Catalyst Decay: Temperature programming.

If a catalyst decays slowly, then the temperature can be increased appropriately so that the conversion is uniform in a continuous reactor. For example, consider a first order reaction and let the decay be given by

$$-\frac{da}{dt} = k_d a^n$$

The reactor may be a PFR or CSTR, but we can increase the feed temperature slowly (and assume that the reactor is also at the same temperature, since the feed temperature will be increased slowly). In this pseudo-isothermal operation, our goal is to ensure that the reaction rate is the same. Determine the temperature profile of the feed necessary to achieve this goal.

Solution:

For a first order reaction, initially the feed is at a temperature $T_{\text{init}}$. The rate constant is $k_{1-\text{init}}$ and the decay constant is at $k_{d-\text{init}}$.

$$k_{1-\text{init}} = k_{10} e^{\frac{-E_a}{RT_{\text{init}}}} \text{ and } k_{d-\text{init}} = k_{d0} e^{\frac{-E_d}{RT_{\text{init}}}}$$

From these two equations we can write

$$k_1 = k_{1-\text{init}} e^{\frac{-E_a}{RT_{\text{init}}}} \frac{1}{T_{\text{init}}} \text{ and } k_d = k_{d-\text{init}} e^{\frac{-E_d}{RT_{\text{init}}}} \frac{1}{T_{\text{init}}}$$

It is assumed that the feed concentration does not change with time. Therefore, for uniform rate, we need to satisfy $k_1 a = k_{1-\text{init}}$. Note that initial activity is 1.

This gives

$$e^{\frac{-E_a}{RT_{\text{init}}}} \frac{1}{T_{\text{init}}} a = 1$$

Therefore,

$$\frac{1}{T} = \frac{1}{T_{\text{init}}} + \frac{R}{E_1} \ln(a)$$

The decay equation is given by

$$-\frac{da}{dt} = k_d a^n = k_{d-\text{init}} e^{\frac{-E_d}{RT_{\text{init}}}} \frac{1}{T_{\text{init}}} a^n$$

$$-\frac{da}{dt} = k_d a^n = k_{d-\text{init}} e^{\frac{-E_d}{RT_{\text{init}}}} e^{\frac{-E_a}{RT_{\text{init}}}} \frac{1}{T_{\text{init}}} \ln(a) \frac{1}{T_{\text{init}}} a^n = k_{d-\text{init}} e^{\frac{-E_a}{RT_{\text{init}}}} \frac{1}{T_{\text{init}}} \ln(a) a^n$$
\[ \frac{da}{dt} = k_{d-init} a^{\frac{-E_d}{E_1}} a^n = k_{d-init} a^{\left(\frac{n}{E_1}E_d\right)} \]

If \( n \neq \frac{E_d}{E_1} \), the initial condition of \( a=1 \) at \( t=0 \) would yield

\[ t = \frac{1}{k_{d-init}} \frac{1-a^{1-n+\frac{E_d}{E_1}}}{1-n+\frac{E_d}{E_1}} \]

Rearrange to get

\[ a = \left(1 - \left(1-n+\frac{E_d}{E_1}\right)k_{d-init}t\right)^{\frac{1}{1-n+\frac{E_d}{E_1}}} \]

(Note: If \( n = \frac{E_d}{E_1} = 1 \), then we will have \( a = e^{-k_{d-init}t} \))

The temperature will be given by

\[ \frac{1}{T} = \frac{1}{T_{init}} + \frac{R}{E_1} \ln (a) = \frac{1}{T_{init}} + \frac{R}{E_1} \ln \left(1 - \left(1-n+\frac{E_d}{E_1}\right)k_{d-init}t\right)^{\frac{1}{1-n+\frac{E_d}{E_1}}} \]

Re arranging this, we get

\[ \frac{1}{T} = \frac{1}{T_{init}} + \frac{R}{E_1} \ln \left(1 - \left(1-n+\frac{E_d}{E_1}\right)k_{d-init}t\right)^{\frac{1}{1-n+\frac{E_d}{E_1}}} \]

For the following values, \( T_{init} = 300 \text{ K}, E_1 = 40000 \text{ J/molA}, E_d = 10000 \text{ J/mol}, k_{d-init} = 2 \times 10^{-5} \text{ s}^{-1}, n = 1.5 \), we get
The temperature has to be raised more or less linearly from 300 to 330 K, in 24 h.

If we have $T_{\text{init}} = 300$ K, $E_1 = 15000$ J/mol, $E_d = 5000$ J/mol, $k_{d\text{-init}} = 1 \times 10^{-4}$ s$^{-1}$, $n = 1.5$, we get

Obviously this is not practical.