

Multiple Reactions

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The multiple reactions may be are four basic types such as

1. series,
2. parallel,
3. complex and
4. independent.

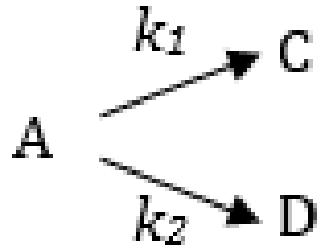
The combination of series and parallel reactions are known as complex reactions.

It may be assumed that the reaction between two reactants

A and B produce two different products C and D
in two separate reactions as

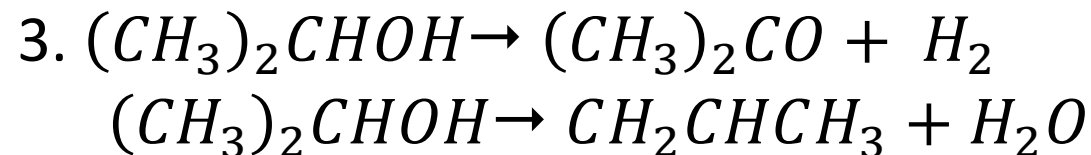
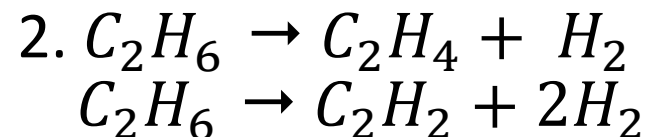
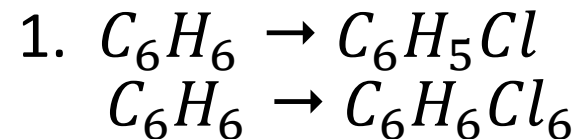
Parallel Reactions

Let us assume the reactions where A reacts to form C and D by two elementary first-order reactions.



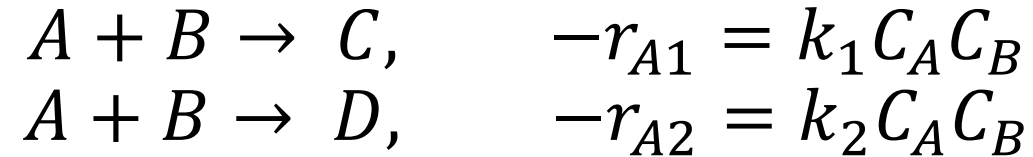
Let, C is the desired product and D is the undesired product.
For these reactions, Conversion, Selectivity and Yield are important.

Some examples of parallel reactions



In all the cases, two products are formed. Any one of these is considered to be as desired product.

Let us consider the following reactions:



Assume 50 moles of A and 50 moles of B are reacted to produce 30 moles of C and 10 moles of D. Say, C is the desired product.

- 30 moles of C produced by consuming 30 moles of A and 30 moles of B. In the second reaction, 10 moles of both A and B are reacted to produce 10 moles of D. Thus, 40 moles of both A and B are reacted in total.
- The relative performance of the reactions can be explained by the terms, Selectivity and Yield.

Selectivity of a desired product is defined as

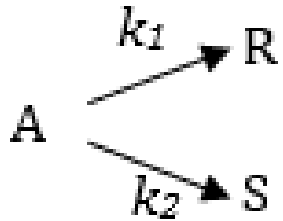
$$\text{Selectivity of C} = \frac{\text{moles of C formed}}{\text{moles of D formed}} = \frac{30}{10} = 3.0$$

The yield of a reaction is defined as

$$\text{Yield of C} = \frac{\text{moles of C formed}}{\text{moles of A reacted}} = \frac{30}{50} \times 100 = 60\%$$

Qualitative Analysis

For the parallel reactions, where two products R and S and R is the desired product.



$$r_R = \frac{dC_R}{dt} = k_1 C_A^{a_1} \quad \text{and} \quad r_S = \frac{dC_S}{dt} = k_2 C_A^{a_2}$$

$$\frac{r_R}{r_S} = \frac{k_1}{k_2} C_A^{(a_1 - a_2)}$$

$(a_1 - a_2)$ may be either zero or positive or negative.

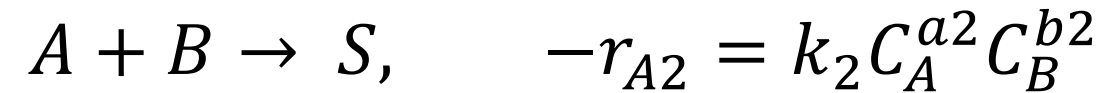
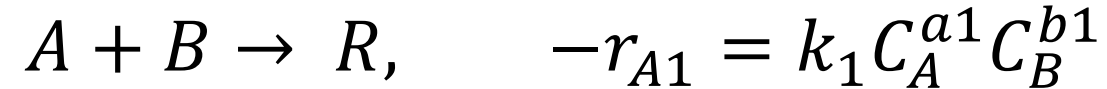
- **Case-1:** If $a_1 = a_2$, $(a_1 - a_2) = 0$

The product distribution $\frac{r_R}{r_S} = \text{constant}$.

It is independent of concentration.

- **Case-2:** if $a_1 > a_2$, $(a_1 - a_2)$ is positive. So with increasing concentration of A, the ratio $\frac{r_R}{r_S}$ increases. The formation of desired product R increases. Batch or plug flow reactor would favor the formation of R and would require a minimum reactor size.
- **Case-3:** if $a_1 < a_2$, $(a_1 - a_2)$ is negative, so with increasing concentration of A, the ratio $\frac{r_R}{r_S}$ decreases. The formation of desired product R decreases. This would require a large mixed reactor as concentration of A to be kept low to favor the formation of R.

If two reactants are involved in a parallel reactions



$$r_R = \frac{dC_R}{dt} = k_1 C_A^{a1} C_B^{b1} \quad \text{and} \quad r_S = \frac{dC_S}{dt} = k_2 C_A^{a2} C_B^{b2}$$

$$\frac{r_R}{r_S} = \frac{k_1}{k_2} C_A^{(a1-a2)} C_B^{(b1-b2)}$$

$$\frac{dC_S}{dC_R} = \frac{r_S}{r_R} = \frac{k_2}{k_1} C_A^{(a2-a1)} C_B^{(b2-b1)}$$

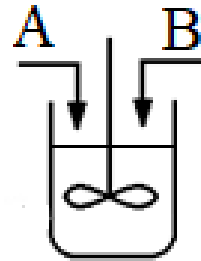
We should check the values of $(a_2 - a_1)$ and $(b_2 - b_1)$

If both a_1 and b_1 are greater than a_2 and b_2 , with increasing C_A and C_B , $\frac{r_S}{r_R}$ ratio decreases. Selectivity of R = $\frac{r_R}{r_S}$ increases.

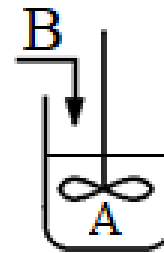
Therefore, depending on the order of the reactions, different combination of concentrations of A and B are desired as follows:

- Both A and B to be kept high
- Both A and B to be kept low
- Either A is high or B is high
- So, the concentration level of reactants is the key control for the distribution of products.

- **Batch reactor**
- When C_A and C_B both high, A and B are to be added at a time.
- When C_A and C_B both low, A and B are added slowly so that liquid level rises slowly.
- When C_A high and C_B low, B is added in a batch reactor containing large quantity of A.



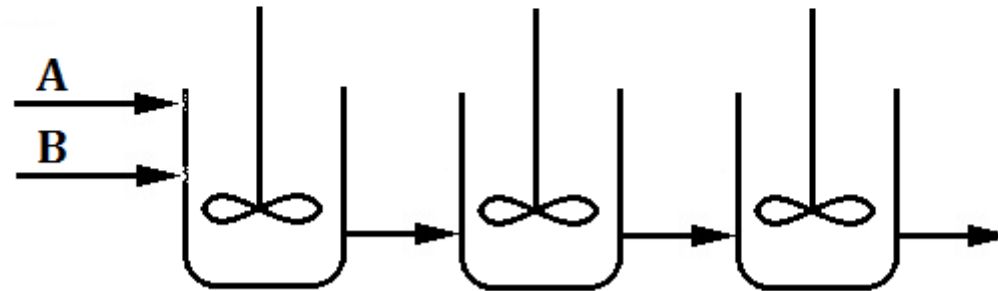
A and B are
added
at a time



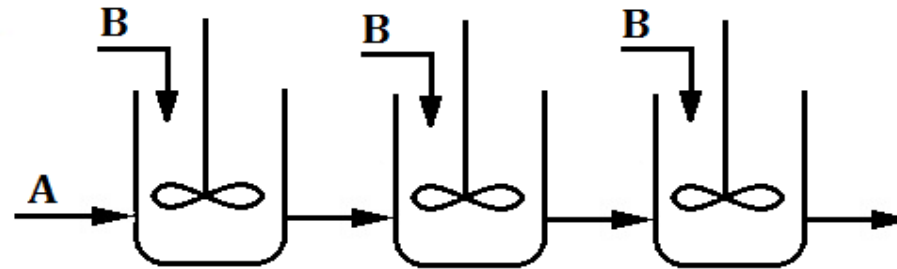
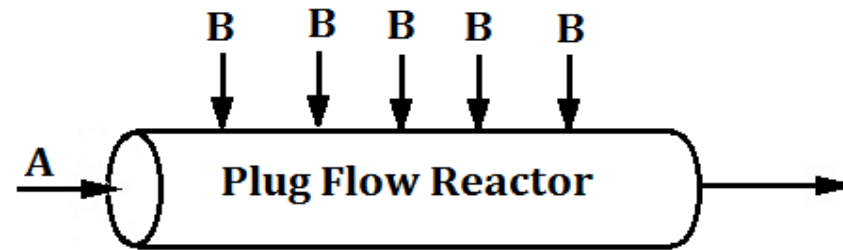
B is added slowly
in a large quantity
of A

Continuous process(PFR or CSTR)

When C_A and C_B both high or both low



- The following arrangements are used when C_A high and C_B low:



Example:1 For the following reactions select a desirable scheme.



$$r_R = \frac{dC_R}{dt} = \frac{dC_T}{dt} = k_1 C_A C_B^{0.3}$$

$$\text{and } r_S = \frac{dC_S}{dt} = \frac{dC_U}{dt} = k_2 C_A^{0.5} C_B^{1.8}$$

$$\frac{dC_S}{dC_R} = \frac{r_S}{r_R} = \frac{k_2}{k_1} C_A^{-0.5} C_B^{1.5}$$

As concentration dependency of B is more pronounced, C_B is to be kept low and C_A high. B is to be added as side streams.

Instantaneous and overall yield of desired product

Instantaneous Fractional Yield of R:

$$\phi = \frac{\text{moles of } R \text{ formed}}{\text{moles of } A \text{ reacted}} = \frac{dC_R}{-dC_A}$$

Overall Yield of R:

$$\Phi = \frac{\text{all } R \text{ formed}}{\text{all } A \text{ reacted}} = \frac{C_{Rf}}{C_{A0} - C_{Af}} = \frac{C_{Rf}}{-\Delta C_A}$$

Exit concentration of R is C_{Rf}

in mixed reactor, $C_{Rf} = \Phi(C_{A0} - C_{Af})$

and in PFR as $\phi = \frac{dC_R}{-dC_A}$, $C_{Rf} = - \int_{C_{A0}}^{C_{Af}} \phi dC_A$

ϕ is function of concentration, as concentration varies, ϕ will change.

So, ϕ is plotted as a function of C_A .

For PFR, area under the curve between C_{A0} to C_{Af} is calculated which is C_{Rf}

Mixed flow reactor

In mixed reactor the concentration is assumed to be same everywhere.

$$\Phi_m = \left(\frac{dC_R}{-dC_A} \right)_{at C_{Af}} = \phi \text{ evaluated at } C_{Af}$$

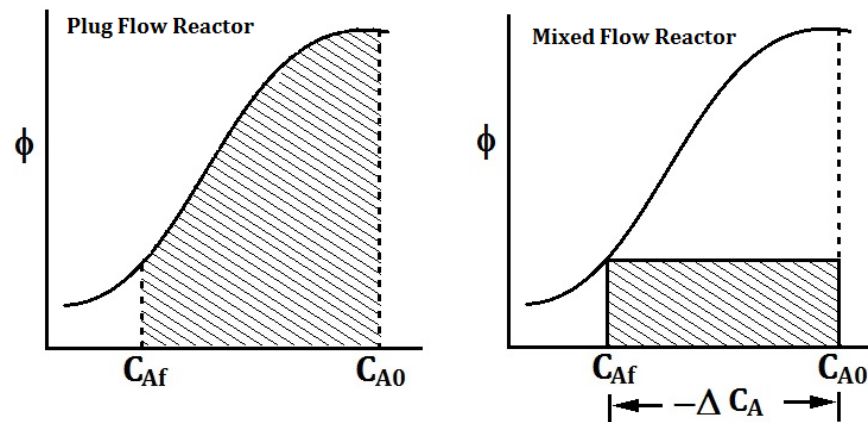
Plug flow reactor

$$\Phi_P = \frac{-1}{C_{A0} - C_{Af}} \int_{C_{A0}}^{C_{Af}} \phi dC_A$$

C_{Rf} determination by graphical method

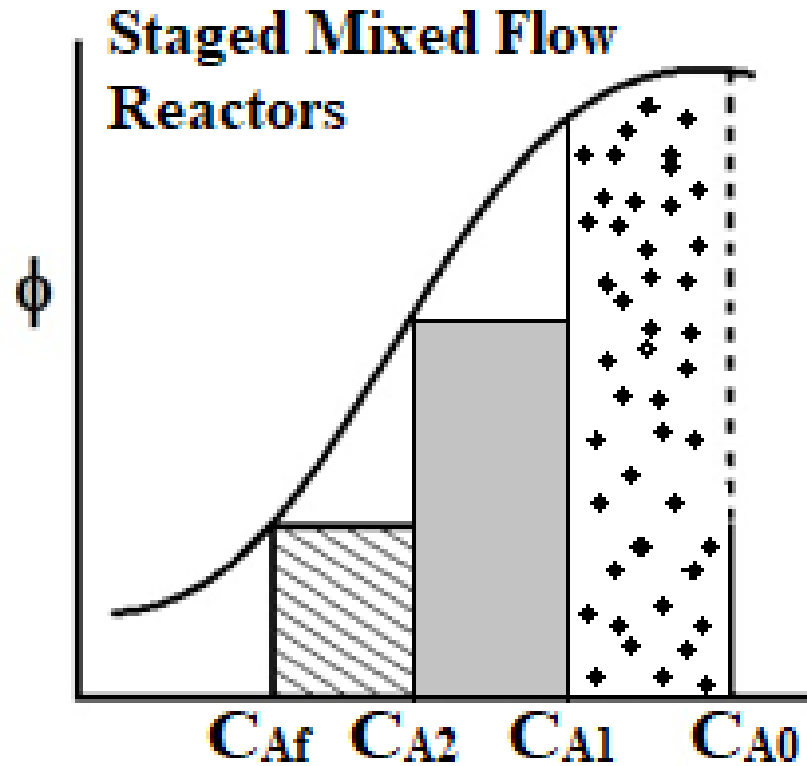
Either from the area under the plot or area of rectangle of ϕ vs C_A plot

$\int_{C_{A0}}^{C_{Af}} \phi dC_A = \text{graphical integration in case of PFR and}$
 $\Phi(C_{A0} - C_{Af}) = \text{rectangle area for mixed flow}$



Series of N- mixed reactors

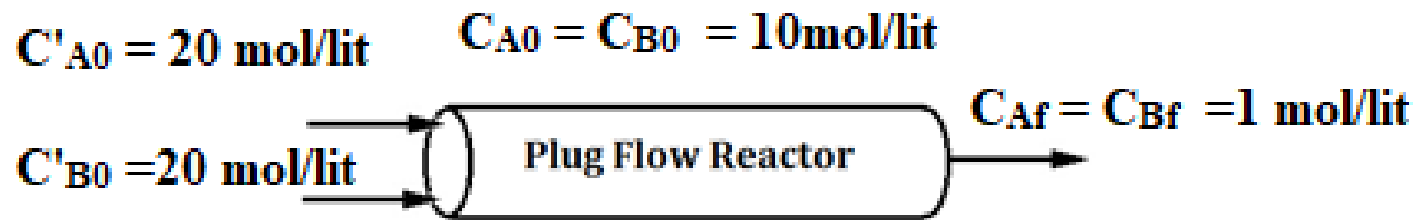
- $\Phi_{N \text{ mixed}}(C_{A0} - C_{AN}) = \varphi_1(C_{A0} - C_{A1}) + \cdots + \varphi_N(C_{A,N-1} - C_{A,N})$
- $\Phi_{N \text{ mixed}} = \frac{\varphi_1(C_{A0}-C_{A1})+\cdots+\varphi_N(C_{A,N-1}-C_{A,N})}{(C_{A0}-C_{A,N})}$



Example-1

- For the competitive liquid-phase reactions
- $A + B \xrightarrow{k_1} R, \quad \dots \text{desired} \quad \frac{dC_R}{dt} = 1.0C_A C_B^{0.3} \text{ mol}/(\text{lit. min})$
- $A + B \xrightarrow{k_1} S, \quad \dots \text{unwanted} \quad \frac{dC_S}{dt} = 1.0C_A^{0.5} C_B^{1.8} \text{ mol}/(\text{lit. min})$
- Find the fraction of impurities in the product stream for 90% conversion of pure A and pure B (each has a density of 20 mol/lit)
- (a) for plug flow reactor
- (b) for mixed flow reactor
- (c) plug-mixed contacting schemes

- Solution:
- For this reactions instantaneous fractional yield of R is given by
- $\varphi = \frac{dC_R}{dC_R + dC_S} = \frac{1.0C_A C_B^{0.3}}{1.0C_A C_B^{0.3} + 1.0C_A^{0.5} C_B^{1.8}} = \frac{1}{1 + C_A^{-0.5} C_B^{1.5}}$
- (a) Plug flow reactor, $C_{A0} = C_{B0} = 10 \text{ mol/lit}$, equimolar flow
- $C'_{A0} = C'_{B0} = 20$ So, $C_A = C_B$ everywhere.



- We have,

$$\Phi = \frac{\text{all } R \text{ formed}}{\text{all } A \text{ reacted}} = \frac{C_{Rf}}{C_{A0} - C_{Af}} = \Phi_P = \frac{-1}{C_{A0} - C_{Af}} \int_{C_{A0}}^{C_{Af}} \phi \, dC_A$$

$$\Phi_P = \frac{-1}{10-1} \int_{10}^1 \frac{1}{1+C_A} dC_A = \frac{1}{9} \ln[1 + C_A]_1^{10} = 0.19$$

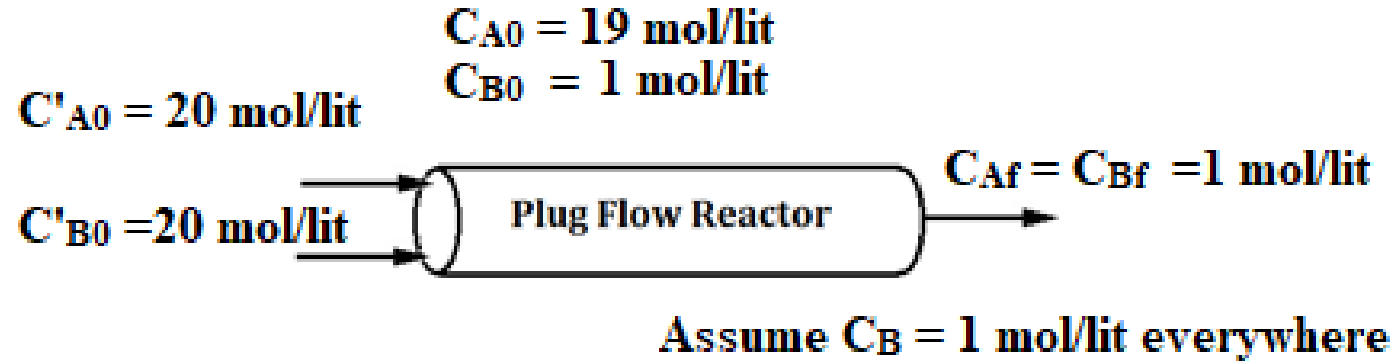
Therefore impurities = 81%

For mixed reactor,

$$\begin{aligned} \Phi_m &= \left(\frac{dC_R}{-dC_A} \right)_{\text{at } C_{Af}} = \phi \text{ evaluated at } C_{Af} \\ &= \frac{1}{1 + C_A} \Big|_{\text{evaluated at } C_{Af}=1} \\ &= \frac{1}{1 + 1} = 0.5 \end{aligned}$$

Therefore impurities = 50%

Plug-mixed combination



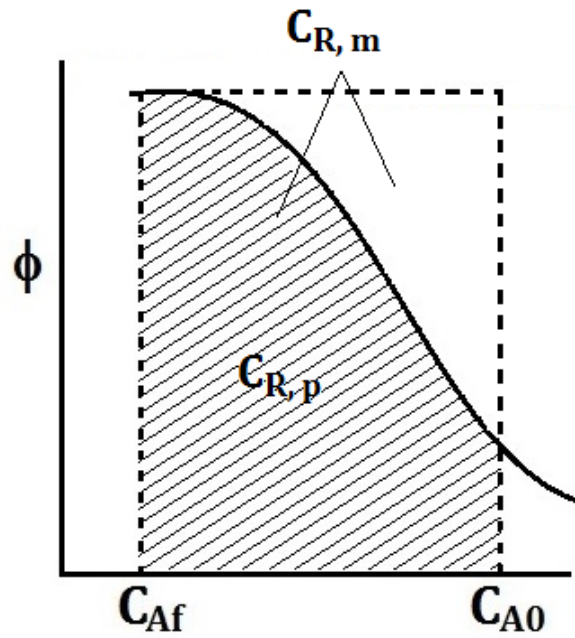
$$\begin{aligned}\Phi_{plug-mixed} &= \frac{-1}{19 - 1} \int_{19}^1 \frac{1}{1 + C_A^{-0.5} C_B^{1.5}} dC_A \\ &= \frac{1}{18} \int_{19}^1 \frac{1}{1 + C_A^{-0.5} 1} dC_A \\ &= \frac{1}{18} \left[(19 - 1) - 2(\sqrt{19} - 1) + 2 \ln \frac{1 + \sqrt{19}}{2} \right] = 0.741\end{aligned}$$

Therefore, impurities = 25.9%

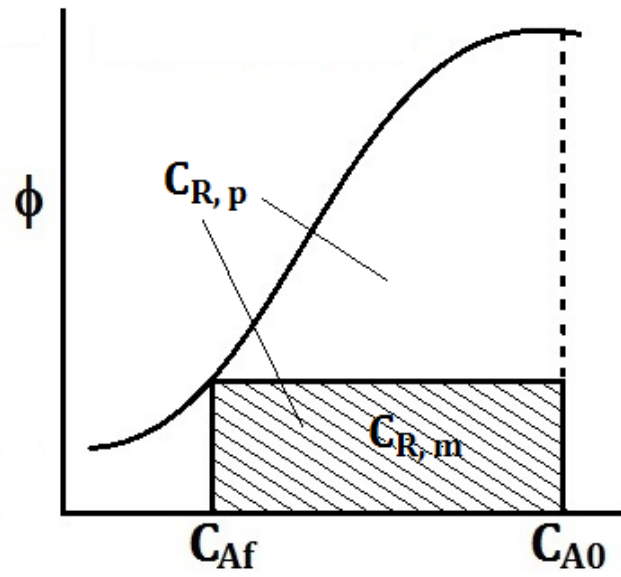
Selection of type of reactor

- In case of single or multiple mixed flow reactors, selection of the best outlet concentration of A is desired, to maximize C_R .
- The maximum area of the rectangle from the plots will give the maximum formation of the product R in mixed flow reactor.
- The shape of fractional yield(ϕ) versus C_A curves describes which type of reactor gives the best product distribution. Different possible shape of the curves are shown below.

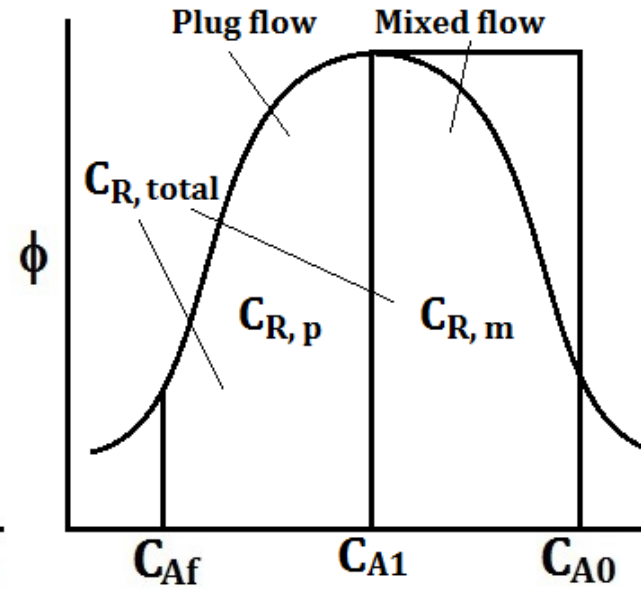
Comparison of different reactors



Mixed flow is the best



Plug flow is the best



Mixed flow followed by plug flow

- Here the fraction yield of A, ϕ is based on A consumed in the reaction.
- If two or more reactants are involved in the reactions, the fractional yield may be computed based on one of the reactants consumed, all reactants consumed, or on products formed.
- Therefore the fractional yield may be defined in general form as (M/N) , which is the instantaneous fractional yield of M based on the consumption or formation of N.