is deactivated may be very fast, such as for hydrocarbon-cracking catalysts, or may be very slow, such as for promoted iron catalysts used for ammonia synthesis, which may remain on-stream for several years without appreciable loss of activity. Nonetheless, the design engineer must account for the inevitable loss of catalyst activity, allowing for either regeneration of the catalyst or its periodic replacement. Since these remedial steps are costly, both in terms of capital cost and loss of production during shutdown, it is preferable to minimize catalyst deactivation if possible.

Fouling

Poisoning is caused by chemisorption of compounds in the process stream; these compounds block or modify active sites on the catalyst. The poison may cause changes in the surface morphology of the catalyst, either by surface reconstruction or surface relaxation, or may modify the bond between the metal catalyst and the support. The toxicity of a poison (*P*) depends upon the enthalpy of adsorption for the poison, and the free energy for the adsorption process, which controls the equilibrium constant for chemisorption of the poison (K_p). The fraction of sites blocked by a reversibly adsorbed poison (θ_P) can be calculated using a Langmuir isotherm :

$$\theta_P = \frac{K_P p_P}{1 + K_A p_A + K_P p_P} \qquad (13)$$

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$$\theta_P = \frac{K_P p_P}{1 + K_A p_A + K_P p_P} \qquad (13)$$

where K_A and K_p are the adsorption constants for the reactant (A) and the poison, respectively, and p_A and p_p are the partial pressures of the reactant and poison. The catalyst activity remaining is proportional to the fraction of unblocked sites, 1 - θ_p.

The compound responsible for poisoning is usually an impurity in the feed stream; however, occasionally, the products of the desired reaction may act as poisons. There are three main types of poisons:

(1) Molecules with reactive heteroatoms (e.g., sulfur);
(2) Molecules with multiple bonds between atoms (e.g., unsaturated hydrocarbons);
(3) Metallic compounds or metal ions (e.g., Hg, Pd, Bi, Sn, Cu, Fe).

Sintering

Sintering is caused by growth or agglomeration of small crystals which make up the catalyst or its support. The structural rearrangement observed during sintering leads to a decrease in surface area of the catalyst, and, consequently, an irreversible reduction in catalyst sites. Sintering generally occurs if the local temperature of the catalyst exceeds approximately one third to one-half of its melting temperature (T_m). The upper limit (i.e., (1/2) T_m) applies under "dry" conditions, whereas the lower temperature limit (i.e., (1/3) T_m) applies if steam is present, since steam facilitates reorganization of many metals, aluminas, and silicas.

To prevent sintering, catalysts may be doped with stabilizers which may have a high melting point and/or prevent agglomeration of small crystals. For example, chromia, alumina, and magnesia, which have high melting points, are often added as stabilizers of finely divided metal catalysts.

Sintering temperatures for common metals

Metal	Sintering temperature/°C;[(1/3)T_m]
Cu	360
Fe	500
Ni	500
Pt	570
Pd	500

How Deactivation Affects Performance

Catalyst deactivation may affect the performance of a reactor in several ways. A reduction in the number of catalyst sites can reduce catalytic activity and decrease fractional conversion. However, some reactions depend solely on the presence of metal, while others depend strongly on the configuration of the metal. Thus, the extent to which performance is affected depends upon the chemical reaction to be catalyzed, and the way in which the catalyst has been deactivated. For example, deposition/chemisorption of sulfur, nitrogen, or carbon on the catalyst generally affects hydrogenation reactions more than exchange reactions. Consequently, if parallel reactions are to be catalyzed, deactivation may cause a shift in selectivity to favor nonhydrogenated products. Similarly, heavy metals (e.g., Ni, Fe) present in the feed stream of catalytic crackers can deposit on the catalyst, and subsequently catalyze dehydrogenation reactions. In this case, the yield of gasoline is reduced, and more light hydrocarbons and hydrogen produced.

Methods for Catalyst Regeneration

In some cases, it is possible to restore partially or completely the activity of a catalyst through chemical treatment. The regeneration process may be slow, either because of thermodynamic limitations or diffusional limitations arising from blockage of catalyst pores. Although the rate of desorption generally increases at high temperatures, prolonged exposure of the catalyst to a high-temperature gas stream can lead to sintering, and irreversible loss of activity. If the bound or deposited species cannot be gasified at temperatures lower than the sintering temperature then the poisoning or fouling is considered to be irreversible.

For catalysts poisoned by sulfur, the metal-sulfur bond is usually broken in the presence of steam, as shown for nickel:

$$\text{Ni-S} + \text{H}_2\text{O} \rightarrow \text{NiO} + \text{H}_2\text{S}$$

$$\text{H}_2\text{S} + 2\text{H}_2\text{O} \rightleftharpoons \text{SO}_2 + 3\text{H}_2$$

The equilibrium for the second reaction favors H_2S until extremely high temperatures are reached (> 700 °C). Thus, sintering of the catalyst could be a problem. Furthermore, SO_2 can act as a poison for some catalysts. If sintering or SO_2 poisoning precludes steam treatment, it is usually possible to remove deposited sulfur by passing a sulfur-free gas stream over the catalyst at moderate temperatures for an extended period of time

Regeneration of coked catalysts may be accomplished by gasification with oxygen, steam, hydrogen, or carbon dioxide:

$$C + O_2 \rightarrow CO_2$$

$$C + H_2O \rightarrow CO + H_2$$

$$C + 2H_2 \rightarrow CH_4$$

$$C + CO_2 \rightarrow 2CO$$

The first reaction is strongly exothermic, and may lead to high local temperatures within the catalyst. Thus, temperature must be carefully controlled to avoid sintering.

7- Preliminary Considerations in Chemical Reaction Engineering

We begin by considering general aspects of reactor selection, performance, and design, primarily from the point of view of process design, but with passing reference to mechanical design. We then present a number of equipment/flow diagrams, some generically schematic and some relating to specific industrial processes, to illustrate many of these aspects.

PROCESS DESIGN AND MECHANICAL DESIGN

Process design has to do with specifying matters relating to the process itself, such as operating conditions, and size, configuration, and mode of operation of the reactor. Mechanical design has to do with specifying matters relating to the equipment itself in the sense of structural and mixing requirements, among others.

Process Design

The problem of process design in CRE typically stems from the requirement to produce a specified product at a particular rate (e.g., 1000 tons day^{-1} of NH_3). Process design then involves making decisions, as quantitatively as possible, about the type of reactor and its mode of operation (e.g., batch or continuous), its size (e.g., volume or amount of catalyst), and processing conditions (e.g., *T*, *P*, product distribution, if relevant).

The design problem usually fits into the spectrum ranging from (1) the rational design of a completely new reactor for a new process, to (2) the analysis of performance of an existing reactor for an existing process. A common situation, between these extremes, even for a new plant, is the modification of an existing type of reactor, the design of which has evolved over time.

1- Matters for Consideration

Process design involves making decisions about a series of matters, on as rational and quantitative a basis as possible, given the information available. The following is an illustrative list of such matters but not an exhaustive one; the items are not all mutually exclusive.

1-	Type of processing	➢ batch ➢ continuous ➢ semibatch or semicontinuous ➢ batch with respect to (specified phase or phases) ➢ continuous with respect to (specified phase or phases)
2-	Type and nature of reacting system	➢ reactant(s) and product(s) ➢ simple ➢ complex (desirable, undesirable products) ➢ stoichiometry ➢ phases, number of phases ➢ catalytic (choice of catalyst) or noncatalytic ➢ endothermic or exothermic ➢ possibility of equilibrium limitation

3-	**Type and size of reactor**	➢ **batch** ➢ **continuous** ➢ **stirred tank** ➢ **tubular, multitubular** ➢ **tower/column** ▪ **spray** ▪ **packed, plate** ▪ **bubble** ➢ **bed** ▪ **fixed** ▪ **fluidized** ▪ **spouted** ▪ **trickle** ➢ **furnace**
4-	**Mode of operation**	➢ **configurational** ▪ **single-stage or multistage (number of)** ▪ **parallel (e.g., multitubular)** ▪ **axial or radial flow (through fixed bed)** ▪ **arrangement of heat transfer surface (if any)** ▪ **flow pattern (backmix flow, tubular flow, etc.)** ▪ **contacting pattern (cocurrent, countercurrent, crosscurrent flow of phases;**
4-	**Mode of operation**	▪ **method of addition of reactants-all at once? in stages? which phase dispersed? continuous?)** ➢ **thermal** ▪ **adiabatic** ▪ **isothermal** ▪ **nonisothermal, nonadiabatic** ➢ **use of recycle**
5-	**Process conditions**	➢ ***T*(*T* profile)** ➢ ***P*(*P* profile)** ➢ **feed (composition, rate)** ➢ **product (composition, rate)**

6-	Optimality	➢ of process conditions ➢ of size ➢ of product distribution ➢ of conversion ➢ of cost (local, global context)
7-	Control and stability of operation	➢ instrumentation ➢ control variables ➢ sensitivity analysis ➢ catalyst life, deactivation, poisons
8-	Socioeconomic	➢ cost ➢ environmental ➢ safety
9-	Materials of construction	➢ type of materials used ➢ corrosion ➢ rate of corrosion, etc.
10-	Startup and shutdown procedures	➢ automatic ➢ manually

2- Data Required

Data required include those specific to the situation in hand (design specifications) and those of a more general nature:

1-	Specifications	➢ reactants ➢ products ➢ throughput or capacity
2-	General data	➢ rate data/parameters relating to ▪ reaction (rate law(s)) ▪ heat transfer ▪ diffusion ▪ mass transfer ▪ pressure drop

3-	General data	➢ equilibrium data ▪ thermodynamic ▪ equation of state ➢ thermochemical data ▪ enthalpy of reaction ▪ heat capacities ➢ other physical property data ▪ density ▪ viscosity ➢ cost data

The lack of appropriate information, particularly rate data over the entire range of operating conditions, is often a major impediment to a complete rational design. If sufficiently important, new experimental data may have to be developed for the situation at hand.

3- Tools Available

The rational design of a chemical reactor is perhaps the most difficult equipment-design task of a chemical engineer. All the tools in the workshop of the chemical engineer may have to be brought to bear on the problem. These include those relating to all of the following:

1-	Rate processes and rate laws	➢ reaction kinetics ▪ development of a reaction model/kinetics scheme ➢ diffusion and mass transfer ▪ diffusion equation ▪ mass transfer model (e.g., two-film model) ➢ heat transfer ▪ as part of thermal characteristics, including T profile ➢ fluid mechanics ▪ flow patterns ▪ mixing ▪ pressure drop
2-	Conservation and balance equations	➢ mass balances, including stoichiometry, continuity equation ➢ energy balance, including energetics of reaction, thermochemistry

3-	Equilibrium	➢ reaction equilibrium, single or multiphase systems; equilibrium conversion for comparison ➢ phase equilibrium, multiphase systems
4-	Mathematics	➢ development of a reactor model from above considerations ➢ analytical or numerical methods for solution of equations, simulation ➢ statistical analysis of rate data
5-	Computers and computer software	➢ use of a PC, workstation, etc., coupled with software packages to solve sets of algebraic and/or differential equations, and to perform statistical analyses necessary for implementation of a reactor model for design or for assessment of reactor performance. ➢ software: spreadsheet packages, simulation software (e.g., CEMCAD), numerical equation solvers, computer algebra system.
6-	Process economics	➢ economic feasibility study

Mechanical Design

The distinction between process design and "mechanical" design (most other aspects!) is somewhat arbitrary. However, in the latter we include the following, which, although important, are outside our scope.

1-	Impeller or agitator design	➢ (as in a stirred tank)
2-	Power requirement	➢ (for above)
3-	Reactor-as-pressure vessel design	➢ wall thickness ➢ over-pressure relief ➢ fabrication
4-	Support-structure design	➢ plant place
5-	Maintenance features	➢ electric workshops ➢ mechanic workshops

EXAMPLES OF REACTORS FOR ILLUSTRATION OF PROCESS DESIGN CONSIDERATIONS

Reactors exist in a variety of types with differing modes of operation for various processes and reacting systems. The following figures illustrate a number of these reactors, some in a schematic, generic sense, and some for specific processes.

1- Batch Reactors

A schematic representation of a batch reactor in Figure (A) shows some of the essential features. A cylindrical vessel is provided with nozzles for adding and removing reactor contents. To ensure adequate mixing, the vessel has a stirrer (turbine) equipped with an external drive, and several vertical baffles to break up vortices around the impeller tips. Temperature control may be achieved with internal heating/cooling coils, as shown, or with an external heat exchanger or jacket. The vessel may be designed as a pressure vessel, in which case a pressure-relief device (e.g., a rupture disc) is required in case over pressure develops, or as an "atmospheric" vessel, in which case a vent is used.

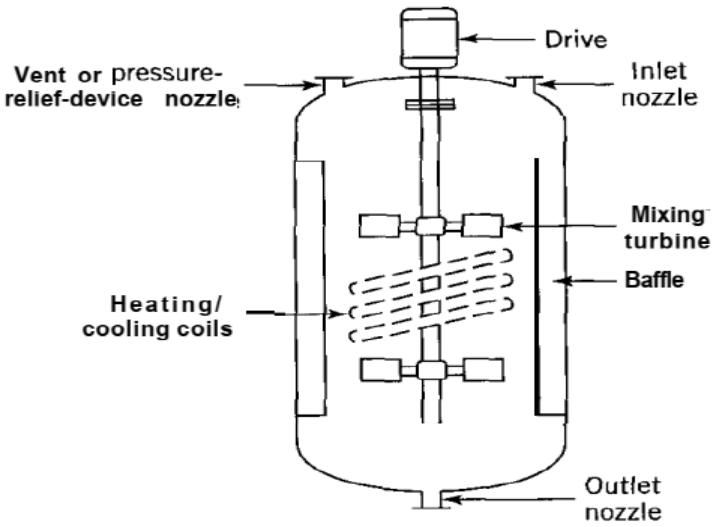


Figure (A) Schematic representation of BR showing some features.

Figure (B) illustrates a pilot plant batch reactor used in the early 1990s for the production of sodium aluminosilicate, from alum and sodium silicate, for use in the pulp and paper industry. The ratio of SiO_2 to Al_2O_3 in the product is controlled by adjustment of the feed amounts from the hoppers above the reactor. Efficient mixing is required for the reacting system (a non Newtonian slurry) to produce the desired amorphous form. For this, baffles on the walls and mixing paddles (not shown) on the central shaft are used. After an appropriate reaction time, the pigment slurry (intermediate product) is removed for further processing.

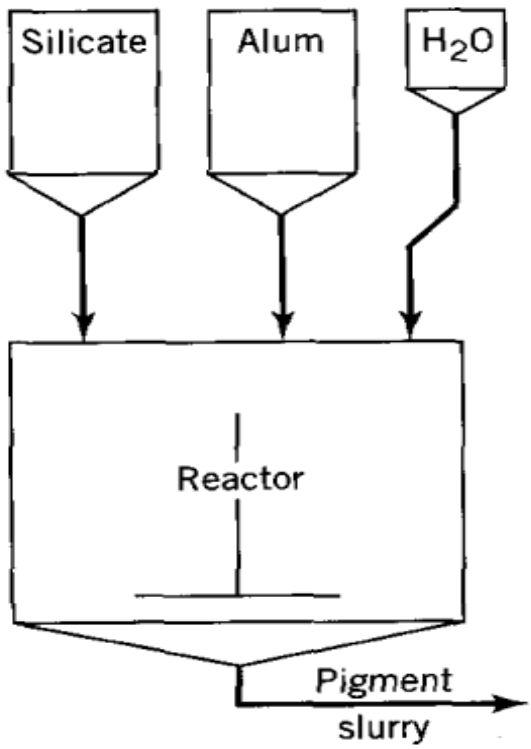


Figure (B) Pilot plant batch reactor for production of sodium aluminosilicate.

2- Stirred-Tank Flow Reactors

A stirred-tank flow reactor may be single-stage or multistage. As an ideal backmix flow reactor, it is referred to as a CSTR or multistage CSTR.

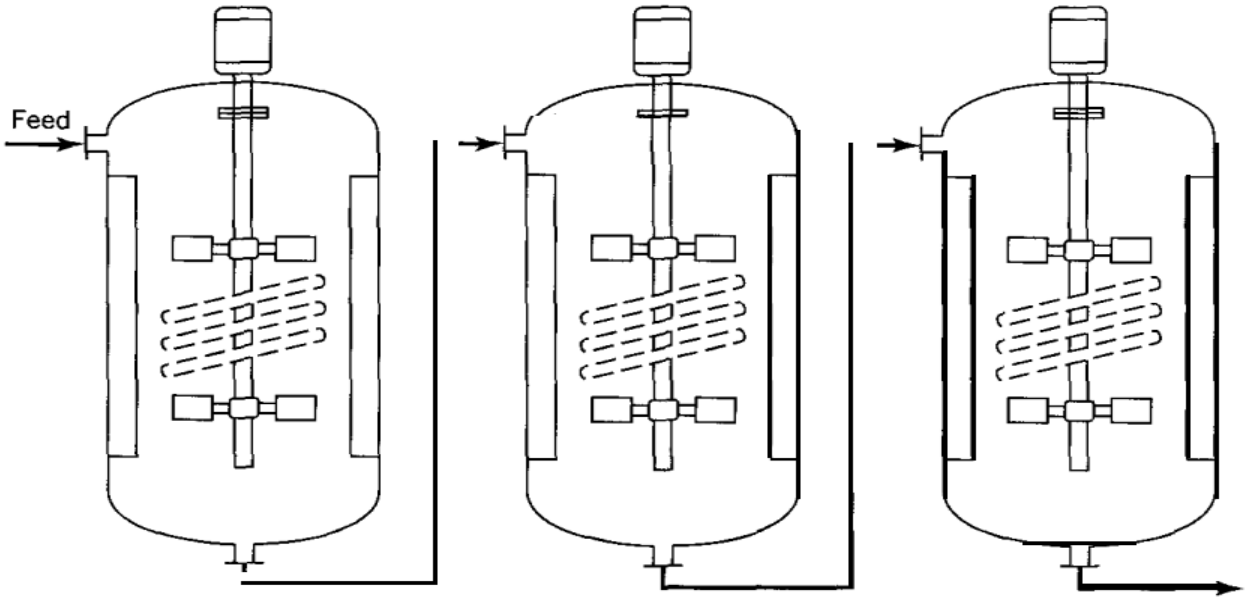


Figure (C) Three-stage stirred-tank flow reactor.

A three-stage stirred-tank flow reactor is illustrated in Figure (C). Mixing and heat transfer features may be similar to those of a batch reactor, but there may be more use of external heat exchangers as preheaters/coolers, interstage heaters/coolers, and after heaters/coolers. In an extreme case of heat-transfer requirement, the reactor may resemble a shell-and-tube heat exchanger, as in a "Stratco" contactor for HF-alkylation of hydrocarbons. A multistage reactor may be contained within a single vessel, as in a Kellogg cascade alkylator. The major difference between a stirred-tank batch reactor and a stirred-tank flow reactor is that, in the latter, provision must be made for continuous flow of material into and out of the reactor by gravity flow or forced-circulation flow with a pump, together with appropriate block and relief valves.

3- Tubular Flow Reactors

The term "tubular flow reactor" is used generically to refer to a reactor in which the flow of fluid is essentially in one direction (e.g., axial flow in a cylindrical vessel) without any attempt to promote backmixing by stirring. Idealized forms are a plug-flow reactor and a laminar-flow reactor. The configuration may vary widely from a very high to a very low length-to-diameter (L/D) ratio, as shown schematically in Figure (D). Tubular flow reactors are also shown in Figures (E), (F) and (G).

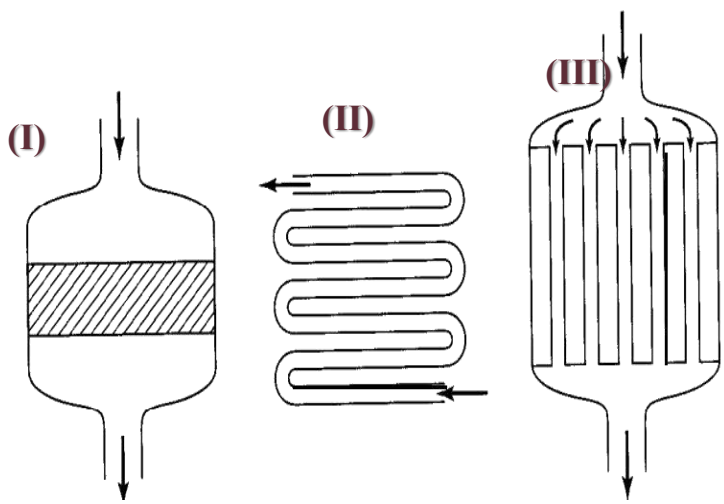


Figure (D) Tubular flow reactor-some possible configurations: (I) low L/D; (II) high L/D; (III) tubular arrangement

3-1 Furnace Reactors

Some endothermic reactions require reactors that can provide high rates of heat transfer at relatively high temperatures (900 to 1100 K). Examples are the dehydrogenation of C_2H_6 to produce C_2H_4 (noncatalytic, low P), and the steam-reforming of natural gas, $CH_4 + H_2O \rightarrow CO + 3H_2$, to produce H_2 for ammonia and methanol syntheses (catalytic, P = 30 bar). The reaction typically takes place as the reacting system (gas) flows through long coils of tubes contained in a combustion chamber (furnace). Heat transfer occurs by radiation and convection in corresponding sections of the reactor. A fuel gas is burned in the combustion chamber. Figure (E) shows a schematic arrangement of a "top-fired" furnace for steam reforming, in which the gas burners are located at the top of the combustion chamber.

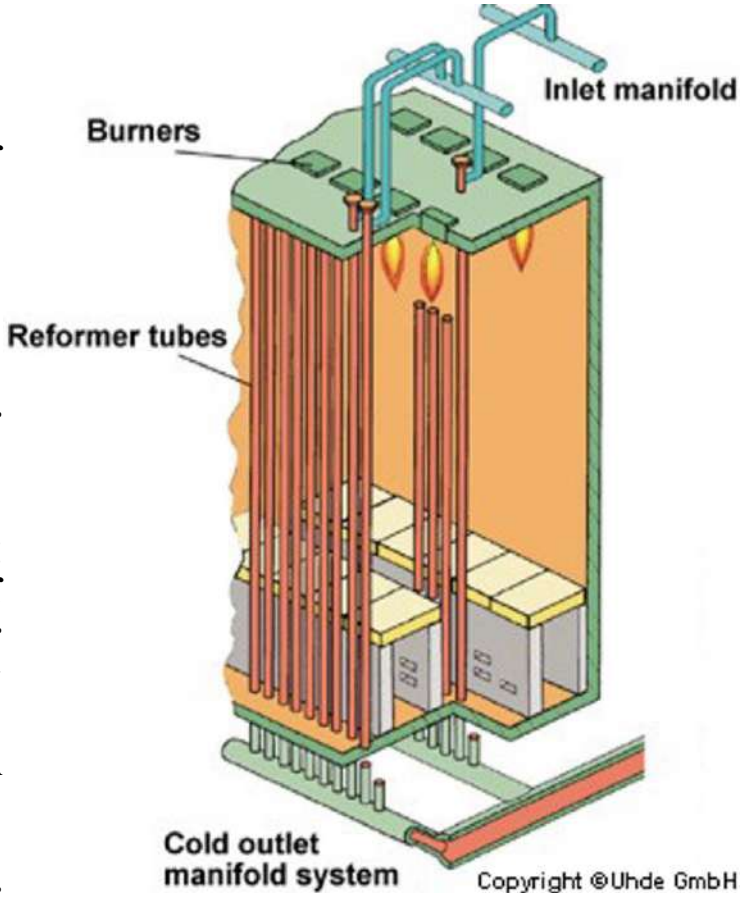


Figure (E) Schematic arrangement of a top-fired furnace for steam-reforming of natural gas

3-2 Fixed-Bed Catalytic Reactors: Ammonia Synthesis

The synthesis of ammonia, $N_2 + 3H_2 = 2NH_3$, like the oxidation of SO_2 is an exothermic, reversible, catalytic reaction carried out in a multistage tubular flow reactor in which each stage consists of a (fixed) bed of catalyst particles. Unlike SO_2 oxidation, it is a high-pressure reaction (150-350 bar, at an average temperature of about 45 0°C). The usual catalyst is metallic Fe. Figure (F) shows Fixed-Bed Catalytic Reactor used for Ammonia Synthesis.

The reactors used can be classified in two main ways:

(1) by type of flow of the gas through the beds: axial, radial, or cross-flow; and

(2) by method used to control T and recover the energy of reaction: indirect cooling with heat exchanger surface or quench cooling.

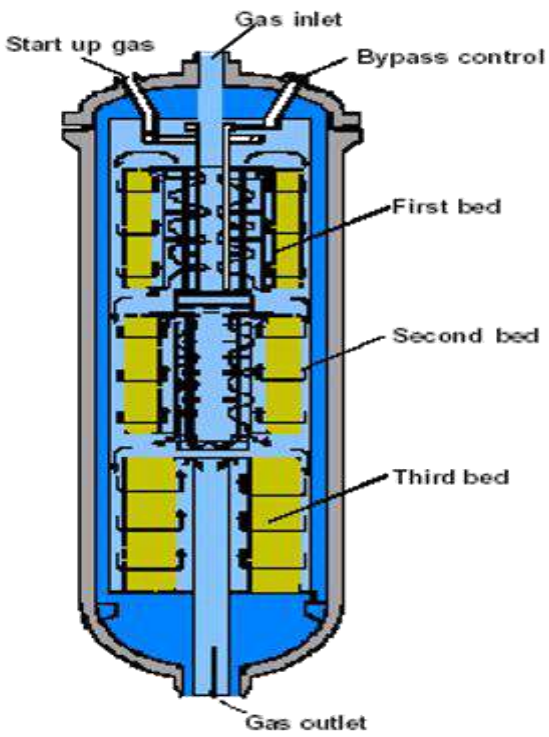


Figure (F) Fixed-Bed Catalytic Reactor used for Ammonia Synthesis.

3-3 Fixed-Bed Catalytic Reactors: Methanol Synthesis

The synthesis of methanol, $CO + 2H_2 = CH_3OH$, like ammonia synthesis, is an exothermic, reversible, catalytic reaction. Unlike a catalyst for ammonia synthesis, a catalyst for methanol synthesis must be selective (as well as active), to avoid formation of species such as CH_4 and C_2H_5OH. The process was formerly carried out at high pressure (100- 300 bar) with a ZnO/Cr_2O_3 catalyst, but a catalyst of $Cu/ZnO/Al_2O_3$ enables the reaction to be carried out at 50-100 bar, which is referred to as low-pressure synthesis. Figure (G) gives an example of converters for low-pressure synthesis of methanol with axial flow. It shows a converter using heat exchanger surface (tube cooling) within a single bed of catalyst. There is another example which shows a converter using quench cooling with quench gas added at three intervals in the bed through lozenge distributors.

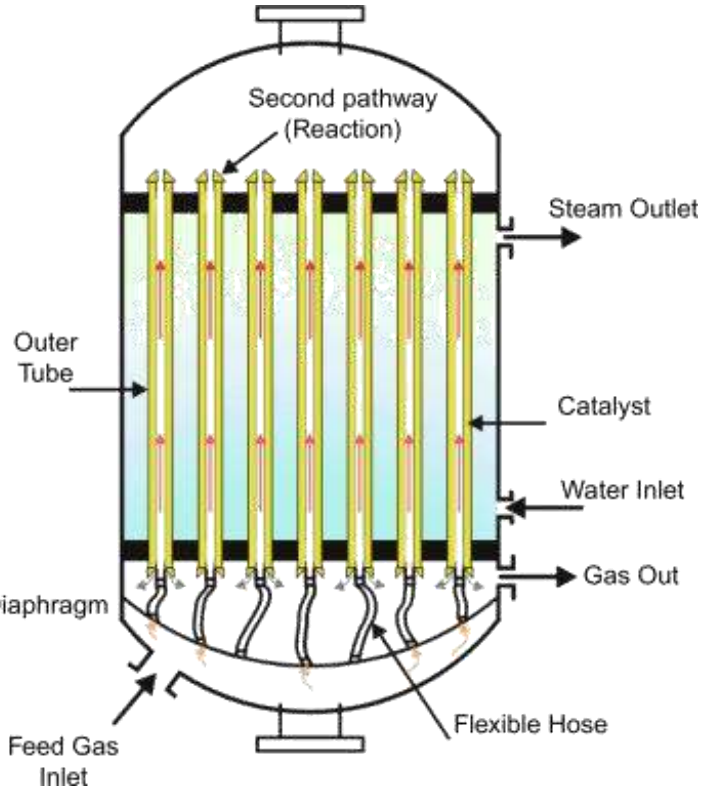


Figure (G) An example of converters for low-pressure synthesis of methanol with axial flow.

4- Fluidized-Bed Reactors

In a fluidized-bed reactor, fluid is introduced at many points and at a sufficiently high velocity that the upward flow through a bed of particles causes the particles to lift and fall back in a recirculating pattern. The result is an expanded "fluidized-bed" of particles + fluid holdup, behaving somewhat like a vigorously boiling liquid. Figure (H) is a schematic diagram of a fluidized-bed "roaster" for oxidizing zinc "concentrate" (ZnS) to ZnO as part of the process for making Zn metal:

$$2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2$$

The fluidized bed occupies the lower part of the vessel, and is supported by a grate containing many openings through which air, entering at the bottom, flows to bring about fluidization. The greater part of the vessel is "freeboard" in which lower gas velocity allows for partial disengagement of entrained particles from the overhead gas stream.

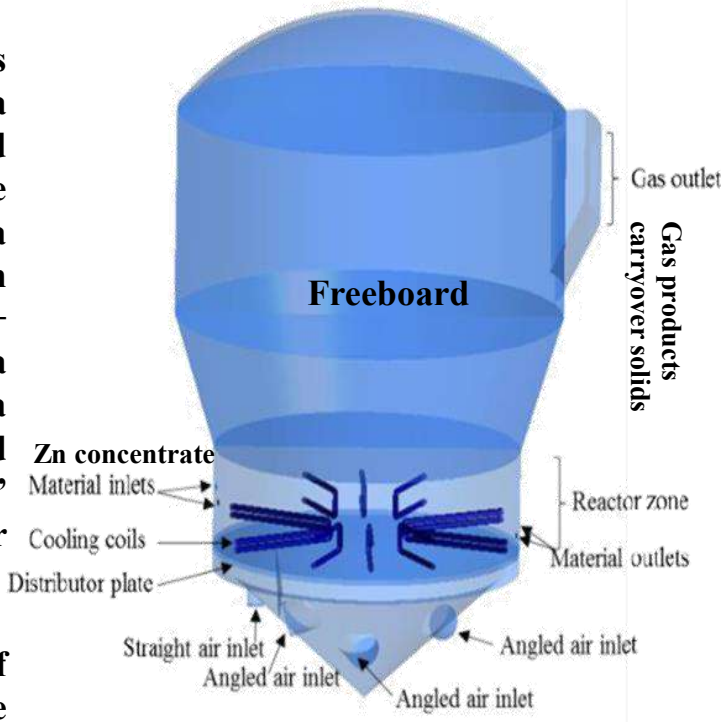


Figure (H) Fluidized-bed reactor for roasting zinc concentrate.

5- Other Types of Reactors

There are many other reactors of various types not included among those discussed here. These include tower reactors, which may be modeled as PF or modified PF reactors. Figure (J) shows the Kvaerner Chemetics electrolytic process for the production of sodium chlorate (in a concentrated solution of "strong liquor") and hydrogen from sodium chloride solution ("brine"). The overall reaction is $NaCl + 3H_2O + NaClO_3 + H_2(g)$. The part of the system shown consists primarily of brine electrolyzers, a degasifier, a chlorate reactor, and an electrolyte cooler.

The reactor is designed to provide sufficient residence time (for recirculating liquid) for the reaction producing chlorate (started in the electrolyzers) to be completed. This involves further reaction of intermediates formed by the complex reactions in the electrolyzer, such as hypochlorite and hypochlorous acid, to produce chlorate.

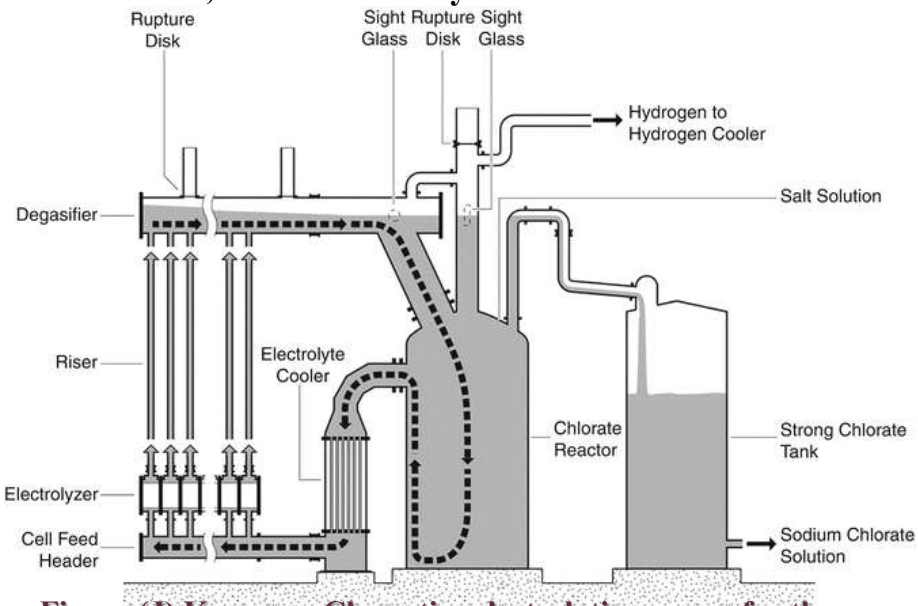


Figure (J) Kvaerner Chemetics electrolytic process for the production of sodium chlorate.

Exercise 7.1

1) For a 1000-ton day^{-1} sulfuric acid plant (100% H_2SO_4 basis), calculate the total molar flow rate (mol s^{-1}) of gas entering the SO_2 converter (for oxidation to SO_3), for steady-state operation, if the fractional conversion (f_{SO2}) in the converter is 0.98, and the feed to the converter is 9.5 mol % SO_2. (1 ton = 1000 kg.)
2) Calculate the (total) volumetric flow rate (m^3 s^{-1}) of gas leaving the reactor of a 1000 – ton day^{-1} ammonia plant, if the gas originates from H_2 and N_2 in the stoichiometric ratio, and 20% conversion to ammonia occurs. T = 450 °C, P = 300 bar, and the compressibility factor z = 1.09. (1 ton = 1000 kg.)
3) The gas leaving an ammonia oxidation unit in a continuous process is cooled rapidly to 20°C and contains 9 mol % NO, 1% NO_2, 8% O_2, and 82% N_2 (all the water formed by reaction is assumed to be condensed). It is desirable to allow oxidation of NO to NO_2 in a continuous reactor to achieve a molar ratio of NO_2 to NO of 5 before absorption of the NO_2 to make HNO_3. Determine the outlet temperature of the reactor, if it operates adiabatically (at essentially 6.9 bar). The following data are to be used; state any assumptions made.

Species	$\Delta H^\circ_{f,298}$/ J mol^{-1}	$\bar{C}_P$ (approx.)/ J mol^{-1} K^{-1}
O_2	0	29.4
NO	+90,291	29.9
NO_2	+33,095	39.0
N_2	0	29.1

8- Some Applications Using Software Programs (CHEMCAD & COCO)

(1) Worked Problem Using CHEMCAD Simulation

Consider the saponification of ethylacetate taking place in a batch reactor at 25 ^{o}C and 1 atm:

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

The charge to the batch reactor is 100 kmol aqueous solution of ethylacetate and sodium hydroxide at a conentration of 0.1 M for both (This is approximately 96 kmol water, 2kmol ethylacetate, and 2 kmol sodium hydroxide). The rate of reaction is given by the relation,

$$(-r_A) = k_A c_{Ester} c_{NaOH} \quad ; \; k_A = 0.126 \; Lmol^{-1}s^{-1}$$

The Arrhenius pre-exponential factor, A is equal to 0.104 $Lmol^{-1}s^{-1}$. Using Chemcad software program, simulate a dynamic batch reactor for the reaction at isothermal condition for 3 minutes and plot the change in moles of sodium hydroxide as a function of time.

Scan the QR code to watch the solution

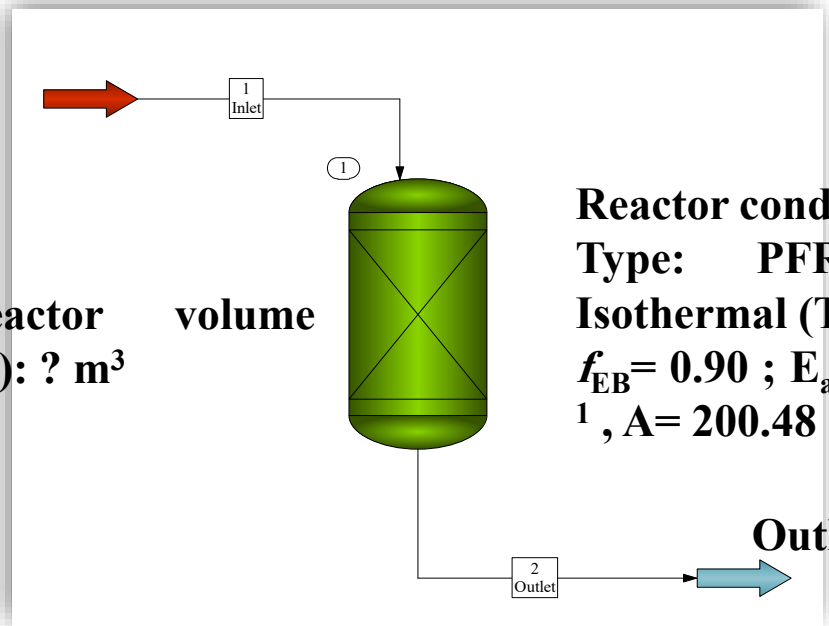
(2) Worked Problem Using CHEMCAD Simulation

Consider the dehydrogenation reaction of ethylbenzene to styrene taking place in either plug- flow reactor or single- stage CSTR at 880 K and 1.378 bar in the presence of water:

$$C_6H_5C_2H_5 \rightarrow C_6H_5CH{=}CH_2 + H_2$$

The feed rate of ethylbenzene and water are 217.5, 2610 mol s^{-1}, respectively at 880 K and 1.378 bar. The reaction is first order; $(-r_{EB}) = k_{EB}P_{EB}$ (P_{EB} in kPa) with activation energy, E_a= 21874 cal mol^{-1}; and Arrhenius pre-exponential factor, A= 200.48 s^{-1}.

Using Chemcad software program, simulate a kinetic reactor for the reaction at isothermal condition with a conversional conversion of ethylbenzene, f_{EB}= 0.90, determine the reactor volume (V), and plot the change in mole fraction of ethylbezene as a function of reactor volume.



Reactor volume (V): ? m^3

Reactor conditions:
Type: PFR or CSTR;
Isothermal (T= 880 K)
f_{EB}= 0.90 ; E_a = 21874 cal mol^{-1} , A= 200.48 s^{-1}.

Outlet conditions: ?

Scan the QR code to watch the solution

(3) Worked Problem Using CHEMCAD Simulation

Consider an ethanol plant designed to produce ethanol from dextrose according to the following stoichiometric reaction:

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$$

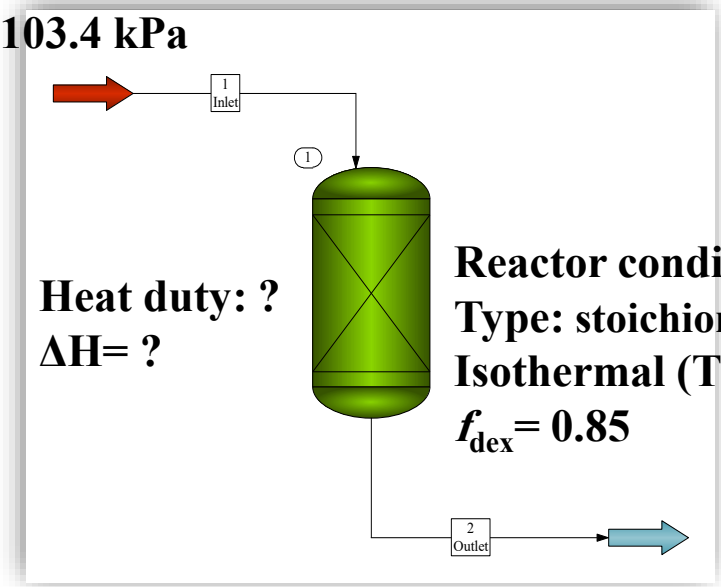
Using Chemcad software program, simulate above reaction using a stoichiometric reactor at isothermal condition (constant temperature, 20 ^oC) and constant pressure, P = 103.4 kPa with a fractional conversion of dextrose, f_{dex}= 0.85..The feed rate of dextrose is 70 kmol h^{-1}. Also, find out the heat duty and enthalpy of reaction.

Inlet conditions:

q_o(dextrose)= 70 kmol h^{-1}

T_o= 20 ^oC

P_o= 103.4 kPa



Heat duty: ?

ΔH= ?

Reactor conditions:

Type: stoichiometric reactor;

Isothermal (T= 20 ^oC)

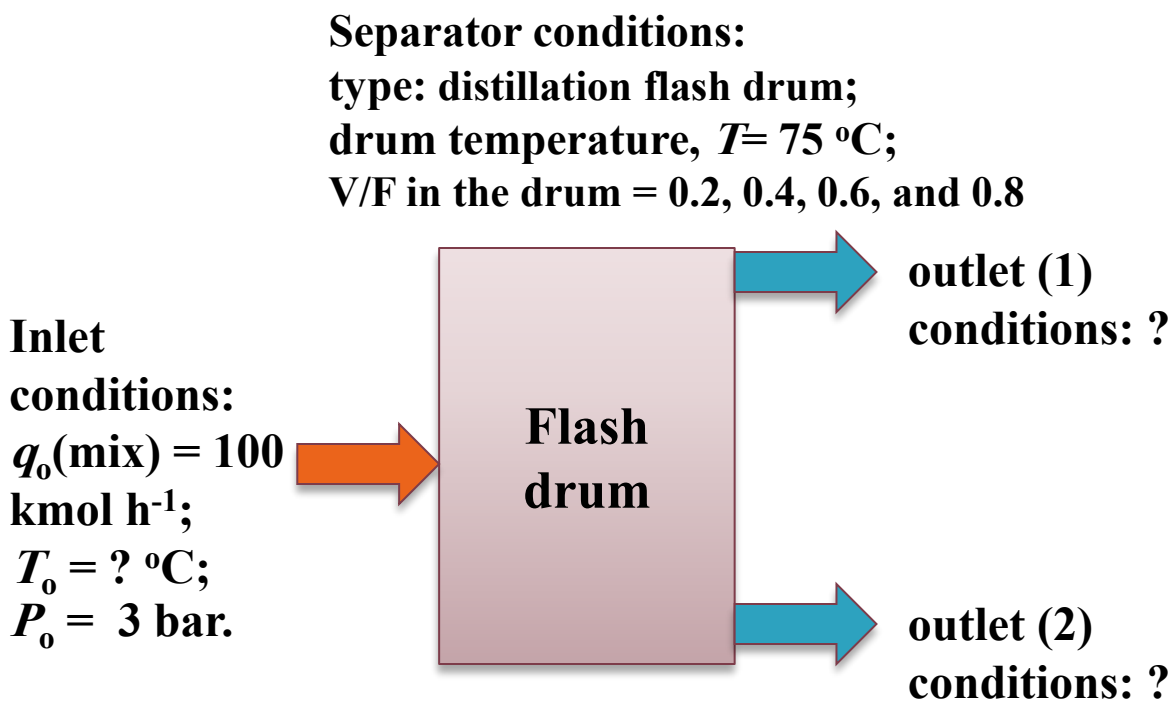
f_{dex}= 0.85

Outlet conditions: ?

Scan the QR code to watch the solution

(4) Worked Problem Using CHEMCAD Simulation

Consider a methanol-water mixture with composition 55 mol % methanol and 45 mol % water. With the help of Chemcad software program, simulate the distillation of this mixture using a flash drum at temperature 75 ^{o}C with feed rate of 100 kmol h^{-1} at 3 bar. Do for mole vapor fraction (V/F) in the drum = 0.2, 0.4, 0.6, and 0.8. Report the feed temperature and flash drum heat duty, Q (kJ/h).



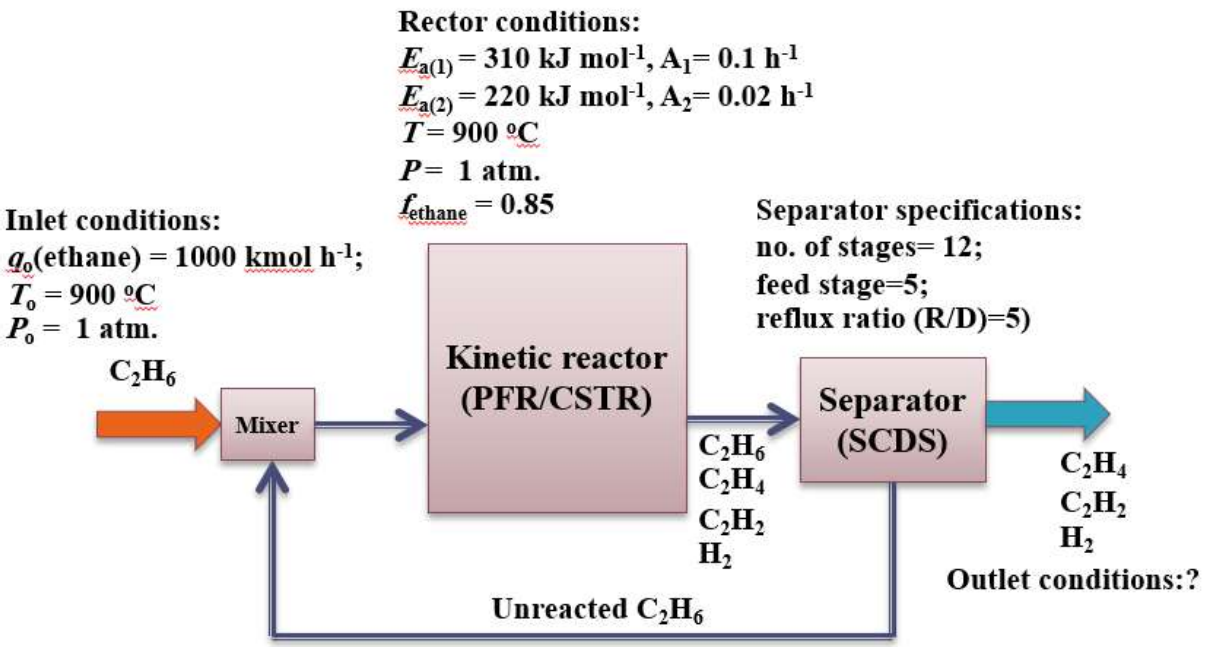
(5) Worked Problem Using CHEMCAD Simulation

Ethane is dehydrogenated to ethylene and acetylene according to the following catalytic reactions:

(1) $C_2H_6 \rightarrow C_2H_4 + H_2$: $E_a = 310$ kJ mol^{-1}, A= 0.1 h^{-1}

(2) $C_2H_6 \rightarrow C_2H_2 + 2\ H_2$: $E_a = 220$ kJ mol^{-1}, A= 0.02 h^{-1}

Using Chemcad software program, simulate the above reactions using a kinetic reactor (PFR/CSTR) at an isothermal condition (constant temperature, 900 °C) and constant pressure, P = 1 atm. with a fractional conversion of ethane, f_{ethane}= 0.85. The feed rate of ethane is 1000 kmol h^{-1}. Also, use the SCDS distillation column (no. of stages= 12; feed stage=5; reflux ratio (R/D)=5) for recycling unreacted ethane to the reactor.

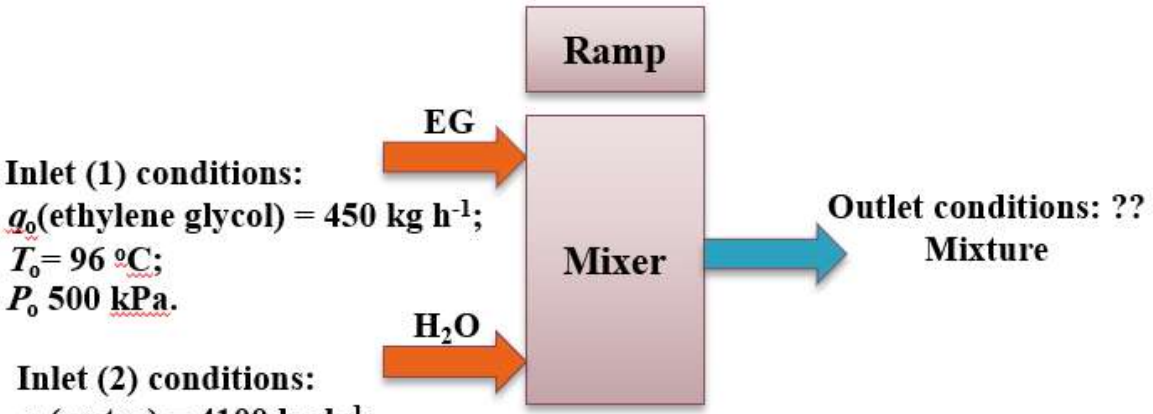


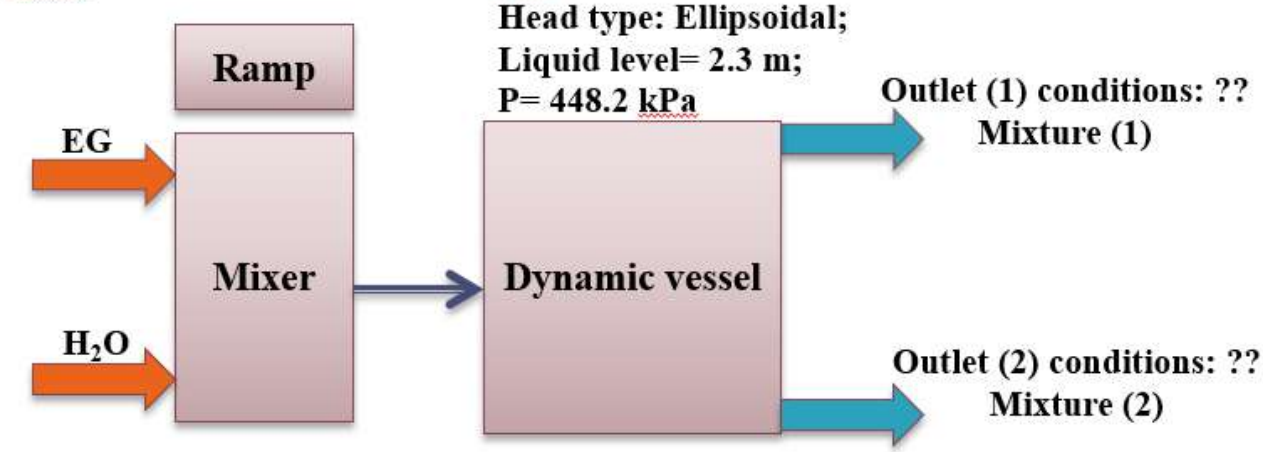
(6) Worked Problem Using CHEMCAD Simulation

Apply dynamic run using Ramp unit operation and/or Dynamic vessel (D= 1.1 m; L= 4.7 m; Head type: Ellipsoidal; Liquid level= 3.3 m; P= 500 kPa) for mixing ethylene glycol and water. The flow rates of ethylene glycol and water are 450 kg h^{-1} and 4100 kg h^{-1}, respectively, at 96 ^{o}C and 500 kPa. On varying the flow rate of ethylene glycol, (a) simulate over 360 minutes with 1 minute time steps; (b) record ethylene glycol stream and product stream; (c) watch ethylene glycol flow and product composition as simulation progresses. Try different modes of inputs: Ramps (Table A), Step changes (Table B), Sinusoidal (Baseline= 800 kg h^{-1}, Amplitude= 400 kg h^{-1}, Period= 60 min, and Offset= 30 min), and Random (from 400 to 1200 kg h^{-1}) modes.

Table (B): Steps	
Time (min)	EG flow rate (kg h^{-1})
0	800
20	800
30	400
89	400
90	1200
119	1200
120	800
360	800

Table (A): Ramps	
Time (min)	EG flow rate (kg h^{-1})
0	800
30	800
90	400
120	1200
240	800
360	800


Ramp
EG
Inlet (1) conditions:
q_0(ethylene glycol) = 450 kg h^{-1};
T_0= 96 ºC;
P_0 500 kPa.
Mixer
Outlet conditions: ??
Mixture
H_2O
Inlet (2) conditions:
q_0(water) = 4100 kg h^{-1};
T_0= 96 ºC;
P_0 500 kPa.


Dynamic vessel
Dia= 1.2 m; L= 3.7 m;
Head type: Ellipsoidal;
Liquid level= 2.3 m;
P= 448.2 kPa
Ramp
EG
Mixer
H_2O
Dynamic vessel
Outlet (1) conditions: ??
Mixture (1)
Outlet (2) conditions: ??
Mixture (2)

(A)

(B)

(7) Worked Problem Using CHEMCAD Simulation

Using Chemcad software program, design biomass- methanol process (the formula of biomass can be modeled as sucrose) that can be represented by the following reactions:

$$(1)\quad C_{12}H_{22}O_{11} + a\,H_2O \rightarrow b\,CO + c\,CO_2 + d\,H_2$$
$$(2)\quad CO_2 + H_2 \rightarrow CO + H_2O$$
$$(3)\quad CO + 2\,H_2 \rightarrow CH_3OH$$

Useful design data and specifications are also presented in the following tables:

Capacity	Biomass Molecular formula	Gasification Temperature	Gasifier Syngas CO_2/CO ratio	Methanol Synthesis Conditions
165 ton d^{-1}	$C_{12}H_{22}O_{11}$	$T = 1200$ K	$CO_2/CO = 1.1$	$T = 550$ K
On-stream factor = 0.9		$P = 20$ atm.		$P = 80$ atm.

➢ **Kinetic parameters for $CO + 2\ H_2 \rightarrow CH_3OH$ at 550 K**

E_a (kJ mol^{-1})	A (mol kg^{-1} s^{-1})	β	Adsorption coefficients& Energies		
			CO	H_2	CH_3OH
152	2.68×10^9	3	6.90×10^{-2} mol kg^{-1} s^{-1} 0.0 kJ mol^{-1}	6.19×10^{-8} mol kg^{-1} s^{-1} -54.96 kJ mol^{-1}	0.0 mol kg^{-1} s^{-1} 0.0 kJ mol^{-1}

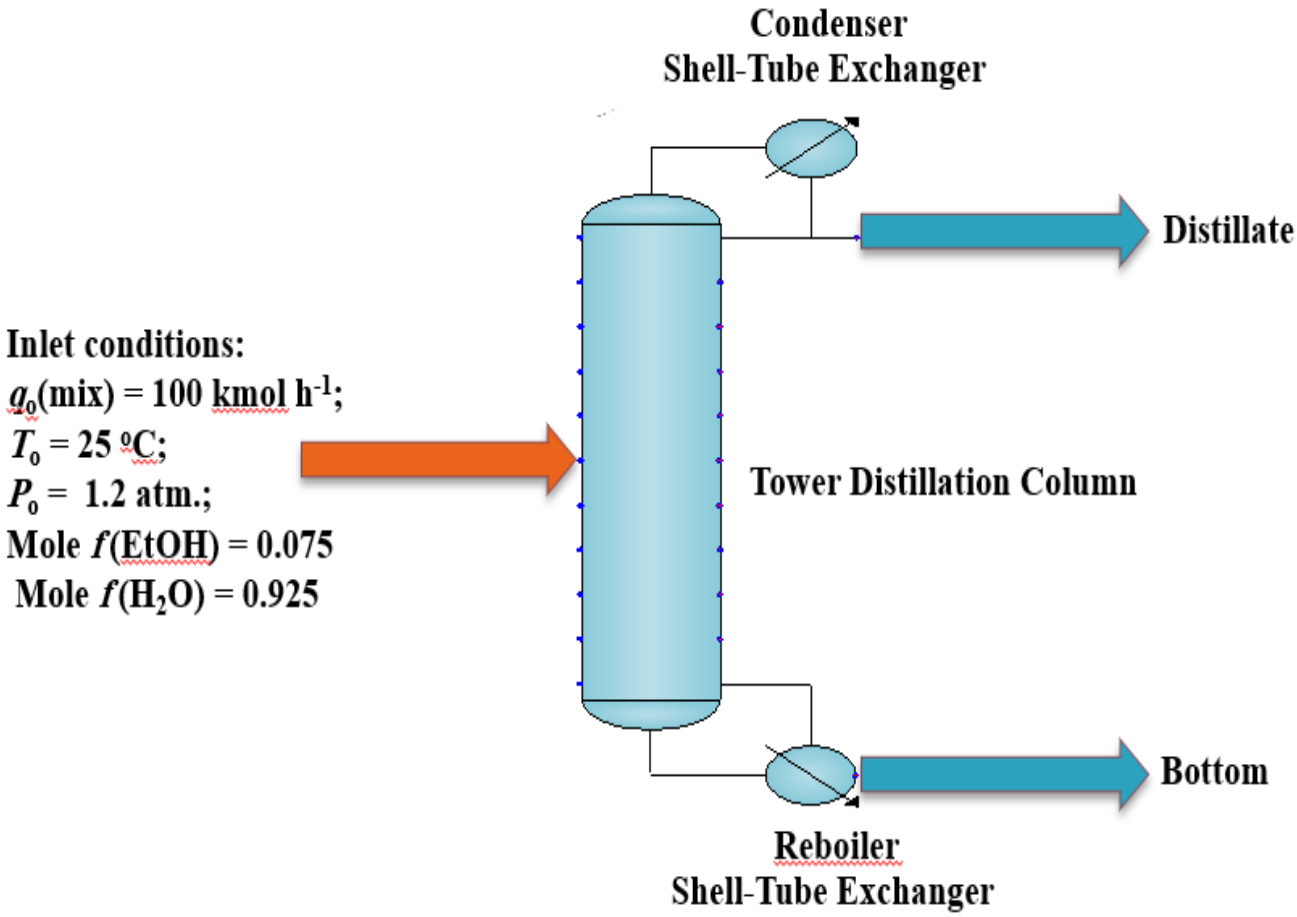
➢ **Kinetic parameters for $CH_3OH \rightarrow CO + 2\ H_2$ 550 K**

E_a (kJ mol^{-1})	A (mol kg^{-1} s^{-1})	β	Adsorption coefficients& Energies		
			CO	H_2	CH_3OH
152	4.46×10^{12}	3	6.90×10^{-2} mol kg^{-1} s^{-1} 0.0 kJ mol^{-1}	6.19×10^{-8} mol kg^{-1} s^{-1} -54.96 kJ mol^{-1}	0.0 mol kg^{-1} s^{-1} 0.0 kJ mol^{-1}

(A) **(B)**

(8) Worked Problem Using CHEMCAD Simulation

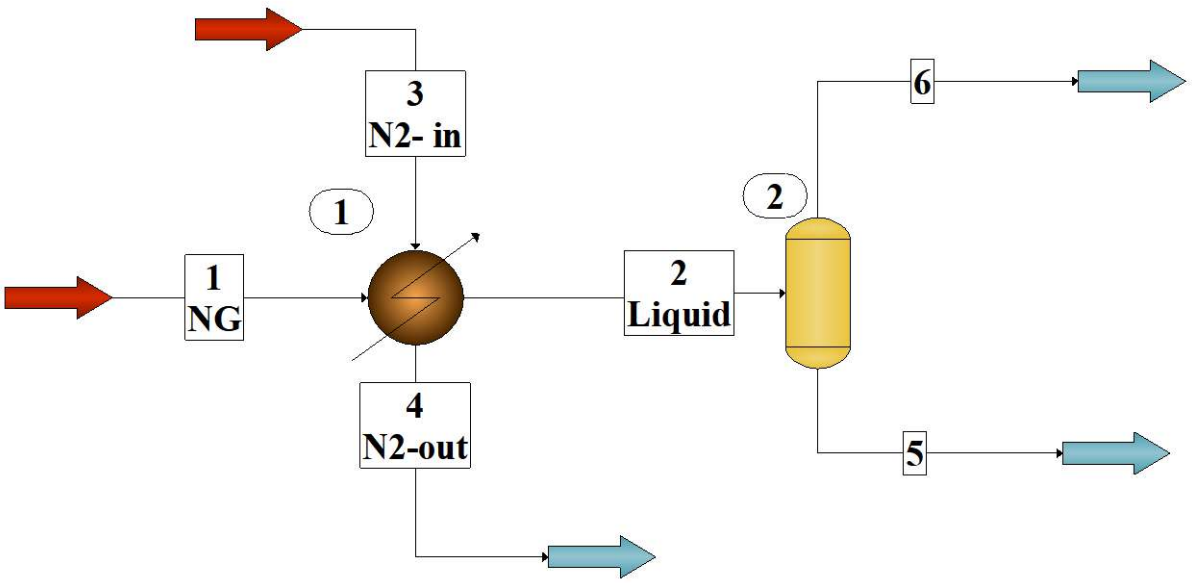
With help of CHEMCAD, use a shortcut column as a starting model to design an efficient distillation column equipped with shell- and- tube heat exchangers for the separation of an ethanol- water mixture with mole fractions of 0.075: 0.925 and total molar flow rate of 100 kmol h^{-1} at 25 ^{o}C and 1.2 atm.
Finally, perform sizing to the designed distillation column and estimate its purchase and installation cost.



(9) Worked Problem Using CHEMCAD Simulation

Design a simple Natural Gas Liquefaction (NGL) unit operating to liquefy 50 tons of natural gas with the following feed properties and composition:

T_o, °C	30
P_o, bar	50
Composition, Wt.%	
Methane	55.4
Ethane	15.9
Propane	10.5
Butane	16.6
Air	1.6



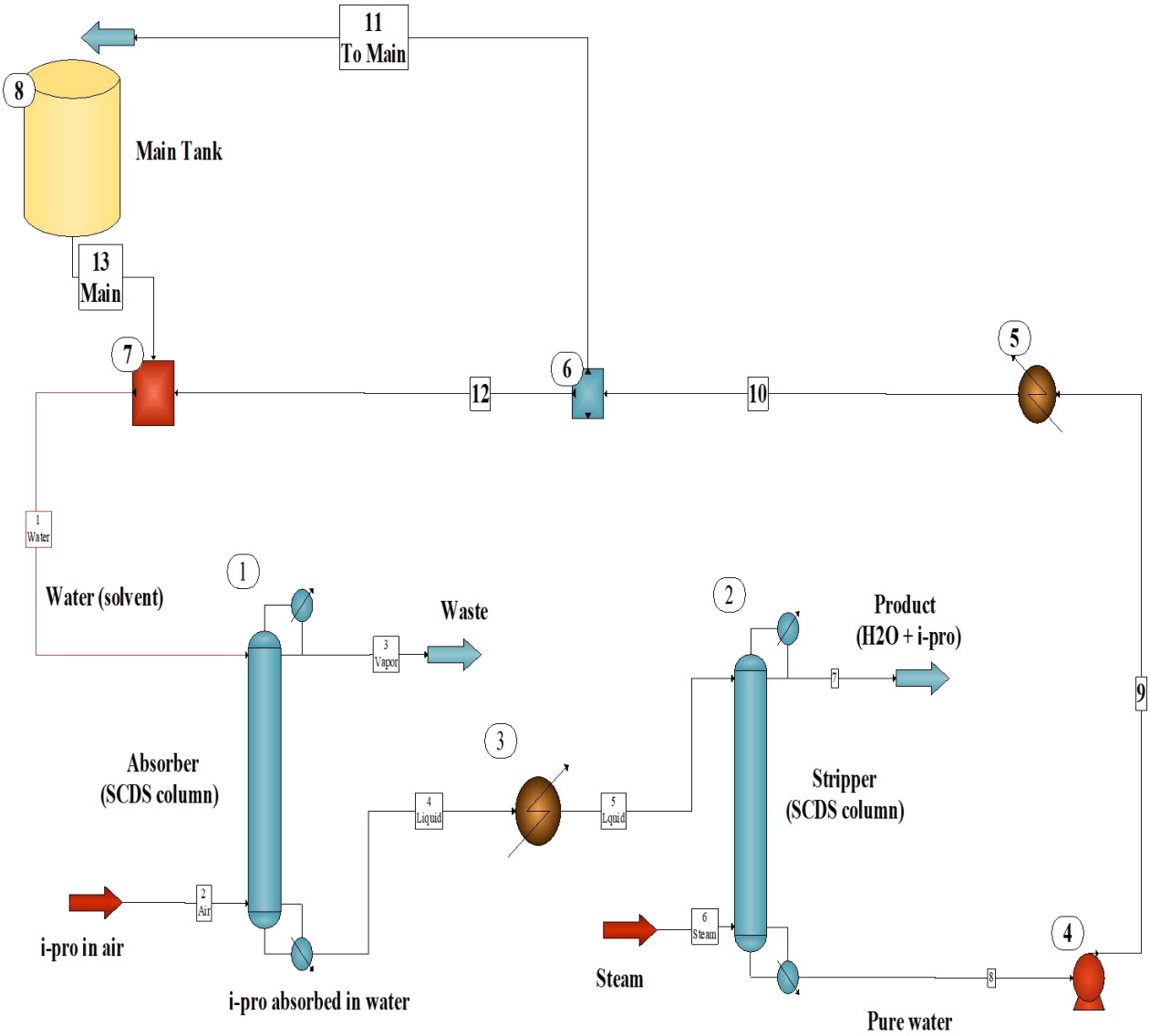
(10) Worked Problem Using CHEMCAD Simulation

For absorbing isopropanol from air into water, design continuous absorption- stripping process, using some appropriate unit operations for separation and recycling, if possible. The following data may be helpful for you design:

Air stream	
T_o, °C	20
P_o, bar	1.8
Isopropanol, mol%	5
Flow rate, kmol h^{-1}	500

Water stream	
T_o, °C	20
P_o, bar	1.8
Water, mol%	100
Flow rate, kmol h^{-1}	1000

Absorber spec.	
Feed T, °C	20
P, bar	1.8
No. of stages	12
Stripper spec.	
Feed T, °C	85
P, bar	1.2
No. of stages	12
Liquid feed	As abs. product
Stripping air feed	Pure water steam at 105 °C and 250 kmol h^{-1}
Isopropanol in liquid outlet, mol %	$< 1 \times 10^{-6}$


11
To Main
8
Main Tank
13
Main
7
12
6
10
5
1
Water
Water (solvent)
1
Waste
3
Vapor
2
Product
(H2O + i-pro)
7
9
Absorber
(SCDS column)
3
4
Liquid
5
Lquid
Stripper
(SCDS column)
2
Air
i-pro in air
6
Steam
Steam
4
8
i-pro absorbed in water
Pure water

(11) Worked Problem Using CHEMCAD Simulation

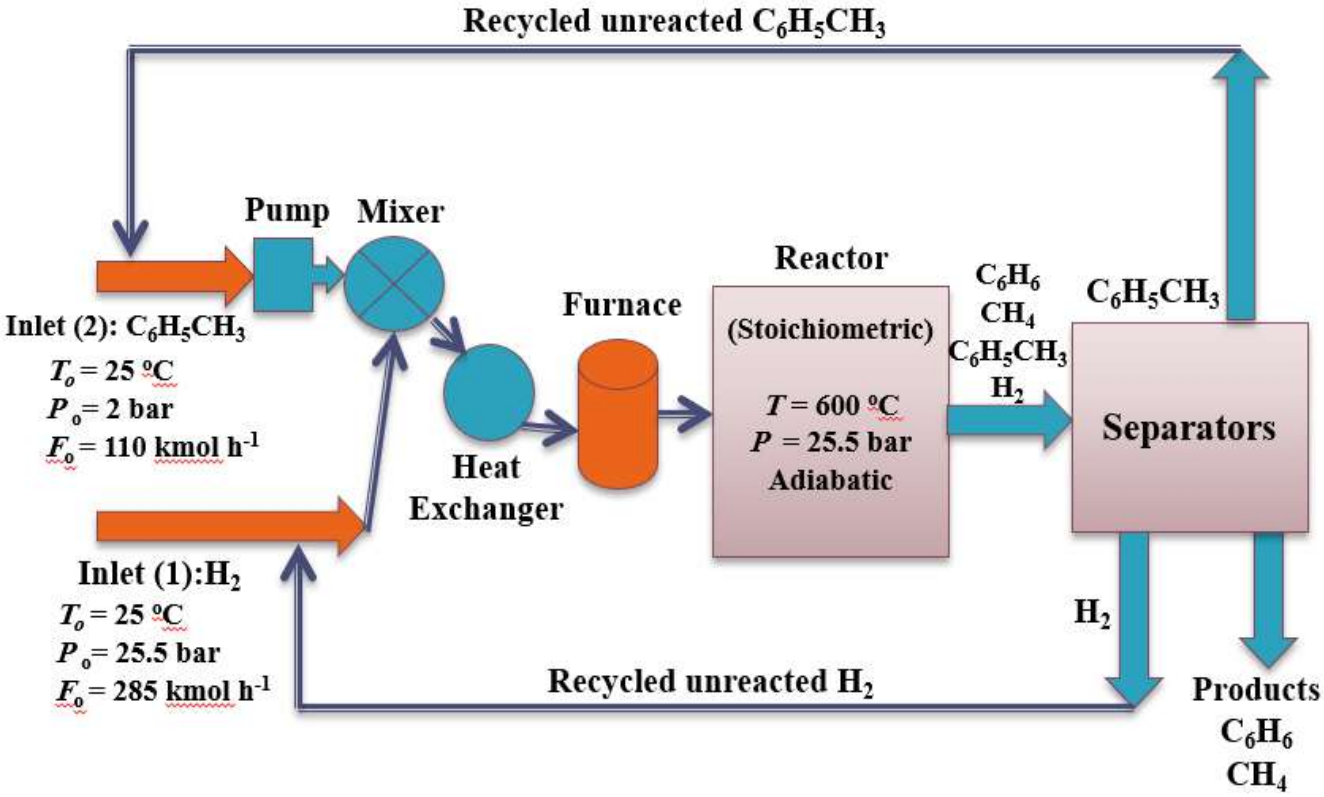
Using the preliminary data shown below, design a plant for production of benzene from toluene with a fractional conversion of 0.80, according to the following exothermic catalytic reaction:

$$C_6H_5CH_3(g) + H_2(g) \rightarrow C_6H_6(g) + CH_4(g) \; ; -r_T = k_T c_T c_{H2}^{1/2}$$

For continuity, the process must include recycling of unreacted toluene and hydrogen. Also, estimate the rate of production of benzene expressed in tons per a year (t/y), based on 7508 hours of plant operation per a year.

Toluene stream	
T_o, °C	25
P_o, bar	2
Molar flow rate (F_o), kmol h^{-1}	110
H_2 stream	
T_o, °C	25
P_o, bar	25.5
Molar flow rate (F_o), kmol h^{-1}	285

Reactor spec.	
Type	Catalytic packed bed (Stoichiometric)
Mode of thermal operation	Adiabatic & exothermic
Feed T, °C	600
Feed P, bar	25.5
No. of phases	Only vapor


Recycled unreacted $C_6H_5CH_3$
Pump
Mixer
Inlet (2): $C_6H_5CH_3$
T_o = 25 ºC
P_o = 2 bar
F_o = 110 kmol h^{-1}
Heat Exchanger
Furnace
Reactor
(Stoichiometric)
T = 600 ºC
P = 25.5 bar
Adiabatic
C_6H_6
CH_4
$C_6H_5CH_3$
H_2
$C_6H_5CH_3$
Separators
Inlet (1):H_2
T_o = 25 ºC
P_o = 25.5 bar
F_o = 285 kmol h^{-1}
H_2
Recycled unreacted H_2
Products
C_6H_6
CH_4

(12) Worked Problem Using COCO Simulator

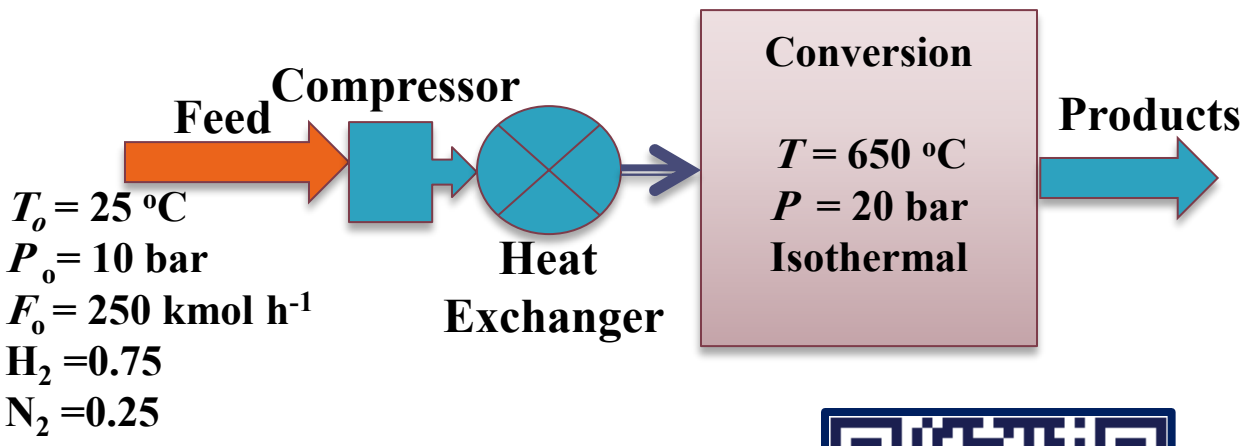
Simulate the ammonia synthesis process at 650 °C with 77.7% conversion of hydrogen, according to the following catalytic reaction:

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3$$

Use the following data for your solution:

Feed stream	
T_o, °C	25
P_o, bar	10
H_2 mole fraction	0.75
N_2 mole fraction	0.25
Total molar flow rate (F_o), kmol h^{-1}	250

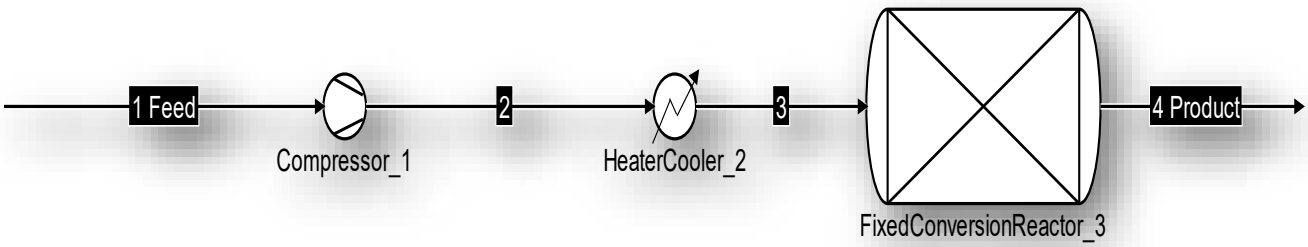
Reactor spec.	
Type	Stoichiometric
Catalyst	Fixed- bed Fe catalyst
Mode of thermal operation	Isothermal
T, °C	650
P, bar	20
No. of phases	1 phase (V)



(13) Worked Problem Using COCO Simulator

1- Separate the produced ammonia in pure liquid form and recycle unreacted H_2 and N_2.

2- Calculate the production rate of ammonia, expressed in tons per year (t/y), based on 7508 hours of plant operation per year.



Stream	1 Feed	2	3	4 Product	Unit
Pressure	10	20	20	20	bar
Temperature	25	112.583	650	650	°C
Flow rate	900	900	900	551.25	kmol / h
Mole frac Nitrogen	0.25	0.25	0.25	0.0918367	
Mole frac Hydrogen	0.75	0.75	0.75	0.27551	
Mole frac Ammonia	0	0	0	0.632653	
EnthalpyF	-14.5128	2530.63	18563.4	-4337.08	J / mol
Volume	0.00248363	0.00161258	0.00385382	0.00384671	m^3 / mol
GibbsEnergy	4285.89	7439.42	6333.19	953.525	J / mol

(14) Worked Problem Using COCO Simulator

Simulate cracking of n-hexane to ethylene and n- butane in PFR using Peng- Robinson thermodynamic model:

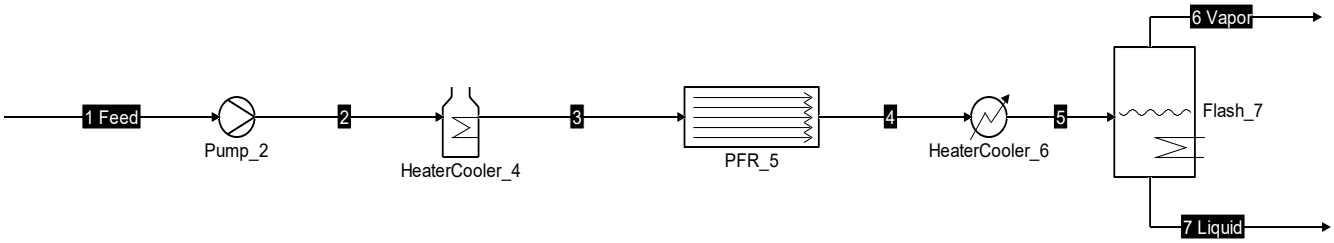
$C_6H_{14} \rightarrow C_2H_4 + C_4H_{10}$, $-r = kP_h$; $k = 1.76 \times 10^{17}\ s^{-1}$ at T = 600 °C and P = 250 kPa (E_a = 263.25 kJ/mol).

Feed stream	
T_o, °C	25
P_o , kPa	100
n-hexane mole fraction	1
n-hexane molar flow rate (F_o), kmol h^{-1}	8200

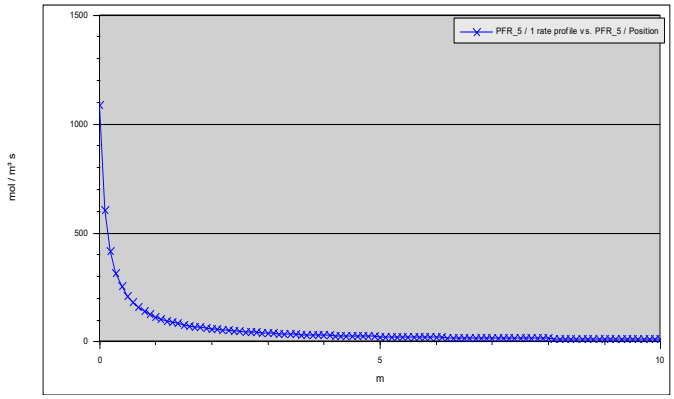
Reactor spec.	
Type	PFR
Reactor length, m	10
Reactor dia., m	1.5
No. of tubes	800
Tube dia., m	0.03
Catalyst	Packed- bed Lime catalyst (load=0.88 kg/m^3; void fra.= 0.027; particle dia.= 0.9 mm)
Mode of thermal operation	Adiabatic
T, °C	600
P , kPa	250

1- Use single and double PFR (series and parallel) and compare between the results.
2- Separate the products using flash drum with recycling the unreacted hexane.
3- Calculate the production rate of products, expressed in tons per year (t/y), based on 7508 hours of plant operation per year.

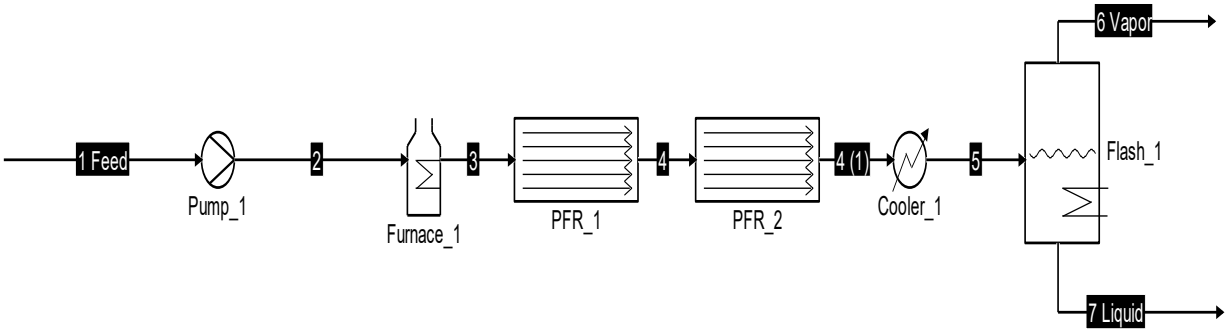
Cracking of n-hexane using single- PFR



Stream	1 Feed	2	3	4	5	6 Vapor	7 Liquid	Unit
Pressure	100	250	250	243.342	243.342	243.342	243.342	kPa
Temperature	25	25.074	600	512.014	5.68434e-14	56.85	56.85	°C
Flow rate	8200	8200	8200	10609.1	10609.1	5365.27	5243.85	kmol / h
Mole frac N-hexane	1	1	1	0.54584	0.54584	0.256922	0.841448	
Mole frac N-butane	0	0	0	0.22708	0.22708	0.309376	0.142879	
Mole frac Ethylene	0	0	0	0.22708	0.22708	0.433702	0.0156732	
Flow N-hexane	8200	8200	8200	5790.88	5790.88	1378.45	4412.43	kmol / h
Flow N-butane	0	0	0	2409.12	2409.12	1659.88	749.234	kmol / h
Flow Ethylene	0	0	0	2409.12	2409.12	2326.93	82.1877	kmol / h

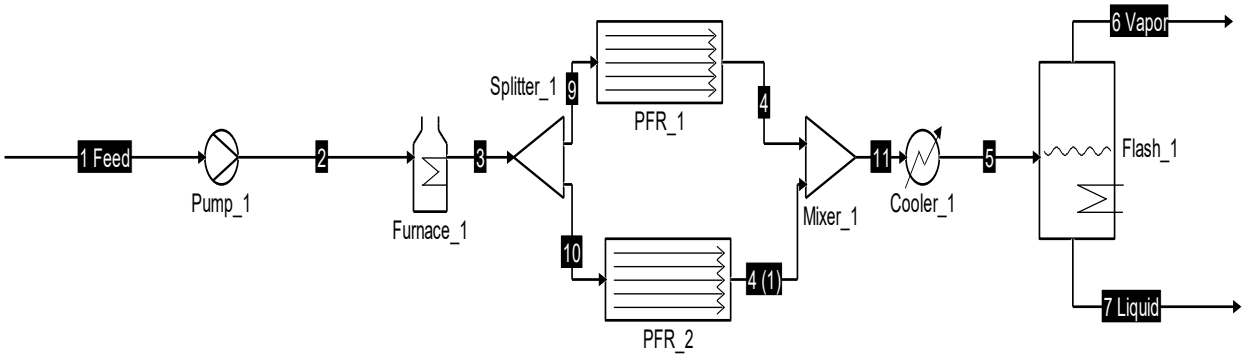


Cracking of n-hexane using series double- PFR



Stream	1 Feed	2	3	4	5	6 Vapor	7 Liquid	4 (1)	Unit
Pressure	100	250	250	243.342	236.268	236.268	236.268	236.268	kPa
Temperature	25	25.074	600	512.014	5.68434e-14	56.85	56.85	499.682	°C
Flow rate	8200	8200	8200	10609.1	10931.2	6447.69	4483.5	10931.2	kmol / h
Mole frac N-hexane	1	1	1	0.54584	0.500294	0.263716	0.840515	0.500294	
Mole frac N-butane	0	0	0	0.22708	0.249853	0.322782	0.144975	0.249853	
Mole frac Ethylene	0	0	0	0.22708	0.249853	0.413502	0.0145105	0.249853	
Flow N-hexane	8200	8200	8200	5790.88	5468.81	1700.36	3768.45	5468.81	kmol / h
Flow N-butane	0	0	0	2409.12	2731.19	2081.2	649.996	2731.19	kmol / h
Flow Ethylene	0	0	0	2409.12	2731.19	2666.14	65.0579	2731.19	kmol / h

Cracking of n-hexane using parallel double- PFR



Stream	1 Feed	2	3	4	5	6 Vapor	7 Liquid	4 (1)	Unit
Pressure	100	250	250	248.146	248.146	248.146	248.146	248.146	kPa
Temperature	25	25.074	600	499.278	5.68434e-14	56.85	56.85	499.278	°C
Flow rate	8200	8200	8200	5471.16	10942.3	6260.88	4681.45	5471.16	kmol / h
Mole frac N-hexane	1	1	1	0.498767	0.498767	0.249625	0.831965	0.498767	
Mole frac N-butane	0	0	0	0.250617	0.250617	0.324081	0.152367	0.250617	
Mole frac Ethylene	0	0	0	0.250617	0.250617	0.426294	0.0156683	0.250617	
Flow N-hexane	8200	8200	8200	2728.84	5457.67	1562.87	3894.8	2728.84	kmol / h
Flow N-butane	0	0	0	1371.16	2742.33	2029.03	713.299	1371.16	kmol / h
Flow Ethylene	0	0	0	1371.16	2742.33	2668.98	73.3504	1371.16	kmol / h

(A)

(B)

(15) Worked Problem Using COCO Simulator

1- Simulate dehydration of ethanol to ethylene and diethyl ether in a single-CSTR using Peng- Robinson thermodynamic model according to the following reactions:

$C_2H_5OH \rightarrow C_2H_4 + H_2O$, $-r_1 = k_1 c$; $k_1 = 0.802\ h^{-1}$ at 523.15 K (E_a= 23.522 J/mol)

$2\ C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O$, $-r_2 = k_2 c^2$; $k_2 = 1.02\ m^3 mol^{-1} h^{-1}$ at 523.15 K (E_a= 94.6216 J/mol)

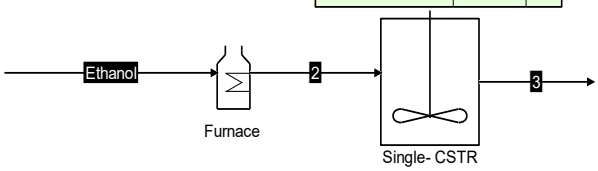
Feed stream (ethanol only)	
T_o , K	298.15
P_o , kPa	300
Molar flow rate (F_o), kmol h^{-1}	500

Reactor spec.	
Type	Single- CSTR
Reactor volume, m^3	100
Catalyst	Fixed- bed ZSM-5 catalyst (V=31.09 m^3; d=0.356 g cm^{-3})
Mode of thermal operation	Adiabatic
T_o , K	523.15
P , kPa	300

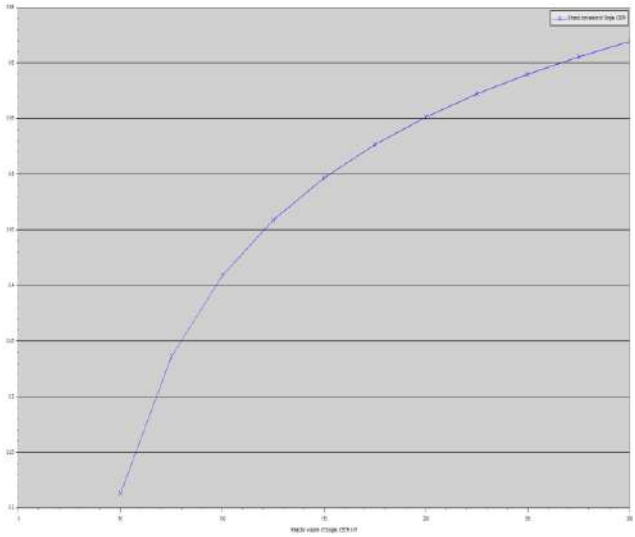
2- Separate the products using simple distillation with recycling the unreacted ethanol.

3- Calculate the production rate of products, expressed in tons per year (t/y), based on 7508 hour of plant operation per year.

Single- CSTR		
Parameter	Value	Unit
Temperature	561.34	K
Reactor volume	100	m³
Ethanol conversion	0.408685	



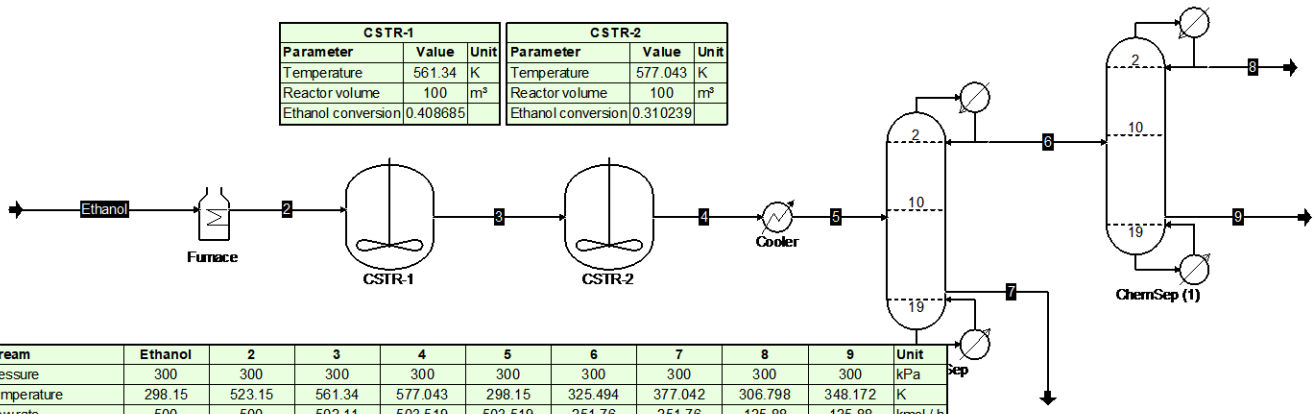
Stream	Ethanol	2	3	Unit
Pressure	300	300	300	kPa
Temperature	298.15	523.15	561.34	K
Flow rate	500	500	502.11	kmol / h
Mole frac Ethanol	1	1	0.58883	
Mole frac Ethylene	0	0	0.00420181	
Mole frac Diethyl ether	0	0	0.201383	
Mole frac Water	0	0	0.205585	
Flow Diethyl ether	0	0	101.116	kmol / h
Flow Ethanol	500	500	295.658	kmol / h
Flow Ethylene	0	0	2.10977	kmol / h
Flow Water	0	0	103.226	kmol / h



Dehydration of Ethanol to Ethylene & Diethyl ether

CSTR-1		
Parameter	Value	Unit
Temperature	561.34	K
Reactor volume	100	m³
Ethanol conversion	0.408685	

CSTR-2		
Parameter	Value	Unit
Temperature	577.043	K
Reactor volume	100	m³
Ethanol conversion	0.310239	



Stream	Ethanol	2	3	4	5	6	7	8	9	Unit
Pressure	300	300	300	300	300	300	300	300	300	kPa
Temperature	298.15	523.15	561.34	577.043	298.15	325.494	377.042	306.798	348.172	K
Flow rate	500	500	502.11	503.519	503.519	251.76	251.76	125.88	125.88	kmol / h
Mole frac Ethanol	1	1	0.58883	0.405015	0.405015	0.174688	0.635341	2.51437e-05	0.349352	
Mole frac Ethylene	0	0	0.00420181	0.00698977	0.00698977	0.0139795	0	0.0279591	5.20785e-11	
Mole frac Diethyl ether	0	0	0.201383	0.290503	0.290503	0.581005	1.9413e-11	0.64519	0.516821	
Mole frac Water	0	0	0.205585	0.297493	0.297493	0.230327	0.364659	0.326826	0.133827	
Flow Diethyl ether	0	0	101.116	146.274	146.274	146.274	4.8874e-09	81.2164	65.0574	kmol / h
Flow Ethanol	500	500	295.658	203.933	203.933	43.9795	159.953	0.00316508	43.9764	kmol / h
Flow Ethylene	0	0	2.10977	3.51949	3.51949	3.51949	0	3.51949	6.55563e-09	kmol / h
Flow Water	0	0	103.226	149.793	149.793	57.9869	91.8063	41.1408	16.8461	kmol / h

(16) Worked Problem Using COCO Simulation

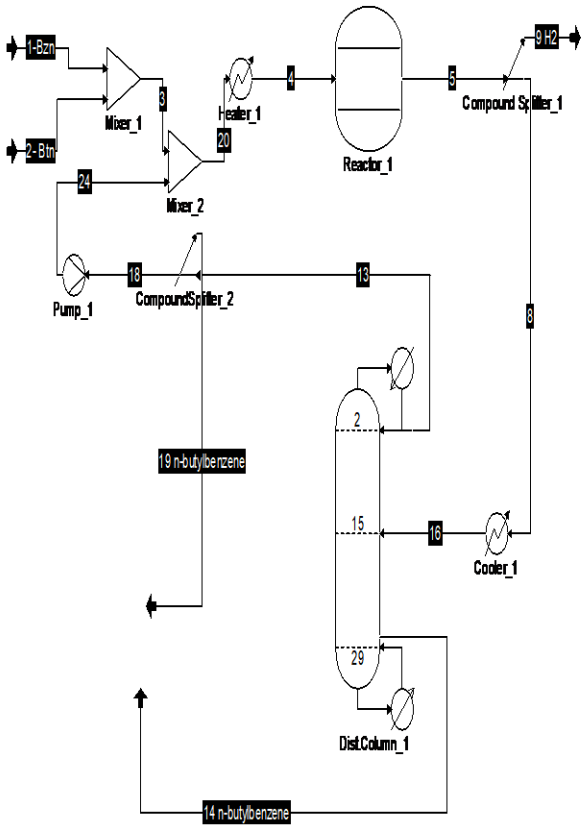
Using the preliminary data shown below, design a plant for production of n-butyl benzene at 84.5 % conversion of benzene, according to the following catalytic reaction:

$$C_6H_6 + \text{n-}C_4H_9Cl \rightarrow \text{n-}C_4H_9C_6H_5 + HCl \quad ; -r = kc_Bc_D$$

For continuity, the process must include recycling of unreacted components. Also, estimate the rate of production of n-butyl benzene expressed in tons per year (t/y), based on 7508 hours of plant operation per a year. Note that n-butyl chloride can be modeled as n-butane and HCl as H_2 for simplicity of simulation.

Benzene stream	
T_o, °C	40
P_o, kPa	200
Molar flow rate (F_o), kmol h^{-1}	1.5
Butyl stream	
T_o, °C	40
P_o, kPa	200
Molar flow rate (F_o), kmol h^{-1}	1.5

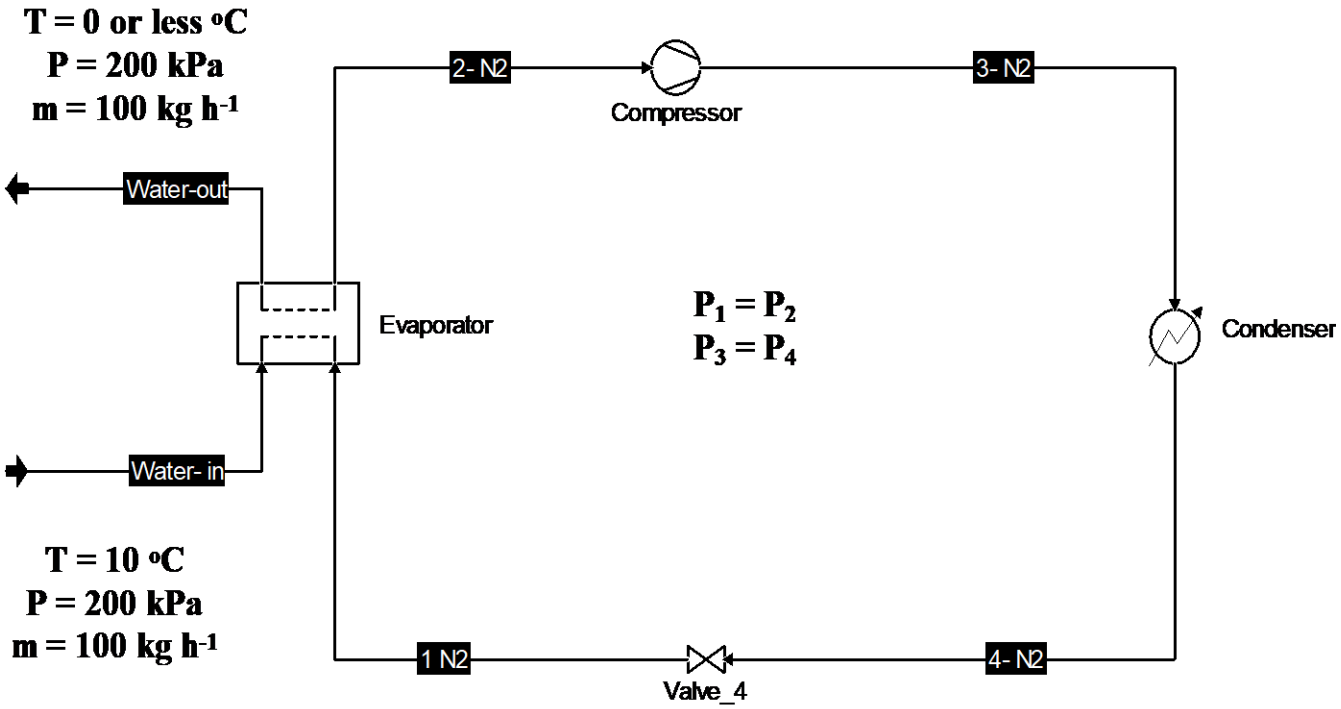
Reactor spec.	
Type	Catalytic packed bed (Stoichiometric)
Catalyst	$AlCl_3$
Mode of thermal operation	Isothermal
Feed T, °C	200
Feed P, kPa	200
No. of phases	2phases (V/L)



Stream	1-Bzn	2-Btn	3	20	4	5	8	16	13	18	24	9 H2	14 n-butylbenzene	19 n-butylbenzene	Unit
Pressure	200	200	200	200	200	200	200	200	101.325	101.325	200	200	101.325	101.325	kPa
Temperature	40	40	52.6465	52.5147	177	177	177	40	34.8993	34.8993	51.8262	177	183.288	34.8993	°C
Flowrate	1.26	1.26	2.52	3	3	3	1.74	1.74	0.87	0.48	0.48	1.26	0.87	0.39	kmol / h
Mole frac N-butane	0	1	0.5	0.5	0.5	0.08	0.137931	0.137931	0.275862	0.5	0.5	0	0	0	
Mole frac N-butylbenzene	0	0	0	0	0	0.42	0.724138	0.724138	0.448276	0	0	0	1	1	
Mole frac Benzene	1	0	0.5	0.5	0.5	0.08	0.137931	0.137931	0.275862	0.5	0.5	0	0	0	
Mole frac Hydrogen	0	0	0	0	0	0.42	0	0	0	0	0	1	0	0	
BubblePointTemperature	103.843	18.8098	37.5289	37.5289	37.5289	N/A	93.1981	93.1981	34.8993	15.3908	37.5289	-250.349	183.288	183.288	°C
FlowN-butane	0	1.26	1.26	1.5	1.5	0.24	0.24	0.24	0.24	0.24	0.24	0	0	0	kmol / h
FlowN-butylbenzene	0	0	0	0	0	1.26	1.26	1.26	0.39	0	0	0	0.87	0.39	kmol / h
FlowBenzene	1.26	0	1.26	1.5	1.5	0.24	0.24	0.24	0.24	0.24	0.24	0	0	0	kmol / h
FlowHydrogen	0	0	0	0	0	1.26	0	0	0	0	0	1.26	0	0	kmol / h
Enthalpy	-30464.8	1384.34	-14540.3	-14609.9	17088.2	18520.4	4740.91	-39435.7	-34779.2	-14982.1	-14975.5	4422.64	-5716.87	-46202	J / mol

(17) Worked Problem Using COCO Simulation

Design a refrigerator working with N_2 as a coolant utility to cool 100 kg h^{-1} water at 10 °C and 200 kPa upto approximately its freezing point.



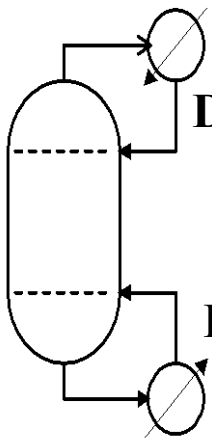
Stream	Water- in	Water-out	1 N2	2- N2	3- N2	4- N2	Unit
Pressure	200	200	2700	2700	6000	6000	kPa
Temperature	10	-0.296183	-29.854	-12	-0.2401	-20	°C
Flow rate	100	100	150	150	150	150	kmol / h
Mole frac Water	1	1	0	0	0	0	
Mole frac Nitrogen	0	0	1	1	1	1	

(18) Worked Problem Using COCO Simulation

Design a distillation column to separate 99 mol% of o-xylene from the following mixture at constant pressure:

Feed stream	
T_o, °C	100
P_o, bar	1
Molar flow rate (F_o), kmol h^{-1}	
Benzene	100
Toluene	100
O-xylene	100

Also, estimate the total annual cost (TAC) of the designed column expressed in US dollars ($).



T_o = 100 °C
P_o = 1 bar
Benzene: 100 kmol h^{-1}
Toluene: 100 kmol h^{-1}
O-xylene: 100 kmol h^{-1}

T = ? °C
P = 1 bar
X (O-xylene): 0.01

T = ? °C
P = 1 bar
X (O-xylene): 0.99

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About the Book

This textbook, "Chemical Engineering: Basics & Applications" provides a comprehensive foundation in Chemical Reaction Engineering (CRE), focusing on the rational design and performance analysis of chemical reactors. It distinguishes CRE from chemical kinetics by positioning the latter as a tool for determining reaction rates and mechanisms, while the former applies this kinetic data to specify reactor size, configuration, .and operating conditions

The core analytical framework is built upon the general balance equation, which accounts for mass or energy across finite or differential control volumes through the summation of input, output, generation, and accumulation rates. The text systematically explores the three primary ideal reactor models: Batch Reactors (BR) for small-volume, high-value production; Continuous Stirred-Tank Reactors (CSTR), characterized by perfect mixing and backmix flow; and Plug-Flow Reactors (PFR), .which model tubular flow without axial mixing

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