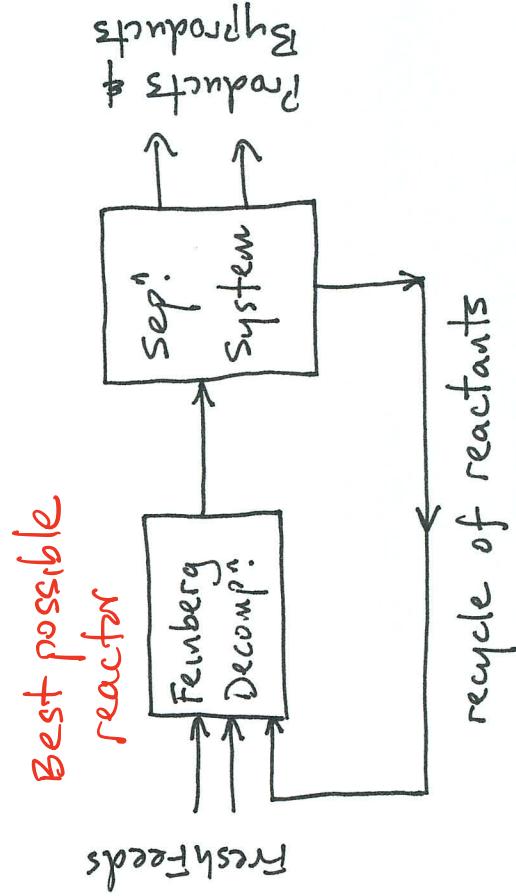
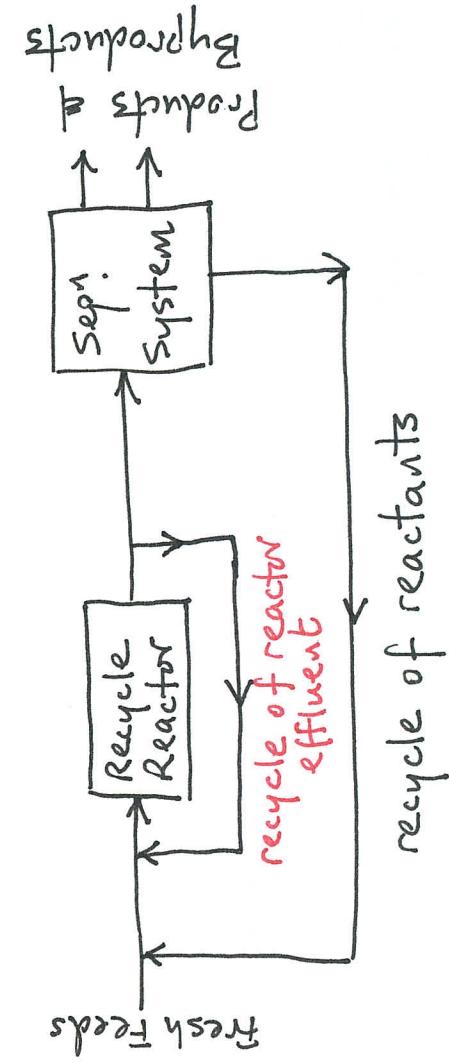
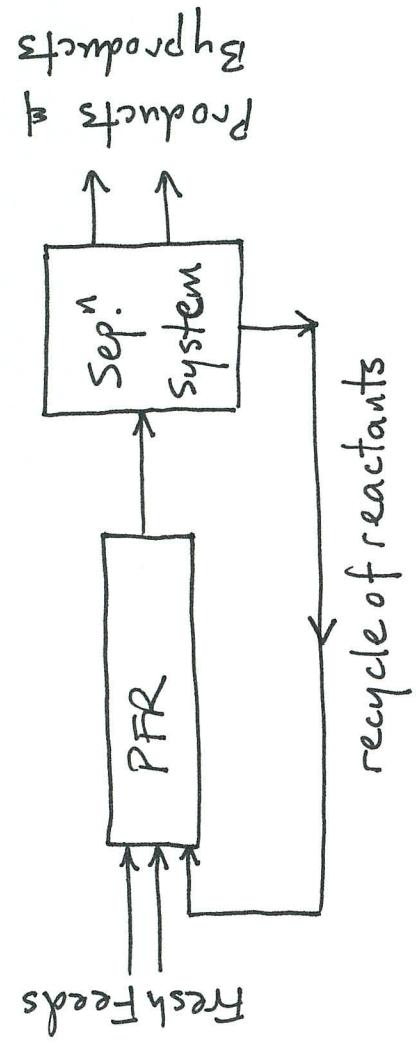
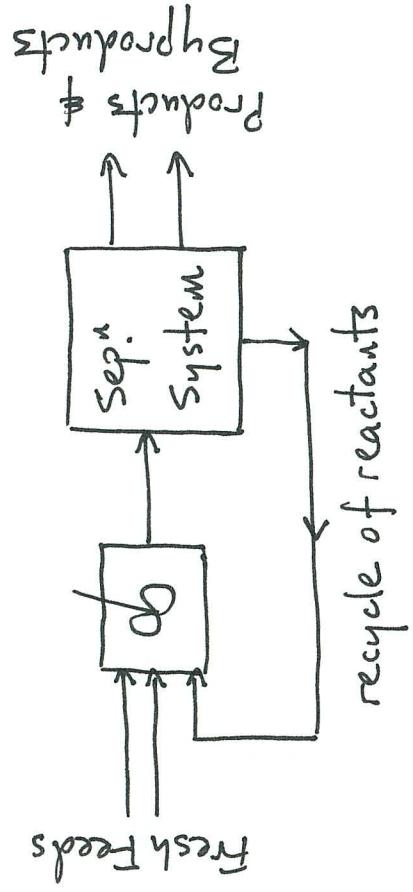
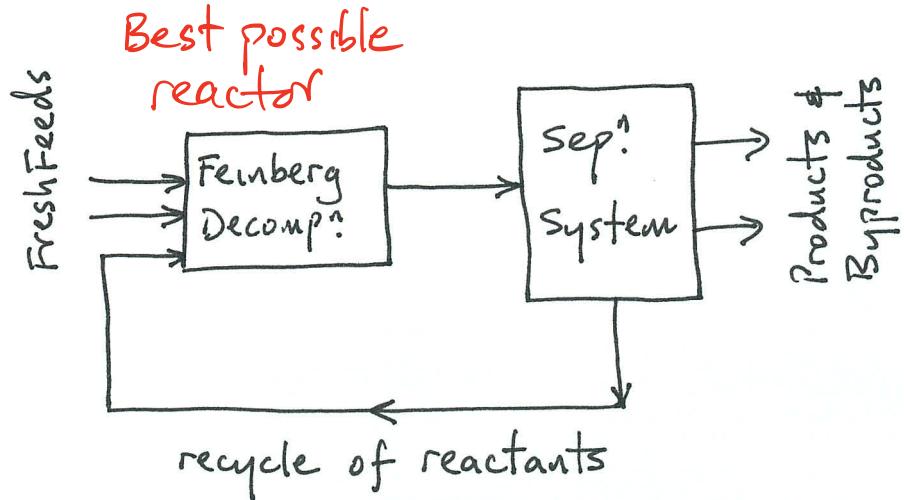
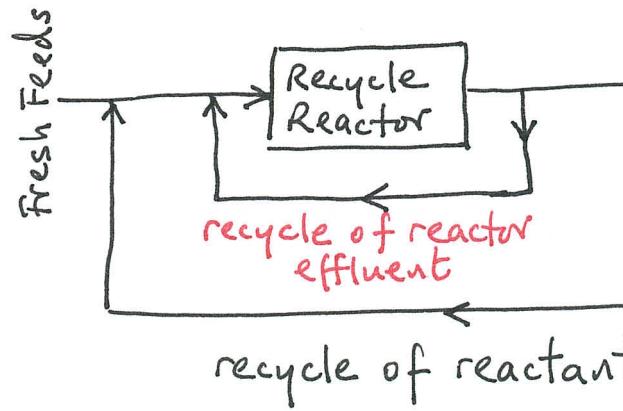
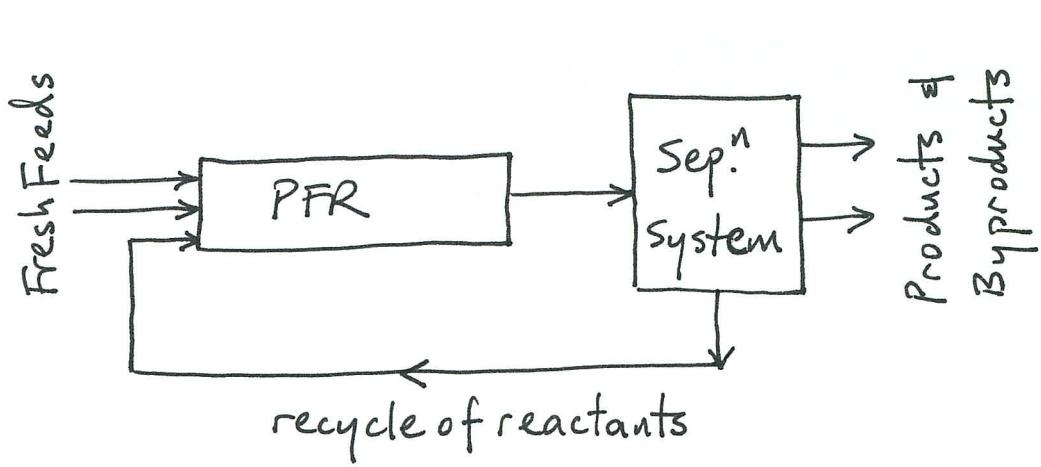
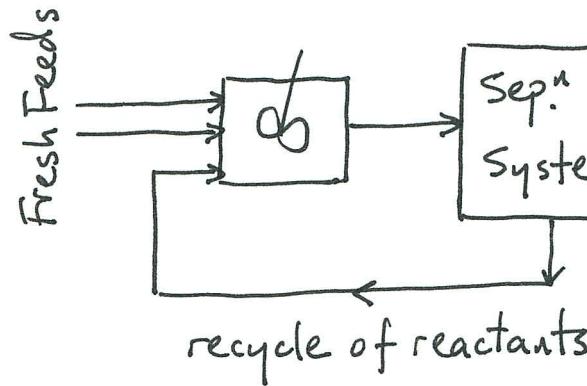


REACTOR DESIGN AT LEVEL 3

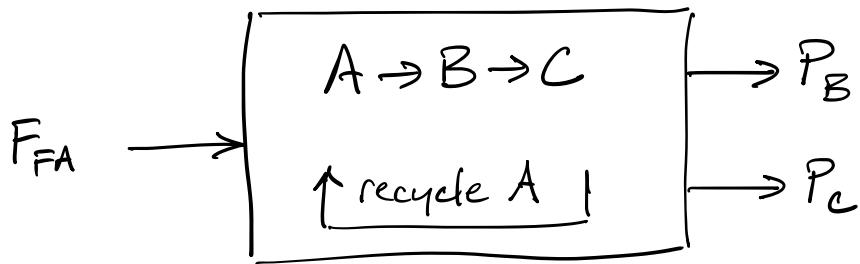


REACTOR DESIGN AT LEVEL 3



Selectivity vs Conversion : A Simple Example

Due to Prof. E.W. M'Farland



Level 2



$$C - R = 3 - 2 = 1 \quad \text{1 mole balance}$$

By inspection it is

$$F_{FA} = P_B + P_C$$

The systematic way

$$\text{balance on } A \quad F_{FA} - 0 - \xi_1 = 0$$

$$\text{balance on } B \quad 0 - P_B + \xi_1 - \xi_2 = 0$$

$$\text{balance on } C \quad 0 - P_C + \xi_2 = 0$$

Reference compnts A & C $\Rightarrow \xi_1 = F_{FA}$
 $\xi_2 = P_C$

Non-reference compnt is B.

The balance on B gives

$$-P_B + F_{FA} - P_C = 0$$

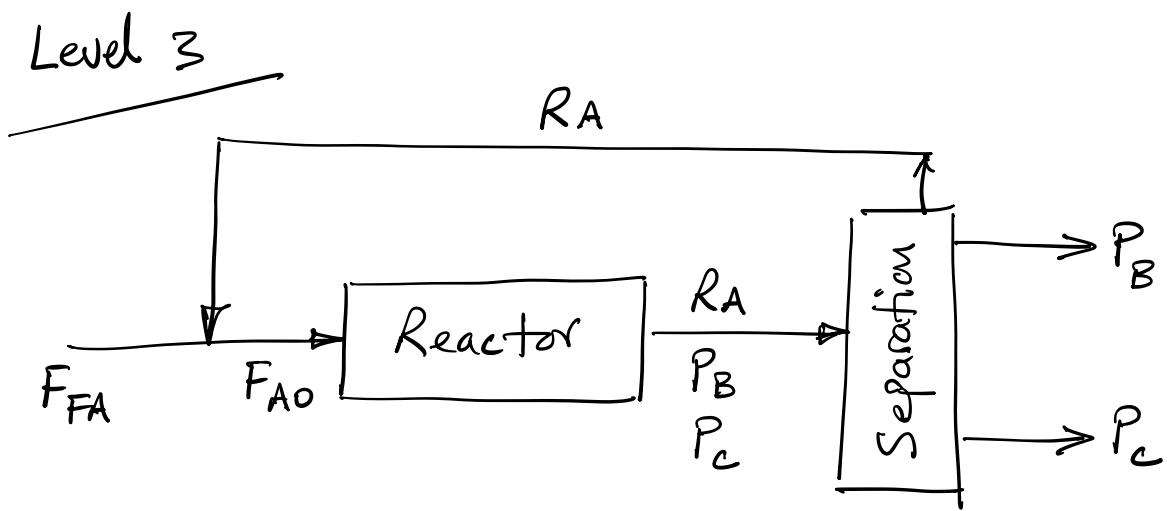
$$\text{Degrees of freedom} = 3 - 1 = 2$$

Specify P_B and s_B

$$s_B = \frac{P_B}{F_{FA}} \Rightarrow F_{FA} = \frac{P_B}{s}$$

\therefore from mole balance

$$P_C = P_B \left(\frac{1 - s_B}{s_B} \right)$$



Balance at recycle mixing point

$$F_{AO} = F_{FA} + R_A$$

\uparrow
 $= F_{AO} (1-x)$

Solve for F_{AO}

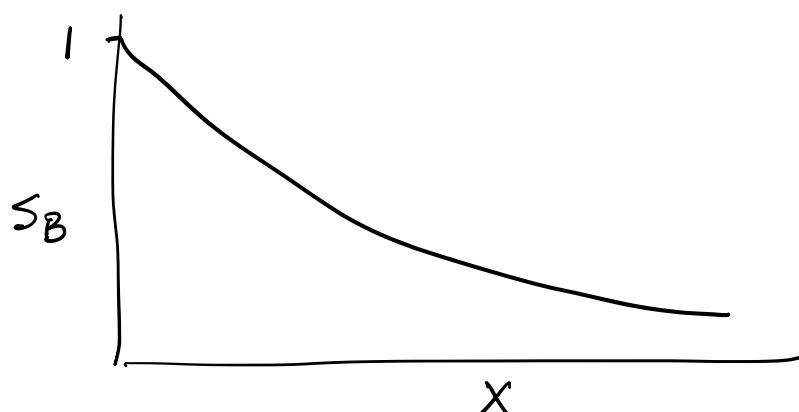
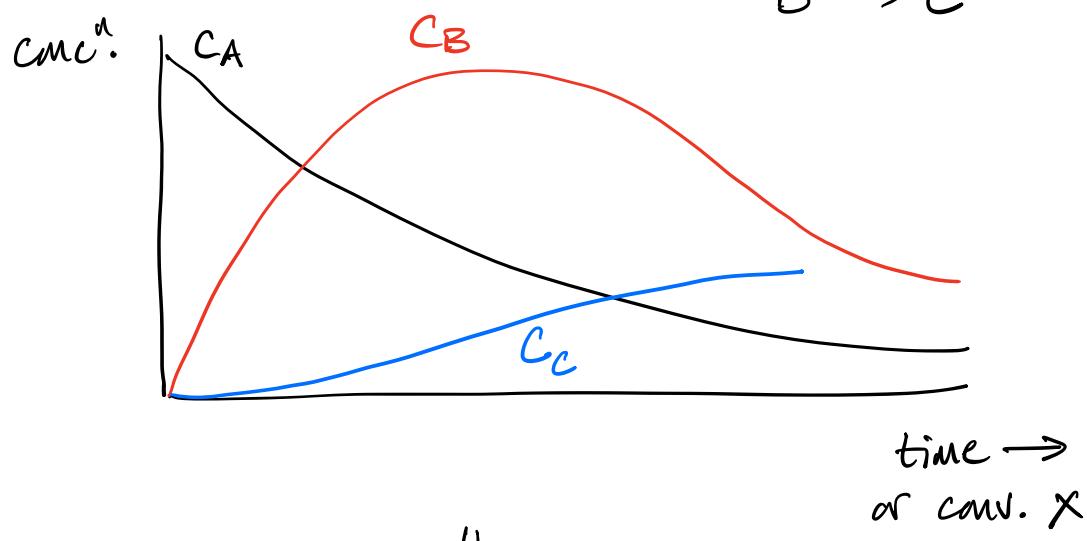
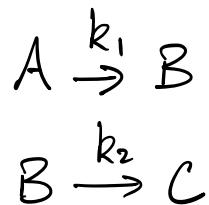
$$F_{AO} = \frac{F_{FA}}{x} = \frac{P_B}{x S_B}$$

Therefore,

$$R_A = \frac{P_B}{S_B} \left(\frac{1-x}{x} \right)$$

Need a relationship between S_B and x
 to understand all flows and reactor/separators
 sizing and cost.

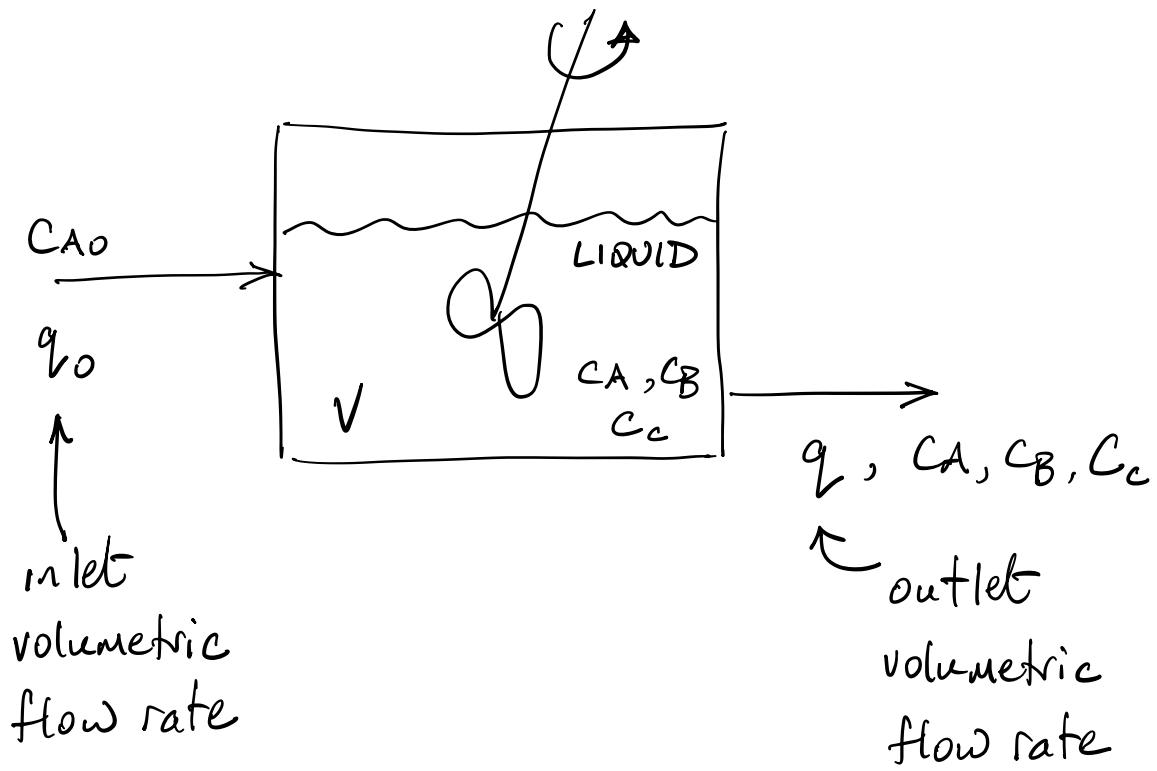
First, let's think



Which way does S_B graph go as $\frac{k_2}{k_1} \downarrow$?

CSTR

Reaction is LIQUID PHASE



Reactor mole balances

$$q_0 C_{A0} - q_1 C_A + V r_A = 0$$

Similar for B & C.

For liquids $q_0 = q_1$ (see later)

\therefore

$$C_{A0} - C_A + \tau (-k_1 C_A) = 0$$

$$0 - C_B + \tau (k_1 C_A - k_2 C_B) = 0$$

$$0 - C_C + \tau (k_2 C_B) = 0$$

$$\tau = \frac{V}{q}$$

Rearrange for τ giving

$$\tau = \frac{C_{A0} - C_A}{k_1 C_A} = \frac{C_B}{k_1 C_A - k_2 C_B} = \frac{C_C}{k_2 C_B}$$

$\underbrace{\hspace{10em}}$

solve for C_B

$$C_B = \frac{C_{A0} - C_A}{1 + \frac{k_2}{k_1} \left(\frac{C_{A0} - C_A}{C_A} \right)}$$

\nearrow

$$= \frac{x}{1-x}$$

$$S_B = \frac{C_B}{C_{A0} - C_A}$$

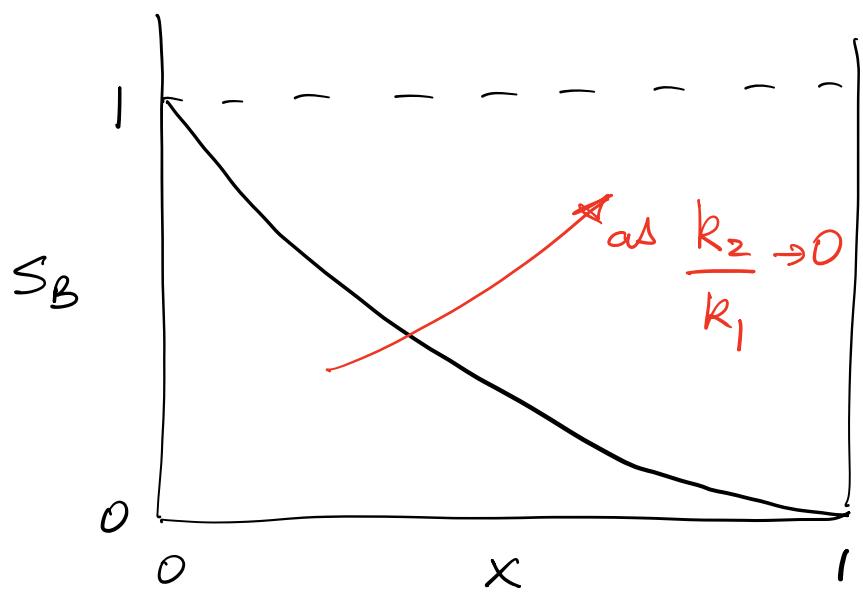
$$\therefore S_B = \frac{1}{1 + \frac{k_2}{k_1} \left(\frac{x}{1-x} \right)}$$

limits

$$x=0 \Rightarrow S_B = 1$$

$$x=1 \Rightarrow S_B = 0$$

$$\frac{k_2}{k_1} \rightarrow 0 \Rightarrow S_B \rightarrow 1 \neq x$$



Butane Alkylation Chemistry

It is desired to produce iso-octane (C_8) from a feed stream containing primarily isobutane (iC_4) and mixed butenes (C_4^{\equiv}). The primary reaction



takes place in the liquid phase in the presence of sulphuric acid catalyst. The typical sulphuric acid to hydrocarbon ratio is 1:1 on a volume basis. The allowable operating temperatures are in the range $4^{\circ}\text{C} \leq T \leq 20^{\circ}\text{C}$. At lower temperature, the reactor contents become extremely viscous and proper mixing is difficult. At higher temperatures, polymerization of the alkenes becomes significant. Within this range, production of dodecanes (C_{12}) is assumed to be the only side reaction.



The dodecanes are unwanted by-products. Both reactions are determined by the process chemists to be irreversible. The desired purity of iso-octane is 99 mol% for gasoline blending. The heavy by-product is used in the process as a fuel.

The rate of reaction of the butene via reactions (1) and (2) is given by

$$r_1 = k_1[iC_4][C_4^{\equiv}] \quad (3)$$

$$r_2 = k_2[C_8][C_4^{\equiv}] \quad (4)$$

where

$$k_1 = 3.66 \times 10^{16} \exp(-101,600/RT) \quad (5)$$

$$k_2 = 4.77 \times 10^{18} \exp(-110,850/RT) \quad (6)$$

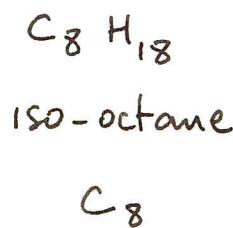
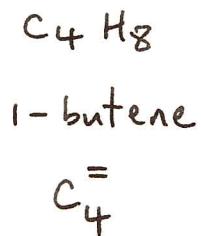
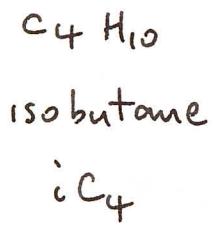
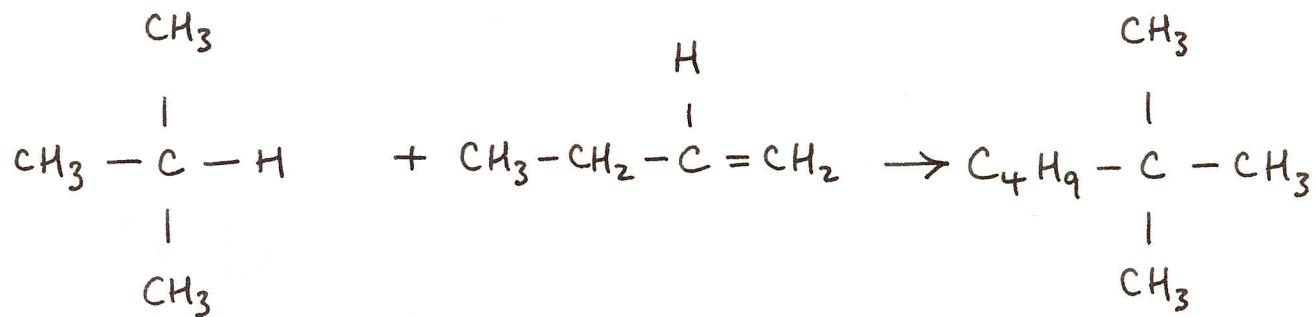
where the temperature, T , is in K, $R = 8.314 \text{ J}/(\text{gmol K})$, the units of k_1 and k_2 are $\text{L}/(\text{gmol s})$, the units of concentration are gmol/L , and the units of r_1 and r_2 are $\text{mol}/(\text{L s})$. The hydrocarbon concentrations are expressed on an acid-free basis. The reaction rate constants are based on a 1:1 acid-to-hydrocarbon ratio (by volume) in the reactor. The heats of reaction are

$$\Delta h_{\text{rxn}1} = -63.7 \text{ kJ/gmol} \quad (7)$$

$$\Delta h_{\text{rxn}2} = -67.5 \text{ kJ/gmol} \quad (8)$$

Butane Alkylation

Main reaction



Side reaction



Q. Which component is the LR ?

Statement of Problem

For a CSTR plot $S \text{ vs } X$ for a selection of reactor T & MR of butane:butene.

where

$$S = \frac{\text{moles of } C_8 \text{ in exit stream}}{\text{moles of } C_4^{\text{reacted}}}$$

$$X = \text{conversion based on } C_4^{\text{reacted}}$$

Key Assumptions for LIQUID phase reactor design.

(1) constant MASS DENSITY of process stream

$$\Rightarrow \text{e.o.s. is } \rho^{\text{mass}} = \text{constant}$$

(2) no volume of mixing

i.e. independent
of T , P and
composition

NOTE

Assumptions (1) + (2) \Rightarrow the mass density of every species is the same, $\rho_1^{\text{mass}} = \rho_2^{\text{mass}} \dots = \rho^{\text{mass}}$

SEE APPENDIX.

Selectivity vs Conversion



$$A = C_4^{\ddagger}, B = C_4, C = C_8, D = C_{12}$$

Let's assume isothermal operation (use energy balance to calculate heat load). The material balances on the species are

$$q_i C_{i0} - q_i C_i + V r_i = 0 \quad i = C_4^{\ddagger}, C_4, C_8, C_{12}$$

or

$$C_{i0} - C_i + \tau r_i = 0 \quad \tau = \frac{V}{q}$$

where

$$r_i = \sum_{r=1}^2 V_{ir} r_r$$

In these material balances we have used

$$q_{in} = q_{out} = q$$

Justified from overall balance on mass basis

$$q_{in} \rho_{in}^{\text{mass}} - q_{out} \rho_{out}^{\text{mass}} + \{\text{generation}\} = 0$$

↑ ↗ ↑
volumetric MASS = 0 on mass basis
flowrate DENSITY

Use the assumption of constant mass density

$$\rho_{in}^{\text{mass}} = \rho_{out}^{\text{mass}} \Rightarrow q_{in} = q_{out}$$

Approach

specify : $C_{1,0}$, T (hence k_1 & k_2), τ

solve : reactor design eq's for C :

$$S = \frac{\cancel{C_8}}{\cancel{C_{4,0}} - \cancel{C_4}} = \frac{C_8}{C_{4,0} - C_4} = \frac{C_c}{C_{A,0} - C_A}$$

$$X = \frac{\cancel{C_{4,0}} - \cancel{C_4}}{\cancel{C_{4,0}}} = \frac{C_{4,0} - C_4}{C_{4,0}} = \frac{C_{A,0} - C_A}{C_{A,0}}$$

Plot S vs X for various MR & T .

Analytical Solution (see Appendix)

It is only possible to solve the reactor design equations analytically for a few special chemistries. Therefore, this is NOT a general solution strategy. However, it is helpful because we can see exactly which parameters the solution depends upon, namely

$$\frac{C_{B0}}{C_{A0}} = MR \neq \frac{k_1}{k_2}$$

Numerical Solution

This approach works for all chemistries and reaction rate expressions.

Numerical solution strategy to find $s \text{ vs } x$ & $V \text{ vs } x$ curves for a CSTR.

The design eq's are:

$$C_{i0} - C_i + \tau r_i = 0 \quad i=1, 2, \dots n$$

where $\tau = \frac{V}{q}$ reactor volume

q total volumetric flow rate
of material at reactor
inlet

To begin we need to decide how to calculate q & C_{i0} .

q For simplicity we assume additivity of volumes.
(i.e., zero volume of mixing)

$$V = V_A + V_B \quad \leftarrow \text{let's assume only A \& B; if}$$

$$\Rightarrow q = q_A + q_B \quad \begin{aligned} &\text{there are more} \\ &\text{species the method} \\ &\text{generalizes.} \end{aligned}$$

$$F_i = P_i q_i \xrightarrow{i} \begin{array}{l} \text{volume/time} \\ \text{moles/time} \end{array}$$

\xleftarrow{i}

$$q_i = \frac{F_i}{P_i} \xrightarrow{i} \begin{array}{l} \text{molar flowrate of } i \\ \text{molar density of pure } i \end{array}$$

$$\therefore q = \frac{F_A}{P_A} + \frac{F_B}{P_B} \quad \text{or in general } q = \sum_i \frac{F_i}{P_i}$$

Giving

$$q = \frac{F_A}{P_A} + \frac{F_B}{P_B} \quad \text{or in general } q = \sum_i \frac{F_i}{P_i}$$

C_{i0}

Divide the boxed eqⁿ throughout by q

$$C_A \frac{F_A}{q P_A} + C_B \frac{F_B}{q P_B} = 1 \quad C_i = \frac{F_i}{q}$$

$$\Rightarrow \frac{C_A}{P_A} + \frac{C_B}{P_B} = 1$$

In general

$$\sum_i \frac{C_i}{P_i} = 1$$

molar concⁿ of each species in process stream

molar density of pure i (KNOWN phys. prop.)

$$\sum_i \frac{c_i}{p_i} = 1$$

→ true everywhere

Therefore, at reactor inlet

$$\frac{C_{A0}}{P_A} + \frac{C_{B0}}{P_B} + \frac{\cancel{C_{CO}^0}}{\cancel{P_C}} + \frac{\cancel{C_{DO}^0}}{\cancel{P_D}} = 1$$

$$MR = \frac{\text{moles B at reactor inlet}}{\text{moles A at reactor inlet}} = \frac{F_B^{in}}{F_A^{in}} = \frac{\frac{F_B^{in}}{q}}{\frac{F_A^{in}}{q}} = \frac{C_{B0}}{C_{A0}}$$

$$\therefore C_{B0} = MR C_{A0}$$

$$\frac{C_{A0}}{P_A} + \frac{C_{B0}}{P_B} = 1 \Rightarrow \frac{C_{A0}}{P_A} + \frac{MR C_{A0}}{P_B} = 1$$

Giving

$$C_{A0} = \frac{1}{\left(\frac{1}{P_A} + \frac{MR}{P_B} \right)} ; C_{B0} = MR C_{A0} = \frac{MR}{\left(\frac{1}{P_A} + \frac{MR}{P_B} \right)}$$

Comments

- (1) The eqⁿ: $\sum_i \frac{c_i}{p_i} = 1$ is equivalent to
additivity of volume fractions. see proof at very end of this section
- (2) Additivity of volumes is NOT the same as additivity of densities. Do not use additivity of densities.

Further explanations of these two comments are given at the end of this section of notes.

NOTE

The mixture density is the HARMONIC MEAN of $p_1, p_2, p_3 \dots$ NOT the arithmetic mean.

Algorithm

- (1) Specify reactor $T \neq MR$
- (2) Calculate $C_{A0} = \frac{1}{\frac{1}{P_A} + \frac{MR}{P_B}}$; $C_{B0} = MR \cdot C_{A0}$
- (3) Pick a value of τ
- (4) Solve the design equations for all $C_i(\tau)$
(nonlinear root finder)
- (5) Calculate s and x
- (6) Calculate all the molar flow rates, F_i ,
at reactor inlet from Level 2 & 3 balances
- (7) Calculate q at reactor inlet; $q = \frac{F_A}{P_A} + \frac{F_B}{P_B}$
- (8) Calculate reactor volume

$$V = \tau q$$

We now have a self-consistent set of values for V, s, x at this value of τ

- (9) loop on τ until x is close to 1
- (10) loop on $MR \neq T$
- (11) Plot graphs of s vs x and V vs x
at several values of $MR \neq T$

Note

This algorithm can be split up into two parts.

First part — calculate all values of $x \& s$
steps $1 \rightarrow 5$ followed by $9 \rightarrow 11$

Second part — from this set of values for $x \& s$
solve steps $6 \rightarrow 8$ followed by $9 \rightarrow 11$
to obtain V vs x

VERY IMPORTANT NOTE

This algorithm proves that you can calculate the s vs x relationship without knowing the flow rate of each species at the reactor inlet. This is a good thing since we cannot calculate these flows until both s and x are known.

You can calculate additional quantities as necessary or as needed, e.g.

$$x_i = \frac{F_i}{\sum_{j=1}^n F_j}$$

mole fraction

Molar density of mixture

$$V = V_1 x_1 + V_2 x_2 \dots \leftarrow \text{additivity of volumes}$$

↑ ↑ ↑
 molar volume of mixture molar volume of pure i

Hence

$$\frac{1}{P} = \frac{x_1}{P_1} + \frac{x_2}{P_2} + \dots = \sum_{i=1}^n \frac{x_i}{P_i}$$

$$P = \frac{1}{\sum_{i=1}^n \frac{x_i}{P_i}}$$

HARMONIC MEAN

$$\therefore P \neq P_1 x_1 + P_2 x_2 + \dots \leftarrow \text{do not use this}$$

The equations and the algorithm must be modified for other situations, such as:

- (1) recycle of some products/by-products or intermediates to reactor inlet;

$$\text{nw } C_{co} \text{ or } C_{DO} \neq 0$$

Must iterate on the unknown inlet conc's
e.g., carbon monoxide intermediate in
SMR process

- (2) non-isothermal or adiabatic operation;
energy balance must be solved together
with material balances

Be on the lookout for multiple steady-states

Self-Consistency Check on your reactor design calc's

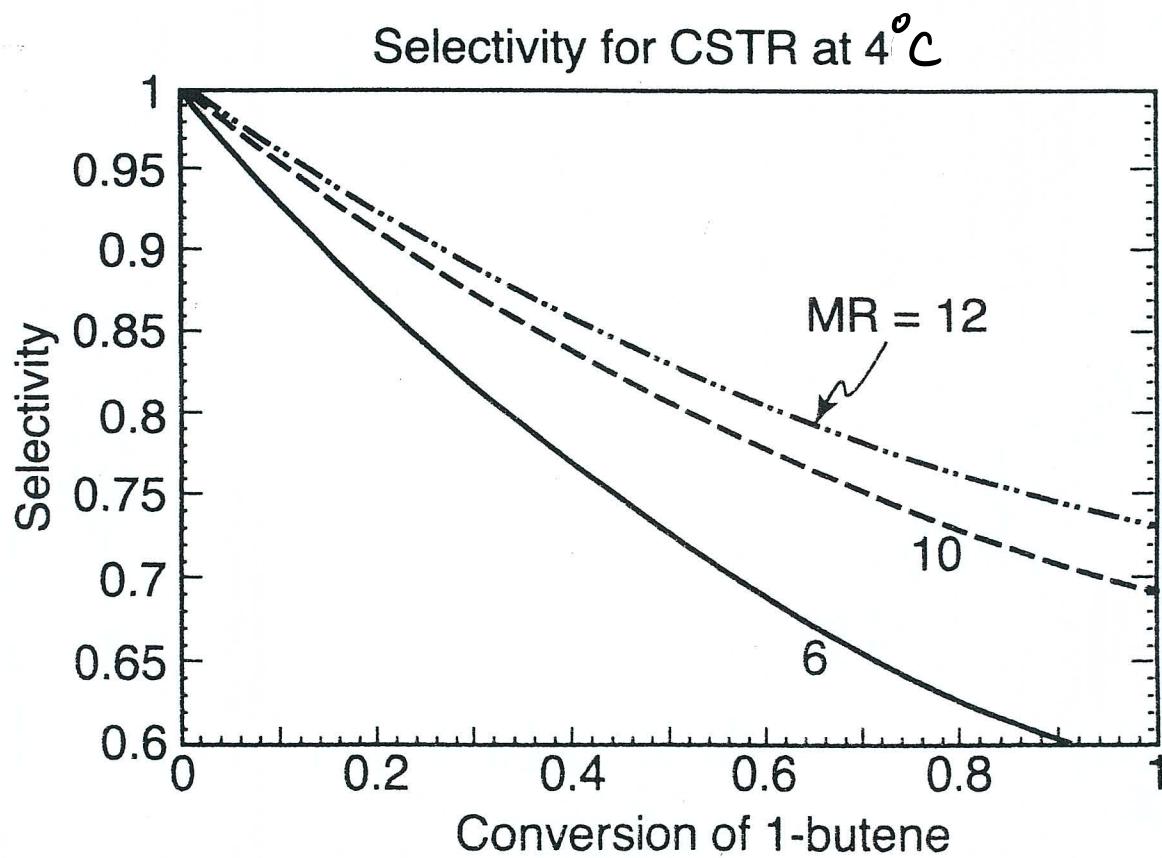
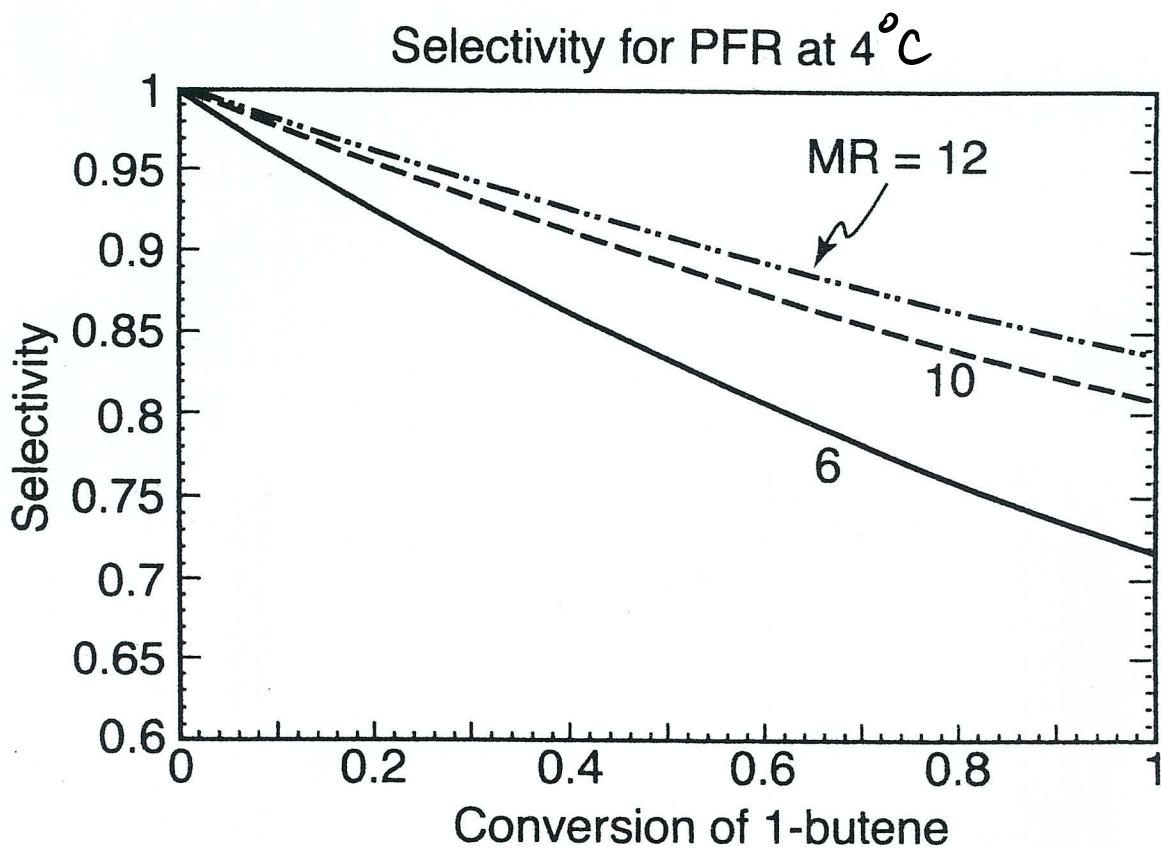
Using your rate expressions and reactor design equations calculate all the outlet concentrations from your reactor $\{C_i\}$.

LIQUID PHASE REACTOR : check $\sum_i \frac{C_i}{P_i} = 1$

If the consistency check is NOT satisfied you have made an error along the way.

Common errors include :

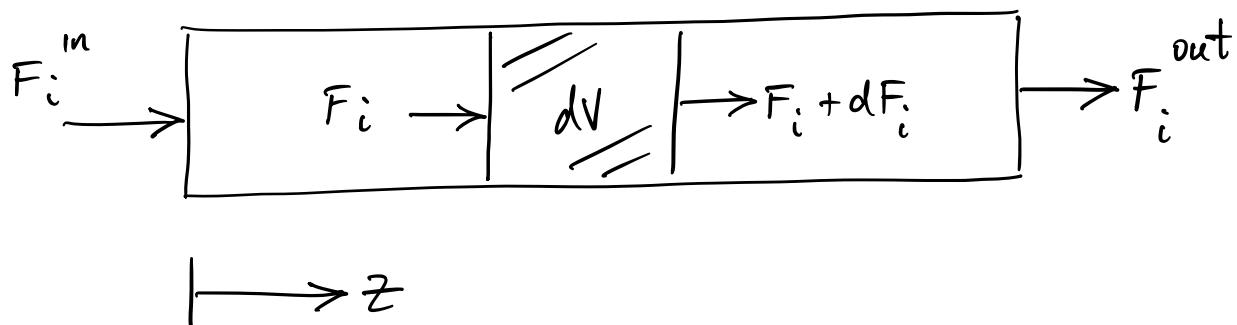
- (a) programming error
- (b) numerical methods error
- (c) problem formulation error, e.g., you have goofed up your rate expressions for species generation rates in your reactor eq's.
- (d) there are also other, more creative, ways of getting the wrong answer!



Plug Flow Reactor

Also called "piston flow reactor" because in this idealized reactor there is no longitudinal mixing or diffusion of the fluid as it moves along the length of the reactor. Thus the fluid moves along the length of the reactor as a piston

- ⇒ each fluid element entering the reactor at the same time leaves at the same time
- ⇒ there is no distribution of residence times



Steady-state mole balance on volume element dV

$$F_i - (F_i + dF_i) + r_i dV = 0$$

where

$$r_i = \sum_{r=1}^R \nu_{ir} r_r$$

↑ ↑
net rate of rate per unit volume
generation of i of reaction r
per unit volume

(negative value
 \Rightarrow depletion)

$$\therefore -dF_i = -r_i dV$$

or

$$\frac{dF_i}{dV} = r_i \quad , \text{ I.C. } F_i(V=0) = F_i^{\text{in}}$$

This is the most general form of the PFR mass balance that applies to both gases & liquids. For gases we must use this form of the equation, but for liquids it simplifies as follows.

Liquids

We again assume

$$\rho_1^{\text{mass}} = \rho_2^{\text{mass}} = \dots = \rho^{\text{mass}}$$

Thus, the mass density of the mixture is independent of composition and pressure (liquids are incompressible), and also T for moderate temperature changes (which must be the case otherwise the liquid would vaporize).

Thus,

q = constant along the length of the reactor

define

$$\tau = \frac{V}{q} \Rightarrow V = q \tau$$

$$\therefore dV = q d\tau$$

Also,

$$F_i = q C_i$$

$$\therefore dF_i = q dC_i$$

$$\therefore \frac{dF_i}{dV} = \frac{q dC_i}{q d\tau} = r_i$$

Giving

$$\frac{dC_i}{d\tau} = r_i , \text{ I.C.}, C_i(\tau=0) = C_i^{\text{in}}$$

Notes:

- (1) The reactor tube will have a constant cross-sectional area, A ,

$$\therefore V = A z$$

and increasing $V \Rightarrow$ increasing z

\Rightarrow moving down the length of the reactor

Exception: DuPont's continuous Nylon 6,6 trumpet reactor where $A \propto \sqrt{z}$

- (2) The inlet concentrations to the reactor are calculated exactly as described above for the CSTR

- (3) PFR's are almost never used for liquid phase reactions! Can you explain why?

BUT, it is important to know the plots

$S \text{ vs } X$

$\frac{d}{dt} V \text{ vs } X$

The selectivity is often much better in a PFR (No distribution of residence times) than in a CSTR (exponential decay of residence times).

When this occurs it motivates using an equivalent embodiment of a PFR (e.g., 3 liquid-phase CSTR's in series, just like the pioneers in the 1950's).

(4) The equation $\frac{dc_i}{dt} = r_i$ is exactly the same as the ODE for a liquid-phase batch reactor.

(5) Units

F_i : moles of i / time

C_i : moles of i / volume

r_i : moles of i / (volume \times time)

Calculations for Liquid-Phase PFR

Use the same algorithm as for a CSTR except in step (4) we integrate the ODE's

$$\frac{dC_i}{d\tau} = r_i \quad ; \quad C_i(\tau=0) = C_{i0}$$

from $\tau=0$ up to the current value of τ .
We could use a Runge - Kutta method.

A particularly simple integration method is the backwards Euler method with a constant time increment, $\delta\tau$.

$$\frac{C_i(n\delta\tau) - C_i((n-1)\delta\tau)}{\delta\tau} = r_i((n-1)\delta\tau)$$

previous step
(KNOWN) ↗

↙ current step

$$\therefore C_i(n) = C_i(n-1) + \delta\tau \cdot r_i(n-1)$$

This equation gives an explicit formula for C_i in step (4).

Self-Consistency Check on your reactor design calc's
Same check as earlier for CSTR

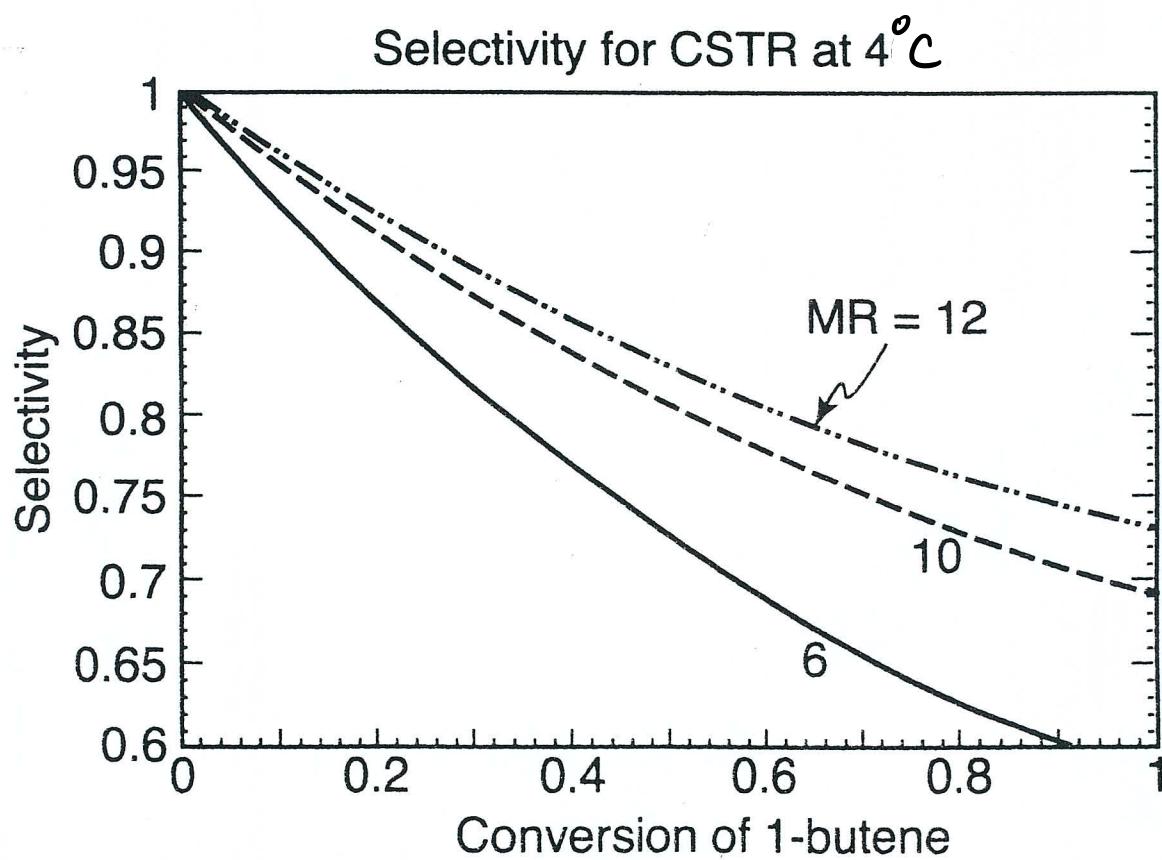
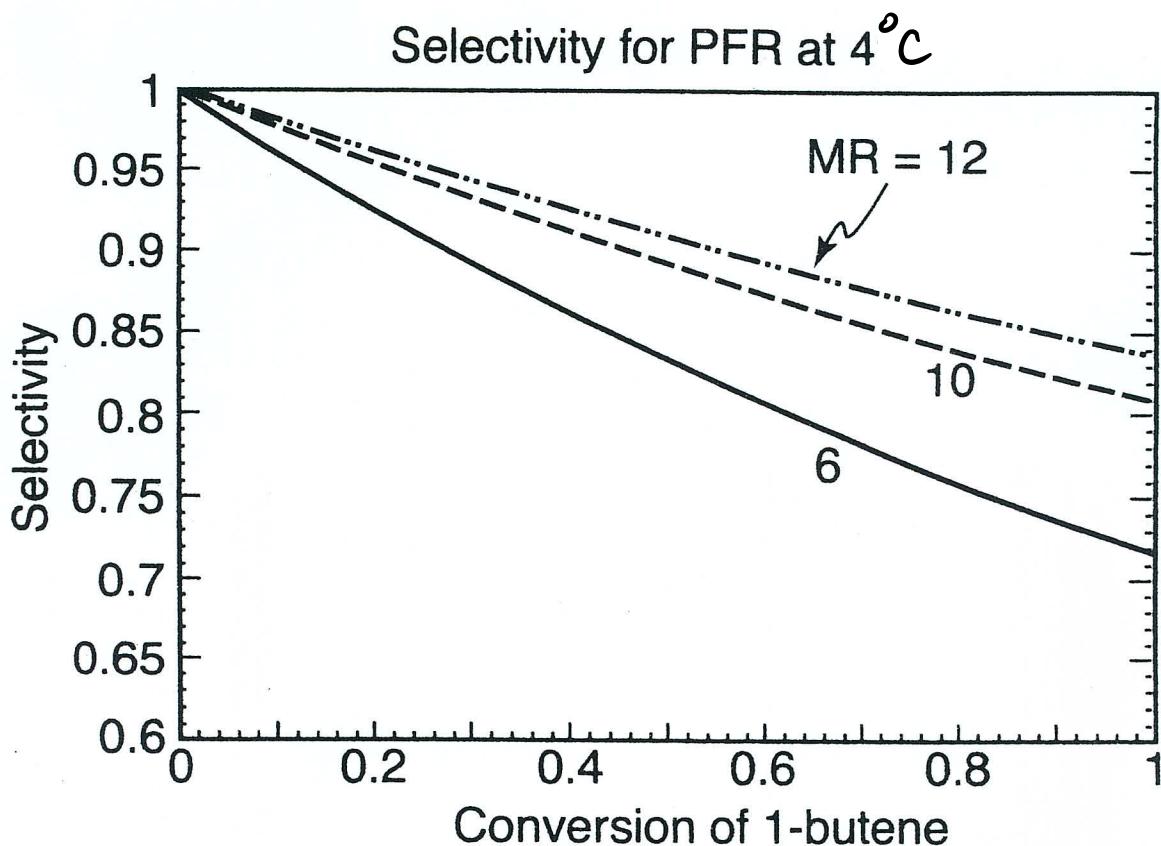
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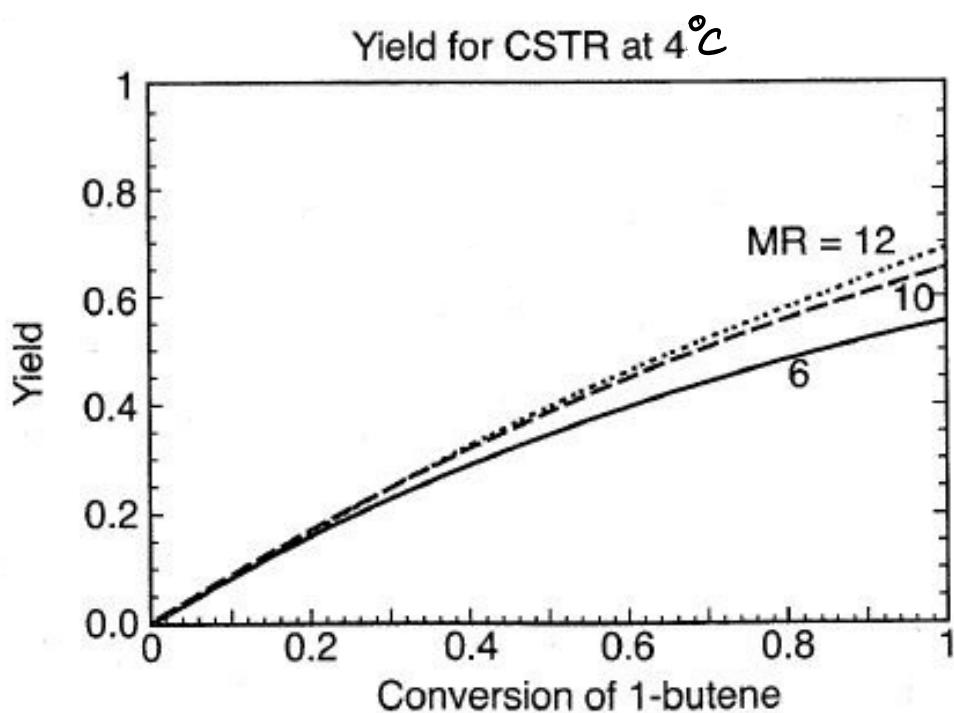
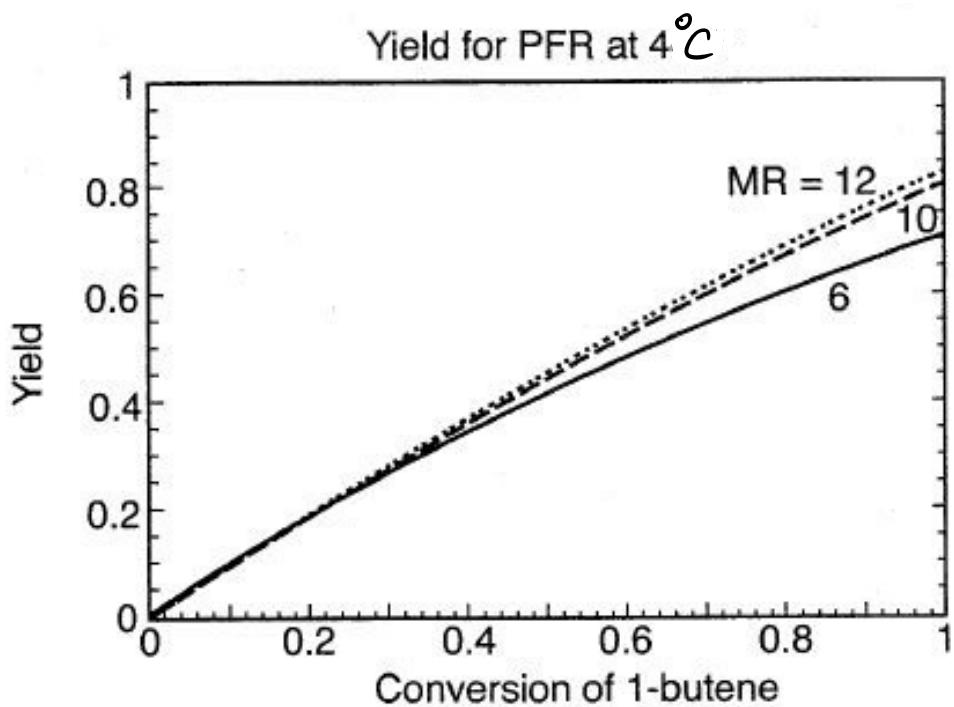
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- (b) numerical methods error
- (c) problem formulation error, e.g., you have goofed up your rate expressions for species generation rates in your reactor eq's.
- (d) there are also other, more creative, ways of getting the wrong answer!





Analytic Solutions

CSTR: $S = \frac{1}{1 + 2K \left(\frac{x_B}{1-x_B} \right)}$

$$x_A = MR \cdot x_B \left\{ \frac{1 + 2K \left(\frac{x_B}{1-x_B} \right)}{1 + K \left(\frac{x_B}{1-x_B} \right)} \right\}$$

$$K = \frac{k_2}{k_1}$$

$$LR = A$$

x_i = conversion of i

PFR: $S = \frac{Z \cdot MR \cdot x_B}{x_A} - 1$

$$x_A = \frac{MR}{1-K} \left\{ x_B (1-2K) + 1 - (1-x_B)^K \right\}$$

Algorithm

- (1) specify MR, T ($\Rightarrow k_1, k_2$)
- (2) specify an initial small value for x_B
- (3) calculate S
- (4) calculate x_A
- (5) STOP if x_A is close to 1.0
- (6) increment x_B
- (7) increment MR & T

Gas-Phase PFR

Gases are compressible and also change their volume with change in moles by reaction, and by change in T . This can be seen from the Perfect Gas Law.

$$V = \frac{nRT}{P}$$

Therefore, we use the general form of the PFR design equation without any attempted simplification,

$$\frac{dF_i}{dV} = r_i \quad , \quad F_i(V=0) = F_i^{\text{in}}$$

F_i = moles of i / time

r_i = moles of i / (volume \times time)

The snag with this equation is that the kinetic rate equations embedded in f_i will be written in terms of either

- partial pressures
- or • concentrations
- or • some other measure of composition

Therefore, before we can integrate the ODE's we must convert the rate expressions from composition variables to molar flow rates.

We do this using the P.G. Law

$$PV = nRT$$

NOTE: This Law implies zero volume of mixing for the constituent gases, therefore, this assumption is already incorporated into the following model.

Consider a mixture of two PG's at total pressure P & temperature T .

All the molecules in the gas experience the same pressure P and the same temperature T .

Therefore, for PG 1 :

$$\rightarrow P_1 = \frac{n_1}{V_1} = \frac{P}{RT}$$

$$PV_1 = n_1 RT$$

\nearrow Volume occupied
by mols 1

\nwarrow number of moles of 1

and for PG 2

$$\rightarrow P_2 = \frac{n_2}{V_2} = \frac{P}{RT}$$

$$PV_2 = n_2 RT$$

Adding these equations gives

$$P(V_1 + V_2) = (n_1 + n_2) RT$$

\nearrow
 V

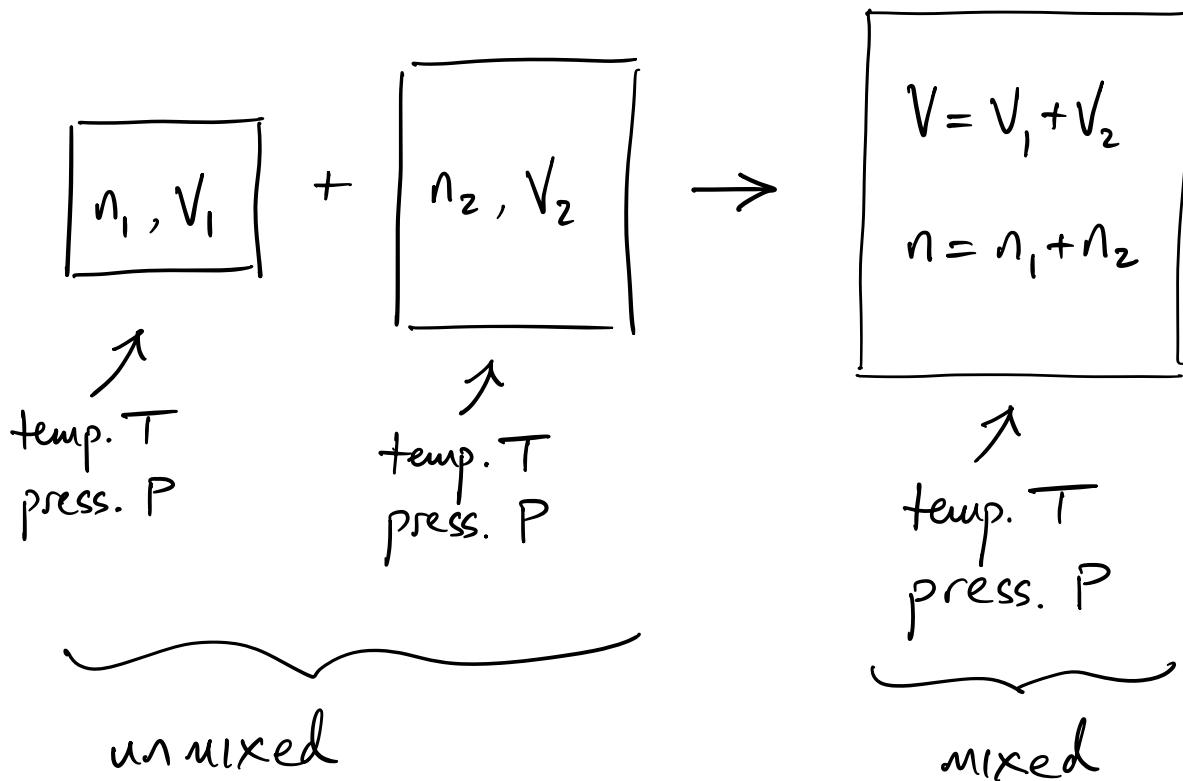
\nearrow
 n

or

$$PV = nRT$$

↑
total volume ↑ total moles

Equivalently



For flow systems we have

$$P_g = FRT$$

↑ ↑
total volume total molar
flowrate flowrate

$$\therefore q = F \left(\frac{RT}{P} \right)$$

$$\text{and } q_i = F_i \left(\frac{RT}{P} \right)$$

Note:

$$P_1 = P_2 = \dots = P_i = P_{\text{overall}} = \frac{P}{RT}$$

since all components are PGs & all have the same molar density at same T & P

$$\therefore q_i = \frac{F_i}{P_i}$$

same functional form as used earlier for liquids but now P_i depends on T & P

Measures of composition in a PG mixture

① mole fraction, y_i :

for a flow system

$$y_i = \frac{n_i}{n} = \frac{F_i}{F_{\text{tot}}}$$

where $n = \sum_{i=1}^c n_i$

② partial pressure, P_i :

$$P_i = P y_i \quad \leftarrow \text{this is a definition of } P_i$$

Notice

$$\sum_i P_i = P \sum_i y_i = P$$

For a flow system, $y_i = \frac{F_i}{F_{\text{total}}}$

$$\therefore P_i = \left(\frac{F_i}{F_{\text{tot}}} \right) P$$

③ Concentration, C_i :

$$C_i = \frac{n_i}{V}$$

moles of i in mixture
total volume of mixture

For a flow system

$$C_i = \frac{F_i}{q}$$

Now, for a PVT mixture

$$P V = n R T$$

↑ ↑ ↗

total pressure total volume total moles

and for a flow system

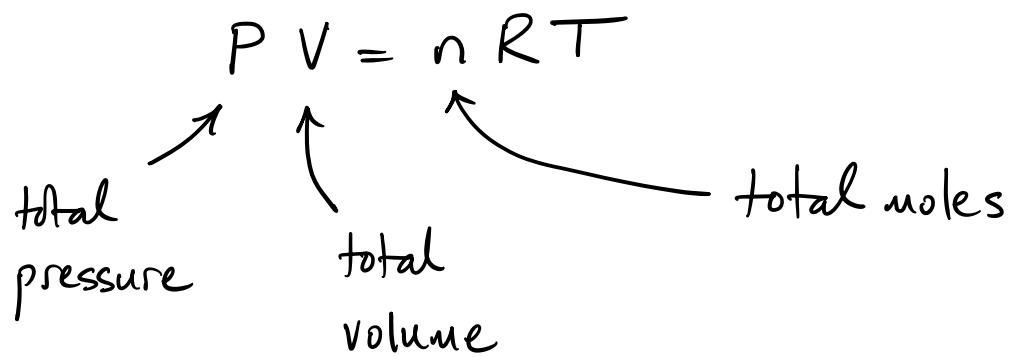
$$P q = F_{\text{total}} R T$$

$$\therefore q = F_{\text{tot}} \frac{R T}{P}$$

Giving

$$C_i = \frac{F_i P}{F_{\text{tot}} RT}$$

(4) Relationship between P_i & C_i :



Multiply each side by y_i :

$$\frac{Py_i}{P_i} V = \frac{ny_i}{n_i} RT$$

$$\therefore P_i = \left(\frac{n_i}{V} \right) RT$$

$\star C_i$

Therefore,

$$P_i = C_i RT$$

use to interchange
molar concentrations
and partial pressures
in rate expressions

Summing both sides over all species in the mixture gives

$$\sum_i C_i = \frac{P}{RT}$$

and noting that at a given T & P we have

$$P_1 = P_2 = \dots = P_{\text{mixture}}$$

we obtain

$$\sum_i \frac{C_i}{P_i} = 1$$

Same equation as for liquids except now the MOLAR DENSITY is the same for each gas

at the same T & P instead of the
MASS DENSITY.

Reactor Volume

Reactor volume increases with increasing conversion of LR. It has the following limits

$$x \rightarrow 1 \quad V \rightarrow \infty$$

(or $x \rightarrow x_{eq}$) \quad \Rightarrow \text{infinite cost}

$$x \rightarrow 0 \quad V \rightarrow \text{constant value} > 0$$

This is true when the production rate is fixed

Let's show this for the simplest case. The result generalizes to all cases.

Consider 1st order LIQUID PHASE reaction



such that

$$r_A = -k C_A$$

Level 2 balance

$$F_{FA} = P_B \xleftarrow{\text{fixed}}$$

Level 3 balances

fresh feed of A to plant

flow rate of A in to reactor $\rightarrow F_A^{\text{in}} = \frac{F_{FA}}{x} = \frac{P_B}{x}$

$$R_A = P_B \left(\frac{1-x}{x} \right)$$

Isothermal, steady-state reactor design equation

$$\frac{C_{A0} - C_A}{C_A} = k \tau$$

dimensionless ratio

dimensionless

$$= \frac{\tau}{\left(\frac{1}{k}\right)} \xleftarrow{\text{process time}} \xleftarrow{\text{reaction time}}$$

Damköhler number

$$Da = k\tau = \frac{kV}{q}$$

$$\therefore \frac{C_{A0} - C_A}{C_A} = Da$$

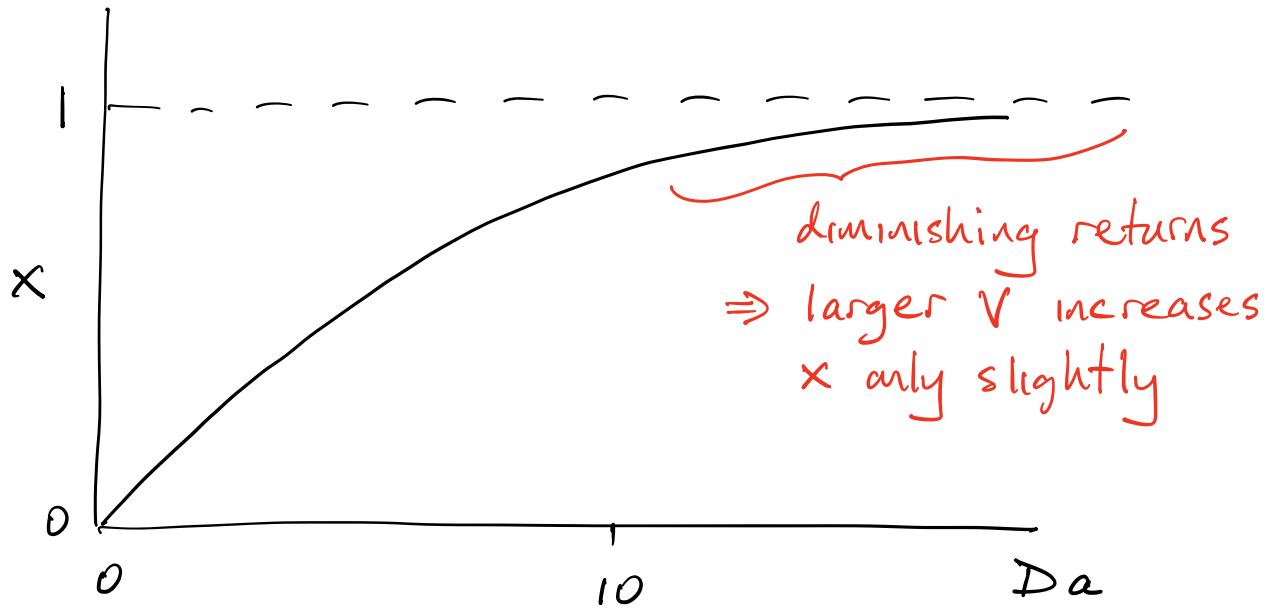
$$x = \frac{C_{A0} - C_A}{C_{A0}} \Rightarrow \frac{C_{A0} - C_A}{C_A} = \frac{x}{1-x}$$

$$\boxed{\frac{x}{1-x} = Da}$$

This is the dimensionless S-S CSTR
design equation for isothermal, liq. phase
 $A \rightarrow B$ reaction.

Plot of x vs Da

$$x = \frac{Da}{1+Da}$$



From the design equation

Da	x	
0.1	0.1	
0.5	0.33	
1	0.5	
10	0.91	
20	0.95	

$\left. \begin{array}{l} \\ \\ \\ \\ \end{array} \right\}$ Normal range of x and Da

Normal reactor design

$$0.5 < Da < 10$$

Scale-up

$$(Da)_{\text{lab reactor}} = (Da)_{\text{commercial reactor}}$$

Reaction Times (determined by chemistry)	Process Times (determined by CHE's)
oxidation $\frac{1}{k} \sim 0.01 \text{ s}$	$\tau \sim 0.1 \text{ s}$
chlorination of propylene @ 400°C	$\tau \sim 1-2 \text{ s}$
esterifications	$\tau \sim 40-60 \text{ min}$

Back to reactor volume

$$\frac{Vk}{q} = \frac{x}{1-x}$$

∴ $V = \frac{q}{k} \left(\frac{x}{1-x} \right)$

use

$$q = \frac{F}{P} \Rightarrow q = \frac{F_A^{\text{in}}}{P_A} \frac{P_B}{x}$$

molar density of pure A

∴ $V = \frac{P_B}{k P_A} \left(\frac{1}{1-x} \right)$

all known constants

∴ $x \rightarrow 1 \Rightarrow V \rightarrow \infty$

$$x \rightarrow 0 \Rightarrow V \rightarrow \frac{P_B}{k P_A} > 0$$

QED

For PFR

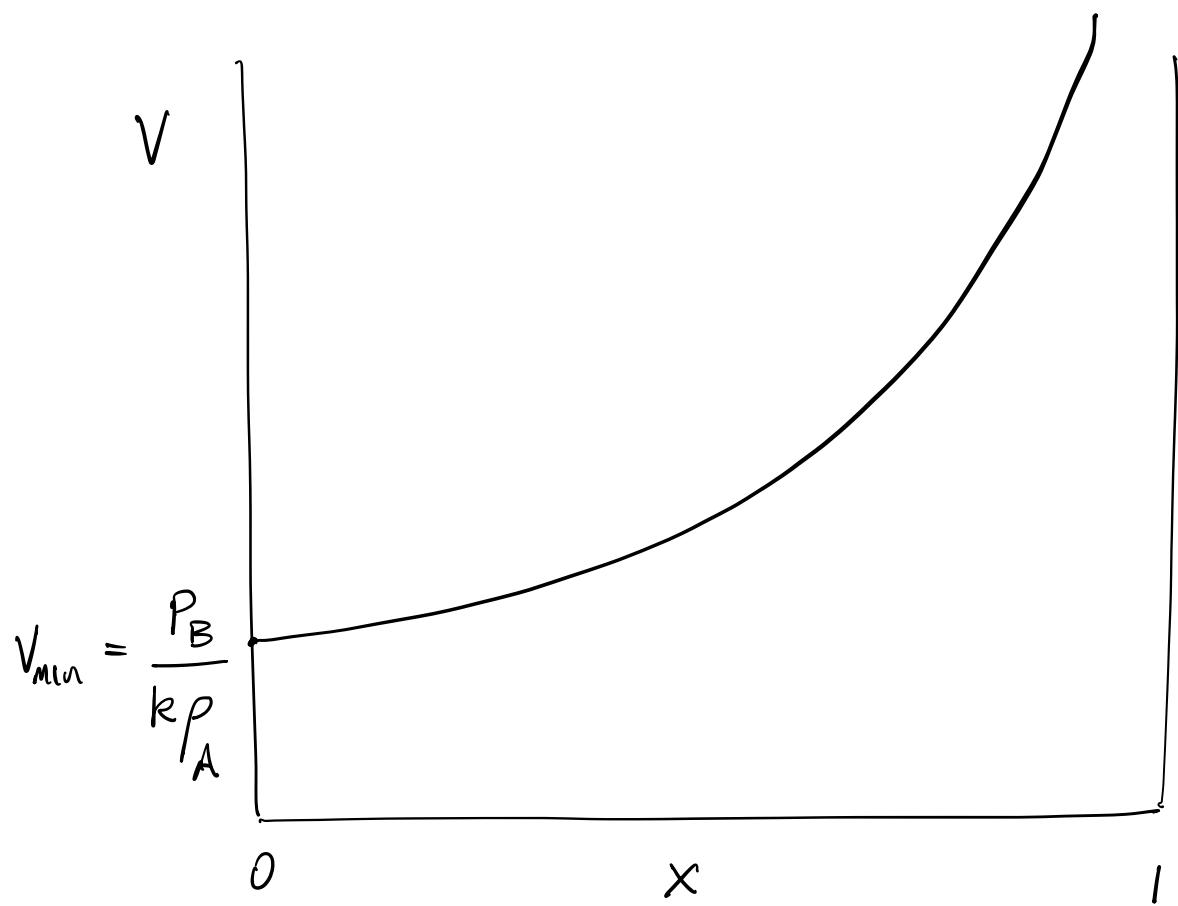
$$\ln\left(\frac{1}{1-x}\right) = Da \quad \text{↑} \\ = \frac{V k}{q}$$

Giving

$$V = \frac{P_B}{k P_A} \cdot \underbrace{\frac{1}{x} \ln\left(\frac{1}{1-x}\right)}_{\text{as } x \rightarrow 0 \text{ this term} \rightarrow 1}$$

\therefore same result as CSTR @ $x=0$ & $x=1$

For generalization to 2nd order reactions
see Appendix



Level 3 Results for HDA Plant

Taken from Vedika Shenoy, Jonathan Chen and Ginny Wang, senior ChE class 2022

Reactor Model

The general PFR design equation for this system are as follows:

$$\frac{dF_T}{dV} = -r_1 \quad (\text{B.1})$$

$$\frac{dF_H}{dV} = -r_1 + r_2 \quad (\text{B.2})$$

$$\frac{dF_M}{dV} = r_1 \quad (\text{B.3})$$

$$\frac{dF_B}{dV} = r_1 - 2r_2 \quad (\text{B.4})$$

$$\frac{dF_D}{dV} = r_2 \quad (\text{B.5})$$

The given rate expressions for the main reaction (r_1) and side reaction (r_2) are as follows:

$$r_1 = k_1 C_T C_H^{0.5} \quad (\text{B.6})$$

$$r_2 = k_2 R^2 T^2 (C_B^2 - \frac{C_D C_H}{K_{eq}}) \quad (\text{B.7})$$

Both rate expressions have units of g mol/(L h).

The following expression can be used to cast the rate equations in terms of molar flow rates of each component:

$$C_i = \frac{F_i}{q} = \frac{F_i P}{F_{tot} RT} \quad (\text{B.8})$$

These expressions can be substituted into the PFR design equations:

$$\frac{dF_T}{dV} = -k_1 \left(\frac{F_T P}{F_{tot} RT} \right) \left(\frac{F_H P}{F_{tot} RT} \right)^{0.5} \quad (\text{B.9})$$

$$\frac{dF_H}{dV} = -k_1 \left(\frac{F_T P}{F_{tot} RT} \right) \left(\frac{F_H P}{F_{tot} RT} \right)^{0.5} + k_2 R^2 T^2 \left[\left(\frac{F_B P}{F_{tot} RT} \right)^2 - \frac{\left(\frac{F_D P}{F_{tot} RT} \right) \left(\frac{F_H P}{F_{tot} RT} \right)}{K_{eq}} \right] \quad (\text{B.10})$$

$$\frac{dF_M}{dV} = k_1 \left(\frac{F_T P}{F_{tot} RT} \right) \left(\frac{F_H P}{F_{tot} RT} \right)^{0.5} \quad (\text{B.11})$$

$$\frac{dF_B}{dV} = k_1 \left(\frac{F_T P}{F_{tot} RT} \right) \left(\frac{F_H P}{F_{tot} RT} \right)^{0.5} - 2k_2 R^2 T^2 \left[\left(\frac{F_B P}{F_{tot} RT} \right)^2 - \frac{\left(\frac{F_D P}{F_{tot} RT} \right) \left(\frac{F_H P}{F_{tot} RT} \right)}{K_{eq}} \right] \quad (\text{B.12})$$

$$\frac{dF_D}{dV} = k_2 R^2 T^2 \left[\left(\frac{F_B P}{F_{tot} RT} \right)^2 - \frac{\left(\frac{F_D P}{F_{tot} RT} \right) \left(\frac{F_H P}{F_{tot} RT} \right)}{K_{eq}} \right] \quad (\text{B.13})$$

$$F_{tot} = F_T + F_H + F_M + F_B + F_D \quad (\text{B.14})$$

The kinetic parameters supplied by the Technical Data Sheet.

PSA Alternative

All methane exits the plant (along with some hydrogen). No methane is recycled, therefore gas recycle flow rate is much smaller than the Recycle & Purge Alternative.

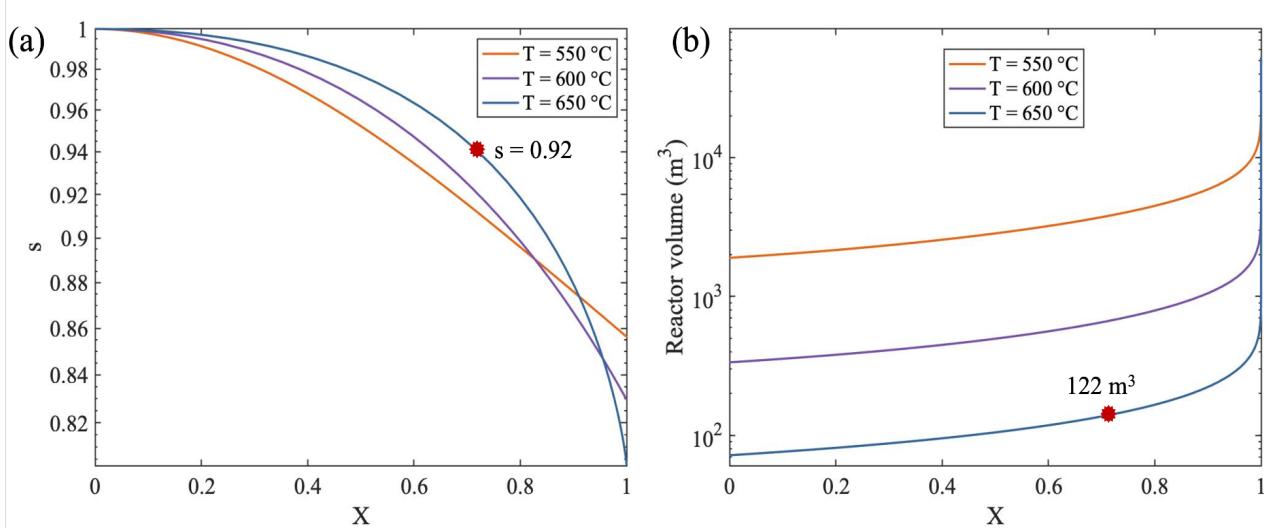


Figure 1. (a) Relationship between benzene selectivity (s) and conversion (X), and (b) between reactor volume and X . Curves are generated for temperatures ranging from $550\text{-}650\text{ }^{\circ}\text{C}$, which are the lower and upper bounds of allowable temperatures, respectively. Plots were generated for $\text{MR} = 5$ and $P = 30\text{ bar}$. The red star indicates the operating conditions in the base-case design, at a conversion of 0.73.

only H₂

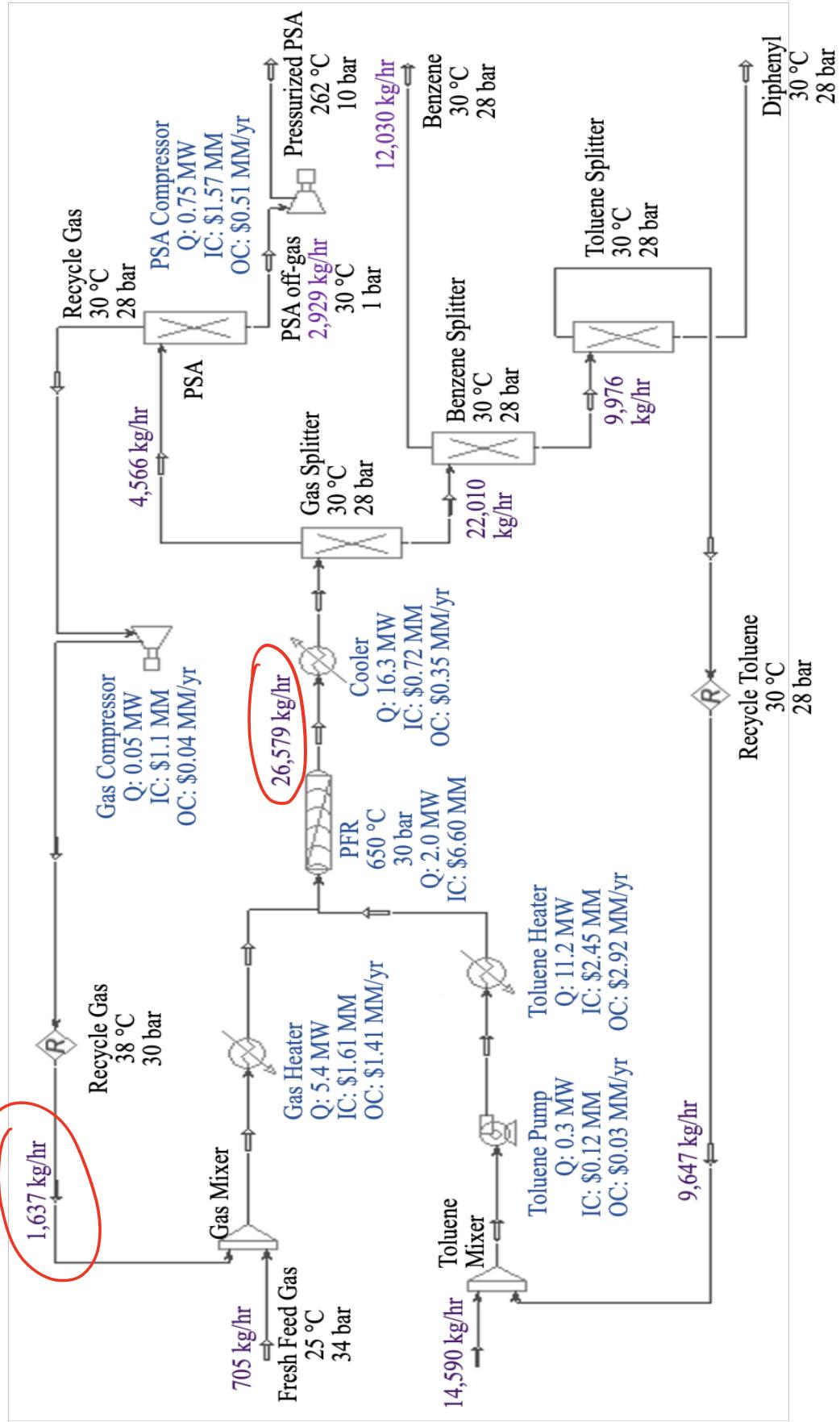


Figure 4 – Converged HYSYS process flow diagram with unit operations labeled in purple, and material streams labeled in black. Included in the unit operations labels are operating conditions, such as temperature and pressure, heat duty, initial costs, and operating costs. Included in the material streams are stream name, temperature, and pressure.

$17,020 \text{ kg/hr}$, mostly CH_4

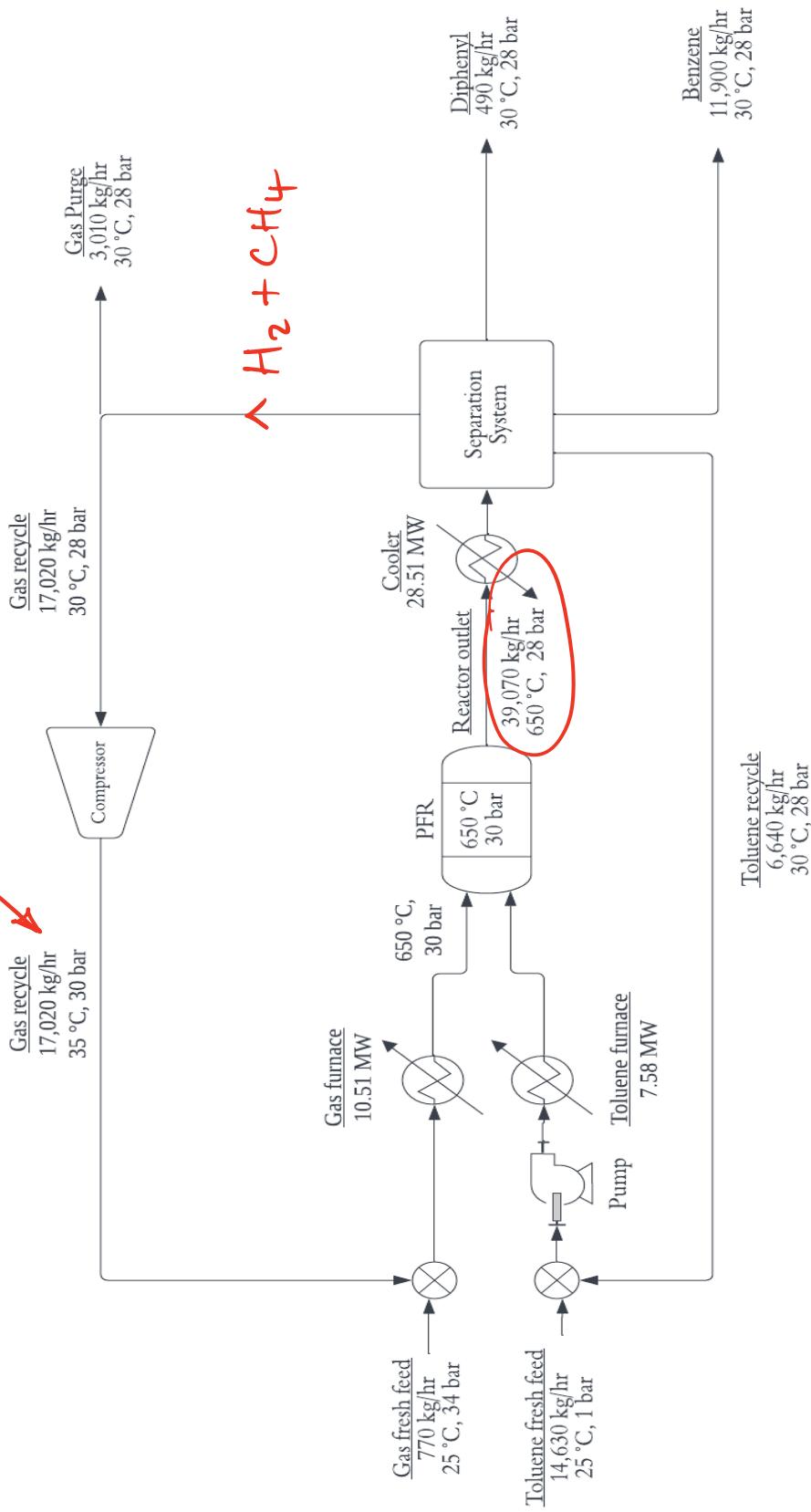


Figure G.2 - Matlab PFD for process alternative with gas purge and recycle.

$$y_{PH} = 0.4$$

Table G.3 - Equipment sizes for the **PSA process alternative**

Equipment	Size
PFR volume	102.9 m ³
Heat exchanger area	766.5 m ²

Table G.6 - Equipment sizes from Matlab conceptual design for the **gas recycle & purge process alternative**

Equipment	Size
PFR volume	306.2 m ³
Heat exchanger area	761.9 m ²

larger because of larger
flow rate through reactor

Preview of Level 4 (PSA Alternative)

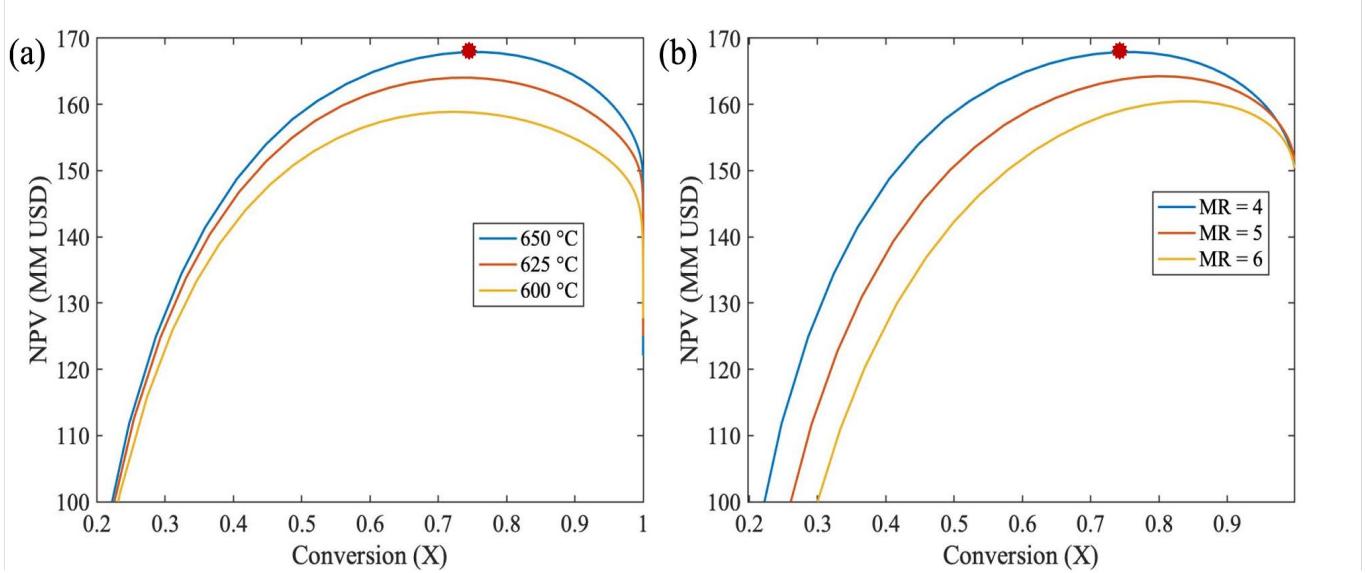


Figure 2. PSA process alternative. (a) NPV in MM USD as a function of conversion, at varied reactor temperatures, and (b) MR of H₂ to toluene. Curves in (a) were generated for MR = 4 and P = 30 bar, and curves in (b) were generated for T = 650 °C and P = 30 bar, with an optimal conversion of 0.73 when MR = 4.

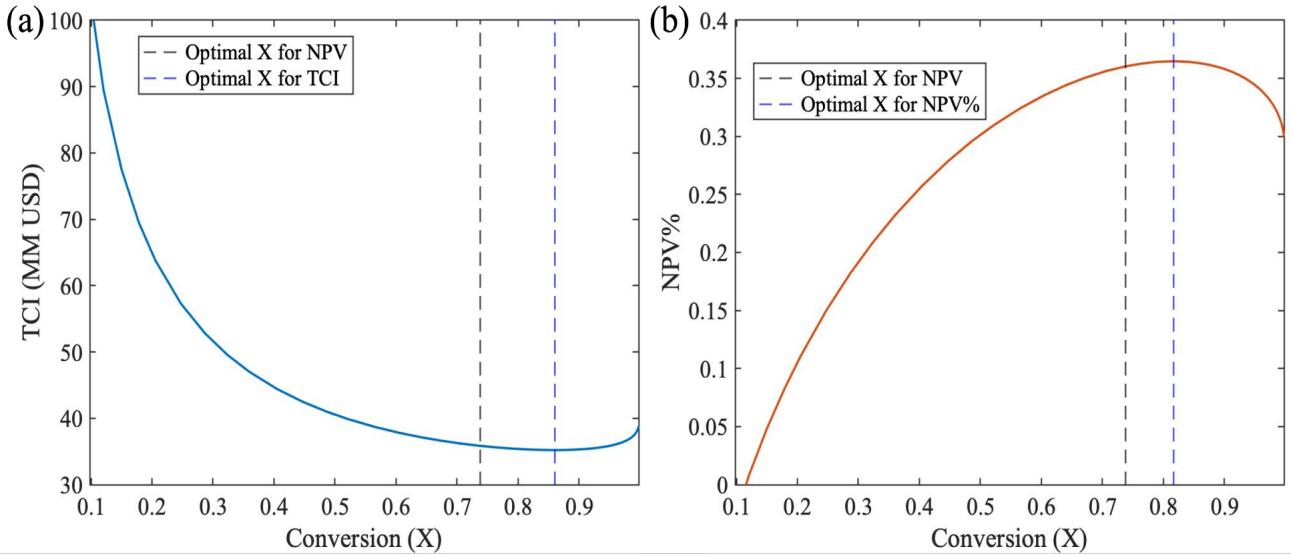
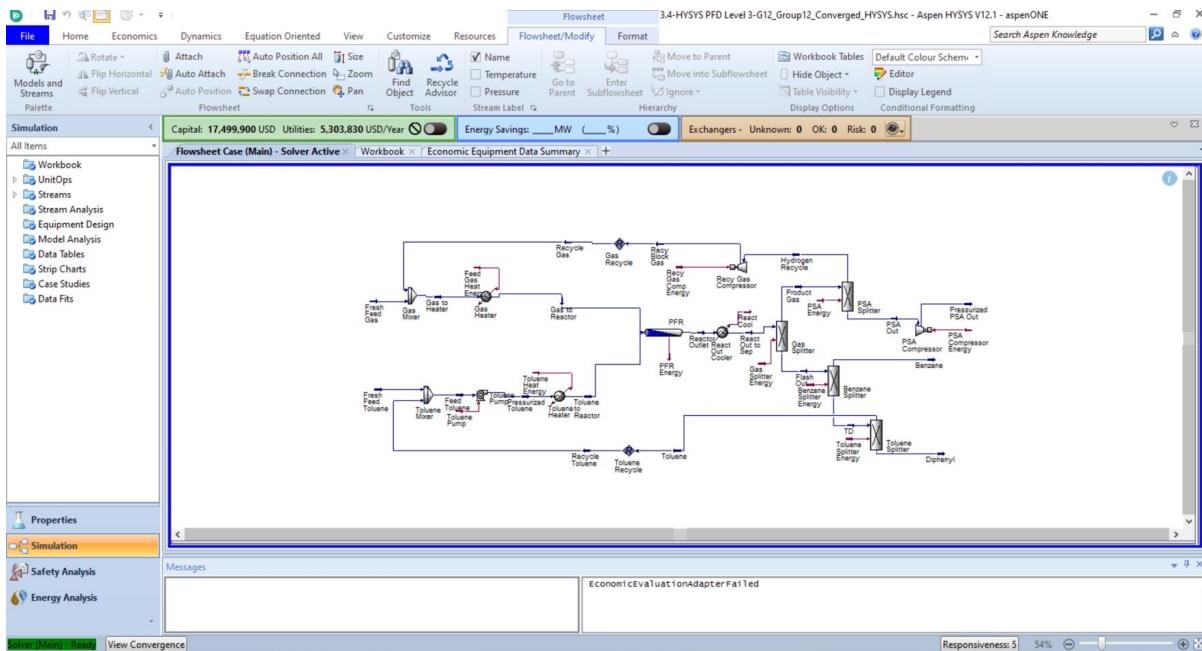


Figure 3. PSA process alternative. Profitability metrics of (a) TCI and (b) NPV% as a function of conversion. Data is generated using the optimal values of $T = 650 \text{ } ^\circ\text{C}$, $P = 30 \text{ bar}$ (reactor temperature and pressure), $MR = 4$, and $X = 0.73$. For this set of variables, the NPV in the Matlab conceptual design was found to be \$167 MM.

Hysys Simulation

- reactor temp. isothermal at 650°C
- ΔP around recycle loop = 2 bar
Notice the compressor in the recycle loop
- PSA \Rightarrow all CH₄ leaves in PSA off-gas
same H₂ $\xrightarrow{\quad\quad\quad}$

open the stream and see the H₂ composition



Proof that $\sum_i \frac{c_i}{\rho_i} = 1$ is equivalent to additivity of volume fractions. This must be true when there is zero volume of mixing.

$$V = V_A + V_B$$

$$\therefore 1 = \frac{V_A}{V} + \frac{V_B}{V} = \phi_A + \phi_B$$

$$\therefore \sum_{i=1}^c \phi_i = 1$$

Now,

$$\begin{aligned} \frac{c_i}{\rho_i} &= \frac{\text{moles of } i}{\text{total volume of mixture, } V} = \frac{1}{V} \\ &\quad \frac{\text{moles of } i}{\text{volume occupied by } i, V_i} \\ &= \frac{V_i}{V} = \phi_i \end{aligned}$$

$$\therefore \sum_i \frac{c_i}{\rho_i} = 1 \iff \sum_i \phi_i = 1$$