ChE 344
Reaction Engineering and Design

Lecture 8: Tuesday, Feb 1, 2022

Isothermal Reactor Design with Pressure Drop

Reading for today's Lecture: Chapter 5.5 (5.6 for process)

Reading for Lecture 9: Chapter 6 (particularly 6.5-6.6)

Lecture 8: Isothermal reactor design – Pressure drop
Related Text: Chapter 5.5-5.6

Pressure drop definition:

$$\Delta P = P_0 - P$$

Pressure drop is how much the total pressure decreases from one point in flowing fluid to another. We will only (in this class) model using pressure drop through PBRs (packed bed reactors). We will assume pressure drop (to drive flow) is negligible in pipes, CSTRs, and PFRs.

The **Ergun equation** for gas-phase pressure drop through a packed bed:

$$\frac{dP}{dz} = \frac{-G}{\rho g_c D_P}\left(\frac{1-\phi_b}{{\phi_b}^3}\right)\left[\underbrace{\frac{150(1-\phi_b)\mu}{D_P}}_{Laminar} + \underbrace{1.75G}_{Turbulent}\right]$$

New variables/parameters related to catalyst:

$$\phi_b = \text{porosity of bed} = \frac{\text{volume of void}}{\text{total bed volume}} = \text{void fraction} = \text{vol. for flow}[=]\text{unitless}$$

$$\rho_c(1-\phi_b) = \rho_b = (\text{catalyst density})\left(\frac{\text{volume of solid}}{\text{total volume}}\right) = \text{density of bed}[=]\frac{\text{mass}}{\text{volume}}$$

$$D_P = \text{diameter of the catalyst pellet/particle}[=]\text{length}$$

New variables/parameters related to fluid:

$$\rho = \text{gas density}[=]\frac{\text{mass}}{\text{volume}}$$

$$G = \rho u = \rho\left(\frac{v}{A_{CS}}\right)[=]\frac{\text{mass}}{\text{area}\cdot\text{time}}$$

$$\mu = \text{fluid viscosity}[=]\frac{\text{mass}}{\text{length}\cdot\text{time}}$$

G is the superficial mass velocity, u is the superficial velocity. A_{CS} is the cross sectional area (of the reactor bed).

150 and 1.75 are from empirically fitting.

g_c is a conversion factor (sometimes called gravitational conversion constant) used to convert between mass and force. For example 32.174 lb_m ft s^{-2} lb_f^{-1}.

Often we will rearrange the Ergun equation:

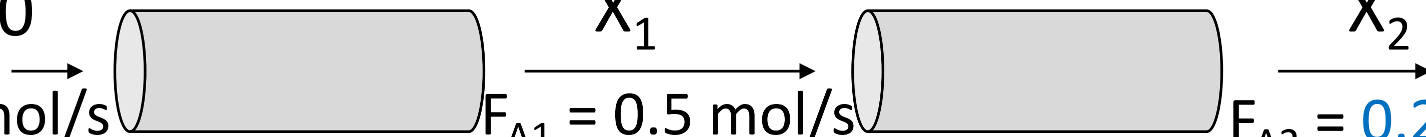
$$\frac{dp}{dW} = -\frac{\alpha}{2p}\frac{T}{T_0}(1+\varepsilon X) = -\frac{\alpha}{2p}\frac{T}{T_0}\frac{F_T}{F_{T0}}$$

$$p \equiv \frac{P}{P_0}[=]\text{unitless};\ \alpha \equiv \frac{2\beta_0}{\rho_c(1-\phi_b)A_{CS}P_0}[=](\text{catalyst mass})^{-1}$$

$$\beta_0 \equiv \frac{G}{\rho_0 g_c D_P}\left(\frac{1-\phi_b}{{\phi_b}^3}\right)\left[\frac{150(1-\phi_b)\mu}{D_P} + 1.75G\right]$$

With your neighbors:

$F_{B1} = F_{A0}(2 - \frac{b}{a}X_1)$ $F_{A1} = F_{A0}(1 - \frac{a}{a}X_1)$



$X_0 = 0$

F_{A0} = 1 mol/s

F_{B0} = 2 mol/s

X_1

F_{A1} = 0.5 mol/s

F_{B1} = 1.5 mol/s

X_2 = 0.75

F_{A2} = 0.25 mol/s

F_{B2} = 1.25 mol/s

Only one reaction is occurring. For X of your limiting reactant defined with respect to the feed into the first reactor:

What is θ_B? F_{B1}/F_{A1}? F_{B2}?

A) θ_B = 2; F_{B1}/F_{A1} = 3; F_{B2} = 1.125

B) θ_B = 3; F_{B1}/F_{A1} = 3; F_{B2} = 1.25

C) θ_B = 2; F_{B1}/F_{A1} = 3; F_{B2} = 2. 25

D) θ_B = 2; F_{B1}/F_{A1} = 3; F_{B2} = 1.25

$$F_{B2} = F_{A0}(2 - X_2)$$

$$F_{B2} \neq F_{A0}(3 - X_2)$$

$$F_{B2} \neq F_{A1}(3 - X_2)$$

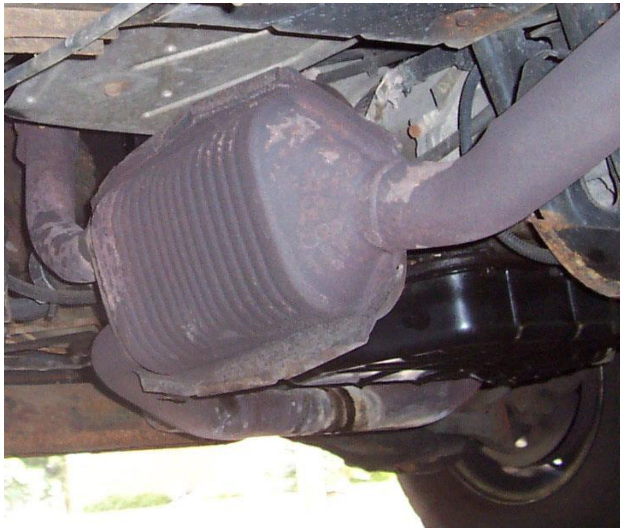
Notice I am not saying anything about concentrations, because we do not have sufficient info to know F_T, v!

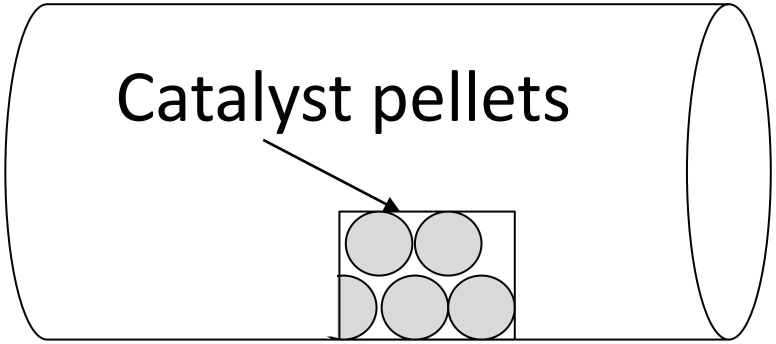
Many industrial reactions are catalytic (>90%), particularly using heterogeneous catalysts,* and so packed bed reactors are common (behave like PFRs for the most part).

PBR (aka fixed bed) with pressure drop today.

- Ammonia synthesis
- Sulfuric acid synthesis
- Hydrocarbon (HC) cracking
- CO, NO_x, HC oxidation (3-way cat. converter)
- Steam reforming (make H_2)
- Desulfurization of natural gas (remove H_2S)

Catalytic converter





*Different phase of catalyst and reactant/product

What is on the horizon for this class?

For Midterm 1, we have been designing reactors with some simplifying assumptions that make our design equations (e.g., isothermal, isobaric flow).

Isothermal reactors:

$T = T_0$ or more rigorously $\frac{dT}{dV} = 0$

Isobaric flow reactors:

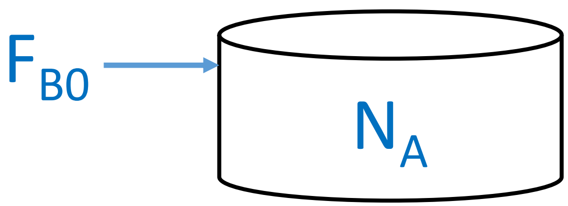
$P = P_0$ or more rigorously $\frac{dP}{dV} = 0$ $\frac{dP}{dW} = 0$

This knowledge can enable you to make excellent approximations and estimations of conversions for a large number of reactions, including many bench scale systems.

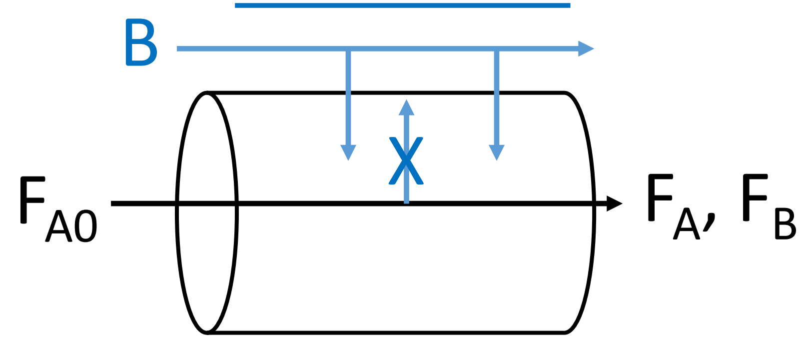
More complex reactors

We can also have more complex reactors (Lecture 9/10)

Semi-batch



Membrane



More complex reactions (Lec. 9 and in more detail in Lec. 12)

Desired product $A \xrightarrow{k_D} D$

Undesired product $A \xrightarrow{k_U} U$

Non-isothermal (Lecture 13)

$$\frac{dT}{dV} \neq 0$$

Pressure drop/pressure change (today)

We have so far considered flow reactors to be isobaric/no pressure drop.

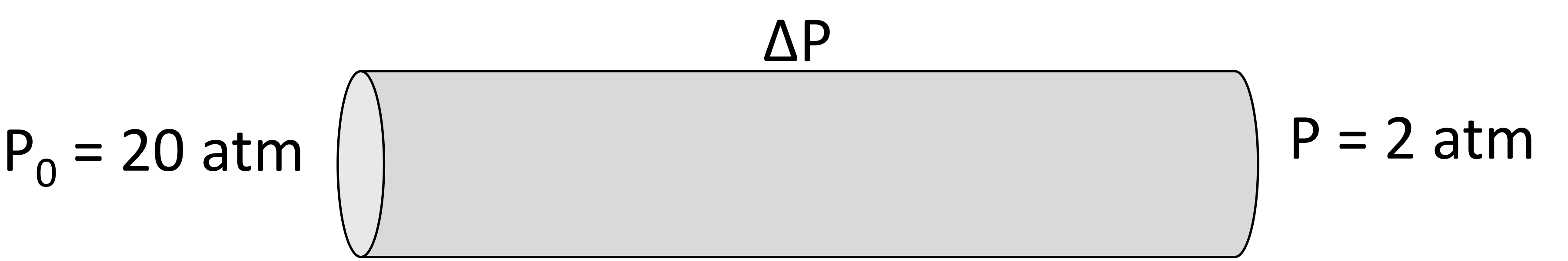
$$P = P_0 \qquad \frac{dP}{dV} = 0 \qquad \frac{dP}{dW} = 0$$

This is not the case in reality because flow may be driven by a pressure gradient.

P_0 (total inlet pressure) > P (total outlet pressure).

This is what we call 'pressure drop'.

So far we have been assuming it is negligible, but not always the case.

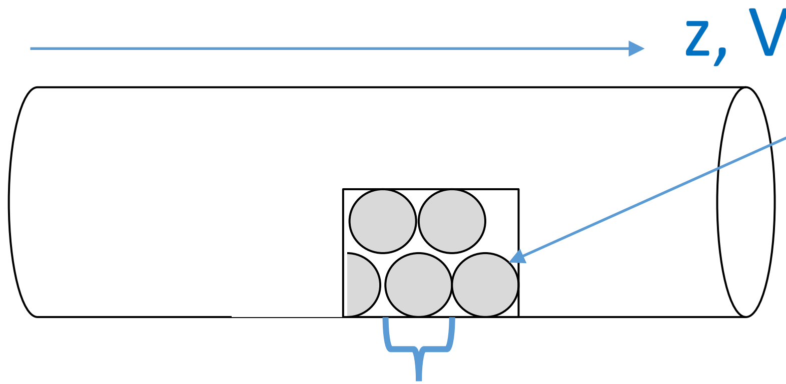


Pressure drop (flow PBR) vs. pressure change in constant V batch reactor

For batch reactors we have usually been considering them to be constant volume ($V = V_0$) and isothermal.*
In these constant volume reactions, if the number of moles of ideal gases change due to reaction, the pressure will change (if isothermal) based on the ideal gas law.
If # of moles increases, the pressure would increase,
if # of moles decreases, the pressure would decrease.
This is not the same as what we refer to as 'pressure drop', as there is no flow for the batch reactor.

*If you assumed constant pressure, the reactor could potentially expand (imagine a reaction occurring in a balloon).

Pressure drop in a **gas-phase** packed bed reactor (PBR)



ρ_c (density of catalyst)

$$\rho_{bed} = \rho_c(1-\phi_b)$$

$$\rho_{bed}V = W$$

Diameter particle/pellet =D_P

Semi-empirical **Ergun equation**

Several mods for non-spherical exist

$$\frac{dP}{dz} = \frac{-G}{\rho g_c D_P}\left(\frac{1-\phi_b}{\phi_b{}^3}\right)\left[\underbrace{\frac{150(1-\phi_b)\mu}{D_P}}_{Laminar} + \underbrace{1.75G}_{Turbulent}\right]$$

The ρ is **gas** density, ϕ_b is the bed void fraction, μ is the viscosity of the **gas**. g_c is gravitational constant. (1.0 kg m/(Ns^2))

If you know the flow regime you can simplify, e.g., in laminar flow, neglect turbulent contribution

$$G \equiv \rho * \underbrace{u}_{superficial\ velocity} = \rho\left(\frac{v}{A_{CS}}\right)$$

Cross sectional area

From conservation of mass:

$$\rho v = \rho_0 v_0$$

From IG law:

$$v = v_0 \frac{P_0}{P}\frac{T}{T_0}\frac{F_T}{F_{T0}} = v_0 \frac{P_0}{P}\frac{T}{T_0}(1 + \varepsilon X)$$

By substituting fluid density for inlet gas density:

$$\frac{dP}{dz} = -\underbrace{\frac{G}{\rho_0 g_c D_P}\left(\frac{1-\phi_b}{{\phi_b}^3}\right)\left[\frac{150(1-\phi_b)\mu}{D_P} + 1.75G\right]}_{\beta_0}\frac{P_0}{P}\frac{T}{T_0}(1 + \varepsilon X)$$

Discuss with your neighbors:

$$\frac{dP}{dz} = -\beta_0 \frac{P_0}{P} \frac{T}{T_0} (1 + \varepsilon X)$$

Looking at the Ergun equation, something should hop out about ε.

For a defined limiting reactant, which of these is **not** a 'possible' value of ε (for our ideal reactors)?

A) ε = 2

B) ε = -3/2

C) ε = 50

D) ε = -0.9

This would give us a negative flow rate. Makes sense in the context that flow would reverse direction (dP/dz = +), but problematic for our ideal PBR where all flow is in one direction.

$$\frac{F_T}{F_{T0}} = (1 + \varepsilon X)$$

If $\varepsilon \leq -1$, F_T will reverse direction (F_T/F_{T0} will be negative)

Why can't this happen? $\varepsilon = y_{A0}\delta$

$$y_{A0} = \frac{F_{A0}}{F_{T0}} > 0 \qquad \delta = \frac{d + c - b - a}{a}$$

$$(y_{A0})_{max} = \frac{a}{a+b}$$

If y_{A0} is higher, A will not be limiting reactant (b/c A will be excess!)

$$(\delta)_{min} > \frac{-b-a}{a}$$

This is the most negative that δ can be. For conservation of mass, some moles must be produced

$$(\varepsilon)_{min} = (y_{A0})_{max}(\delta)_{min} > \frac{a}{a+b}\frac{-b-a}{a} = -1$$

$$\varepsilon > -1$$

$$\frac{dP}{dz} = -\beta_0 \frac{P_0}{P} \frac{T}{T_0} (1 + \varepsilon X)$$

<u>We want to couple with our PFR/PBR equation</u>

Let's first re-derive PBR, starting with the PFR design equation

$$F_{A0} \frac{dX}{dV} = -r_A$$

r_A is rate per unit volume (of reactor)

r'_A is rate per unit mass (of catalyst)

$$\rho_b V = W$$

$$r_A = \rho_b r'_A$$

Rewrite PFR design equation in terms of mass of catalyst (W)

W_{cat} = V_{cat} * density catalyst = $V_{reactor}$ * density catalyst bed

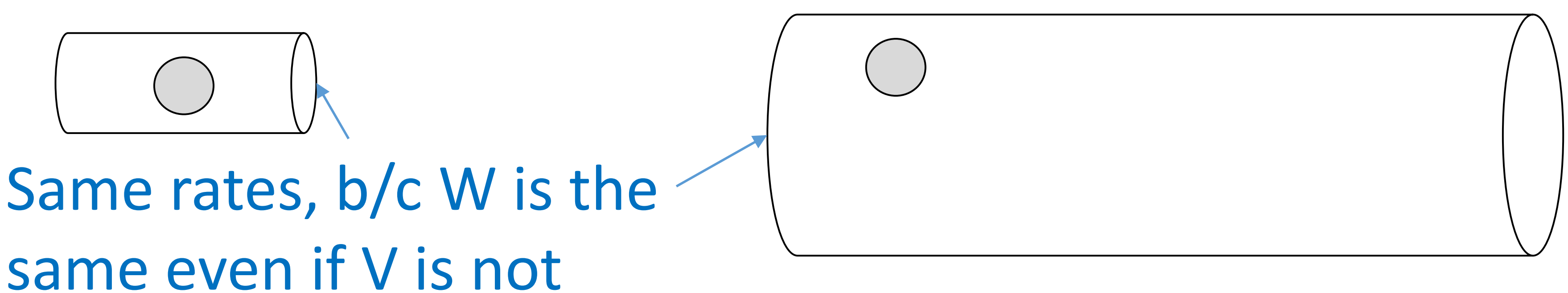
$$F_{A0} \frac{dX}{dV} = F_{A0} \frac{dX}{dW} \frac{dW}{dV} = F_{A0} \frac{dX}{dW} \rho_b = -r_A = -\rho_b r'_A$$

$$F_{A0}\frac{dX}{dW}\rho_b = -\rho_b r_A'$$

This gives us the PBR design equation

$$F_{A0}\frac{dX}{dW} = -r_A'$$

Why do we bother doing this? For catalytic reactions, when we measure the reaction rate to get rate laws, etc. we care about the amount of catalyst, b/c that controls the rate, not the reactor volume.



For the gas reaction A → bB with $r_A = -kC_A$

$$F_{A0}\frac{dX}{dW} = -r_A' = kC_A = k\frac{C_{A0}(1-X)}{1+\varepsilon X}\frac{P}{P_0}\frac{T_0}{T}$$

For a P**F**R:

k is rate constant in terms of volume for a PFR

For a P**B**R:

k is rate constant in terms of catalyst mass for a PBR

How can we link catalyst weight to the z down the PBR we used in the Ergun equation?

$$W = \rho_c(1-\phi_b)A_{CS}z$$

$$\frac{dP}{dz} = \frac{dP}{dW}\frac{dW}{dz}$$

Back to Ergun equation:

$$\frac{dP}{dz} = -\beta_0 \frac{P_0}{P} \frac{T}{T_0} (1 + \varepsilon X)$$

$$\frac{dP}{dW} = -\frac{\beta_0}{\rho_c (1 - \phi_b) A_{CS}} \frac{P_0}{P} \frac{T}{T_0} (1 + \varepsilon X)$$

$$\alpha \equiv \frac{2\beta_0}{\rho_c (1 - \phi_b) A_{CS} P_0}$$

$$p \equiv \frac{P}{P_0}$$

Ergun:

$$\frac{dp}{dW} = -\frac{\alpha}{2p} \frac{T}{T_0} (1 + \varepsilon X)$$

Gas only!

Design:

$$F_{A0} \frac{dX}{dW} = k \frac{C_{A0}(1 - X)}{1 + \varepsilon X} p \frac{T_0}{T}$$

Example problem:

Make ethylene oxide from ethylene and air in a PBR:

$$C_2H_4 + \frac{1}{2}O_2 \rightarrow C_2H_4O; A + \frac{1}{2}B \rightarrow C$$

Conditions: $ $$$

Stoichiometric feed, F_{A0} = 0.3 lbmol/second @ 10 atm

Isothermal PBR @ 260 °C

10 banks of 1 ½" tube x 100 tubes/batch, 1,000 tubes

Assume reaction gas properties are the same as air

ρ_c = 120 lbm/ft^3, ¼" catalyst pellets and void fraction = 0.45

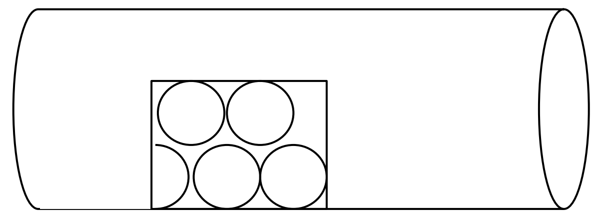
$$r_A' = -kP_A^{1/3}P_B^{2/3}$$

Rate law given for pressures not C_j

k = 0.0141 lbmol/(lbm$_{cat}$ * atm * hr)

- Plot X and concentration profile vs. W
- Calculate X at W = 50 lb_{cat} (single tube)
- Calculate W where X = 0.6
- Calculate the pressure drop at that weight of catalyst

F_{A0} = 0.003 lbmol/s
(1,000 tubes total)



Consider single tube

F_{B0} = 0.0015 lbmol/s

F_{C0} = 0 lbmol/s

$F_{N2,0}$ = 0.0015 lbmol/s *0.79 mol N_2/ 0.21 mol O_2
= 0.005643 lbmol/s of inert nitrogen

Design Equation
+ Rate Law

$$F_{A0}\frac{dX}{dW} = -r_A' = kP_A^{1/3}P_B^{2/3}$$

$$= k(C_A RT)^{1/3}(C_B RT)^{2/3}$$

$$F_{A0}\frac{dX}{dW} = kRTC_A^{1/3}C_B^{2/3}$$

Stoichiometry:

Reactant A (ethylene)

Isothermal

$$C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}\frac{P}{P_0}\frac{T_0}{T} = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}p$$

Reactant B (oxygen)

$$C_B = \frac{C_{A0}(\theta_B - \frac{b}{a}X)}{(1+\varepsilon X)}p$$

$$C_B = \frac{C_{A0}(0.5-0.5X)}{(1+\varepsilon X)}p$$

Combine (Design Eqn, Rate Law, Stoichiometry (for gases), and now also have Ergun Eqn):

$$C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}p \quad C_B = \frac{C_{A0}(0.5-0.5X)}{(1+\varepsilon X)}p$$

Not pseudo

$$k' = \frac{kRTC_{A0}}{2^{2/3}}$$

$$\frac{dX}{dW} = \frac{-r_A'}{F_{A0}} = \frac{k}{F_{A0}}RTC_A^{1/3}C_B^{2/3} = \frac{k'}{F_{A0}}\frac{(1-X)}{(1+\varepsilon X)}p$$

Ergun Equation:

Isothermal

$$\frac{dp}{dW} = -\frac{\alpha}{2p}\frac{T}{T_0}(1+\varepsilon X) \qquad \alpha \equiv \frac{2\beta_0}{\rho_c(1-\phi_b)A_{CS}P_0}$$

$$\beta_0 \equiv \frac{G}{\rho_0 g_c D_P}\left(\frac{1-\phi_b}{{\phi_b}^3}\right)\left[\frac{150(1-\phi_b)\mu}{D_P} + 1.75G\right]$$

Solve using Polymath, Mathematica, Matlab, etc.

$$\frac{dX}{dW} = \frac{k'}{F_{A0}} \frac{(1 - X)}{(1 + \varepsilon X)} p \qquad \frac{dp}{dW} = -\frac{\alpha}{2p}(1 + \varepsilon X)$$

ICs: p(W = 0) = 1, X(W=0) = 0

Per (identical) tube:

$$A + \frac{1}{2}B \rightarrow C$$

F_{A0} = 0.003 lbmol/s

F_{B0} = 0.0015 lbmol/s

$F_{N2,0}$ = 0.005643 lbmol/s

$F_{A0} = 1.08$ lbmol/**hr**

$$\varepsilon = y_{A0}\delta = \frac{F_{A0}}{F_{T0}}(-1/2) = -0.15$$

$$P_{A0} = y_{A0}P = 0.3(10\ atm)$$

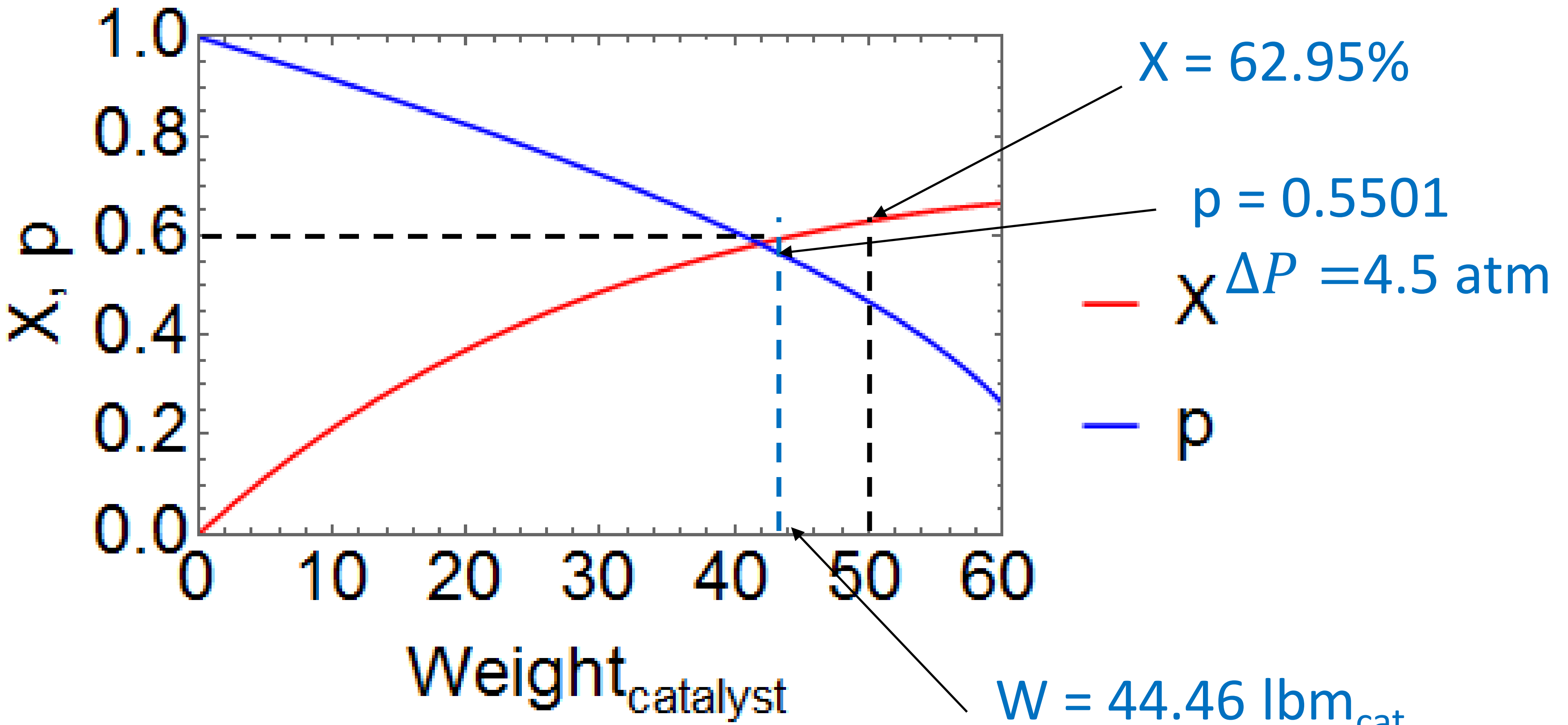
k = 0.0141 lbmol/(lbm_{cat} * atm * hr)

$$k' = \frac{kRTC_{A0}}{2^{2/3}} = \frac{k}{2^{2/3}} RT \frac{P_{A0}}{RT} = 0.0266 \text{ lbmol/(lbmcat*hr)}$$

$\alpha = 0.0166\ 1/\text{lbm}_{cat}$

g_c= 32.174 lb_m*ft/(s^2*lb_f) (convert from mass to force)

$$\frac{dX}{dW} = \frac{k'}{F_{A0}} \frac{(1-X)}{(1+\varepsilon X)} p \qquad \frac{dp}{dW} = -\frac{\alpha}{2p}(1+\varepsilon X)$$



Example PBR pressure drop

$$\frac{dX}{dW} = \frac{k'}{F_{A0}} \frac{(1-X)}{(1+\varepsilon X)} p$$

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

```
(* Define terms for Ergun equation, rate *)

α = 0.0166; ϵ = -0.15; F = 1.08; k1 = 0.0266;

sol1 = NDSolve[{y'[w] == -α / (2 * y[w]) * (1 + ϵ * X[w]),
    X'[w] == k1 / F * (1 - X[w]) / (1 + ϵ * X[w]) * y[w], X[0] == 0, y[0] == 1},
   {y[w], X[w]}, {w, 64.6}];

(* Plot X as a function of catalyst weight,
pressure ratio as a function of weight *)

Show[Plot[X[w] /. sol1, {w, 0, 64}, Frame → True, PlotRange → {{0, 60}, {0, 1}},
  FrameLabel → {"Weight_catalyst", "X, y"}, PlotStyle → Red, PlotLegends → {"X"},
  LabelStyle → {Large, Black}],
 Plot[y[w] /. sol1, {w, 0, 64}, PlotRange → {{0, 60}, {0, 1}}, PlotStyle → Blue,
  PlotLegends → {"y"}, LabelStyle → {Large, Black}]]
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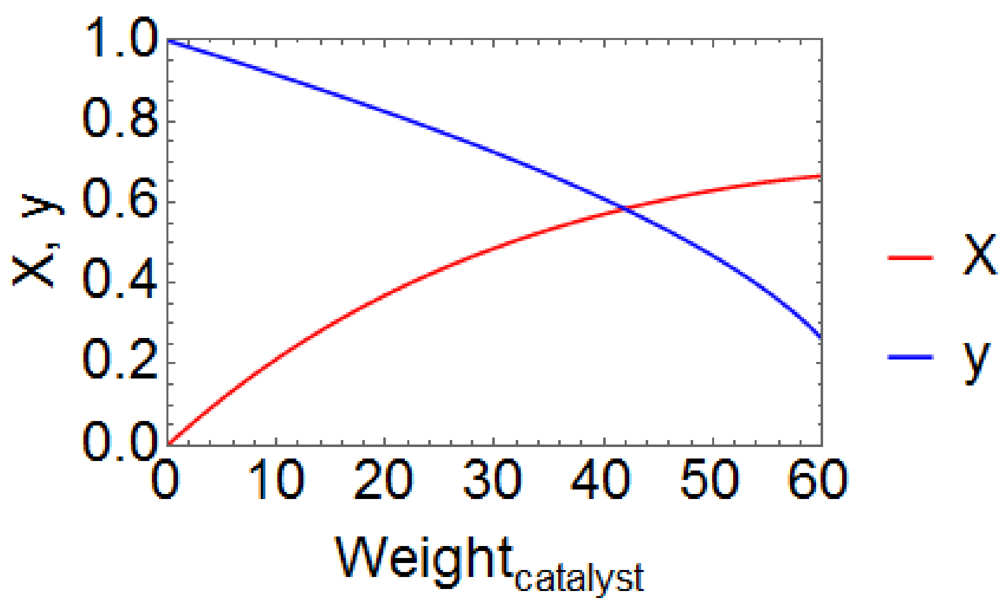

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(* Function applying interpolating function for conversion solved above *)

In[4]:= ex[w_] = X[w] /. sol1[[1]];

ex[50]

0.629527

(* Solve for value of w when X = 0.6 *)

In[5]:= NSolve[ex[w] == 0.6, w]

Out[5]= {{w → 44.4604}}

(* Find the pressure drop for this weight of catayst *)

(* Another way to do it with mma using FindRoot *)

In[54]:= FindRoot[(X[w] /. sol1) == 0.6, {w, 50}]

Out[54]= {w → 44.4604}

In[48]:= why[w_] = y[w] /. sol1[[1]];

In[55]:= why[44.4604]

Out[55]= 0.550114

In[56]:= % * 10 (* y = P/P0 and P0 = 10 atm *)

Out[56]= 5.50114

(* ΔP = 10 atmospheres - 5.5 atmosphere = 4.5 atm drop through the PBR *)
```

Calculate X at W = 50 lbm

Calculate W where X = 0.6

Calculate the pressure drop at that weight of catalyst