

Chapter 1

Overview of Chemical Reaction Engineering

Every industrial chemical process is designed to produce economically a desired product from a variety of starting materials through a succession of treatment steps. Figure 1.1 shows a typical situation. The raw materials undergo a number of physical treatment steps to put them in the form in which they can be reacted chemically. Then they pass through the reactor. The products of the reaction must then undergo further physical treatment—separations, purifications, etc.—

Chemical kinetics deals with: -

- how fast or slow chemical reactions proceed (occur), i.e. reaction rate,
- what chemical reactions occurs in a chemical process, i.e. reaction mechanisms (reaction mechanisms that cause reactions to occur).

The study of chemical reaction engineering (CRE) combines the study of chemical kinetics with the reactors in which the reactions occur. Chemical kinetics and reactor design are at the heart of producing almost all industrial chemicals.

Reactor design uses information, knowledge, and experience from a variety of areas—thermodynamics, chemical kinetics, fluid mechanics, heat transfer, mass transfer, and economics. Chemical reaction engineering is the synthesis of all these factors with the aim of properly designing a chemical reactor.

To find what a reactor is able to do we need to know the kinetics, the contacting pattern and the performance equation. We show this schematically in Fig. 1.2.

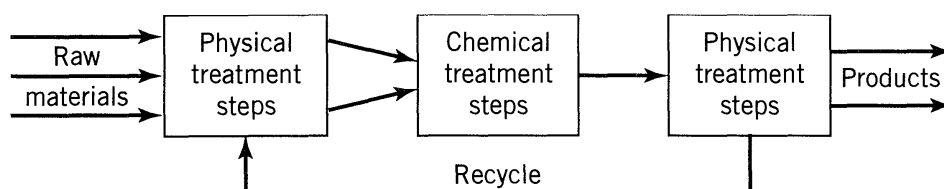


Figure 1.1 Typical chemical process.

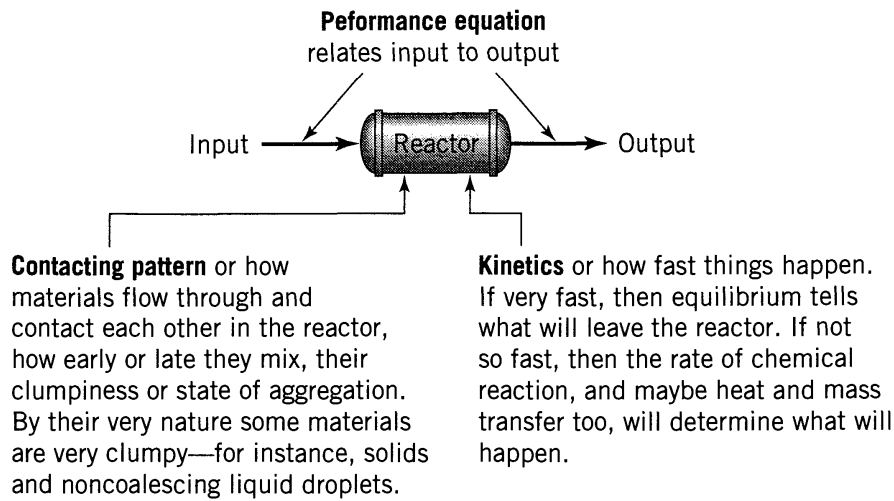
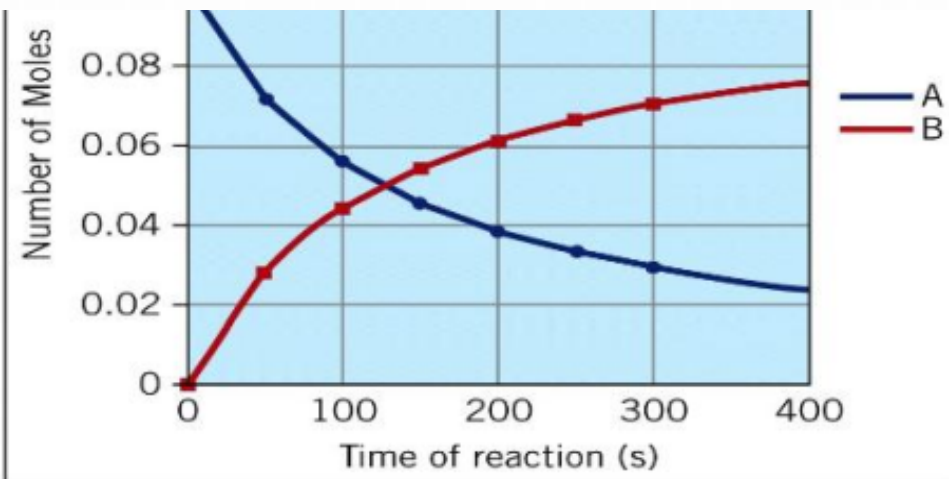


Figure 1.2 Information needed to predict what a reactor can do.

$$\text{Output} = f [\text{input, kinetics, contacting}] \dots\dots\dots (1)$$

o **Homogeneous reaction** : it takes place in one phase alone.

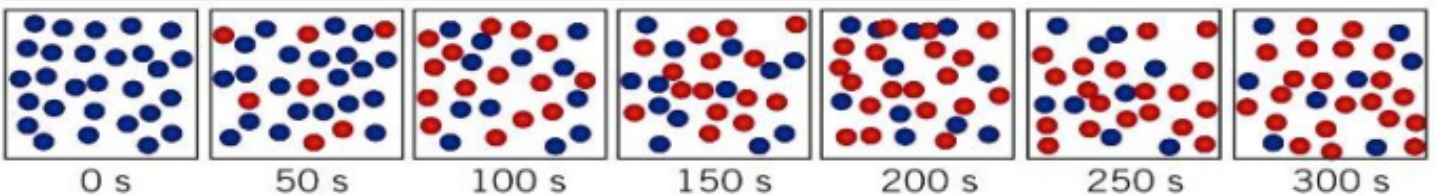
o **Heterogeneous reaction** : multiple phases, reaction usually occurs at the interface



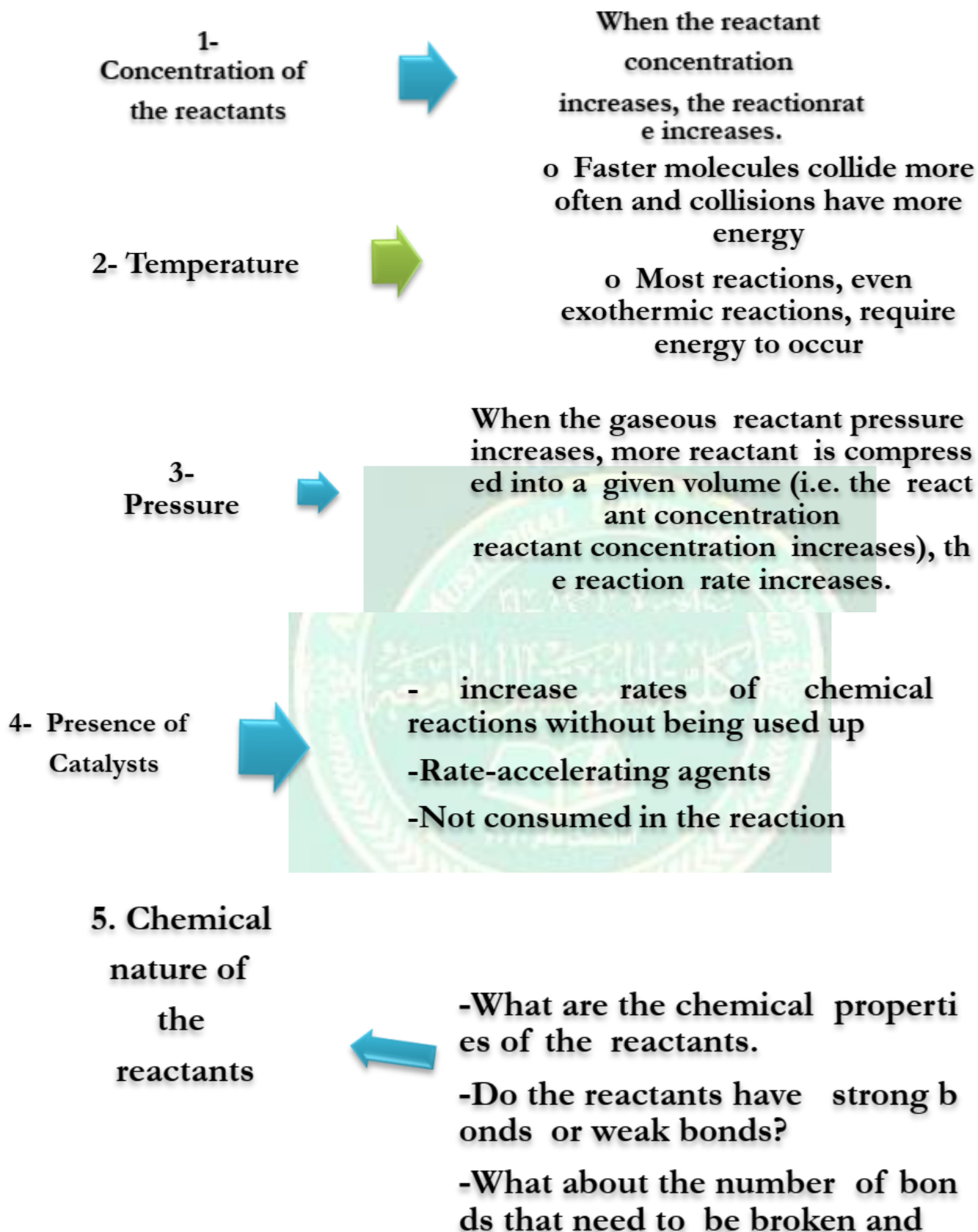
By the amount of **product** produced or **reactants** consumed per unit time.

o **[B]** concentration of products will increase over time

o **[A]** concentration of reactants will decrease over



Factors Affecting Reaction Rates



Definition of Reaction Rate

We next ask how to *define* the rate of reaction in meaningful and useful ways. To answer this, let us adopt a number of definitions of rate of reaction, all

interrelated and all intensive rather than extensive measures. But first we must select one reaction component for consideration and define the rate in terms of this component i . If the rate of change in number of moles of this component due to reaction is dN_i/dt , then the rate of reaction in its various forms is defined as follows. Based on unit volume of reacting fluid,

$$r_i = \frac{1}{V} \frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of fluid}) (\text{time})} \quad (2)$$

Based on unit mass of solid in fluid-solid systems,

$$r'_i = \frac{1}{W} \frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{mass of solid}) (\text{time})} \quad (3)$$

Based on unit interfacial surface in two-fluid systems or based on unit surface of solid in gas-solid systems,

$$r''_i = \frac{1}{S} \frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{surface}) (\text{time})} \quad (4)$$

Based on unit volume of solid in gas-solid systems

$$r'''_i = \frac{1}{V_s} \frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of solid}) (\text{time})} \quad (5)$$

Based on unit volume of reactor, if different from the rate based on unit volume of fluid,

$$r''''_i = \frac{1}{V_r} \frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of reactor}) (\text{time})} \quad (6)$$

In homogeneous systems the volume of fluid in the reactor is often identical to the volume of reactor. In such a case V and V_r are identical and Eqs. 2 and 6 are used interchangeably. In heterogeneous systems all the above definitions of reaction rate are encountered, the definition used in any particular situation often being a matter of convenience.

From Eqs. 2 to 6 these intensive definitions of reaction rate are related by

$$\left(\frac{\text{volume}}{\text{of fluid}}\right) r_i = \left(\frac{\text{mass of}}{\text{solid}}\right) r'_i = \left(\frac{\text{surface}}{\text{of solid}}\right) r''_i = \left(\frac{\text{volume}}{\text{of solid}}\right) r'''_i = \left(\frac{\text{volume}}{\text{of reactor}}\right) r''''_i$$

or

$$Vr_i = Wr'_i = Sr''_i = V_s r'''_i = V_r r''''_i \quad (7)$$

Speed of Chemical Reactions

Some reactions occur very rapidly; others very, very slowly. For example, in the production of polyethylene, one of our most important plastics, or in the production of gasoline from crude petroleum, we want the reaction step to be complete in less than one second, while in waste water treatment, reaction may take days and days to do the job.

Figure 1.3 indicates the relative rates at which reactions occur. To give you an appreciation of the relative rates or relative values between what goes on in sewage treatment plants and in rocket engines, this is equivalent to

1 sec to 3 yr

With such a large ratio, of course the design of reactors will be quite different in these cases.

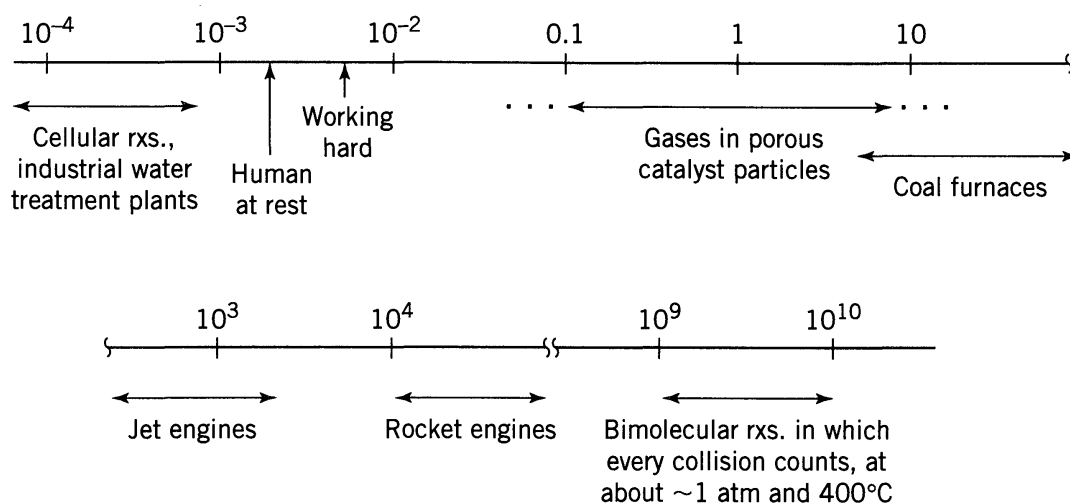


Figure 1.3 Rate of reactions $-r_A''' = \frac{\text{moles of A disappearing}}{\text{m}^3 \text{ of thing} \cdot \text{s}}$

Overall Plan

Reactors come in all colors, shapes, and sizes and are used for all sorts of reactions. As a brief sampling we have the giant cat crackers for oil refining; the monster blast furnaces for iron making; the crafty activated sludge ponds for sewage treatment; the amazing polymerization tanks for plastics, paints, and fibers; the critically important pharmaceutical vats for producing aspirin, penicillin, and birth control drugs; the happy-go-lucky fermentation jugs for moonshine; and, of course, the beastly cigarette.

Such reactions are so different in rates and types that it would be awkward to try to treat them all in one way. So we treat them by type in this book because each type requires developing the appropriate set of performance equations.

EXAMPLE 1.1 THE ROCKET ENGINE

A rocket engine, Fig. E1.1, burns a stoichiometric mixture of fuel (liquid hydrogen) in oxidant (liquid oxygen). The combustion chamber is cylindrical, 75 cm long and 60 cm in diameter, and the combustion process produces 108 kg/s of exhaust gases. If combustion is complete, find the rate of reaction of hydrogen and of oxygen.

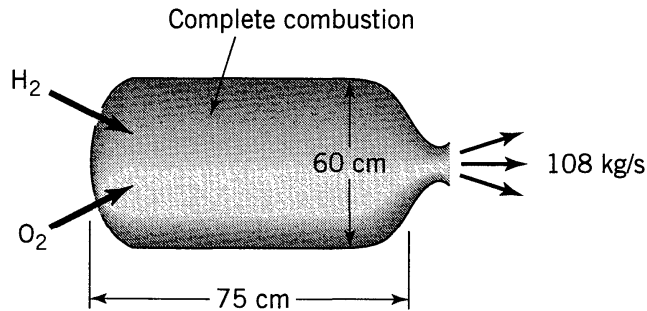


Figure E1.1

SOLUTION

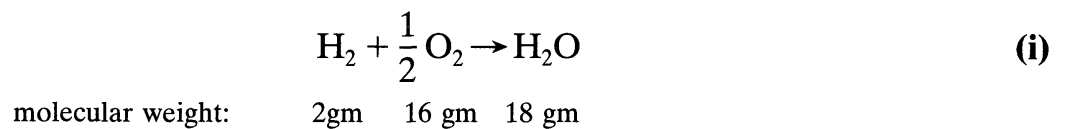
We want to evaluate

$$-r_{\text{H}_2} = \frac{1}{V} \frac{dN_{\text{H}_2}}{dt} \quad \text{and} \quad -r_{\text{O}_2} = \frac{1}{V} \frac{dN_{\text{O}_2}}{dt}$$

Let us evaluate terms. The reactor volume and the volume in which reaction takes place are identical. Thus,

$$V = \frac{\pi}{4} (0.6)^2 (0.75) = 0.2121 \text{ m}^3$$

Next, let us look at the reaction occurring.



Therefore,

$$\text{H}_2\text{O produced/s} = 108 \text{ kg/s} \left(\frac{1 \text{ kmol}}{18 \text{ kg}} \right) = 6 \text{ kmol/s}$$

So from Eq. (i)

$$\text{H}_2 \text{ used} = 6 \text{ kmol/s}$$

$$\text{O}_2 \text{ used} = 3 \text{ kmol/s}$$

and the rate of reaction is

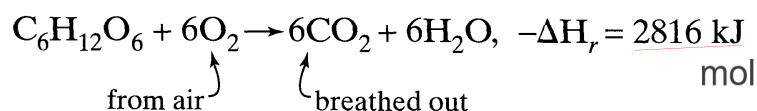
$$\underline{\underline{-r_{\text{H}_2}}} = -\frac{1}{0.2121 \text{ m}^3} \cdot \frac{6 \text{ kmol}}{\text{s}} = \underline{\underline{2.829 \times 10^4 \frac{\text{mol used}}{(\text{m}^3 \text{ of rocket}) \cdot \text{s}}}}$$

$$\underline{\underline{-r_{\text{O}_2}}} = -\frac{1}{0.2121 \text{ m}^3} \cdot 3 \frac{\text{kmol}}{\text{s}} = \underline{\underline{1.415 \times 10^4 \frac{\text{mol}}{\text{m}^3 \cdot \text{s}}}}$$

Note: Compare these rates with the values given in Figure 1.3. ■

EXAMPLE 1.2 THE LIVING PERSON

A human being (75 kg) consumes about 6000 kJ of food per day. Assume that the food is all glucose and that the overall reaction is



Find man's metabolic rate (the rate of living, loving, and laughing) in terms of moles of oxygen used per m³ of person per second.

SOLUTION

We want to find

$$-r'''_{\text{O}_2} = -\frac{1}{V_{\text{person}}} \frac{dN_{\text{O}_2}}{dt} = \frac{\text{mol O}_2 \text{ used}}{(\text{m}^3 \text{ of person})\text{s}} \quad \text{(i)}$$

Let us evaluate the two terms in this equation. First of all, from our life experience we estimate the density of man to be

$$\rho = 1000 \frac{\text{kg}}{\text{m}^3}$$

Therefore, for the person in question

$$V_{\text{person}} = \frac{75 \text{ kg}}{1000 \text{ kg/m}^3} = 0.075 \text{ m}^3$$

Next, noting that each mole of glucose consumed uses 6 moles of oxygen and releases 2816 kJ of energy, we see that we need

$$\frac{dN_{\text{O}_2}}{dt} = \left(\frac{6000 \text{ kJ/day}}{2816 \text{ kJ/mol glucose}} \right) \left(\frac{6 \text{ mol O}_2}{1 \text{ mol glucose}} \right) = 12.8 \frac{\text{mol O}_2}{\text{day}}$$

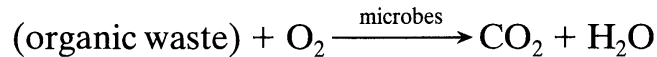
Inserting into Eq. (i)

$$-r''_{\text{O}_2} = \frac{1}{0.075 \text{ m}^3} \cdot \frac{12.8 \text{ mol O}_2 \text{ used}}{\text{day}} \frac{1 \text{ day}}{24 \times 3600 \text{ s}} = \underline{\underline{0.002 \frac{\text{mol O}_2 \text{ used}}{\text{m}^3 \cdot \text{s}}}}$$

Note: Compare this value with those listed in Figure 1.3.

PROBLEMS

1.1. Municipal waste water treatment plant. Consider a municipal water treatment plant for a small community (Fig. P1.1). Waste water, 32 000 m³/day, flows through the treatment plant with a mean residence time of 8 hr, air is bubbled through the tanks, and microbes in the tank attack and break down the organic material



A typical entering feed has a BOD (biological oxygen demand) of 200 mg O₂/liter, while the effluent has a negligible BOD. Find the rate of reaction, or decrease in BOD in the treatment tanks.

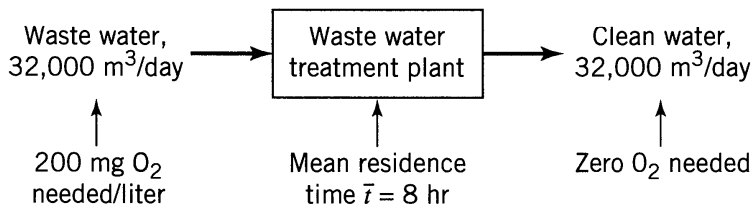


Figure P1.1

1.2. Coal burning electrical power station. Large central power stations (about 1000 MW electrical) using fluidized bed combustors may be built some day (see Fig. P1.2). These giants would be fed 240 tons of coal/hr (90% C, 10%

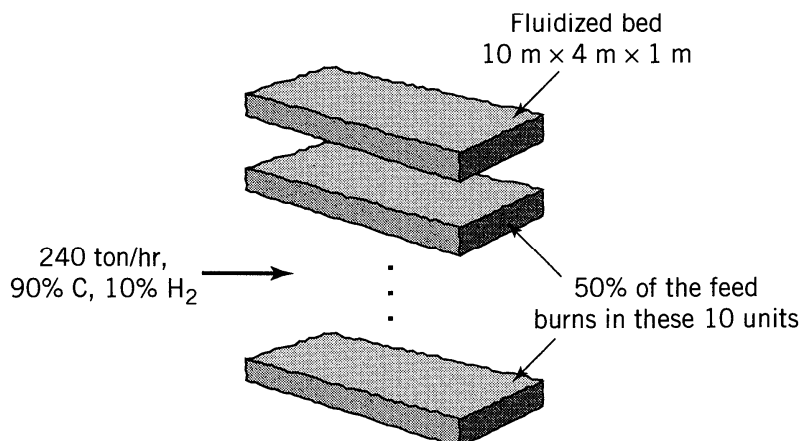
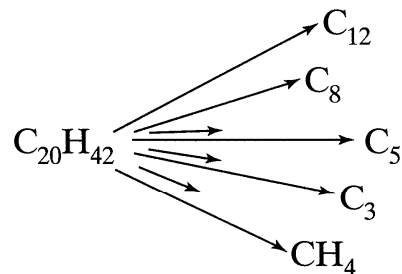


Figure P1.2

H₂), 50% of which would burn within the battery of primary fluidized beds, the other 50% elsewhere in the system. One suggested design would use a battery of 10 fluidized beds, each 20 m long, 4 m wide, and containing solids to a depth of 1 m. Find the rate of reaction within the beds, based on the oxygen used.

1.3. Fluid cracking crackers (FCC). FCC reactors are among the largest processing units used in the petroleum industry. Figure P1.3 shows an example of such units. A typical unit is 4-10 m ID and 10-20 m high and contains about 50 tons of $\rho = 800 \text{ kg/m}^3$ porous catalyst. It is fed about 38 000 barrels of crude oil per day ($6000 \text{ m}^3/\text{day}$ at a density $\rho \cong 900 \text{ kg/m}^3$), and it cracks these long chain hydrocarbons into shorter molecules.

To get an idea of the rate of reaction in these giant units, let us simplify and suppose that the feed consists of just C₂₀ hydrocarbon, or



If 60% of the vaporized feed is cracked in the unit, what is the rate of reaction, expressed as $-r'$ (mols reacted/kg cat · s) and as r''' (mols reacted/ $\text{m}^3 \text{ cat} \cdot \text{s}$)?

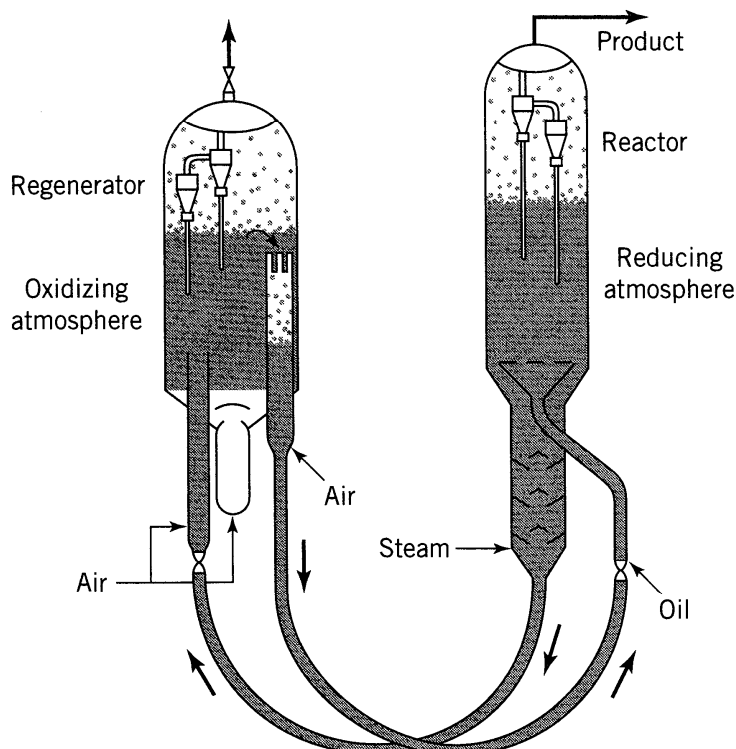


Figure P1.3 The Exxon Model IV FCC unit.