Web Example W10–A  Catalyst Decay in a Fluidized Bed Modeled as a CSTR

The gas-phase cracking reaction

\[ \text{Gas oil (g)} \rightarrow \text{Products (g)} \]

\[ \text{A} \rightarrow \text{B} + \text{C} \]

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 m\(^3\)/h. There are 50,000 kg of catalyst in the reactor and the bulk density is 500 kg/m\(^3\).

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:

   \[ v_0 C_{A0} - v C_A + r_A W = \frac{dN_A}{dt} \quad \text{(WE10-A.1)} \]

   Recalling \( N_A = C_A V \) and \( r_A V = r_A' W \), then for constant volume we have

   \[ v_0 C_{A0} - v C_A + r_A V = V \frac{dC_A}{dt} \quad \text{(WE10-A.2)} \]

2. **Rate Law**:

   \[ -r_A = k a C_A \quad \text{(WE10-A.3)} \]

3. **Decay Law**:

   \[ -\frac{d a}{dt} = k_d a C_A \quad \text{(WE10-A.4)} \]

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

   \[ \frac{v}{v_0} = \frac{F}{F_{T0}} = (1 + \epsilon X) \quad \text{(WE10-A.5)} \]

\(^\dagger\) For 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.
\[ X = 1 - \frac{F_A}{F_{A0}} = 1 - \frac{C_A^v}{C_{A0}v_0} \]

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

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

\[ \frac{v}{v_0} = 1 + y_{A0} - \frac{C_A}{C_{T0}v_0} \quad (\text{WE10-A.6}) \]

Solving for \( v \) yields
\[ v = v_0 \frac{1 + y_{A0}}{1 + C_A/C_{T0}} \quad (\text{WE10-A.7}) \]

5. Combining gives us
\[ v_0 C_{A0} - \frac{v_0 (1 + y_{A0})}{1 + C_A/C_{T0}} C_A - kaC_A V = V \frac{dC_A}{dt} \quad (\text{WE10-A.8}) \]

Dividing both sides of Equation (WE10-A.8) by the volume and writing the equation in terms of \( \tau = V/v_0 \), we obtain
\[ \frac{dC_A}{d\tau} = \frac{C_{A0}}{\tau} \left( \frac{1 + y_{A0}}{1 + C_A/C_{T0}} + \frac{a \tau k}{\tau} \right) C_A \quad (\text{WE10-A.9}) \]

As an approximation we assume the conversion to be
\[ X = \frac{F_{A0} - F_A}{F_{A0}} = 1 - \frac{v C_A}{v_0 C_{A0}} = 1 - \left( \frac{1 + y_{A0}}{1 + C_A/C_{T0}} \right) \left( \frac{C_A}{C_{A0}} \right) \quad (\text{WE10-A.10}) \]

Calculation of reactor volume and space time yields
\[ V = \frac{W}{\rho_b} = \frac{50,000}{500 \text{ kg/m}^3} = 100 \text{ m}^3 \]
Equations (WE10-A.4), (WE10-A.9), and (WE10-A.10) are solved using Polymath as the ODE solver. The Polymath program is shown in Table WE10-A.1. The solution is shown in Figure WE10-A.1.

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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 ($\tau = 0.02$ 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 (WE10-A.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.
Web—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

$$Q_p = h \tilde{a}_p (T - T_s)$$  \hspace{1cm} (W10-129)

where $h$ = heat transfer coefficient, kJ/m$^2$·s·K

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

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

The energy balance on the gas phase is

$$\frac{dT}{dW} = \frac{U \tilde{a}_w (T_a - T) + h \tilde{a}_p (T_s - T)}{\Sigma F_i C_{P_i}}$$  \hspace{1cm} (W10-130)

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

$$\tilde{a}_w = \frac{4}{D_p \rho_p}$$  \hspace{1cm} (W10-131)

The energy balance on the solid catalyst is

$$\frac{dT_s}{dW} = \frac{h \tilde{a}_p (T_s - T) + (r'_{\Delta})(\Delta H_{Rx})}{U_s C_{P_s}}$$  \hspace{1cm} (W10-132)

where $C_{P_s}$ (J/kg·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:

$$\tilde{a}_p = \frac{6}{d_p \rho_p}$$  \hspace{1cm} (W10-133)

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

$$\frac{dT}{dW} = \frac{U \tilde{a}_w (T_a - T) + (r'_{\Delta})(\Delta H_{Rx})}{U_s C_{P_s} + \Sigma F_i C_{P_i}}$$  \hspace{1cm} (W10-134)
The elementary irreversible gas-phase catalytic reaction

\[ \text{A} \xrightarrow{k_1} \text{B} \]

is carried out isothermally in a batch reactor. The catalyst deactivation follows a first-order decay law and is independent of the concentrations of both A and B.

(a) Determine a general expression for catalyst activity as a function of time.

(b) Make a qualitative sketch of catalyst activity as a function of time. Does \( a(t) \) ever equal zero for a first-order decay law?

(c) Write out the general algorithm and derive an expression for conversion as a function of time, the reactor parameters, and the catalyst parameters.

Fill in the following algorithm

\[ \text{Mole balance} \]
\[ \text{Rate law} \]
\[ \text{Decay law} \]
\[ \text{Stoichiometry} \]
\[ \text{Combine} \]
\[ \text{Solve} \]

1. Separate
2. Integrate

\[ \text{Ans.:} \quad X = 1 - \exp \left[ \frac{k_1 W}{k_d V_0} (1 - \exp(-k_d t)) \right] \]

(d) Calculate the conversion and catalyst activity in the reactor after 10 minutes at 300 K.

(e) How would you expect your results in parts (b) and (d) to change if the reaction were run at 400 K? Briefly describe the trends qualitatively.

(f) Calculate the conversion and catalyst activity in the reactor after 10 minutes if the reaction were run at 400 K instead of 300 K. Do your results match the predictions in part (e)?

Additional information:

- \( C_{A0} = 1 \text{ mol/dm}^3 \)
- \( V_0 = 1 \text{ dm}^3 \)
- \( W = 1 \text{ kg} \)
- \( k_d = 0.1 \text{ min}^{-1} \text{ at } 300 \text{ K} \)
- \( k_1 = 0.2 \text{ dm}^3/(\text{kg cat} \cdot \text{min}) \text{ at } 300 \text{ K} \)
- \( E_d/R = 2000 \text{ K} \)
- \( E_A/R = 500 \text{ K} \)