

Catalyst Decay DVD 10

10.7 Catalyst Deactivation

In designing fixed and ideal fluidized-bed catalytic reactors, we have assumed up to now that the activity of the catalyst remains constant throughout the catalyst's life. That is, the total concentration of active sites, C_t , accessible to the reaction does not change with time. Unfortunately, Mother Nature is not so kind as to allow this behavior to be the case in most industrially significant catalytic reactions. One of the most insidious problems in catalysis is the loss of catalytic activity that occurs as the reaction takes place on the catalyst. A wide variety of mechanisms have been proposed by Butt and Petersen,¹ to explain and model catalyst deactivation.

Catalytic deactivation adds another level of complexity to sorting out the reaction rate law parameters and pathways. In addition, we need to make adjustments for the decay of the catalysts in the design of catalytic reactors. This adjustment is usually made by a quantitative specification of the catalyst's activity, $a(t)$. In analyzing reactions over decaying catalysts we divide the reactions into two categories: *separable kinetics* and *nonseparable kinetics*. In separable kinetics, we separate the rate law and activity:

$$\text{Separable kinetics: } -r'_A = a(\text{Past history}) \times -r'_A \text{ (Fresh catalyst)}$$

When the kinetics and activity are separable, it is possible to study catalyst decay and reaction kinetics independently. However, nonseparability,

$$\text{Nonseparable kinetics: } -r'_A = -r'_A \text{ (Past history, Fresh catalyst)}$$

must be accounted for by assuming the existence of a nonideal surface or by describing deactivation by a mechanism composed of several elementary steps.²

In this section we shall consider only *separable kinetics* and define the activity of the catalyst at time t , $a(t)$, as the ratio of the rate of reaction on a catalyst that has been used for a time t to the rate of reaction on a fresh catalyst ($t = 0$):

$a(t)$: catalyst activity

$$a(t) = \frac{2r'_A(t)}{2r'_A(t=0)} \quad (10-92)$$

¹ J. B. Butt and E. E. Petersen, *Activation, Deactivation and Poisoning of Catalysts* (New York: Academic Press, 1988). See also S. Szépe and O. Levenspiel, *Chem. Eng. Sci.*, 23, 881–894 (1968).

² D. T. Lynch and G. Emig, *Chem. Eng. Sci.*, 44(6), 1275–1280 (1989).

Because of the catalyst decay, the activity decreases with time and a typical curve of the activity as a function of time is shown in Figure 10-22.

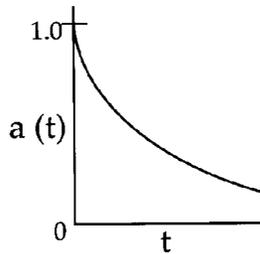


Figure 10-22 Activity as a function of time.

Combining Equations (10-92) and (3-2), the rate of disappearance of reactant A on a catalyst that has been utilized for a time t is

Reaction rate law
accounting for
catalyst activity

$$2r'_A = a(t)k(T) \text{fn}(C_A, C_B, \dots, C_P) \quad (10-93)$$

where $a(t)$ = catalytic activity, time-dependent

$k(T)$ = specific reaction rate, temperature-dependent

C_i = gas-phase concentration of reactants, products, or contaminant

The rate of catalyst decay, r_d , can be expressed in a rate law analogous to Equation (10-93):

Catalyst decay
rate law

$$r_d = -\frac{da}{dt} = p[a(t)]k_d(T)h(C_A, C_B, \dots, C_P) \quad (10-94)$$

where $p[a(t)]$ is some function of the activity, k_d is the specific decay constant, and $h(C_i)$ is the functionality of r_d on the reacting species concentrations. For the cases presented in this chapter, this functionality either will be independent of concentration (i.e., $h = 1$) or will be a linear function of species concentration (i.e., $h = C_i$).

The functionality of the activity term, $p[a(t)]$, in the decay law can take a variety of forms. For example, for a first-order decay,

$$p(a) = a \quad (10-95)$$

and for a second-order decay,

$$p(a) = a^2 \quad (10-96)$$

The particular function, $p(a)$, will vary with the gas catalytic system being used and the reason or mechanism for catalytic decay.

10.7.1 Types of Catalyst Deactivation

- Sintering
- Fouling
- Poisoning

There are three categories into which the loss of catalytic activity can traditionally be divided: sintering or aging, fouling or coking, and poisoning.

Deactivation by Sintering (Aging).³ Sintering, also referred to as aging, is the loss of catalytic activity due to a loss of active surface area resulting from the prolonged exposure to high gas-phase temperatures. The active surface area may be lost either by crystal agglomeration and growth of the metals deposited on the support or by narrowing or closing of the pores inside the catalyst pellet. A change in the surface structure may also result from either surface recrystallization or the formation or elimination of surface defects (active sites). The reforming of heptane over platinum on alumina is an example of catalyst deactivation as a result of sintering.

Figure 10-23 shows the loss of surface area resulting from the flow of the solid porous catalyst support at high temperatures to cause pore closure. Figure 10-24 shows the loss of surface area by atomic migration and agglomeration of small metal sites deposited on the surface into a larger site where the interior atoms are not accessible to the reaction. Sintering is usually negligible at temperatures below 40% of the melting temperature of the solid.⁴

The catalyst support becomes soft and flows, resulting in pore closure.

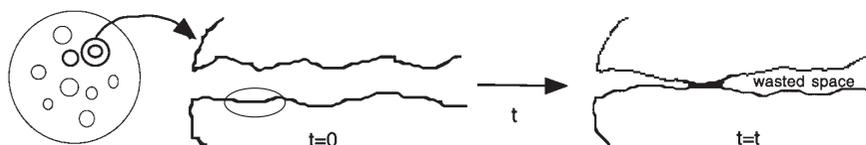


Figure 10-23 Decay by sintering: pore closure.

The atoms move along the surface and agglomerate.

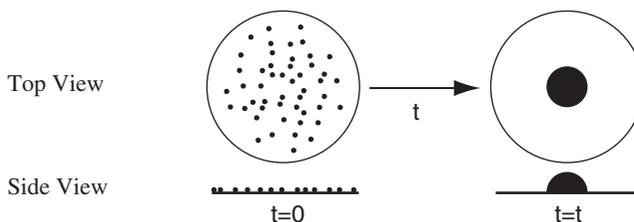


Figure 10-24 Decay by sintering: agglomeration of deposited metal sites.

Deactivation by sintering may in some cases be a function of the mainstream gas concentration. Although other forms of the sintering decay rate laws exist, one of the most commonly used decay laws is second order with respect to the present activity:

$$r_d = k_d a^2 = - \frac{da}{dt} \quad (10-97)$$

³ See G. C. Kuczynski, Ed., *Sintering and Catalysis*, Vol. 10 of *Materials Science Research* (New York: Plenum Press, 1975).

⁴ R. Hughes, *Deactivation of Catalysts* (San Diego: Academic Press, 1984).

Integrating, with $a = 1$ at time $t = 0$, yields

Sintering: second-order decay

$$a(t) = \frac{1}{1 + k_d t} \quad (10-98)$$

The amount of sintering is usually measured in terms of the active surface area of the catalyst S_a :

$$S_a = \frac{S_{a0}}{1 + k_d t} \quad (10-99)$$

The sintering decay constant, k_d , follows the Arrhenius equation

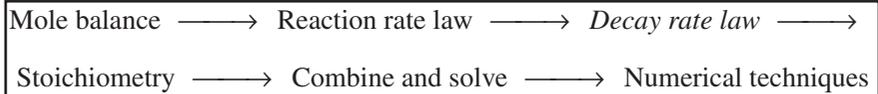
$$k_d = k_d(T_0) \exp \left[\frac{E_d}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (10-100)$$

Minimizing sintering

The decay activation energy, E_d , for the reforming of heptane on Pt/Al₂O₃ is on the order of 70 kcal/mol, which is rather high. As mentioned earlier sintering can be reduced by keeping the temperature below 0.3 to 0.4 times the metal's melting point.

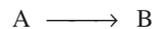
We will now stop and consider reactor design for a fluid–solid system with decaying catalyst. To analyze these reactors, we only add one step to our algorithm, that is, determine the catalyst decay law. The sequence is shown here.

The algorithm



Example 10–5 *Calculating Conversion with Catalyst Decay in Batch Reactors*

The first-order isomerization



is being carried out isothermally in a batch reactor on a catalyst that is decaying as a result of aging. Derive an equation for conversion as a function of time.

Solution

1. **Design equation:**

$$N_{A0} \frac{dX}{dt} = 2r'_A W \quad (E10-5.1)$$

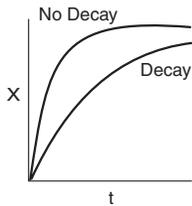
2. **Reaction rate law:**

$$2r'_A = k' a(t) C_A \quad (E10-5.2)$$

One extra step (number 3) is added to the algorithm.



Following the Algorithm



3. **Decay law.** For second-order decay by sintering:

$$a(t) = \frac{1}{1+k_d t} \quad (10-98)$$

4. **Stoichiometry:**

$$C_A = C_{A0}(1 - X) = \frac{N_{A0}}{V} (1 - X) \quad (E10-5.3)$$

5. **Combining** gives us

$$\frac{dX}{dt} = \frac{W}{V} k' a(t) (1-X) \quad (E10-5.4)$$

Let $k = k'W/V$. Then, separating variables, we have

$$\frac{dX}{1-X} = ka(t) dt \quad (E10-5.5)$$

Substituting for a and integrating yields

$$\int_0^X \frac{dX}{1-X} = k \int_0^t \frac{dt}{1+k_d t} \quad (E10-5.6)$$

$$\ln \frac{1}{1-X} = \frac{k}{k_d} \ln(1+k_d t) \quad (E10-5.7)$$

6. **Solving** for the conversion X at any time t , we find that

$$X = 1 - \frac{1}{(1+k_d t)^{k/k_d}} \quad (E10-5.8)$$

This is the conversion that will be achieved in a batch reactor for a first-order reaction when the catalyst decay law is second order. The purpose of this example was to demonstrate the algorithm for isothermal catalytic reactor design for a decaying catalyst. In problem 10-2(e) you are asked to sketch the temperature–time trajectories for various values of k and k_d .

Deactivation by Coking or Fouling. This mechanism of decay (see Figures 10-25 and 10-26) is common to reactions involving hydrocarbons. It results from a carbonaceous (coke) material being deposited on the surface of a catalyst.

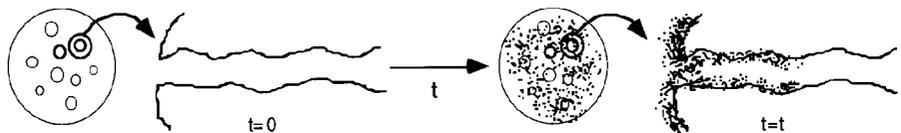
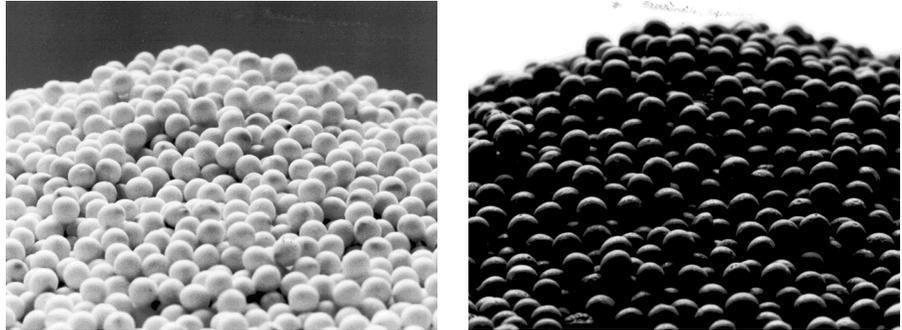


Figure 10-25 Schematic of decay by coking.



(a) Fresh catalyst

(b) Spent catalyst

Figure 10-26 Decay by coking. (Photos courtesy of Engelhard catalyst, copyright by Michael Gaffney Photographer, Mendham, N.J.)

The amount of coke on the surface after a time t has been found to obey the following empirical relationship:

$$C_C = At^n \quad (10-101)$$

where C_C is the concentration of carbon on the surface (g/m^2) and n and A are fouling parameters, which can be functions of the feed rate. This expression was originally developed by Voorhies⁵ and has been found to hold for a wide variety of catalysts and feed streams. Representative values of A and n for the cracking of East Texas light gas oil⁶ yield

$$\% \text{ coke} = 0.47 \sqrt{t(\text{min})}$$

Different functionalities between the activity and amount of coke on the surface have been observed. One commonly used form is

$$a = \frac{1}{k_{Ck} C_C^p + 1} \quad (10-102)$$

or, in terms of time,

$$a = \frac{1}{k_{Ck} A^p t^{np} + 1} = \frac{1}{1 + k' t^m} \quad (10-103)$$

For light Texas gas oil being cracked at 750°F over a synthetic catalyst for short times, the decay law is

$$a = \frac{1}{1 + 7.6 t^{1/2}} \quad (10-104)$$

where t is in seconds.

⁵ A. Voorhies, *Ind. Eng. Chem.*, 37, 318 (1945).

⁶ C. O. Prater and R. M. Lago, *Adv. Catal.*, 8, 293 (1956).

Activity for
deactivation by
coking

Other commonly used forms are

$$a = e^{2\alpha_1 C_C} \quad (10-105)$$

and

$$a = \frac{1}{1 + \alpha_2 C_C} \quad (10-106)$$

A dimensionless fouling correlation has been developed by Pacheco and Petersen.⁷

Minimizing coking

When possible, coking can be reduced by running at elevated pressures (2000 to 3000 kPa) and hydrogen-rich streams. A number of other techniques for minimizing fouling are discussed by Bartholomew.⁸ Catalysts deactivated by coking can usually be regenerated by burning off the carbon. The use of the shrinking core model to describe regeneration is discussed in Section 11.5.1.

Deactivation by Poisoning. Deactivation by this mechanism occurs when the poisoning molecules become irreversibly chemisorbed to active sites, thereby reducing the number of sites available for the main reaction. The poisoning molecule, P, may be a reactant and/or a product in the main reaction, or it may be an impurity in the feed stream.

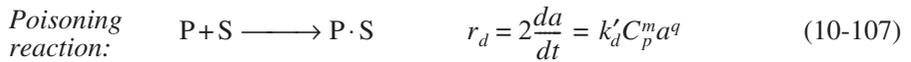
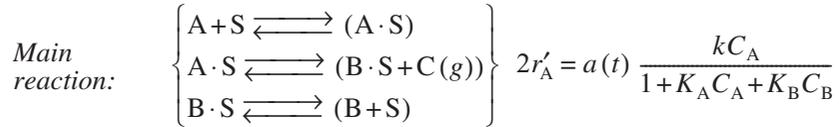
It's going to
cost you.

Side Note. One of the most significant examples of catalyst poisoning occurred at the gasoline pump. Oil companies found that adding lead to the gasoline increased the octane number. The television commercials said “We are going to enhance your gasoline, *but it's going to cost you* for the added tetra-ethyl lead.” So for many years they used lead as an antiknock component. As awareness grew about NO, HC, and CO emission from the engine, it was decided to add a catalytic afterburner in the exhaust system to reduce these emissions. Unfortunately, it was found that the lead in the gasoline poisoned the reactive catalytic sites. So, the television commercials now said “We are going to take the lead out of gasoline but to receive the same level of performance as without lead, *but it's going to cost you* because of the added refining costs to raise the octane number.” Do you think that financially, the consumer would have been better off if they never put the lead in the gasoline in the first place??

Poison in the Feed. Many petroleum feed stocks contain trace impurities such as sulfur, lead, and other components which are too costly to remove, yet poison the catalyst slowly over time. For the case of an impurity, P, in the feed stream, such as sulfur, for example, in the reaction sequence

⁷ M. A. Pacheco and E. E. Petersen, *J. Catal.*, 86, 75 (1984).

⁸ C. Bartholomew, *Chem. Eng.*, Sept. 12, 1984, p. 96.



the surface sites would change with time as shown in Figure 10-27.

Progression of sites
being poisoned

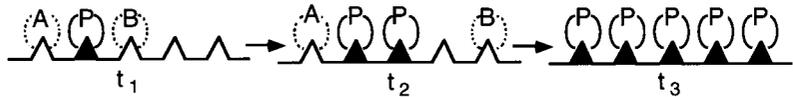


Figure 10-27 Decay by poisoning.

If we assume the rate of removal of the poison, $r_{\text{P}\cdot\text{S}}$, from the reactant gas stream onto the catalyst sites is proportional to the number of sites that are unpoisoned ($C_{t0} - C_{\text{P}\cdot\text{S}}$) and the concentration of poison in the gas phase, C_{P} :

$$r_{\text{P}\cdot\text{S}} = k_d (C_{t0} - C_{\text{P}\cdot\text{S}}) C_{\text{P}}$$

where $C_{\text{P}\cdot\text{S}}$ is the concentration of poisoned sites and C_{t0} is the total number of sites initially available. Because every molecule that is adsorbed from the gas phase onto a site is assumed to poison the site, this rate is also equal to the rate of removal of total active sites (C_t) from the surface:

$$-\frac{dC_t}{dt} = \frac{dC_{\text{P}\cdot\text{S}}}{dt} = r_{\text{P}\cdot\text{S}} = k_d (C_{t0} - C_{\text{P}\cdot\text{S}}) C_{\text{P}}$$

Dividing through by C_{t0} and letting f be the fraction of the total number of sites that have been poisoned yields

$$\frac{df}{dt} = k_d (1 - f) C_{\text{P}} \quad (10-108)$$

The fraction of sites available for adsorption ($1 - f$) is essentially the activity $a(t)$. Consequently, Equation (10-108) becomes

$$2 \frac{da}{dt} = a(t) k_d C_{\text{P}} \quad (10-109)$$

A number of examples of catalysts with their corresponding catalyst poisons are given by Farrauto and Bartholomew.⁹

⁹ R. J. Farrauto and C. H. Bartholomew, *Fundamentals of Industrial Catalytic Processes* (New York: Blackie Academic and Professional, 1997). This book is one of the definitive resources on catalyst decay.

Packed-Bed Reactors. In packed-bed reactors where the poison is removed from the gas phase by being adsorbed on the specific catalytic sites, the deactivation process can move through the packed bed as a wave front. Here, at the start of the operation, only those sites near the entrance to the reactor will be deactivated because the poison (which is usually present in trace amounts) is removed from the gas phase by the adsorption; consequently, the catalyst sites farther down the reactor will not be affected. However, as time continues, the sites near the entrance of the reactor become saturated, and the poison must travel farther downstream before being adsorbed (removed) from the gas phase and attaching to a site to deactivate it. Figure 10-28 shows the corresponding activity profile for this type of poisoning process. We see in Figure 10-28 that by time t_4 the entire bed has become deactivated. The corresponding overall conversion at the exit of the reactor might vary with time as shown in Figure 10-29.

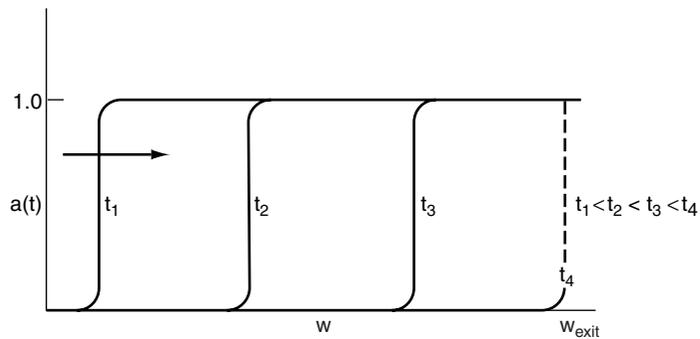


Figure 10-28 Movement of activity front in a packed bed.

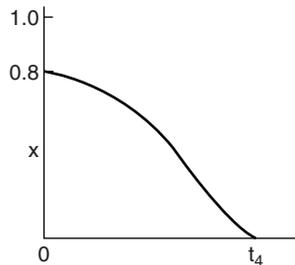


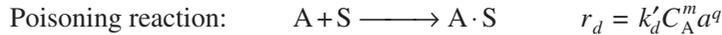
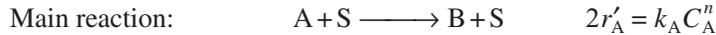
Figure 10-29 Exit conversion as a function of time.



Summary Notes

The partial differential equations that describe the movement of the reaction front shown in Figure 10-28 are derived and solved in an example in the CD-ROM/Web Summary Notes for Chapter 10.

Poisoning by Either Reactants or Products. For the case where the main reactant also acts as a poison, the rate laws are:



An example where one of the reactants acts as a poison is in the reaction of CO and H₂ over ruthenium to form methane, with

$$-r_{\text{CO}} = ka(t)C_{\text{CO}}$$

$$2\frac{da}{dt} = r_d = k'_d a(t) C_{\text{CO}}$$

Similar rate laws can be written for the case when the product B acts as a poison.

For *separable deactivation kinetics* resulting from contacting a poison at a constant concentration C_{P_0} and no spatial variation:

Separable
deactivation
kinetics

$$2\frac{da}{dt} = r_d = k'_d C_{P_0}^n a^n(t) = k_d a^n \quad (10-110)$$

The solution to this equation for the case of first-order decay, $n = 1$

$$2\frac{da}{dt} = k_d a \quad (10-111)$$

is

$$a = e^{2k_d t} \quad (10-112)$$

Empirical Decay Laws. Table 10-7 gives a number of empirical decay laws along with the reaction systems to which they apply.

Key Resource for
catalyst deactivation

One should also see *Fundamentals of Industrial Catalytic Processes*, by Farrauto and Bartholomew,¹⁰ which contains rate laws similar to those in Table 10-7, and also gives a comprehensive treatment of catalyst deactivation.

¹⁰Ibid.

TABLE 10-7. DECAY RATE LAWS

<i>Functional Form of Activity</i>	<i>Decay Reaction Order</i>	<i>Differential Form</i>	<i>Integral Form</i>	<i>Examples</i>
Linear	0	$2\frac{da}{dt} = \beta_0$	$a = 1 - \beta_0 t$	Conversion of <i>para</i> -hydrogen on tungsten when poisoned with oxygen*
Exponential	1	$2\frac{da}{dt} = \beta_1 a$	$a = e^{2\beta_1 t}$	Ethylene hydrogenation on Cu poisoned with CO ^b Paraffin dehydrogenation on Cr·Al ₂ O ₃ ^c Cracking of gas oil ^d Vinyl chloride monomer formation ^e
Hyperbolic	2	$2\frac{da}{dt} = \beta_2 a^2$	$\frac{1}{a} = 1 + \beta_2 t$	Vinyl chloride monomer formation ^f Cyclohexane dehydrogenation on Pt/Al ₂ O ₃ ^g Isobutylene hydrogenation on Ni ^h
Reciprocal power	$\frac{\beta_3 + 1}{\beta_3} = \gamma$ $\frac{\beta_4 + 1}{\beta_4} = n$	$2\frac{da}{dt} = \beta_3 a^n A_0^{1/5}$ $2\frac{da}{dt} = \beta_4 a^n A_0^{1/5}$	$a = A_0 t^{2\beta_3}$ $a = A_0 t^{2\beta_4}$	Cracking of gas oil and gasoline on clay ⁱ Cyclohexane aromatization on NiAl ^j

*D. D. Eley and E. J. Rideal, *Proc. R. Soc. London*, A178, 429 (1941).

^bR. N. Pease and L. Y. Steward, *J. Am. Chem. Soc.*, 47, 1235 (1925).

^cE. F. K. Herington and E. J. Rideal, *Proc. R. Soc. London*, A184, 434 (1945).

^dV. W. Weekman, *Ind. Eng. Chem. Process Des. Dev.*, 7, 90 (1968).

^eA. F. Ogunye and W. H. Ray, *Ind. Eng. Chem. Process Des. Dev.*, 9, 619 (1970).

^fA. F. Ogunye and W. H. Ray, *Ind. Eng. Chem. Process Des. Dev.*, 10, 410 (1971).

^gH. V. Maat and L. Moscou, *Proc. 3rd Int. Congr. Catal.* (Amsterdam: North-Holland, 1965), p. 1277.

^hA. L. Pozzi and H. F. Rase, *Ind. Eng. Chem.*, 50, 1075 (1958).

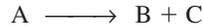
ⁱA. Voorhies, Jr., *Ind. Eng. Chem.*, 37, 318 (1945); E. B. Maxted, *Adv. Catal.*, 3, 129 (1951).

^jC. G. Ruderhausen and C. C. Watson, *Chem. Eng. Sci.*, 3, 110 (1954).

Source: J. B. Butt, *Chemical Reactor Engineering—Washington, Advances in Chemistry Series 109* (Washington, D.C.: American Chemical Society, 1972), p. 259. Also see CES 23, 881(1968)

Example 10-6 Catalyst Decay in a Fluidized Bed Modeled as a CSTR

The gas-phase cracking reaction¹¹



is carried out in a *fluidized* CSTR reactor. The feed stream contains 80% gas oil (A) and 20% inert I. The gas oil contains sulfur compounds, which poison the catalyst. As a first approximation we will assume that the cracking reaction is first order in the gas oil concentration. The rate of catalyst decay is first order in the present activity, and first order in the reactant concentration. Assuming that the bed can be modeled as a well-mixed CSTR, determine the reactant concentration, activity, and conversion as a function of time. The volumetric feed rate to the reactor is 5000 m³/h. There are 50,000 kg of catalyst in the reactor and the bulk density is 500 kg/m³.

Additional information:

$$C_{A0} = 0.8 \text{ mol/dm}^3 \quad k = \rho_B k' = 45 \text{ h}^{-1}$$

$$C_{T0} = 1.0 \text{ mol/dm}^3 \quad k_d = 9 \text{ dm}^3/\text{mol} \cdot \text{h}$$

Solution

1. **Mole Balance** on reactant:

$$v_0 C_{A0} - v C_A + r'_A W = \frac{dN_A}{dt} \quad (\text{E10-6.1})$$

Recalling $N_A = C_A V$ and $r'_A V = r'_A W$, then for constant volume we have

$$v_0 C_{A0} - v C_A + r'_A V = V \frac{dC_A}{dt} \quad (\text{E10-6.2})$$

2. **Rate Law:**

$$-r'_A = k a C_A \quad (\text{E10-6.3})$$

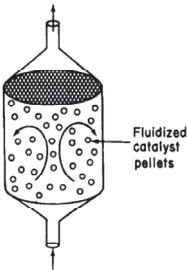
3. **Decay Law:**

$$2 \frac{da}{dt} = k_d a C_A \quad (\text{E10-6.4})$$

4. **Stoichiometry** (gas phase, $P = P_0$, $T = T_0$). From Equation (3-41) we have

$$\frac{v}{v_0} = \frac{F_T}{F_{T0}} = (1 + \epsilon X) \quad (\text{E10-6.5})$$

¹¹For simplicity, gas oil is used to represent the reactive portion of the feed. In actuality, gas oil, distilled from crude, is made up of complex hydrocarbons, which can be cracked, and simple hydrocarbons, which will not crack and are therefore inert in this application.



$$X = 1 - \frac{F_A}{F_{A0}} = 1 - \frac{C_A v}{C_{A0} v_0}$$

$$\frac{v}{v_0} = 1 + \varepsilon - \varepsilon \frac{C_A v}{C_{A0} v_0}$$

$$\varepsilon = y_{A0} \delta = (1 + 1 - 1) y_{A0} = y_{A0} = \frac{C_{A0}}{C_{T0}}$$

$$\frac{v}{v_0} = 1 + y_{A0} - \frac{C_A v}{C_{T0} v_0} \quad (\text{E10-6.6})$$

Solving for v yields

$$v = v_0 \frac{1 + y_{A0}}{1 + C_A / C_{T0}} \quad (\text{E10-6.7})$$

5. **Combining** gives us

$$v_0 C_{A0} - \frac{v_0 (1 + y_{A0})}{1 + C_A / C_{T0}} C_A - k_a C_A V = V \frac{dC_A}{dt} \quad (\text{E10-6.8})$$

Dividing both sides of Equation (E10-6.8) by the volume and writing the equation in terms of $t = V/v_0$, we obtain

$$\frac{dC_A}{dt} = \frac{C_{A0}}{t} - \frac{(1 + y_{A0}) / (1 + C_A / C_{T0}) + atk}{t} C_A \quad (\text{E10-6.9})$$

As an approximation we assume the conversion to be

$$X = \frac{F_{A0} - F_A}{F_{A0}} = 1 - \frac{v C_A}{v_0 C_{A0}} = 1 - \left(\frac{1 + y_{A0}}{1 + C_A / C_{T0}} \right) \left(\frac{C_A}{C_{A0}} \right) \quad (\text{E10-6.10})$$

Calculation of reactor volume and space time yields

$$V = \frac{W}{\rho_b} = \frac{50,000}{500 \text{ kg/m}^3} = 100 \text{ m}^3$$

$$t = \frac{V}{v_0} = \frac{100 \text{ m}^3}{5000 \text{ m}^3/\text{h}} = 0.02 \text{ h}$$

Equations (E10-6.4), (E10-6.9), and (E10-6.10) are solved using Polymath as the ODE solver. The Polymath program is shown in Table E10-6.1. The solution is shown in Figure E10-6.1.

TABLE E10-6.1. POLYMATH PROGRAM

ODE Report (RK45)

Differential equations as entered by the user

$$\begin{aligned} [1] \quad & d(a)/d(t) = -kd \cdot a \cdot Ca \\ [2] \quad & d(Ca)/d(t) = Ca0/tau - ((1+yao)/(1+Ca/Ct0) + tau \cdot a \cdot k) \cdot Ca/tau \end{aligned}$$

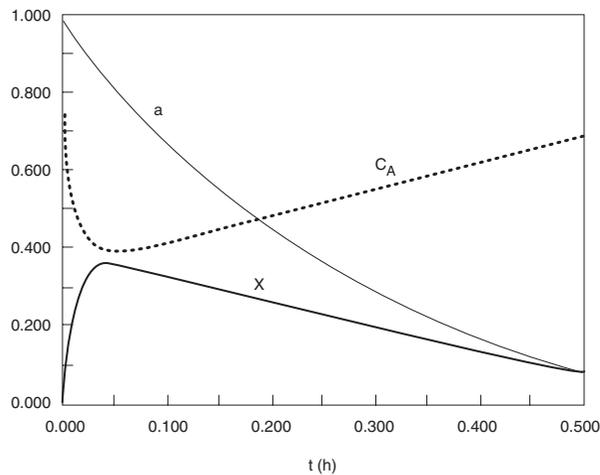
Explicit equations as entered by the user

$$\begin{aligned} [1] \quad & kd = 9 \\ [2] \quad & Ca0 = .8 \\ [3] \quad & tau = .02 \\ [4] \quad & Ct0 = 1. \\ [5] \quad & k = 45 \\ [6] \quad & yao = Ca0/Ct0 \\ [7] \quad & X = 1 - (1+yao)/(1+Ca/Ct0) \cdot Ca/Ca0 \end{aligned}$$



Living Example Problem

C_A , X , and a time trajectories in a CSTR *not* at steady state

**Figure E10-6.1** Variation of C_A (mol/dm³), a , and X with time in a CSTR.

The conversion variable X does not have much meaning in flow systems not at steady state, owing to the accumulation of reactant. However, here the space time is relatively short ($t = 0.02$ h) in comparison with the time of decay $t = 0.5$ h. Consequently, we can assume a quasi-steady state and consider the conversion as defined by Equation (E10-6.10) valid. Because the catalyst decays in less than an hour, a fluidized bed would not be a good choice to carry out this reaction.

We will now consider three reaction systems that can be used to handle systems with decaying catalyst. We will classify these systems as those having slow, moderate, and rapid losses of catalytic activity. To offset the decline in chemical reactivity of decaying catalysts in continuous flow reactors, the following three methods are commonly used:

Matching the reactor type with speed of catalyst decay

- Slow decay – *Temperature–Time Trajectories* (10.7.2)
- Moderate decay – *Moving-Bed Reactors* (10.7.3)
- Rapid decay – *Straight-Through Transport Reactors* (10.7.4)

10.7.2 Temperature–Time Trajectories

In many large-scale reactors, such as those used for hydrotreating, and reaction systems where deactivation by poisoning occurs, the catalyst decay is relatively slow. In these continuous flow systems, constant conversion is usually necessary in order that subsequent processing steps (e.g., separation) are not upset. One way to maintain a constant conversion with a decaying catalyst in a packed or fluidized bed is to increase the reaction rate by steadily increasing the feed temperature to the reactor. Operation of a “fluidized” bed in this manner is shown in Figure 10-30.

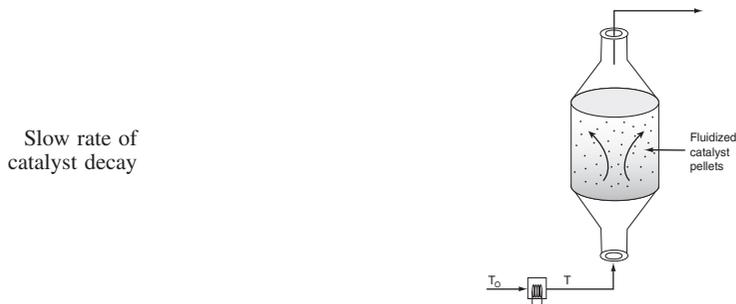


Figure 10-30 Reactor with preheater to increase feed temperature.

We are going to increase the feed temperature in such a manner that the reaction rate remains constant with time:

$$2r'_A(t=0, T_0) = 2r'_A(t, T) = a(t, T)[2r'_A(t=0, T)]$$

For a first-order reaction we have

$$k(T_0)C_A = a(t, T)k(T)C_A$$

We will neglect any variations in concentration so that the product of the activity (a) and specific reaction rate (k) is constant and equal to the specific reaction rate, k_0 at time $t = 0$ and temperature T_0 ; that is,

$$k(T)a(t, T) = k_0 \quad (10-113)$$

Gradually raising the temperature can help offset effects of catalyst decay.

The goal is to find *how* the temperature should be increased with time (i.e., the temperature–time trajectory) to maintain constant conversion. Using the Arrhenius equation to substitute for k in terms of the activation energy, E_A , gives

$$k_0 e^{(E_A/R)(1/T_0 - 1/T)} a = k_0 \quad (10-114)$$

Solving for $1/T$ yields

$$\frac{1}{T} = \frac{R}{E_A} \ln a + \frac{1}{T_0} \quad (10-115)$$

The decay law also follows an Arrhenius-type temperature dependence.

$$2 \frac{da}{dt} = k_{d0} e^{(E_d/R)(1/T_0 - 21/T)} a^n \quad (10-116)$$

where k_{d0} = decay constant at temperature T_0 , s^{-1}

Comparing theory
and experiment

E_A = activation energy for the main reaction (e.g., $A \rightarrow B$), kJ/mol

E_d = activation energy for catalyst decay, kJ/mol

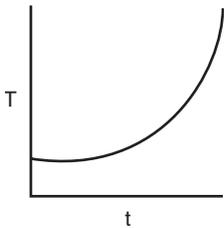
Substituting Equation (10-115) into (10-116) and rearranging yields

$$2 \frac{da}{dt} = k_{d0} \exp\left(2 \frac{E_d}{E_A} \ln a\right) a^n = k_{d0} a^{(n + 2E_d/E_A)} \quad (10-117)$$

Integrating with $a = 1$ at $t = 0$ for the case $n \neq (1 + E_d/E_A)$, we obtain

$$t = \frac{1 - a^{1 + 2nE_d/E_A}}{k_{d0}(1 - n + E_d/E_A)} \quad (10-118)$$

Solving Equation (10-114) for a and substituting in (10-118) gives



$$t = \frac{1 - \exp\left[\frac{E_A - nE_A + E_d}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]}{k_{d0}(1 - n + E_d/E_A)} \quad (10-119)$$

Equation (10-119) tells us how the temperature of the catalytic reactor should be increased with time in order for the reaction rate to remain constant.

In many industrial reactions, the decay rate law changes as temperature increases. In hydrocracking, the temperature–time trajectories are divided into three regimes. Initially, there is fouling of the acidic sites of the catalyst followed by a linear regime due to slow coking, and finally, accelerated coking characterized by an exponential increase in temperature. The temperature–time trajectory for a deactivating hydrocracking catalyst is shown in Figure 10-31.

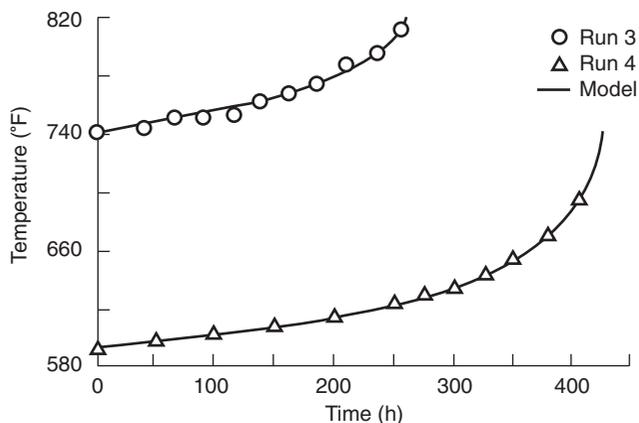
For a first-order decay, Krishnaswamy and Kittrell's expression [Equation (10-119)] for the temperature–time trajectory reduces to

$$t = \frac{E_A}{k_{d0}E_d} [1 - e^{(E_d/R)(1/T_0 - 1/T)}] \quad (10-120)$$

10.7.3 Moving-Bed Reactors

Reaction systems with significant catalyst decay require the continual regeneration and/or replacement of the catalyst. Two types of reactors currently in commercial use that accommodate production with decaying catalysts are the moving-bed and straight-through transport reactor. A schematic diagram of a moving-bed reactor (used for catalytic cracking) is shown in Figure 10-32.

Moving bed reactor:
Used for reactions
with moderate rate
of catalyst decay.



Run	E_A (cal/mol)	A (h^{-1})	E_d (cal/mol)	A_d (h^{-1})
3	30.0	0.52×10^{12}	42.145	1.54×10^{11}
4	30.0	0.52×10^{12}	37.581	2.08×10^{11}

Figure 10-31 Temperature–time trajectories for deactivating hydrocracking catalyst, runs 3 and 4. [Reprinted with permission from S. Krishnaswamy and J. R. Kittrell, *Ind. Eng. Chem. Process Des. Dev.*, 18, 399 (1979). Copyright © 1979 American Chemical Society.]

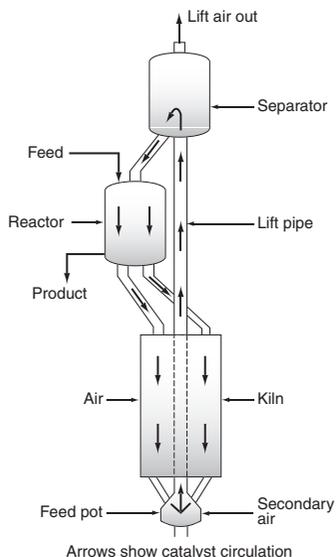


Figure 10-32 Thermoform catalytic cracking (TCC) unit. [From V. Weekman, *AIChE Monogr. Ser.*, 75(11), 4 (1979). With permission of the AIChE. Copyright © 1979 AIChE. All rights reserved.]

The value of the catalyst contained in a reactor of this type is approximately \$1 million

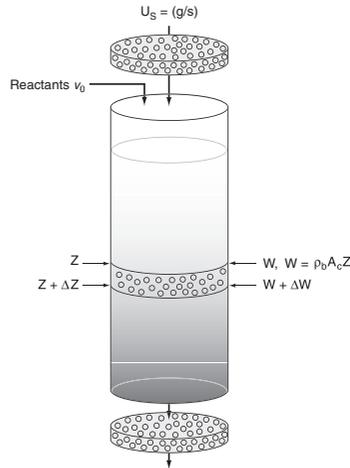


Figure 10-33 Moving-bed reactor—schematic.

The freshly regenerated catalyst enters the top of the reactor and then moves through the reactor as a compact packed bed. The catalyst is coked continually as it moves through the reactor until it exits the reactor into the kiln, where air is used to burn off the carbon. The regenerated catalyst is lifted from the kiln by an airstream and then fed into a separator before it is returned to the reactor. The catalyst pellets are typically between $\frac{1}{8}$ and $\frac{1}{4}$ in. in diameter.

The reactant feed stream enters at the top of the reactor and flows rapidly through the reactor relative to the flow of the catalyst through the reactor (Figure 10-33). If the feed rates of the catalyst and the reactants do not vary with time, the reactor operates at steady state; that is, conditions at any point in the reactor do not change with time. The mole balance on reactant A over ΔW is

$$\left[\begin{array}{c} \text{Molar} \\ \text{flow} \\ \text{rate of A in} \end{array} \right] - \left[\begin{array}{c} \text{Molar} \\ \text{flow} \\ \text{rate of A out} \end{array} \right] + \left[\begin{array}{c} \text{Molar} \\ \text{rate of} \\ \text{generation of A} \end{array} \right] = \left[\begin{array}{c} \text{Molar} \\ \text{rate of} \\ \text{accumulation of A} \end{array} \right]$$

$$F_A(W) - F_A(W+\Delta W) + r'_A \Delta W = 0 \quad (10-121)$$

Dividing by ΔW , letting ΔW approach zero, and expressing the flow rate in terms of conversion gives

$$F_{A0} \frac{dX}{dW} = 2r'_A \quad (2-17)$$

The rate of reaction at any time t is

$$2r'_A = a(t)[2r'_A(t=0)] = a(t)[k \text{ fn}(C_A, C_B, \dots, C_p)] \quad (10-93)$$

The activity, as before, is a function of the time the catalyst has been in contact with the reacting gas stream. The decay rate law is

$$2 \frac{da}{dt} = k_d a^n \quad (10-110)$$

We now need to relate the contact time to the weight of the catalyst. Consider a point z in the reactor, where the reactant gas has passed cocurrently through a catalyst weight W . Since the solid catalyst is moving through the bed at a rate U_s (mass per unit time), the time t that the catalyst has been in contact with the gas when the catalyst reaches a point z is

$$t = \frac{W}{U_s} \quad (10-122)$$

If we now differentiate Equation (10-122)

$$dt = \frac{dW}{U_s} \quad (10-123)$$

and combine it with the decay rate law, we obtain

$$\boxed{2 \frac{da}{dW} = \frac{k_d}{U_s} a^n} \quad (10-124)$$

The activity equation is combined with the mole balance:

$$\boxed{\frac{dX}{dW} = \frac{a[2r'_A(t=0)]}{F_{A0}}} \quad (10-125)$$

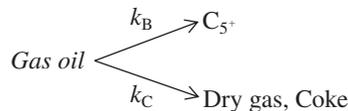
The design equation
for moving-bed
reactors



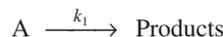
Living Example Problem

Example 10-7 Catalytic Cracking in a Moving-Bed Reactor

The catalytic cracking of a gas oil charge, A, to form C_5^+ (B) and to form coke and dry gas (C) is to be carried out in a screw-type conveyor moving-bed reactor at 900°F :



This reaction can also be written as



While pure hydrocarbons are known to crack according to a first-order rate law, the fact that the gas oil exhibits a wide spectrum of cracking rates gives rise to the fact that the lumped cracking rate is well represented by a second-order rate law (see Problem CDP5-H_B) with the following specific reaction rate:¹²

¹² Estimated from V. W. Weekman and D. M. Nace, *AIChE J.*, 16, 397 (1970).

$$2r'_A = 0.60 \frac{(\text{dm})^6}{(\text{g cat})(\text{mol})(\text{min})} C_A^2$$

The catalytic deactivation is independent of gas-phase concentration and follows a first-order decay rate law, with a decay constant of 0.72 reciprocal minutes. The feed stream is diluted with nitrogen so that as a first approximation, volume changes can be neglected with reaction. The reactor contains 22 kg of catalyst that moves through the reactor at a rate of 10 kg/min. The gas oil is fed at a rate of 30 mol/min at a concentration of 0.075 mol/dm³. Determine the conversion that can be achieved in this reactor.

Solution

1. Design Equation:

$$F_{A0} \frac{dX}{dW} = a (2r'_A) \quad (\text{E10-7.1})$$

2. Rate Law:

$$2r'_A = kC_A^2 \quad (\text{E10-7.2})$$

3. Decay Law. First-order decay

$$2 \frac{da}{dt} = k_d a$$

Using Equation (10-124), we obtain

$$2 \frac{da}{dW} = \frac{k_d}{U_s} a \quad (\text{E10-7.3})$$

Integrating

$$a = e^{2(k_d/U_s)W} \quad (\text{E10-7.4})$$

4. Stoichiometry. If $v \approx v_0$ [see Problem P10-2(g)] then

$$C_A = C_{A0}(1 - X) \quad (\text{E10-7.5})$$

5. Combining, we have

$$F_{A0} \frac{dX}{dW} = e^{2(k_d/U_s)W} kC_{A0}^2 (1-X)^2 \quad (\text{E10-7.6})$$

6. Separating and integrating yields

$$\frac{F_{A0}}{kC_{A0}^2} \int_0^X \frac{dX}{(1-X)^2} = \int_0^W e^{2(k_d/U_s)W} dW \quad (\text{E10-7.7})$$

$$\frac{X}{1-X} = \frac{kC_{A0}^2 U_s}{F_{A0} k_d} (1 - e^{2k_d W/U_s}) \quad (\text{E10-7.8})$$

Moving beds:
moderate rate of
catalyst decay

7. Numerical evaluation:

$$\frac{X}{1-X} = \frac{0.6 \text{ dm}^6}{\text{mol} \cdot \text{g cat} \cdot \text{min}} \times \frac{(0.075 \text{ mol/dm}^3)^2}{30 \text{ mol/min}} \frac{10,000 \text{ g cat/min}}{0.72 \text{ min}^{-1}}$$

$$\times \left(1 - \exp \left[\frac{(-0.72 \text{ min}^{-1})(22 \text{ kg})}{10 \text{ kg/min}} \right] \right)$$

$$\frac{X}{1-X} = 1.24$$

$$X = 55\%$$

We will now rearrange Equation (E10-7.8) to a form more commonly found in the literature. Let λ be a dimensionless decay time:

$$\lambda = k_d t = \frac{k_d W}{U_s} \quad (10-126)$$

and Da_2 be the Damköhler number for a second-order reaction (*a reaction rate divided by a transport rate*) for a packed-bed reactor:

$$\text{Da}_2 = \frac{(k C_{A0}^2)(W)}{F_{A0}} = \frac{k C_{A0} W}{v_0} \quad (10-127)$$

Through a series of manipulations we arrive at the equation for the conversion in a *moving bed* where a second-order reaction is taking place:¹³

Second-order
reaction in a
moving-bed reactor

$$X = \frac{\text{Da}_2(1 - e^{-2\lambda})}{\lambda + \text{Da}_2(1 - e^{-2\lambda})} \quad (10-128)$$

Similar equations are given or can easily be obtained for other reaction orders or decay laws.

Heat Effects in Moving Beds. We shall consider two cases for modeling the temperature profile in the moving-bed reactor. In one case the temperature of the solid catalyst and the temperature of the gas are different and in the other case they are the same.

Case 1 ($T \neq T_s$). The rate of heat transfer between the gas at temperature T and the solid catalyst particles at temperature T_s is

$$Q_p = h \tilde{a}_p (T - T_s) \quad (10-129)$$

where h = heat transfer coefficient, $\text{kJ/m}^2 \cdot \text{s} \cdot \text{K}$

\tilde{a}_p = solid catalyst surface area per mass of catalyst in the bed, $\text{m}^2/\text{kg cat}$

T_s = temperature of the solid, K. Also, T_a = temperature of heat exchange fluid, K

¹³Ibid.

The energy balance on the gas phase is

$$\text{Energy balance} \quad \frac{dT}{dW} = \frac{U\tilde{a}_w(T_a - T) + h\tilde{a}_p(T_s - T)}{\Sigma F_i C_{P_i}} \quad (10-130)$$

If D_p is the pipe diameter (m), ρ_B is the bulk catalyst density (kg/m^3), and \tilde{a}_w is the wall surface area per mass of catalyst (m^2/kg)

$$\tilde{a}_w = \frac{4}{D_p \rho_B} \quad (10-131)$$

The energy balance on the solid catalyst is

$$\text{Heat exchange between catalyst particle and gas} \quad \frac{dT_s}{dW} = -\frac{h\tilde{a}_p(T_s - T) + (r'_A)(\Delta H_{R_x})}{U_s C_{P_s}} \quad (10-132)$$

where C_{P_s} ($\text{J/kg}\cdot\text{K}$) is the heat capacity of the solids, U_s (kg/s) the catalyst loading, and \tilde{a}_p is the external surface area of the catalyst pellet per unit mass of catalyst bed:

$$\tilde{a}_p = \frac{6}{d_p \rho_b} \quad (10-133)$$

where d_p is the pellet diameter.

Case 2 ($T_s = T$). If the product of the heat transfer coefficient, h , and the surface area, \tilde{a}_p , is very large, we can assume that the solid and gas temperatures are identical. Under these circumstances the energy balance becomes

$$\frac{dT}{dW} = \frac{U\tilde{a}_w(T_a - T) + (r'_A)(\Delta H_{R_x})}{U_s C_{P_s} + \Sigma F_i C_{P_i}} \quad (10-134)$$

10.7.4 Straight-Through Transport Reactors (STTR)

This reactor is used for reaction systems in which the catalyst deactivates very rapidly. Commercially, the STTR is used in the production of gasoline from the cracking of heavier petroleum fractions where coking of the catalyst pellets occurs very rapidly. In the STTR, the catalyst pellets and the reactant feed enter together and are transported very rapidly through the reactor. The bulk density of the catalyst particle in the STTR is significantly smaller than in moving-bed reactors, and often the particles are carried through at the same velocity as the gas velocity. In some places the STTR is also referred to as a circulating fluidized bed (CFB). A schematic diagram is shown in Figure 10-34.

STTR: Used when catalyst decay (usually coking) is very rapid

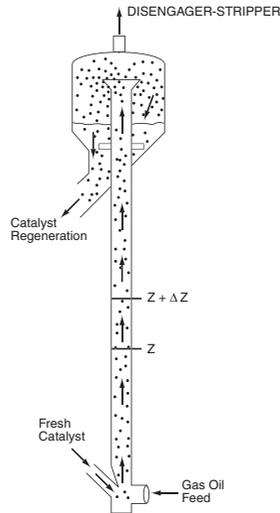


Figure 10-34 Straight-through transport reactor.

A mole balance on the reactant A over the differential reactor volume

$$\Delta V = A_C \Delta z$$

is

$$F_A|_z - F_A|_{z+\Delta z} + r_A A_C \Delta z = 0$$

Dividing by Δz and taking the limit as $\Delta z \rightarrow 0$ and recalling that $r_A = \rho_B r'_A$, we obtain

$$\frac{dF_A}{dz} = r_A A_C = r'_A \rho_B A_C \quad (10-135)$$

In terms of conversion and catalyst activity,

$$\frac{dX}{dz} = \left(\frac{\rho_B A_C}{F_{A0}} \right) [2r'_A(t=0)] a(t) \quad (10-136)$$

For a catalyst particle traveling through the reactor with a velocity U_p , the time the catalyst pellet has been in the reactor when it reaches a height z is just

$$t = \frac{z}{U_p} \quad (10-137)$$

Substituting for time t in terms of distance z [i.e., $a(t) = a(z/U_p)$], the mole balance now becomes

$$\frac{dX}{dz} = \frac{\rho_B A_C [2r'_A(t=0)] a(z/U_p)}{F_{A0}}$$

The entering molar flow rate, F_{A0} , can be expressed in terms of the gas velocity U_g , C_{A0} , and A_C :

$$F_{A0} = U_o A_C C_{A0}$$

Substituting for F_{A0} , we have

$$\frac{dX}{dz} = \frac{\rho_B a(z/U_p) [2r'_A(t=0)]}{C_{A0} U_o} \quad (10-138)$$



Living Example Problem

A typical cost of the catalyst in the system is \$1 million

Example 10-8 Decay in a Straight-Through Transport Reactor

The vapor-phase cracking of a gas oil is to be carried out in a straight-through transport reactor (STTR) that is 10 m high and 1.5 m in diameter. Gas-oil is a mixture of normal and branched paraffins (C_{12} – C_{40}), naphthenes, and aromatics, all of which will be lumped as a single species, A. We shall lump the primary hydrocarbon products according to distillate temperature into two respective groups, dry gas (C – C_4) B and gasoline (C_5 – C_{14}) C. The reaction



can be written symbolically as



Both B and C are adsorbed on the surface. The rate law for a gas-oil cracking reaction on fresh catalyst can be approximated by

$$-r'_A = \frac{k' P_A}{1 + K_A P_A + K_B P_B + K_C P_C}$$

with $k' = 0.0014$ kmol/kg cat \cdot s \cdot atm, $K_A = 0.05$ atm $^{-1}$, $K_B = 0.15$ atm $^{-1}$, and $K_C = 0.1$ atm $^{-1}$. The catalyst decays by the deposition of coke, which is produced in most cracking reactions along with the reaction products. The decay law is

$$a = \frac{1}{1 + At^{1/2}} \quad \text{with } A = 7.6 \text{ s}^{-1/2}$$

Pure gas-oil enters at a pressure of 12 atm and a temperature of 400°C. The bulk density of catalyst in the STTR is 80 kg cat/m 3 . Plot the activity and conversion of gas oil up the reactor for entering gas velocity $U_0 = 2.5$ m/s.

Solution

Mole Balance:

$$F_{A0} \frac{dX}{dz} = -r_A A_C$$

$$\frac{dX}{dz} = \frac{-r_A}{U_o C_{A0}} \quad (E10-8.1)$$

The height of the catalyst particle at time “t” after entering the STTR is

$$z = \int_0^t U dt$$

Differentiating, we can find a relation between the time the catalyst particle has been in the STTR and reached a height z which we can use to find the activity a.

$$\frac{dt}{dz} = \frac{1}{U}$$

Rate Law:

$$-r_A = \rho_B(-r'_A) \quad (\text{E10-8.2})$$

$$-r'_A = a[-r'_A(t=0)] \quad (\text{E10-8.3})$$

On fresh catalyst

$$-r'_A(t=0) = k' \frac{P_A}{1 + K_A P_A + K_B P_B + K_C P_C} \quad (\text{E10-8.4})$$

Combining Equations (E10-8.2) through (E10-8.4) gives

$$-r_A = a \left(\rho_B k' \frac{P_A}{1 + K_A P_A + K_B P_B + K_C P_C} \right) \quad (\text{E10-8.5})$$

Decay law. Assuming that the catalyst particle and gas travel up the reactor at the velocity $U_p = U_g = U$, we obtain

$$t = \frac{z}{U} \quad (\text{E10-8.6})$$

$$a = \frac{1}{1 + A(z/U)^{1/2}} \quad (\text{E10-8.7})$$

where $U = v/A_C = v_0(1 + 'X)/A_C$ and $A_C = \pi D^2/4$.

Stoichiometry (gas phase isothermal and no pressure drop):

$$P_A = P_{A0} \frac{1-X}{1+'X} \quad (\text{E10-8.8})$$

$$P_B = \frac{P_{A0} X}{1+'X} \quad (\text{E10-8.9})$$

$$P_C = P_B \quad (\text{E10-8.10})$$

Parameter Evaluation:

$$' = y_{A0} \delta = (1 + 1 - 1) = 1$$

$$U = U_0(1 + 'X)$$

$$C_{A0} = \frac{P_{A0}}{RT_0} = \frac{12 \text{ atm}}{(0.082 \text{ m}^3 \cdot \text{atm}/\text{kmol} \cdot \text{K})(673 \text{ K})} = 0.22 \frac{\text{kmol}}{\text{m}^3}$$



Following the Algorithm

Equations (E10-8.1), (E10-8.5), (E10-8.7), and (E10-8.8) through (E10-8.10) are now combined and solved using an ODE solver. The Polymath program is shown in Table E10-8.1, and the computer output is shown in Figure E10-8.1.

TABLE E10-8.1. EQUATIONS FOR THE STTR: LANGMUIR–HINSHELWOOD KINETICS

ODE Report (RK45)

Differential equations as entered by the user

[1] $d(X)/d(z) = -ra/Uo/Cao$

Explicit equations as entered by the user

[1] $Ka = 0.05$
 [2] $Kb = .15$
 [3] $Pao = 12$
 [4] $eps = 1$
 [5] $A = 7.6$
 [6] $R = 0.082$
 [7] $T = 400+273$
 [8] $\rho = 80$
 [9] $kprime = 0.0014$
 [10] $D = 1.5$
 [11] $Uo = 2.5$
 [12] $Kc = 0.1$
 [13] $U = Uo*(1+eps*X)$
 [14] $Pa = Pao*(1-X)/(1+eps*X)$
 [15] $Pb = Pao*X/(1+eps*X)$
 [16] $vo = Uo*3.1416*D*D/4$
 [17] $Cao = Pao/R/T$
 [18] $Kca = Ka*R*T$
 [19] $Pc = Pb$
 [20] $a = 1/(1+A*(z/U)^{0.5})$
 [21] $raprime = a*(-kprime*Pa/(1+Ka*Pa+Kb*Pb+Kc*Pc))$
 [22] $ra = \rho*raprime$



Living Example Problem

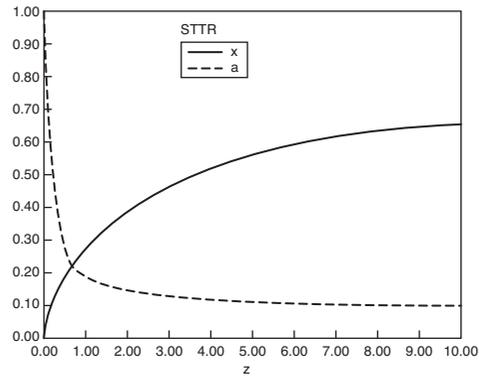


Figure E10-8.1 Activity and conversion profiles.

SUMMARY

1. **Catalyst deactivation.** The catalyst activity is defined as

$$a(t) = \frac{2r'_A(t)}{2r'_A(t=0)} \quad (\text{S10-13})$$

The rate of reaction at any time t is

$$2r'_A = a(t)k(T) \text{fn}(C_A, C_B, \dots, C_P) \quad (\text{S10-14})$$

The rate of catalyst decay is

$$r_d = -\frac{da}{dt} = p[a(t)]k_d(T)g(C_A, C_B, \dots, C_P) \quad (\text{S10-15})$$

For first-order decay:

$$p(a) = a \quad (\text{S10-16})$$

For second-order decay:

$$p(a) = a^2 \quad (\text{S10-17})$$

2. For slow catalyst decay the idea of a **temperature–time trajectory** is to increase the temperature in such a way that the rate of reaction remains constant.

3. The coupled differential equations to be solved for a **moving-bed reactor** are

$$F_{A0} \frac{dX}{dW} = a(2r'_A) \quad (\text{S10-18})$$

For n th-order activity decay and m order in a gas-phase concentration of species i ,

$$2 \frac{da}{dW} = \frac{k_d a^n C_i^m}{U_s} \quad (\text{S10-19})$$

$$t = \frac{W}{U_s} \quad (\text{S10-20})$$

4. The coupled differential equations to be solved in a **straight-through transport reactor** for the case when the particle and gas velocities, U , are identical are

$$\frac{dX}{dz} = \frac{a(t)[-r'_A(t=0)]l \left(\frac{\rho_b A_c}{C_{A0}} \right)}{U_g} \quad (\text{S10-21})$$

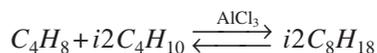
$$t = \frac{z}{U_g} \quad (\text{S10-22})$$

For coking

$$a(t) = \frac{1}{1 + At^{1/2}} \quad (\text{S10-23})$$

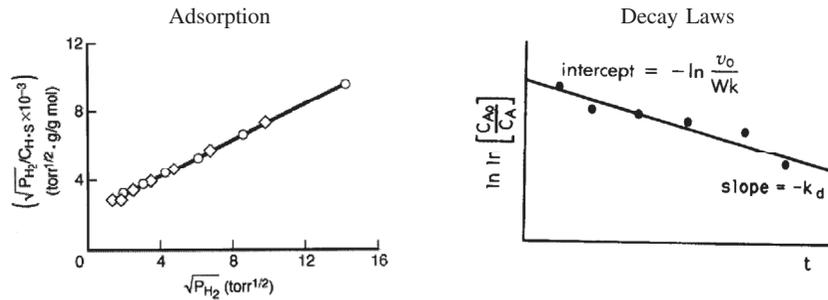
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Alkylation and Dealkylation Reactions. *Alkylation* is the addition of an alkyl group to an organic compound. This type of reaction is commonly carried out in the presence of the Friedel–Crafts catalysts, AlCl_3 along with a trace of HCl . One such reaction is



A similar alkylation is the formation of ethyl benzene from benzene and ethylene:





P10-10C The following data for the hydrogenation of *i*-octene to form *i*-octane were obtained using a differential reactor operated at 200°C.

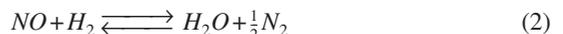
Run	Rate (mol/g·h)	Partial Pressure (atm)		
		Hydrogen	<i>i</i> -Octene	<i>i</i> -Octane
1	0.0362	1	1	0
2	0.0239	1	1	1
3	0.0390	3	1	1
4	0.0351	1	3	1
5	0.0114	1	1	3
6	0.0534	10	1	0
7	0.0280	1	10	0
8	0.0033	1	1	10
9	0.0380	2	2	2
10	0.0090	1	1	4
11	0.0127	0.6	0.6	0.6
12	0.0566	5	5	5

- Develop a rate law, and evaluate all the rate law parameters.
- Suggest a mechanism consistent with the experimental data.
Hydrogen and *i*-octene are to be fed in stoichiometric proportions at a total rate of 5 mol/min at 200°C and 3 atm.
- Neglecting pressure drop, calculate the catalyst weight necessary to achieve 80% conversion of *i*-octene in a CSTR and in a plug-flow reactor.
- If pressure drop is taken into account and the $\frac{1}{8}$ -in. catalyst pellets are packed in $1\frac{1}{2}$ -in. schedule 80 pipes 35 ft long, what catalyst weight is necessary to achieve 80% conversion? The void fraction is 40% and the density of the catalyst is 2.6 g/cm³.

P10-16b In the production of ammonia



the following side reaction occurs:



Ayen and Peters [*Ind. Eng. Chem. Process Des. Dev.*, 1, 204 (1962)] studied the catalytic reaction of nitric oxide with Girdler G-50 catalyst in a differential reactor at atmospheric pressure. Table P10-16_B shows the reaction rate of the side reaction as a function of P_{H_2} and P_{NO} at a temperature of 375°C.

TABLE P10-16. FORMATION OF WATER

P_{H_2} (atm)	P_{NO} (atm)	Reaction Rate
		$r_{H_2O} \times 10^5$ (g mol/min · g cat) $T = 375^\circ\text{C}, W = 2.39$ g
0.00922	0.0500	1.60
0.0136	0.0500	2.56
0.0197	0.0500	3.27
0.0280	0.0500	3.64
0.0291	0.0500	3.48
0.0389	0.0500	4.46
0.0485	0.0500	4.75
0.0500	0.00918	1.47
0.0500	0.0184	2.48
0.0500	0.0298	3.45
0.0500	0.0378	4.06
0.0500	0.0491	4.75

The following rate laws for side reaction (2), based on various catalytic mechanisms, were suggested:

$$r_{H_2O} = \frac{kK_{NO}P_{NO}P_{H_2}}{1 + K_{NO}P_{NO} + K_{H_2}P_{H_2}} \quad (3)$$

$$r_{H_2O} = \frac{kK_{H_2}K_{NO}P_{NO}}{1 + K_{NO}P_{NO} + K_{H_2}P_{H_2}} \quad (4)$$

$$r_{H_2O} = \frac{k_1K_{H_2}K_{NO}P_{NO}P_{H_2}}{(1 + K_{NO}P_{NO} + K_{H_2}P_{H_2})^2} \quad (5)$$

Find the parameter values of the different rate laws and determine which rate law best represents the experimental data.