

## Ideal Reactors and Multiple Reactions Isothermal Operation

Selection of a proper flow pattern is the key factor in achieving desired selectivities and yields in multiple reactions. For every multiple reaction system of known stoichiometry it is possible to determine “a priori” which limiting flow pattern – complete backmixing (CSTR) or no mixing (PFR) will yield superior yields or selectivities. The consideration of yields often is more important than reactor size in choosing the preferred reactor flow pattern.

From Lecture 1 we know that all multiple reaction systems can be represented by a set of  $R$  independent reactions among the  $S$  chemical species present in the system:

$$\sum_{j=1}^S \nu_{ij} A_j = 0 \quad \text{for } i=1,2,3\dots R \quad (1^*)$$

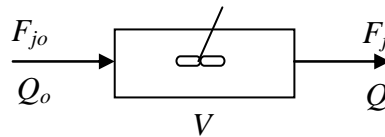
These stoichiometric relationships allow one to relate moles produced (or depleted) of each species to the molar extents of the  $R$  reactions:

$$F_j = F_{j0} + \sum_{i=1}^R \nu_{ij} \dot{X}_i \quad (1)$$

The rate of reaction of each species is given through the rates of the  $R$  independent reactions,  $r_i$ ,  $i = 1,2,\dots,R$ .

$$R_j = \sum_{i=1}^R \nu_{ij} r_i \quad (2)$$

### CSTR – Ideal Stirred Tank Continuous Flow Reactor



The design equation (i.e., the mass balance for species  $j$ ) can be written for  $R$  species,  $j = 1,2,3,\dots,R$ :

$$F_{j0} - F_j + \sum_{i=1}^R \nu_{ij} r_i V = 0 \quad (3)$$

for  $j = 1, 2, \dots, R$

If the reaction rate  $r_i$  for each independent reaction  $i$  can be represented by an  $n$ -th order form, of eq (4a)

$$r_i = k_i \prod_{j=1}^S C_j^{\alpha_{ij}} \quad (4a)$$

then at  $P = \text{const}$ ,  $T = \text{const}$ , the rate of the  $i$ -th reaction,  $r_i$ , can be represented in terms of molar extents  $\dot{X}_i$  of the reactions by:

$$r_i = k_i \prod_{j=1}^S C_{tot,o}^{\alpha_{ij}} \left( \frac{F_{jo} + \sum_{i=1}^R \nu_{ij} \dot{X}_i}{F_{tot,o} + \sum_{j=1}^S \sum_{i=1}^R \nu_{ij} \dot{X}_i} \right)^{\alpha_{ij}} \quad (4b)$$

where  $\alpha_{ij}$  is the reaction order of reaction  $i$  with respect to species  $j$ ,  $F_{tot,o}$  is the total initial molar flow rate.

Substitution of equations (2) and (4b) into (3) results in set of  $R$  nonlinear equations in  $\dot{X}_i$ . Three types of problems described below arise:

- a) Given the feed flow rates, reactor size  $V$  and rate forms for all reactions one can calculate all the reaction extents  $\dot{X}_i$ 's and from equation (1) get the composition of the outlet stream.

In addition, from Lecture 1, at  $P = \text{const}$ ,  $T = \text{const}$ :

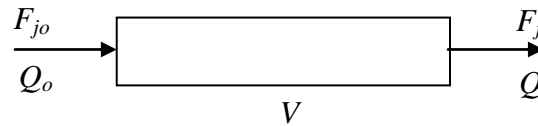
$$Q = Q_o \left( 1 + \sum_{i=1}^R \sum_{j=1}^S \nu_{ij} \dot{X}_i / F_{tot,o} \right) \quad (5)$$

The exit volumetric flow rate can be computed and effluent concentrations calculated

$$C_j = \frac{F_j}{Q} \quad (6)$$

- b) Given the feed molar flow rates and composition, and the desired partial composition of the outflow, as well as the reaction rates, one can calculate the reactor size from equation (3) and the composition of other species in the outflow.
- c) Given molar feed rates and outflow molar flow rates for a given reactor size the rate of reaction for each species can be found from equation (3).
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## PFR – Plug Flow Reactor



The design equation (i.e. the differential mass balance for species j) can be written for R species

$$\frac{dF_j}{dV} = \sum_{i=1}^R \nu_{ij} r_i \quad (7)$$

$j = 1, 2, \dots, R$

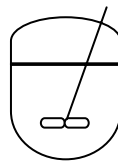
The initial conditions are

$$V = 0 \quad F_j = F_{j0} \quad (7a)$$

Using equations (1) and (4b) the above set of R first order differential equations can be integrated simultaneously and solved for  $\dot{X}_i$ 's as functions of V.

- a) Given the feed flow rate and composition, and the form of the reaction rates, one could determine what volume V is required to attain the desired product distribution.
- b) Given the feed and reactor volume and reaction rate forms, one can determine the exit product distribution.

## Batch Reactor – Autoclave of Constant Volume



The R species (for  $j=1, 2, 3..R$ ) mass balances yield:

$$\frac{dn_j}{dt} = \sum_{i=1}^R \nu_{ij} r_i \quad (8)$$

Initial conditions are:

$$t = 0 \quad n_j = n_{j0} \quad (8a)$$

Moles and extents are related by:

$$n_j = n_{j0} + \sum_{i=1}^R \nu_{ij} X_i \quad (9)$$

For  $j = 1, 2, 3 \dots S$

The rate form as a function of extents is given by

$$r_i = k_i \prod_{j=1}^S C_{j0}^{\alpha_{ij}} \left( 1 + \frac{\sum_{i=1}^R \nu_{ij} X_i}{n_{j0}} \right)^{\alpha_{ij}} \quad (10)$$

$$r_i = k_i \prod_{j=1}^S \left( C_{j0} + \sum_{i=1}^R \nu_{ij} \xi_i \right)^{\alpha_{ij}} \quad (10a)$$

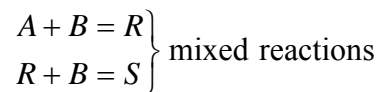
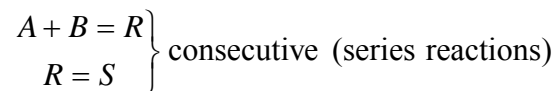
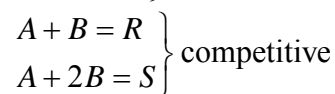
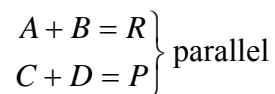
where  $\xi_i = \frac{X_i}{V}$  (10b)

One can solve the set of R first order differential equations to calculate the product distribution in time, or the desired time needed for a prescribed product distribution.

The above approach, while well suited for the computer, does not provide us with the insight as to which flow pattern is better in a given process until we actually compute the answers for both limiting cases.

In order to get better insight in the role of the flow pattern in product distribution in multiple reactions we will consider some simple systems and use the notions of yields and selectivity.

### Classification of Multiple Reactions



In Lecture 1 we have defined the various yields

$$y\left(\frac{P}{A}\right) = \frac{R_P}{-R_A} = \frac{\sum_{i=1}^R \nu_{ip} r_i}{-\sum_{i=1}^R \nu_{iA} r_i} \quad \{\text{point (relative) yield}\}$$

Point (relative) yield measures the ratio of the production rate of a desired product P and the rate of disappearance of the key reactant A. Point yield is a function of composition and this varies along a PFR reactor, varies in time in a batch reactor, and is a constant number in a CSTR.

$$Y\left(\frac{P}{A}\right) = \frac{F_P - F_{Po}}{F_{Ao} - F_A} \quad \{\text{overall (relative) yield}\}$$

Overall (relative) yield gives the ratio of the overall product P produced and the total consumption of reactant A.

In a CSTR the overall and point yield are identical.

$$Y\left(\frac{P}{A}\right) = y\left(\frac{P}{A}\right)$$

In a PFR the overall yield is the integral average of the point yield:

$$Y\left(\frac{P}{A}\right) = \frac{1}{F_{Ao} - F_A} \int_{F_A}^{F_{Ao}} y\left(\frac{P}{A}\right) dF_A$$

Overall operational yield is also often used, defined as the number of moles of the desired product produced per mole of key reactant fed to the system.

$$\star\left(\frac{P}{A}\right) = \frac{F_P - F_{Po}}{F_{Ao}}$$

The relationship to overall relative yield is obvious

$$\star\left(\frac{P}{A}\right) = Y\left(\frac{P}{A}\right) x_A$$

where  $x_A$  is the overall conversion of A

$$x_A = \frac{F_{Ao} - F_A}{F_{Ao}}$$

None of the above yields has been normalized, i.e., their maximum theoretical value may be more or less than one as dictated by stoichiometric coefficients.

A normalized yield can be introduced by

$$\bar{y}\left(\frac{P}{A}\right) = \frac{y\left(\frac{P}{A}\right)}{y_{\max}\left(\frac{P}{A}\right)}$$

where  $y_{\max}\left(\frac{P}{A}\right)$  is obtained by assuming that only the reactions leading from A to R occur.

Point selectivity and overall selectivity measure the ratio of formation of the desired product and one or more of the unwanted products, e.g.

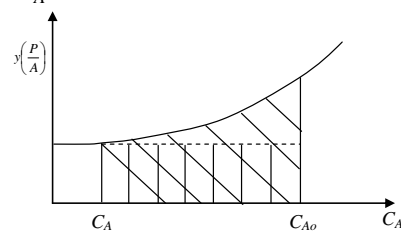
$$s\left(\frac{P}{U}\right) = \frac{R_p}{R_u} \quad S = \frac{F_p - F_{po}}{F_u - F_{uo}}$$

A general rule:

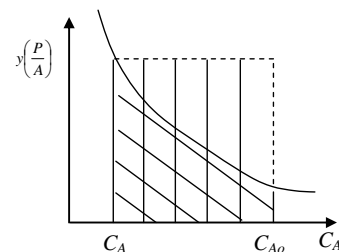
If  $\frac{dy\left(\frac{P}{A}\right)}{dC_A} > 0$  PFR produces more P.

If  $\frac{dy\left(\frac{P}{A}\right)}{dC_A} < 0$  CSTR produces more P

If  $y\left(\frac{P}{A}\right)$  is not a monotonic function of  $C_A$  either reactor type may produce more P depending on operating conditions. The case of monotonic point yield is illustrated below for the case with  $\varepsilon_A = 0$ .

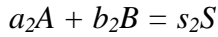
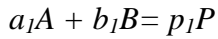


\\ \\ Area = Cp in PFR  
| | | Area = Cp in CSTR



I. Liquid Systems or Gases With  $\sum_{i=1}^R \sum_{j=1}^S \nu_{ij} = 0$

Competitive Reactions



Given the rate

$$r_1 = k_1 C_A^{\alpha_{1A}} C_B^{\alpha_{1B}}$$

$$r_2 = k_2 C_A^{\alpha_{2A}} C_B^{\alpha_{2B}}$$

Point yield then is:

$$y\left(\frac{P}{A}\right) = \frac{R_p}{-R_A} = \frac{p_1 r_1}{a_1 r_1 + a_2 r_2} = \frac{\frac{p_1}{a_1}}{1 + \frac{a_2 r_2}{a_1 r_1}}$$

$$y\left(\frac{P}{A}\right) = \frac{\frac{p_1}{a_1}}{1 + \frac{a_2 k_2}{a_1 k_1} C_A^{(\alpha_{2A} - \alpha_{1A})} C_B^{(\alpha_{2B} - \alpha_{1B})}}$$

$$y_{\max}\left(\frac{P}{A}\right) = \frac{p_1}{a_1}$$

$$\bar{y}\left(\frac{P}{A}\right) = \frac{1}{1 + \frac{a_2 k_2}{a_1 k_1} C_A^{(\alpha_{2A} - \alpha_{1A})} C_B^{(\alpha_{2B} - \alpha_{1B})}}$$

We want  $\bar{y}\left(\frac{P}{A}\right)$  to be as high as possible. This implies:

- i) if  $\alpha_{2A} < \alpha_{1A}$ ,  $\alpha_{2B} < \alpha_{1B}$ , keep  $C_A$  and  $C_B$  as high as possible. PFR is better than CSTR.
- ii) if  $\alpha_{2A} = \alpha_{1A}$ ,  $\alpha_{2B} < \alpha_{1B}$ , keep  $C_B$  as high as possible. PFR is better than CSTR.
- iii) if  $\alpha_{2A} = \alpha_{1A}$ ,  $\alpha_{2B} > \alpha_{1B}$ , keep  $C_B$  as low as possible. CSTR is better than PFR. Try for yourself other combinations.

Example 1

$$\begin{aligned} A = P & & R_P = 1.0 C_A \text{ (kmol/m}^3\text{s)} \\ 2A = S & & R_S = 0.5 C_A^2 \text{ (kmol/m}^3\text{s)} \end{aligned}$$

Determine  $C_p$  in a) CSTR, b) PFR. The feed contains  $C_{A0} = 1$  (kmol/ms),  $C_{p0} = 0$ . Conversion of 98% is desired.

$$y\left(\frac{P}{A}\right) = \frac{R_p}{-R_A} = \frac{R_p}{R_p + 2R_s} = \frac{1}{1 + C_A}$$

$$y_{\max}\left(\frac{P}{A}\right) = 1 \quad \bar{y}\left(\frac{P}{A}\right) = y\left(\frac{P}{A}\right)$$

To keep point yield as high as possible, it is necessary to keep  $C_A$  low everywhere. CSTR will be better than PFR. Let us show this quantitatively.

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a) CSTR

By setting the overall yield equal to the point yield we can solve for the exit concentration of product P.

$$Y\left(\frac{P}{A}\right) = \frac{C_p}{C_{A0} - C_A} = y\left(\frac{P}{A}\right) = \frac{1}{1 + C_A}$$

$$C_p = \frac{C_{A0} - C_A}{1 + C_A} = \frac{C_{A0} x_A}{1 + C_{A0}(1 - x_A)} = \frac{1 \times 0.98}{1 + 1 - 0.98} = 0.961 \text{ (kmol / m}^3\text{)}$$

Overall yield  $Y\left(\frac{P}{A}\right) = \frac{C_p}{C_{A0} - C_A} = 0.980$

Overall operational yield  $\star\left(\frac{P}{A}\right) = 0.961$

Required reactor size (space time)

$$\tau = \frac{C_{A0} - C_A}{-R_A} = \frac{C_{A0} x_A}{C_{A0}(1 - x_A) + C_{A0}^2(1 - x_A)^2} = \underline{48.0(s)}$$



b) PFR

Product concentration is obtained by integration of the point yield

$$C_p = \int_{C_A}^{C_{Ao}} y\left(\frac{P}{A}\right) dC_A = \int_{C_A}^{C_{Ao}} \frac{dC_A}{1 + C_A}$$

$$C_p = \ln\left(\frac{1 + C_{Ao}}{1 + C_A}\right) = \ln\left(\frac{1 + 1}{1 + 1 - 0.98}\right) = 0.673(\text{kmol} / \text{m}^3)$$

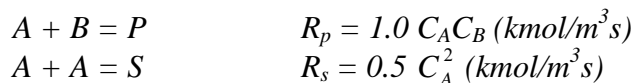
$$\text{Overall yield } Y\left(\frac{P}{A}\right) = 0.687$$

$$\text{Overall operational yield } \star\left(\frac{P}{A}\right) = 0.673$$

$$\text{Required reactor size } \tau = \int_{C_A}^{C_{Ao}} \frac{dC_A}{-R_A} = \int_{C_A}^{C_{Ao}} \frac{dC_A}{C_A(1 + C_A)}$$

$$\tau = \ln\left(\frac{C_{Ao}(1 + C_A)}{C_A(1 + C_{Ao})}\right) = \ln\left[\frac{1 + 1 - 0.98}{(1 - 0.98)(1 + 1)}\right] = \underline{3.2(s)}$$

Plug flow reactor is considerably smaller but CSTR gives a better yield and higher concentration of the desired product.

Example 2

Given  $F_{Ao} = F_{Bo} = 1$  (kmol/s;  $C_{Ao} = C_{Bo} = 1$  (kmol/m<sup>3</sup>)  $C_{Po} = C_{So} = 0$  and desired conversion  $x_A = 0.98$ , determine  $C_p, Y\left(\frac{P}{A}\right), \star\left(\frac{P}{A}\right), S\left(\frac{P}{S}\right)$  and required reactor space time for

a) CSTR, b) PFR.

$$y\left(\frac{P}{A}\right) = \frac{R_p}{-R_A} = \frac{R_p}{R_p + 2R_s} = \frac{C_B}{C_B + C_A} = \frac{1}{1 + \frac{C_A}{C_B}}$$

To maximize point yield one should keep the reactant concentration ratio  $C_A/C_B$  as low as possible everywhere.

Eliminate  $C_B$  in terms of  $C_p$  and  $C_A$  using  $C_j = C_{j0} + \sum_{i=1}^R \nu_{ij} \xi_i \quad i = 1, R$

$$C_A = C_{A0} - \xi_1 - 2\xi_2$$

$$C_P = C_{P0} + \xi_1$$

$$\xi_1 = C_P - C_{P0} \quad \xi_2 = \frac{1}{2}[C_{A0} - C_A - C_P]$$

Now:

$$C_B = C_{A0} - \xi_1 = C_{B0} - C_P$$

$$\begin{aligned} C_S &= C_{S0} + \xi_2 = 0 + \frac{1}{2}[C_{A0} - C_A - C_P] \\ &= \frac{1}{2}[C_{A0} - C_A - C_{B0} + C_B] \end{aligned}$$

a) CSTR

$$Y\left(\frac{P}{A}\right) = \frac{C_P}{C_{A0} - C_A} = y\left(\frac{P}{A}\right) = \frac{C_{A0} - C_P}{C_{A0} - C_P + C_A}$$

Solve for  $C_p$

$$C_P^2 - (C_{A0} - C_{B0})C_P + C_{B0}(C_{A0} - C_A) = 0$$

$$C_{A0} = C_{B0} = 1; \quad C_A = C_{A0}(1 - x_A) = 1 - 0.98$$

$$C_P^2 - 2C_P + 0.98 = 0$$

$$\left. \begin{aligned} C_P &= 1 - \sqrt{1 - 0.98} = 0.859 \text{ (kmol/m}^3\text{)} \\ C_A &= 0.02 \text{ kmol/m}^3 \\ C_B &= 0.141 \text{ kmol/m}^3 \\ C_S &= 0.061 \text{ kmol/m}^3 \end{aligned} \right\} \text{exit stream composition}$$

$$\text{Overall yield } Y\left(\frac{P}{A}\right) = 0.877$$

Overall operational yield  $\star \left( \frac{P}{A} \right) = 0.859$

Overall selectivity  $S \left( \frac{P}{S} \right) = \frac{C_p}{C_s} = 14.2$

Required Reactor Size

$$\tau = \frac{C_{Bo} - C_B}{-R_B} = \frac{C_{Ao} - C_B}{C_A C_B} = \frac{1 - 0.141}{0.02 \times 0.141} = 306(s)$$

b) PFR

$$\frac{dF_p}{dF_A} = \frac{R_p}{R_A} = -y \left( \frac{P}{A} \right)$$

Since  $F_j = QC_j$  and  $Q = \text{const}$

$$\frac{dC_p}{dC_A} = -\frac{C_{Bo} - C_p}{C_{Bo} - C_p + C_A}$$

$$\text{at } C_A = C_{Ao}, C_p = 0$$

Rearrange:

$$\frac{dC_A}{dC_p} + \frac{C_A}{C_{Bo} - C_p} = -1$$

$$\frac{d}{dC_p} \left( \frac{C_A}{C_{Bo} - C_p} \right) = \frac{-1}{C_{Bo} - C_p}$$

$$\text{at } C_p = 0 \quad C_A = C_{Ao}$$

Integrate from the indicated initial condition:

$$\frac{C_A}{C_{Ao} - C_p} - \frac{C_{Ao}}{C_{Bo}} = \ln \left( \frac{C_{Bo} - C_p}{C_{Bo}} \right)$$

$$\frac{C_A}{1 - C_p} = 1 + \ln(1 - C_p) (*)$$

Substitute known quantities:

$$C_A = C_{Ao} (1 - x_A) = 1 - 0.98 = 0.02 \text{ (kmol/m}^3\text{)}$$

Solve for  $C_p$  by trial and error:

$$\phi(C_p) = C_p - 0.98 - (1 - C_p)\ln(1 - C_p) = 0$$

$$D\phi(C_p) = 2 + \ln(1 - C_p)$$

$$C_p^{n+1} = C_p^n - \frac{\phi(C_p^n)}{D\phi(C_p^n)} \quad \text{Newton-Raphson Algorithm}$$

This yields:

$$\left. \begin{aligned} C_p &= 0.613 \text{ kmol/m}^3 \\ C_A &= 0.02 \text{ kmol/m}^3 \\ C_B &= 0.387 \text{ kmol/m}^3 \\ C_s &= 0.184 \text{ kmol/m}^3 \end{aligned} \right\} \text{Exit stream composition}$$

The last two concentrations above are evaluated using the stoichiometric relationship.

$$\text{Overall yield} \quad Y\left(\frac{P}{A}\right) = 0.626$$

$$\text{Overall operational yield} \quad \star\left(\frac{P}{A}\right) = 0.613$$

$$\text{Overall selectivity} \quad S\left(\frac{P}{S}\right) = 3.33$$

Required reactor space time:

$$\tau = \int_{C_B}^{C_{Bo}} \frac{dC_B}{-R_B} = \int_{C_B=0.387}^{C_{Bo}=1} \frac{dC_B}{C_A C_B}$$

From (\*)

$$C_A = (1 - C_p)[1 + \ln(1 - C_p)]$$

From stoichiometry

$$C_B = C_{Bo} - C_p = 1 - C_p$$

Thus

$$C_A = C_B(1 + \ln C_B)$$

$$\tau = \int_{C_B=0.387}^{C_{B_0}=1} \frac{dC_B}{C_B^2(1 + \ell n C_B)} = e \int_{1+\ell n C_B}^{1+\ell n C_{B_0}} \frac{e^{-u}}{u} du$$

$$\begin{aligned} \tau &= e \{E_1(1 + \ell n C_B) - E_1(1 + \ell n C_{B_0})\} = e \{E_1(0.05) - E_1(1)\} \\ &= 2.71 \{2.4679 - 0.2194\} = \underline{6.1(s)} \end{aligned}$$

where

$$E_1(z) = \int_z^{\infty} \frac{e^{-u}}{u} du \quad \text{exponential integral}$$

$E_1(z)$  values tabulated in M. Abramowitz & A. Stegun "Handbook of Mathematical Functions", Dover Press, N.Y. 1964.

### Comparison of CSTR & PFR

Reaction System:            A + B = P (desired)  
                                      A + A = S

Decision variables:         $x_A = 0.98$   
                                       $M_{B/A} = \frac{F_{B_0}}{F_{A_0}} = 1$

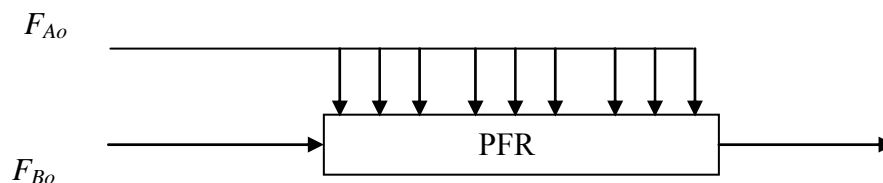
Rate Form:                     $r_1 = 10 C_A C_B$  (kmol/m<sup>3</sup>s)  
                                       $r_2 = 0.5 C_A^2$  (kmol/m<sup>3</sup>s)

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	<u>CSTR</u>	<u>PFR</u>	<u>Optimal Ideal Reactor</u>
Operational yield	0.859	0.613	0.950
Overall selectivity	14.2	3.3	63.0
Reactor space time	306 (s)	6.1 (s)	150 (s)

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The last column of the above Table was computed based on an ideal reactor model shown below. We have B entering a plug flow reactor while  $F_{A_0}$  is distributed from the side stream into the reactor in such a manner that  $C_A = 0.02$  kmol/m<sup>3</sup> everywhere in the reactor.



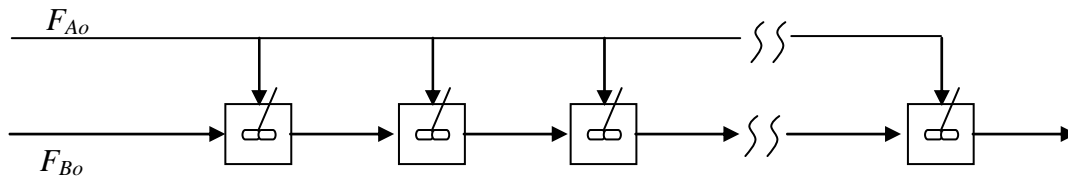
From the expression for the point yield

$$y\left(\frac{P}{A}\right) = \frac{C_B}{C_B + C_A} = \frac{1}{1 + \frac{C_A}{C_B}}$$

it is clear that one needs to keep  $C_A$  low and  $C_B$  high. With the constraint of  $F_{A0} = F_{B0}$  the above ideal reactor accomplishes that requirement in an optimal manner.

Could such a “porous wall” reactor with plug flow be constructed? It depends on the nature of the reaction mixture.

However, we learn from the above that with our choice of decision variables maximum selectivity is 63, we can never do better than that! We also learn that a good reactor set up is a cascade of CSTR's.



The total number of reactors used will depend on economics. With 2 reactors we get selectivity of over 20, with five we are close to optimum.

Examining the effect of decision variables we see that  $C_p$  increases with increased conversion of A. For conversions larger than 0.98 the reactor volume becomes excessive.

If we took  $M_{B/A} > 1$  that would improve the yield and selectivity but at the expense of having to recycle more unreacted B.

Let us ask the following question. How much excess B would we have to use in a PFR in order to bring its overall selectivity to the level of a single CSTR i.e.,  $S = \frac{C_p}{C_s} = 14.2$  at  $C_{A0} = 1$  ( $\text{kmol/m}^3$ ) and  $x_A = 0.98$ . So the goal is to choose  $C_{B0}$  in order to get at the exit of plug flow:

$$\frac{C_p}{C_s} = 14.2$$

From stoichiometry:

$$C_s = \frac{1}{2}[C_{A0} - C_A - C_p] = \frac{1}{2}[C_{A0}x_A - C_p] = \frac{1}{2}[0.98 - C_p]$$

The prescribed desired selectivity is:

$$\frac{2C_p}{0.98 - C_p} = 14.2 \Rightarrow C_p = 0.859 (\text{kmol} / \text{m}^3)$$

$$C_s = 0.061 (\text{kmol} / \text{m}^3)$$

The integrated equation for PFR is:

$$\frac{C_A}{C_{Bo} - C_p} - \frac{C_{Ao}}{C_{Bo}} = \ell n \left( 1 - \frac{C_p}{C_{Ao}} \right)$$

The initial concentration of B is now the only unknown. Evaluate it by trial & error.

$$\frac{0.02}{C_{Bo} - 0.859} - \frac{1}{C_{Bo}} = \ell n \left( 1 - \frac{0.859}{C_{Bo}} \right) \text{ gives}$$

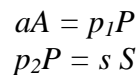
$$C_{Bo} = 3.79 \frac{\text{kmol}}{\text{m}^3}$$

Since  $C_{Ao} = 1$  (kmol/m<sup>3</sup>),  $M_{B/A} = 3.79$  – almost four times more B than A should be introduced in the feed to get the selectivity in a PFR to the level of a CSTR.

A great excess of unreacted B has to be separated in the effluent:

$$C_B = C_{Bo} - C_p = 3.790 - 0.859 = 2.931 \text{ (kmol/m}^3\text{)}$$

### Consecutive Reactions



Two basic problems arise:

- conduct the reaction to completion,
- promote production of the intermediate.

The first problem is trivial and can be reduced to a single reaction problem. Use the slowest reaction in the sequence to design the reactor.

In order to maximize the production of intermediates PFR flow pattern is always superior to a CSTR flow pattern.

$$y\left(\frac{P}{A}\right) = \frac{R_p}{-R_A} = \frac{p_1 r_1 - p_2 r_2}{a r_1} = \frac{p_1}{a} - \frac{p_2}{a} \frac{r_2}{r_1}$$

$$y_{\max}\left(\frac{P}{A}\right) = \frac{p_1}{a}$$

$$\bar{y}\left(\frac{P}{A}\right) = 1 - \frac{p_2}{p_1} \frac{r_2}{r_1} = 1 - \frac{p_2 k_2 C_P^\beta}{p_1 k_1 C_A^\alpha}$$

One needs to keep  $C_A$  high and  $C_P/C_A$  low which is best accomplished in a PFR.

### Example 1

$$\begin{aligned} A = P & & r_1 = 1.0 C_A \text{ (kmol/m}^3\text{s)} & \alpha = 1 \\ P = S & & r_2 = 0.5 C_P \text{ (kmol/m}^3\text{s)} & \beta = 1 \end{aligned}$$

Starting with  $C_{A0} = 1$  (kmol/m<sup>3</sup>) and  $C_{P0} = C_{S0} = 0$  find the maximum attainable  $C_P$  in  
a) CSTR, b) PFR.

We could continue to use the point yield approach.

### CSTR Stirred Tank Reactor

$$C_P = y\left(\frac{P}{A}\right)(C_{A0} - C_A) = \frac{C_A - 0.5C_P}{C_A}(C_{A0} - C_A)$$

Solve for  $C_P$

$$C_P = \frac{C_A(C_{A0} - C_A)}{0.5(C_{A0} + C_A)}$$

Find optimal  $C_A$  at which the CSTR should operate.

$$\frac{dC_P}{dC_A} = 0 \Rightarrow (C_{A0} - 2C_A)(C_{A0} + C_A) - C_A(C_{A0} - C_A) = 0$$

$$C_A^2 + 2C_{A0}C_A - C_{A0}^2 = 0$$

$$C_{A_{opt}} = C_{A0}[\sqrt{2} - 1] = \underline{0.414 \text{ (kmol/m}^3\text{)}}$$

$$C_{P_{\max}} = \frac{0.414(1 - 0.414)}{0.5(1 + 0.414)} = \underline{0.343 \text{ (kmol/m}^3\text{)}}$$

$$C_S = C_{A0} - C_A - C_P = \underline{0.243 \text{ kmol/m}^3}$$

Overall yield  $Y\left(\frac{P}{A}\right) = 0.585$



Operational yield  $\star \left( \frac{P}{A} \right) = 0.343$

Overall selectivity  $S \left( \frac{P}{S} \right) = 1.4$

Required reactor space time:

$$\tau = \frac{C_{A_0} - C_{A_{opt}}}{-R_A} = \frac{C_{A_0} - C_{A_{opt}}}{C_{A_{opt}}} = \frac{1 - 0.414}{0.414} = \underline{1.4(s)}$$


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b) PFR Plug Flow Reactor

$$\frac{dC_P}{dC_A} = -y \left( \frac{P}{A} \right) = \frac{0.5C_P - C_A}{C_A}$$

at  $C_A = C_{A_0}$ ,  $C_P = 0$

$$\frac{dC_P}{dC_A} - \frac{0.5C_P}{C_A} = -1$$

$$\frac{d}{dC_A} \left[ \frac{C_P}{\sqrt{C_A}} \right] = -\frac{1}{\sqrt{C_A}}$$

$$\frac{C_P}{\sqrt{C_A}} = 2 \left[ \sqrt{C_{A_0}} - \sqrt{C_A} \right]$$

$$C_P = 2\sqrt{C_A} \left[ \sqrt{C_{A_0}} - \sqrt{C_A} \right]$$

Find  $C_A$  at the reactor exit by

$$\frac{dC_P}{dC_A} = 0 \Rightarrow \sqrt{C_{A_0}} - 2\sqrt{C_A} = 0$$

$$C_{A_{opt}} = \frac{C_{A_0}}{4}$$

$$C_{A_{opt}} = 0.25(\text{kmol} / \text{m}^3)$$

$$C_{P_{max}} = 2\sqrt{0.25} \left[ 1 - \sqrt{0.25} \right] = \underline{0.5(\text{kmol} / \text{m}^3)}$$

$$C_s = 1 - 0.5 - 0.25 = \underline{0.25(\text{kmol} / \text{m}^3)}$$

Overall yield  $Y \left( \frac{P}{A} \right) = \frac{2}{3} = 0.667$

Operational yield  $\star \left( \frac{P}{A} \right) = 0.5$

Overall selectivity  $S\left(\frac{P}{A}\right) = 2.0$

Required space time:

$$\tau = \int_{C_{A_{opt}}}^{C_{A_0}} \frac{dC_A}{C_A} = \ln \frac{C_{A_0}}{C_{A_{opt}}} = \ln 4 = 2 \ln 2 = 1.39(s)$$

The same results can be obtained by using the design equations (i.e. mass balance) for P & A.

### CSTR

$$\tau = \frac{C_{A_0} - C_A}{C_A} \quad C_A = \frac{C_{A_0}}{1 + \tau}$$

$$\tau = \frac{C_P}{C_A - 0.5C_P} \quad C_P = \frac{C_A \tau}{1 + 0.5\tau} = \frac{C_{A_0} \tau}{(1 + \tau)(1 + 0.5\tau)}$$

$$\frac{dC_P}{d\tau} = 0 \Rightarrow \text{gives } \tau_{opt} = 1.4(s), \text{ etc.}$$

### PFR

$$\frac{dC_A}{d\tau} = -C_A \quad C_A = C_{A_0} e^{-\tau}$$

$$\tau = 0, \quad C_A = C_{A_0} = 1$$

$$\frac{dC_P}{d\tau} = C_A - 0.5C_P$$

$$\tau = 0 \quad C_P = 0$$

$$\frac{d}{d\tau} (e^{0.5\tau} C_P) = C_{A_0} e^{-\tau} e^{0.5\tau} = C_{A_0} e^{-0.5\tau}$$

$$C_P = 2(e^{-0.5\tau} - e^{-\tau})$$

$$\frac{dC_P}{d\tau} = 0 \Rightarrow \tau_{opt} = 2 \ln 2, \text{ etc.}$$

**Mixed Reactions**

This is the most frequently encountered type of multiple reactions which can be viewed as a combination of competitive and consecutive reactions. We can solve the problems involving these reactions either by setting R design equations for R components or by utilizing the concept of the point yield in simpler reaction schemes.

**Example 1**

$k_1 = 10$   $k_2 = 1$  ( $\text{m}^3/\text{kmol min}$ ). R is the desired product. Find  $C_R$  in a) CSTR, b) PFR, when  $C_{R0} = C_{S0} = 0$ . Decision variable  $C_{A0} = C_{B0} = 1$  ( $\text{kmol/m}^3$ ).

We can write two point yields:

$$y\left(\frac{R}{A}\right) = \frac{R_R}{-R_A} = \frac{k_1 C_A C_B - k_2 C_B C_R}{2k_1 C_A C_B} = \frac{1}{2} \left[ 1 - \frac{k_2 C_R}{k_1 C_A} \right]$$

$$y\left(\frac{R}{B}\right) = \frac{R_R}{-R_B} = \frac{k_1 C_A C_B - k_2 C_B C_R}{k_1 C_A C_B + 2k_2 C_B C_R} = \frac{C_A - \frac{k_2}{k_1} C_R}{C_A + \frac{2k_2}{k_1} C_R}$$

The point yield  $y\left(\frac{R}{A}\right)$  depends only on  $C_R$  and  $C_A$  and is simpler to use.

a) CSTR      Stirred Tank Reactor

$$C_R = y\left(\frac{R}{A}\right)(C_{A0} - C_A) = \frac{C_A - \frac{k_2}{k_1} C_R}{2C_A} (C_{A0} - C_A)$$

$$C_R = \frac{C_A (C_{A0} - C_A)}{\left(2 - \frac{k_2}{k_1}\right) C_A + \frac{k_2}{k_1} C_{A0}} = \frac{C_A (C_{A0} - C_A)}{1.9C_A + 0.1C_{A0}}$$

Find optimum  $C_A$  in a CSTR.

$$\frac{dC_R}{dC_A} = 0 \Rightarrow \left(2 - \frac{k_2}{k_1}\right) C_A^2 + 2 \frac{k_2}{k_1} C_{A0} C_A - \frac{k_2}{k_1} C_{A0}^2 = 0$$

$$C_{A_{opt}} = \frac{C_{Ao}}{\sqrt{2\frac{k_1}{k_2} + 1}}$$

$$C_{A_{opt}} = \frac{1}{\sqrt{2 \times 10 + 1}} = \underline{0.183 \text{ (kmol/m}^3\text{)}}$$

$$C_{R_{max}} = \frac{0.183(1 - 0.183)}{1.9 \times 0.183 + 0.1} = \underline{0.334 \text{ (kmol/m}^3\text{)}}$$

From stoichiometry

$$C_B - C_{Bo} - \frac{3}{2}(C_{Ao} - C_A) + 2C_R = 1 - \frac{3}{2}(1 - 0.183) + 2 \times 0.334$$

$$C_S = \frac{1}{2}(C_{Ao} - C_A) - C_R = \frac{1}{2}(1 - 0.183) - 0.334$$

$$C_B = 0.443 \text{ (kmol/m}^3\text{)}; C_S = 0.0745 \text{ (kmol/m}^3\text{)}$$

Overall yield  $Y\left(\frac{R}{A}\right) = 0.409; Y\left(\frac{R}{B}\right) = 0.600$

Operational yield  $\star\left(\frac{R}{A}\right) = 0.334; \star\left(\frac{R}{B}\right) = 0.334$

Overall selectivity  $S\left(\frac{R}{S}\right) = 4.48 = 4.5$

Required reactor space time:

$$\tau = \frac{C_{Ao} - C_A}{2k_1 C_A C_B} = \frac{1 - 0.183}{2 \times 1 \times 0.183 \times 0.443} = \underline{5.0 \text{ (min)}}$$

b) PFR Plug Flow Reactor

$$\frac{dC_R}{dC_A} = -y\left(\frac{R}{A}\right) = -\frac{1}{2} + \frac{k_2}{2k_1} \frac{C_R}{C_A}$$

$$C_A = C_{Ao}, C_R = 0$$

$$\frac{d}{dC_A} \left( C_A - \frac{k_2}{2k_1} C_R \right) = -\frac{1}{2} C_A - \frac{k_2}{2k_1}$$

$$C_R = \frac{C_{Ao} \left( 1 - \frac{k_2}{2k_1} \right) \frac{k_2}{2k_1} C_A^{0.95} - C_A}{\left( 2 - \frac{k_2}{k_1} \right) 1.9}$$

For optimal  $C_A$  at reactor exit:

$$\frac{dC_R}{dC_A} = 0 \Rightarrow C_{A_{opt}} = \left( \frac{k_2}{2k_1} \right)^{\left( \frac{1}{1-k_2} \right)}$$

$$C_{A_{opt}} = (0.05)^{0.95} = \underline{0.0427(\text{kmol} / \text{m}^3)}$$

$$C_{R_{max}} = \frac{1^{0.95} \times 0.0427^{0.05} - 0.0427}{1.9} = \underline{0.427(\text{kmol} / \text{m}^3)}$$

$$C_B = 1 - \frac{3}{2}(1 - 0.0427) + 2 \times 0.427 = \underline{0.418(\text{kmol} / \text{m}^3)}$$

$$C_S = \frac{1}{2}(1 - 0.0427) - 0.427 = \underline{0.0517(\text{kmol} / \text{m}^3)}$$

Overall yield  $Y\left(\frac{R}{A}\right) = 0.446; \quad Y\left(\frac{R}{B}\right) = 0.734$

Operational yield  $\star\left(\frac{R}{A}\right) = 0.427; \quad \star\left(\frac{R}{B}\right) = 0.427$

Overall selectivity  $S\left(\frac{R}{S}\right) = 8.27 = 8.3$

Reactor space time:

$$\tau = \int_{C_A}^{C_{A_0}} \frac{dC_A}{2C_A C_B}$$

From stoichiometry

$$C_B = C_{B_0} - \frac{3}{2}(C_{A_0} - C_A) + 2C_R$$

but all along the PFR

$$C_R = \frac{C_A^{0.05} - C_A}{1.9}$$

$$C_B = C_{Bo} - \frac{3}{2}(C_{Ao} - C_A) + \frac{2}{1.9}(C_A^{0.05} - C_A)$$

$$C_B = \left(1.5 - \frac{2}{1.9}\right)C_A + \frac{2}{1.9}C_A^{0.05} - 0.5$$

$$C_B = 0.447C_A + 1.05C_A^{0.05} - 0.5$$

$$\tau = 0.5 \int_{0.0427}^1 \frac{dC_A}{0.447C_A^2 + 1.05C_A^{1.05} - 0.5C_A} \text{ integrate numerically (2.759 min)}$$

**Caution must be exercised when using the point yield concept and finding maximum concentrations in mixed reactions. Sometimes formal answers will lie outside the physically permissible range if the other reactant is rate limiting.**

For example in Example 1 if we take

$$C_{Ao} = 2 \left( \frac{\text{kmol}}{\text{m}^3} \right) \quad ; \quad C_{Bo} = 1 \left( \frac{\text{kmol}}{\text{m}^3} \right)$$

We are feeding the reactants in stoichiometric ratio for reaction 1.

Following the above described procedure in a CSTR we would find

$$C_{A_{opt}} = \frac{C_{Ao}}{\sqrt{2 \times 10 + 1}} = 0.366 (\text{kmol} / \text{m}^3)$$

$$C_{R_{max}} = \frac{0.366(2 - 0.366)}{1.9 \times 0.366 + 0.2} = 0.668 (\text{kmol} / \text{m}^3)$$

However these values are not attainable since from stoichiometry it follows that:

$$C_B = 1 - \frac{3}{2}(2 - 0.366) + 2 \times 0.668 = -0.115 < 0$$

This indicates that B is not introduced in sufficient amount to allow the reactions to proceed to that point.

If  $C_{Bo} = 1.115$  (kmol/m<sup>3</sup>) then the above  $C_{R_{max}}$  can be obtained (theoretically) at  $C_B = 0$  and that would require an infinitely large reactor.

Thus the maximum reactor size that is allowed would determine  $C_{B_{min}}$ . Say  $C_{B_{min}} = 0.01$  (kmol/m<sup>3</sup>) (99% conversion of B).

Calculate the resulting  $C_A$  and  $C_R$  from

$$C_A = C_{Ao} - \frac{4}{3}C_R - \frac{2}{3}(C_{Bo} - C_{B_{\min}})$$

$$C_R = \frac{C_A(C_{Ao} - C_A)}{1.9C_A + 0.1C_{Ao}}$$

$$C_A = 0.461(\text{kmol} / \text{m}^3)$$

That yields:  $C_R = 0.660(\text{kmol} / \text{m}^3)$

$$C_S = 0.110(\text{kmol} / \text{m}^3)$$

Overall yield  $Y\left(\frac{R}{A}\right) = 0.429$ ;  $Y\left(\frac{R}{B}\right) = 0.667$

Operational yield  $\star\left(\frac{R}{A}\right) = 0.330$ ;  $\star\left(\frac{R}{B}\right) = 0.660$

Overall selectivity  $S\left(\frac{R}{S}\right) = 6.0$

Reactor space time:

$$\tau = \frac{2 - 0.461}{2 \times 1 \times 0.461 \times 0.01} = 170 \text{min}$$

II. Systems with change in total volumetric flow rate ( $\varepsilon_A \neq 0$ ) gases

Same approach may be used but one needs to deal with  $\dot{X}_i$  extents rather than concentrations. Use relationships from Lecture 1.

### Summary

PFR promotes more reactions of higher order with respect to reactions of lower order.

CSTR favors reactions of lower order with respect to those of higher order.

In consecutive reactions better yields are achieved always in PFR than in a CSTR for an intermediate product.

Select judiciously the objective function to be optimized.

Remember: Optimizing overall yield does not necessarily lead to the same result as maximizing the production rate (or concentration) of the desired product or as maximizing selectivity.

Be aware of the relationship of the design equations and reaction stoichiometry.