

Heterogenous Data Analysis for Reactor Design

Book: *Elements of Chemical Reaction Engineering*, H.S. Fogler, 4th Edition (Chapter 10)

A packed bed reactor (PBR) and a fluidized CSTR needs to be designed to process a feed consisting of 30% toluene, 45% hydrogen, and 25% inerts. Toluene is fed at a rate of 50 mol/min at a temperature of 640°C and a pressure of 40 atm (4052 kPa). Calculate the catalyst weight necessary to achieve 65% conversion in a CSTR and a PBR (neglect pressure drop)

Design of CSTR

In - Out + Generation = Accumulation

$$F_{T0} - F_T + (r_T)W = 0$$

$$F_{T0} - F_{T0}(1 - X) + (r_T)W = 0$$

$$W = \frac{F_{T0}X}{(-r_T)}$$

$$W = \frac{F_{T0}X}{\frac{144.77 \times 10^{-10} [p_T p_H]}{1 + 1.3905 p_B + 1.0384 p_T}}$$

Now, $p_T = p_{T0}(1 - X)$ and, $p_H = p_{T0}(M - X)$ where $M = \frac{p_{H0}}{p_{T0}}$ and $p_B = p_{T0}X$

$$W = \frac{F_{T0}X(1 + 1.3905 p_B + 1.0384 p_T)}{144.77 \times 10^{-10} [p_T p_H]} = \frac{F_{T0}X[1 + 1.3905 p_{T0}X + 1.0384 p_{T0}(1 - X)]}{144.77 \times 10^{-10} [p_{T0}^2 (1 - X)(M - X)]}$$

$$F_{TO} = 50 \frac{\text{mol}}{\text{min}} = \frac{50 \text{ mol}}{60 \text{ s}} = 0.83333 \text{ mol/s}$$

$$p_{TO} = y_T P_{total} = 0.3 \times 40 = 12 \text{ atm} \quad M = \frac{0.45}{0.30} = 1.5 \quad X = 0.65$$

$$W = \frac{F_{TO} X [1 + 1.3905 p_{TO} X + 1.0384 p_{TO} (1 - X)]}{144.77 \times 10^{-10} [p_{TO}^2 (1 - X)(M - X)]}$$

$$W = \frac{[0.83333 \times 0.65] [1 + 1.3905 \times 12 \times 0.65 + 1.0384 \times 12 \times (1 - 0.65)]}{144.77 \times 10^{-10} [12^2 (1 - 0.65)(1.5 - 0.65)]}$$

$$W = \frac{[0.54166] [1 + 10.842 + 4.36128]}{6.20195 \times 10^{-7}}$$

$$W = 14151466.3 \text{ g} = 1.41515 \times 10^4 \text{ kg}$$

Design of PBR

$$F_{A,W} - F_{A,W+\Delta W} + (r_A)\Delta W = 0$$

Dividing by ΔW and taking limit as $\Delta W \rightarrow 0$, we have, $F_{A0} \frac{dX}{dW} = (-r_A)$

We know $F_A = F_{A0} - F_{A0}X$ and $dF_A = -F_{A0} dX$

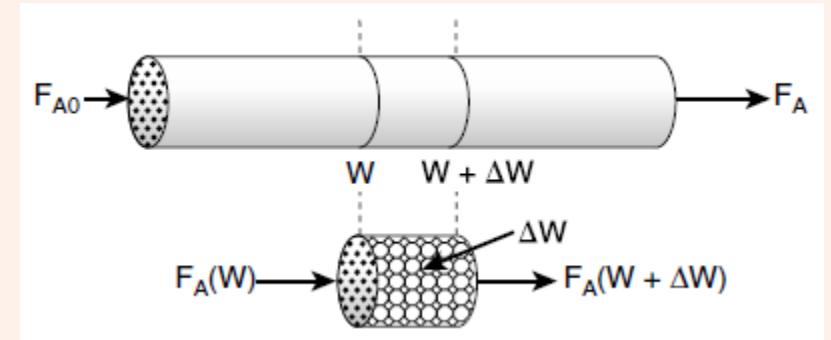
$$\therefore \boxed{F_{A0} \frac{dX}{dW} = (-r_A)}$$

In the absence of pressure drop in the packed bed, this equation can be integrated as $W = F_{A0} \int_0^{X_A} \frac{dX}{(-r_A)}$

For this problem, $W = F_{T0} \int_0^X \frac{dX}{(-r_T)}$ [Pressure drop = 0]

$$W = F_{T0} \int_0^X \frac{dX}{\frac{144.77 \times 10^{-10} [p_T p_H]}{1 + 1.3905 p_B + 1.0384 p_T}} = F_{T0} \int_0^X \frac{dX}{\frac{144.77 \times 10^{-10} [p_{T0}^2 (1-X)(M-X)]}{[1 + 1.3905 p_{T0} X + 1.0384 p_{T0} (1-X)]}}$$

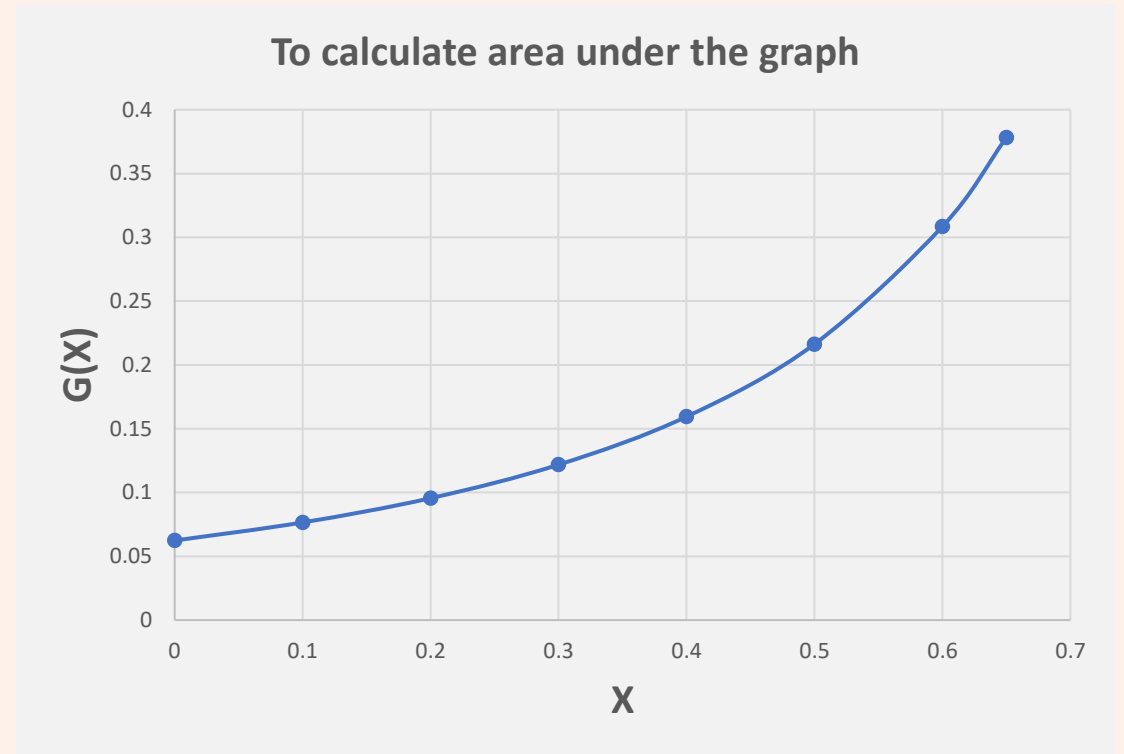
$$W = \frac{0.83333}{144.77 \times 10^{-10}} \int_0^X \frac{[1 + 1.3905 p_{T0} X + 1.0384 p_{T0} (1-X)] dX}{p_{T0}^2 (1-X)(M-X)}$$



$$W = \frac{0.83333}{144.77 \times 10^{-10}} \int_0^{0.65} \frac{[1 + 1.3905 \times 12 \times X + 1.0384 \times 12 \times (1 - X)] dX}{12^2 (1 - X)(1.5 - X)}$$

$$W = 57562340.26 \int_0^{0.65} G(X) dX$$

X	G(X)
0	0.062319
0.1	0.076517
0.2	0.095525
0.3	0.121762
0.4	0.159416
0.5	0.216297
0.6	0.308563
0.65	0.378319



$$\begin{aligned} \text{Area under the curve} &= 0.006942 + 0.008602 + 0.010864 + 0.014059 + 0.018786 + 0.026243 + 0.017172 \\ &= 0.102668 \end{aligned}$$

$$\begin{aligned} W &= 57562340.26 \times 0.102668 = 5909810.35 \text{ g} \\ &= \underline{5909.810 \text{ kg catalyst}} \end{aligned}$$

The design of the previous packed bed reactor done previously without considering pressure drop inside the reactor. In real life industrial reactors for gas phase reactions, pressure drop in the packed bed has a strong effect on the conversion

Pressure drop in packed bed reactors (Fogler, Chapter 4, Pg 175)

For gas phase reaction, the concentration of the reacting species is proportional to the total pressure and pressure drop in the packed bed affects the reactor operation

The concentration of reactant species i is $C_i = C_{Ao} \left[\frac{M_i + \nu_i X}{1 + \epsilon X} \right] \frac{P}{P_o} \frac{T_o}{T}$

where ν_i = stoichiometric coefficient, $M_i = \frac{F_{io}}{F_{Ao}}$, P_o, T_o = initial pressure and temperature,

P, T = pressure and temperature at any X

Example: If $(-r_A) = \frac{kC_A}{1 + K_A C_A}$ and $C_A = \frac{C_{Ao}(1 - X_A)}{(1 + \epsilon_A X_A)} \cdot \frac{P}{P_o} \cdot \frac{T_o}{T}$

$$(-r_A) = \frac{k \left[\frac{C_{Ao}(1 - X_A)}{(1 + \epsilon_A X_A)} \cdot \frac{P}{P_o} \cdot \frac{T_o}{T} \right]}{1 + K_A \left[\frac{C_{Ao}(1 - X_A)}{(1 + \epsilon_A X_A)} \cdot \frac{P}{P_o} \cdot \frac{T_o}{T} \right]}$$

Putting this in the mass balance equation, $F_{Ao} \frac{dX}{dW} = (-r_A)$ we get,

$$F_{Ao} \frac{dX}{dW} = v_o C_{Ao} \frac{dX}{dW} = \frac{k \left[\frac{C_{Ao}(1-X_A)}{(1+\epsilon_A X_A)} \cdot \frac{P}{P_o} \cdot \frac{T_o}{T} \right]}{1+K_A \left[\frac{C_{Ao}(1-X_A)}{(1+\epsilon_A X_A)} \cdot \frac{P}{P_o} \cdot \frac{T_o}{T} \right]}$$

For isothermal conditions ($T = T_o$), $\frac{dX}{dW} = \frac{\frac{k \left[\frac{(1-X_A)}{(1+\epsilon_A X_A)} \cdot \frac{P}{P_o} \right]}{v_o}}{1+K_A \left[\frac{C_{Ao}(1-X_A)}{(1+\epsilon_A X_A)} \cdot \frac{P}{P_o} \right]}$

Thus , $\frac{dX}{dW} = F_1(X, P)$

RHS of the balance equation is a function of only conversion and pressure for isothermal reactors

It is now necessary to relate the pressure drop through the catalyst bed to the catalyst weight in order to determine the conversion as a function of catalyst weight

For flow through packed bed, the Ergun equation is used to calculate the pressure drop

$$\frac{dP}{dz} = -\frac{G}{\rho g_c D_p} \left(\frac{1-\phi}{\phi^3} \right) \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right]$$

where P = pressure (kPa) ϕ = void fraction = vol of void/total bed vol $1-\phi$ = vol of solid/total bed vol
 D_p = diameter of particles in the bed $g_c = 32.17 \text{ ft lb}_m/\text{lb}_f \text{ m}^2$ (for metric system, $g_c = 1$) z = length of packed bed
 μ = viscosity of gas passing through bed $G = \rho u$ = superficial mass velocity ρ = gas density u = superficial velocity

The only parameter in the right hand side of the Ergun equation that varies with pressure (P) is gas density (ρ)

At steady state, the mass flow rate at any point in the reactor (\dot{m}) is equal to the mass flow rate at the entrance (\dot{m}_o)

$$\dot{m}_o = \dot{m}$$

$$\therefore \rho_o v_o = \rho v \text{ (continuity equation)}$$

$$\text{Now, } v = v_o \left(\frac{F_T}{F_{T_o}} \right) \left(\frac{P_o}{P} \right) \left(\frac{T}{T_o} \right) \text{ and}$$

$$\rho = \frac{\rho_o v_o}{v} = \rho_o \left(\frac{F_{T_o}}{F_T} \right) \left(\frac{P}{P_o} \right) \left(\frac{T_o}{T} \right)$$

$$C_T = \frac{F_T}{v} = \frac{P}{zRT} \text{ at any point in the reactor}$$

$$C_{T_o} = \frac{F_{T_o}}{v_o} = \frac{P_o}{z_o R T_o} \text{ at entrance}$$

$$\frac{C_T}{C_{T_o}} = \frac{\frac{F_T}{v}}{\frac{F_{T_o}}{v_o}} = \left(\frac{P}{P_o} \right) \left(\frac{T_o}{T} \right)$$

$$\frac{v}{v_o} = \frac{F_T}{F_{T_o}} \left(\frac{P_o}{P} \right) \left(\frac{T}{T_o} \right)$$

The value of $\rho = \rho_o \left(\frac{F_{T0}}{F_T}\right) \left(\frac{P}{P_o}\right) \left(\frac{T_o}{T}\right)$ is now put in the Ergun equation to get

$$\frac{dP}{dz} = -\frac{G}{\rho_o g_c D_p} \left(\frac{1-\phi}{\phi^3}\right) \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G\right] \left(\frac{F_T}{F_{T0}}\right) \left(\frac{P_o}{P}\right) \left(\frac{T}{T_o}\right)$$

Simplifying, $\boxed{\frac{dP}{dz} = -\beta_o \left(\frac{F_T}{F_{T0}}\right) \left(\frac{P_o}{P}\right) \left(\frac{T}{T_o}\right)}$ $\beta_o = \frac{G}{\rho_o g_c D_p} \left(\frac{1-\phi}{\phi^3}\right) \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G\right]$

For packed bed reactors, weight of catalyst W is more important than bed height z

$\boxed{W = (1-\phi)A_c z \rho_c}$ where $(1-\phi)A_c z =$ volume of solids, $A_c =$ column cross-sectional area and $\rho_c =$ density of solid catalyst

Now, $dz = \frac{dW}{(1-\phi)A_c \rho_c}$

Putting this value of dz in the above simplified Ergun equation, we get, $\frac{dP}{dW} = -\frac{\beta_o}{(1-\phi)A_c \rho_c} \left(\frac{F_T}{F_{T0}}\right) \left(\frac{P_o}{P}\right) \left(\frac{T}{T_o}\right)$

On further simplifying, $\frac{dP}{dW} = -\frac{\alpha}{2} \left(\frac{F_T}{F_{T0}}\right) \left(\frac{P_o}{P/P_o}\right) \left(\frac{T}{T_o}\right)$ where $\alpha = \frac{2\beta_o}{(1-\phi)A_c \rho_c P_o}$

If $P/P_o = y$, $\boxed{\frac{dy}{dW} = -\frac{\alpha}{2y} \left(\frac{F_T}{F_{T0}}\right) \left(\frac{T}{T_o}\right)}$

Since $F_T = F_{T0} (1 + \varepsilon X)$, $\boxed{\frac{dy}{dW} = -\frac{\alpha}{2y} (1 + \varepsilon X) \left(\frac{T}{T_o}\right)}$

For isothermal conditions, ($T = T_o$)

$$\frac{dy}{dW} = -\frac{\alpha}{2y}(1 + \varepsilon X)$$

Putting the values of y and α ,

$$\frac{d(P/P_o)}{dW} = -\frac{\frac{2\beta_o}{(1-\phi)A_c\rho_c P_o}}{2P/P_o}(1 + \varepsilon X)$$

Thus , $\frac{dP}{dW} = F_2(X, P)$ Here, the RHS is a function of only conversion and pressure for isothermal reactors

This equation, $\frac{dP}{dW} = F_2(X, P)$ and the one derived earlier, $\frac{dX}{dW} = F_1(X, P)$ form a set of coupled first order differential equations, that needs to be solved simultaneously

This solution can be done using numerical methods or a software package

Analytical solution for this particular problem (no volume change, $\varepsilon = 0$)

$$\frac{dy}{dW} = -\frac{\alpha}{2y}(1 + \varepsilon X)$$

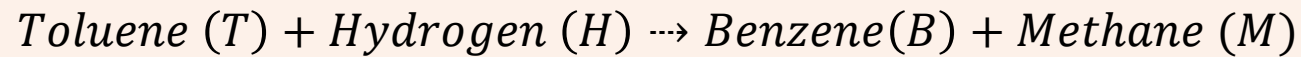
$$\int_1^y 2y dy = -\alpha \int_0^W dW \quad \Rightarrow \quad 2 \left[\frac{y^2}{2} - \frac{1}{2} \right] = -\alpha W \quad \Rightarrow \quad y^2 = 1 - \alpha W$$

$$y = P/P_o = (1 - \alpha W)^{1/2} \quad \text{where} \quad \alpha = \frac{2\beta_o}{(1-\phi)A_c\rho_c P_o}$$

This expression for P can be substituted in the rate law and the mole balance can be written solely as a function of X and W and then solved

Example for PBR reactor design after considering pressure drop in packed bed

A packed bed reactor (PBR) needs to be designed to process a feed consisting of 30% toluene, 45% hydrogen, and 25% inerts. Toluene is fed at a rate of 50 mol/min at a temperature of 640°C and a pressure of 40 atm (4052 kPa). Hydrogen is used in excess to help prevent coking. The pressure drop parameter, α is $9.8 \times 10^{-5} \text{ kg}^{-1}$. Plot the conversion, the pressure ratio, y and the partial pressure of toluene, hydrogen and benzene as a function of catalyst weight.



$$\frac{dF_T}{dW} = r_T \quad \text{or} \quad \frac{dX}{dW} = \frac{(-r_T)}{F_{T0}} \quad \dots\dots\dots (1)$$

$$\text{From earlier derivations, } (-r_T) = \frac{k[p_T p_H]}{1 + K_B p_B + K_T p_T} \quad \dots\dots\dots (2)$$

$$\text{where } k = 144.77 \times 10^{-10}, \quad K_T = 1.0384, \quad K_B = 1.3905$$

$$p_T = C_T RT = C_{T0} RT_0 \left(\frac{1-X}{1+\varepsilon X} \right) \left(\frac{P}{P_0} \right) = p_{T0} \left(\frac{1-X}{1+\varepsilon X} \right) y$$

For this reaction, $\varepsilon = 0$

$$p_T = p_{T0}(1 - X)y \quad \dots\dots\dots (3)$$

$$p_B = p_{T0} X y \quad \dots\dots\dots (4)$$

$$p_H = p_{T0}(M - X)y \quad \quad \quad M = \frac{0.45}{0.30} = 1.5$$

$$p_H = p_{T0}(1.5 - X)y \quad \dots\dots\dots (5)$$

Since $\varepsilon = 0$, $y = P/P_o = (1 - \alpha W)^{1/2}$ (6)

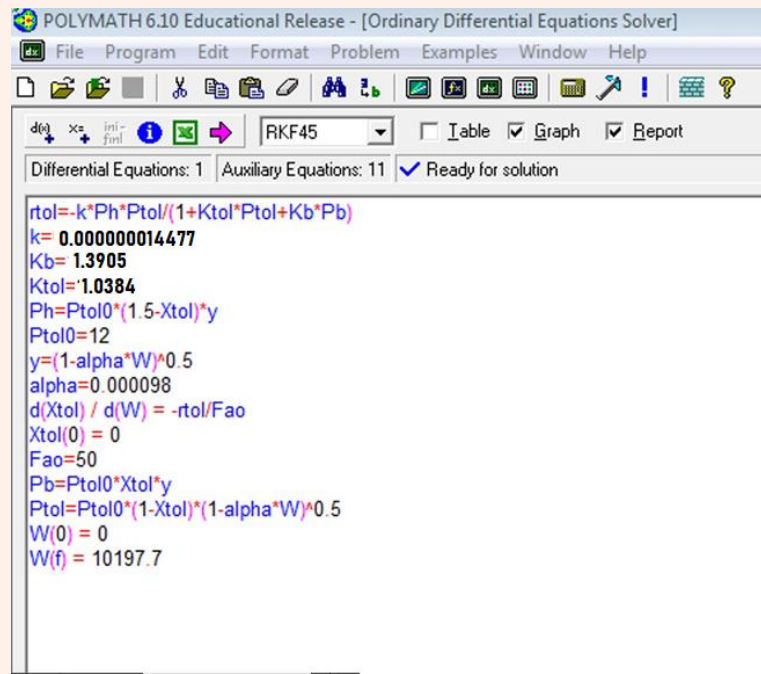
The maximum catalyst weight that will result in a final pressure of 1 atm (outlet pressure from reactor) is given as,

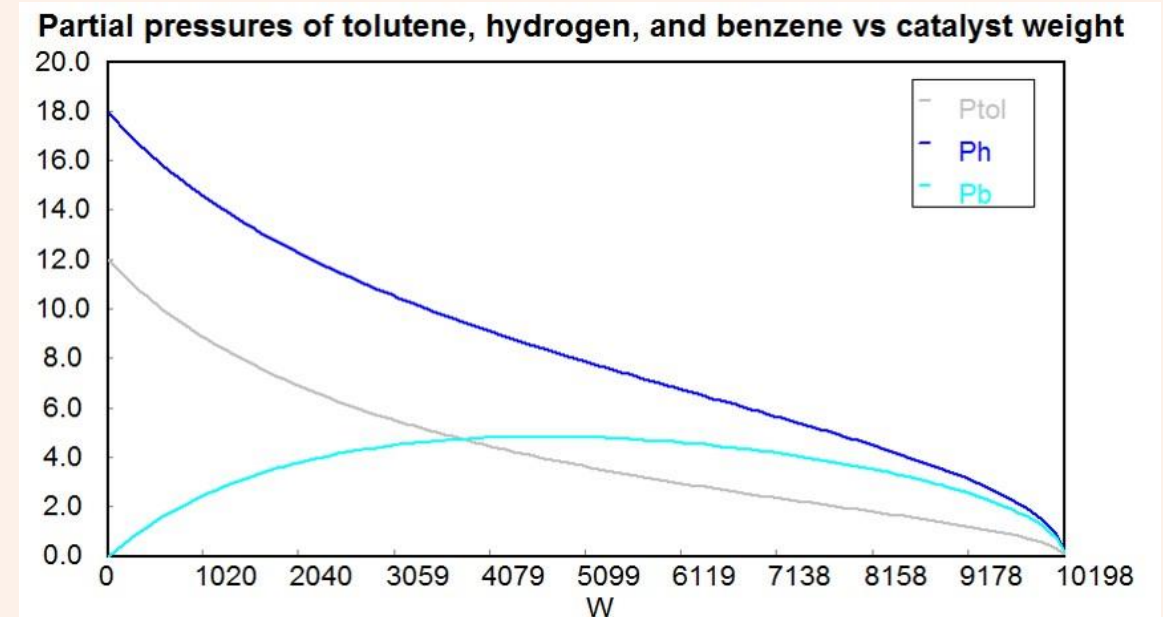
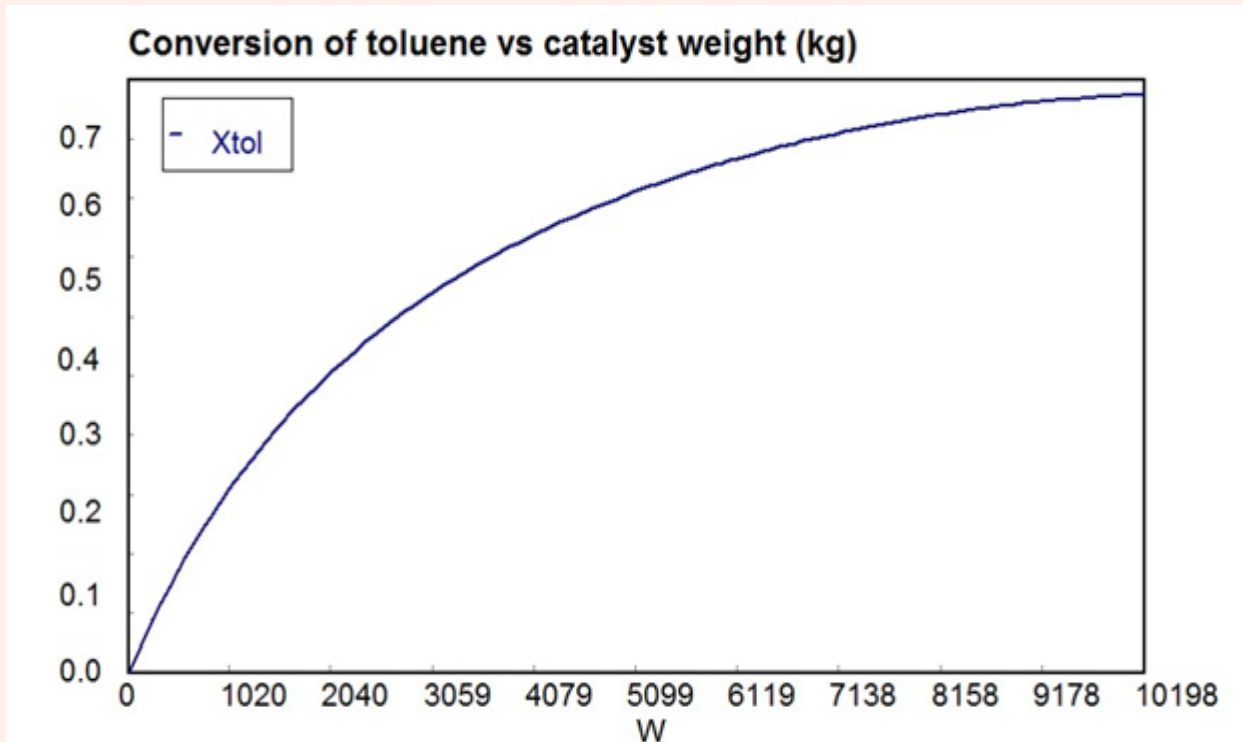
$$1/40 = (1 - 9.8 \times 10^{-5} W)^{1/2}$$

$$W = 10197.7 \text{ kg}$$

The equations (1) and (6) are related by X , W and P .

An ODE solver can be used to find the X versus W plot. The value of W is chosen 0 and 10,000 kg. These equations (1-6) are plugged into Polymath 6.1 to solve





With 10,000 kg catalyst, a conversion of 78.17% can be achieved in a packed bed reactor when pressure drop is not considered

With consideration of pressure drop, this value drops to 69%

Minimizing pressure drop can increase production rate

Experimental methods of finding rates

Values of experimentally determined rates and partial pressures were used for heterogenous data analysis. This was used to find the appropriate reaction model (and rate expression) and kinetic parameters for a reaction

But what type of reactors are used to find these experimental rate values?

Differential reactor

- A differential reactor is usually used to determine the rate of reaction as a function of either concentration or partial pressure
- A very, small amount of catalyst in the form of a thin wafer or disk is used in a differential reactor
- The conversion in the catalyst bed is low, < 10%
- The change in temperature and reactant concentration through the bed is small (reactor is gradientless)
- Rate is constant at all points in the catalyst bed and the operation is isothermal

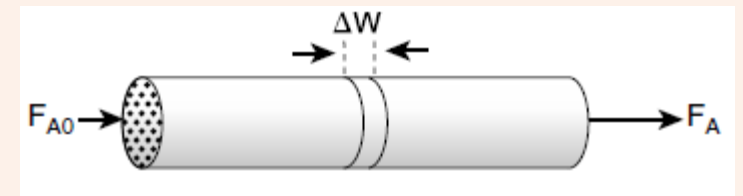
$$F_{Ao} - F_{Ae} + (r_A)(\Delta W) = 0$$

$$F_{Ao} - F_{Ao}(1 - X_A) = (-r_A)(\Delta W)$$

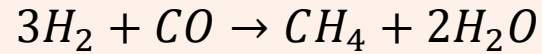
$$F_{Ao}X_A = (-r_A)(\Delta W)$$

$$(-r_A) = \frac{F_{Ao}X_A}{\Delta W}$$

$$(-r_A) = \frac{F_{Ao}X_A}{\Delta W} = \frac{F_B}{\Delta W} = \frac{v_o(C_{Ao} - C_{Ae})}{\Delta W} = \frac{C_B v_o}{\Delta W} \quad \text{for a reaction of } A \rightarrow B$$



The reaction of hydrogen with carbon monoxide was carried out at 500° F in a differential reactor



The exit volumetric flow rate from the bed containing 10 g catalyst was maintained at 300 dm³/min for each run. The partial pressures of H₂ and CO at the entrance and the CH₄ concentration at the exit was measured. Calculate the reaction rate

Run	p _{CO} (atm)	p _{H₂} (atm)	C _{CH₄} (mol/dm ³)	r _{CH₄} (mol CH ₄ /g cat.min)
1	1	1	1.73 x 10 ⁻⁴	5.2 x 10 ⁻³
2	1.8	1	4.40 x 10 ⁻⁴	13.2 x 10 ⁻³
3	4.08	1	10 x 10 ⁻⁴	30 x 10 ⁻³
4	1	0.1	1.65 x 10 ⁻⁴	4.95 x 10 ⁻³
5	1	0.5	2.47 x 10 ⁻⁴	7.42 x 10 ⁻³
6	1	4.0	1.75 x 10 ⁻⁴	5.25 x 10 ⁻³

$$(-r_{CO}) = (r_{CH_4}) = \frac{F_{CO}X}{W} = \frac{F_{CH_4}}{W} = \frac{C_{CH_4}v_o}{W}$$

$$(r_{CH_4}) = \frac{300 \times 1.73 \times 10^{-4}}{10} = 5.2 \times 10^{-3} \text{ mol CH}_4/\text{g cat.min}$$

The rest of the values in the last column (reaction rate) are calculated in a similar manner

Integral reactor

- In the integral reactor, there is a variation in the reaction rate within the reactor
- For large conversions, the concentration of the reactant varies significantly throughout the reactor, as does the rate
- The reaction rate can be found by two means using such a reactor
- Integral analysis: Here, a specific mechanism with its corresponding rate equation is put to test by integrating the performance equation

$$W = F_{A0} \int_0^X \frac{dX_A}{(-r_A)}$$

However, as the rate expressions become more complicated, this method becomes more cumbersome

- Differential analysis: The conversion is plotted versus W/F_{A0} and the slopes at each W/F_{A0} denotes the rate

$$(-r_A) = \frac{dX_A}{d(W/F_{A0})}$$

