BT209

Bioreaction Engineering

29/03/2023

Deign for Multiple reactions
(Series reaction and combined series and parallel reactions)

Design for multiple reaction: Series and combination of series- parallel

- Different types of series reaction and combined series and parallel reactions

$$A \rightarrow R \rightarrow S \rightarrow T$$

Series

$$\begin{aligned} A + B &\rightarrow R \\ R + B &\rightarrow S \\ S + B &\rightarrow T \end{aligned}$$

Series parallel, or consecutive-competitive

$$\begin{array}{ccccc} A & \rightarrow & R & \rightarrow & S \\ \searrow & & \searrow & & \\ T & & U & & \end{array}$$

Denbigh system

$$A \rightleftarrows R \rightarrow S$$

Reversible and irreversible

$$A \rightleftarrows R \rightleftarrows S$$

Reversible

$$\begin{array}{ccc} & A & \\ \swarrow\nearrow & & \searrow\nwarrow \\ R & \rightleftarrows & S \end{array}$$

Reversible network

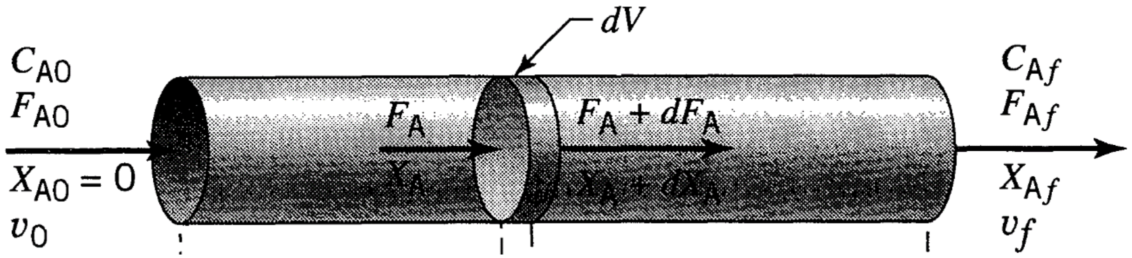
Irreversible first order series reaction: Distribution in Plug Flow (PFR)

$$\boxed{A \xrightarrow{k_1} R \xrightarrow{k_2} S}$$

What is C_R^{max} (INTERMEDIATE PRODUCT) (PFR) for pure feed of A?

Kinetics

$$\left.\begin{aligned} r_A &= -k_1 C_A \\ r_R &= k_1 C_A - k_2 C_R \\ r_S &= k_2 C_R \end{aligned}\right\}$$



$$F_A = (F_A + dF_A) + (-r_A)dV$$

$$dF_A = d[F_{A0}(1 - X_A)] = -F_{A0}dX_A$$

$$F_{A0}dX_A = (-r_A)dV$$

For constant volume (liquid)

$\vartheta_0 = \vartheta_f$

Similarly for R and S

$$\left\{\begin{aligned} F_{A0}\frac{dX_A}{dV} &= -r_A = k_1 C_A \\ F_{R0}\frac{dX_R}{dV} &= r_R = k_1 C_A - k_2 C_R \\ F_{S0}\frac{dX_S}{dV} &= r_S = k_2 C_R \end{aligned}\right.$$

Assume R increasing

Assume S increasing

Cont..

$$Using, X_A = \frac{C_{A0}-C_A}{C_{A0}}, \quad F_{A0}=C_{A0}\vartheta_0 \quad and \quad \tau = \frac{V}{\vartheta_0}$$

$$X_R = \frac{C_R - C_{R0}}{C_{R0}}, \quad F_{R0}=C_{R0}\vartheta_0$$ (Assume R increasing)

$$X_S = \frac{C_S - C_{S0}}{C_{S0}}, \quad F_{S0}=C_{S0}\vartheta_0$$ (Assume R increasing)

Solution of differential equations (profiles of A, R and S)

$$F_{A0}\frac{dX_A}{dV} = -r_A = k_1 C_A$$

$$-\vartheta_0 \frac{dC_A}{dV} = -r_A = k_1 C_A$$

$$\frac{dC_A}{d\tau} = -k_1 C_A$$

$$\boxed{\frac{C_A}{C_{A0}} = e^{-k_1\tau}}$$

$$F_{R0}\frac{dX_R}{dV} = -r_R = -k_1 C_A + k_2 C_R$$

$$\vartheta_0 \frac{dC_R}{dV} = k_1 C_A - k_2 C_R$$

$$\frac{dC_R}{d\tau} = k_1 C_A - k_2 C_R$$

$$\frac{dC_R}{d\tau} + k_2 C_R = k_1 C_{A0} e^{-k_1\tau}$$

(Method use: Multiplying integration factor)

$$\boxed{\frac{C_R}{C_{A0}} = \frac{k_1}{k_2 - k_1}\left(e^{-k_1\tau} - e^{-k_2\tau}\right)}$$

Cont..

$$\frac{C_A}{C_{A0}} = e^{-k_1\tau}$$

$$\frac{C_R}{C_{A0}} = \frac{k_1}{k_2 - k_1}\left(e^{-k_1\tau} - e^{-k_2\tau}\right)$$

$$r_A + r_R + r_S = -k_1 C_A + k_1 C_A - k_2 C_R + k_2 C_R = 0$$

$$\frac{dC_A}{dt} + \frac{dC_R}{dt} + \frac{dC_S}{dt} = 0$$

$C_A + C_R + C_s$=constant

$at, t = 0, C_{A0} + C_{R0} + C_{s0}$=constant

$constant = C_{A0}$, as pure feed C_{R0}=0, C_{s0}=0

$$C_S = C_{A0} - C_A - C_R$$

Cont..

For C_R^{max}

Put $dC_R/d\tau = 0$ where,

$$\frac{C_R}{C_{A0}} = \frac{k_1}{k_2 - k_1}\left(e^{-k_1\tau} - e^{-k_2\tau}\right)$$

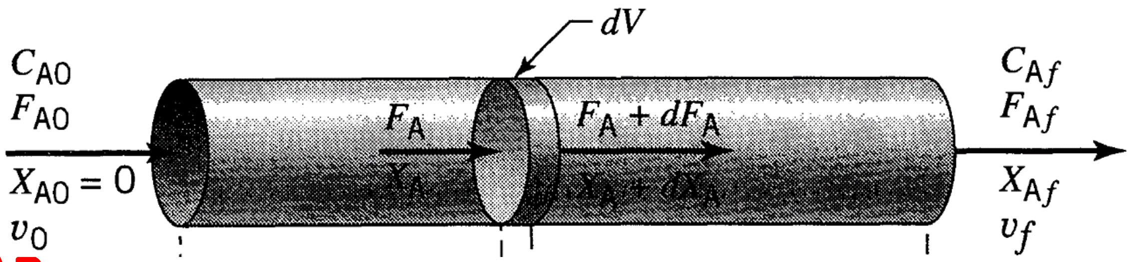
$$\boxed{\begin{aligned} \frac{C_{R,max}}{C_{A0}} &= \left(\frac{k_1}{k_2}\right)^{k_2/(k_2-k_1)} \\ \tau_{p,opt} &= \frac{1}{k_{\text{log mean}}} = \frac{\ln(k_2/k_1)}{k_2 - k_1} \end{aligned}}$$

Try it?

Similar to batch reactor

Different method to solve

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$



What is C_R^{max} in a Plug flow reactor (PFR)?

$$r_A = -k_1 C_A$$

$$r_R = k_1 C_A - k_2 C_R$$

$$r_S = k_2 C_R$$

Directly you can use

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

$$\frac{V}{F_{R0}} = \frac{\tau}{C_{R0}} = \int_0^{X_{Rf}} \frac{dX_R}{r_R} \quad \text{(Assume R increasing)}$$

$$\frac{V}{F_{S0}} = \frac{\tau}{C_{S0}} = \int_0^{X_{Sf}} \frac{dX_S}{r_S} \quad \text{(Assume R increasing)}$$

Get same expression of C_A, C_R, and Cs

Distribution at different k_2/k_1 in a PFR

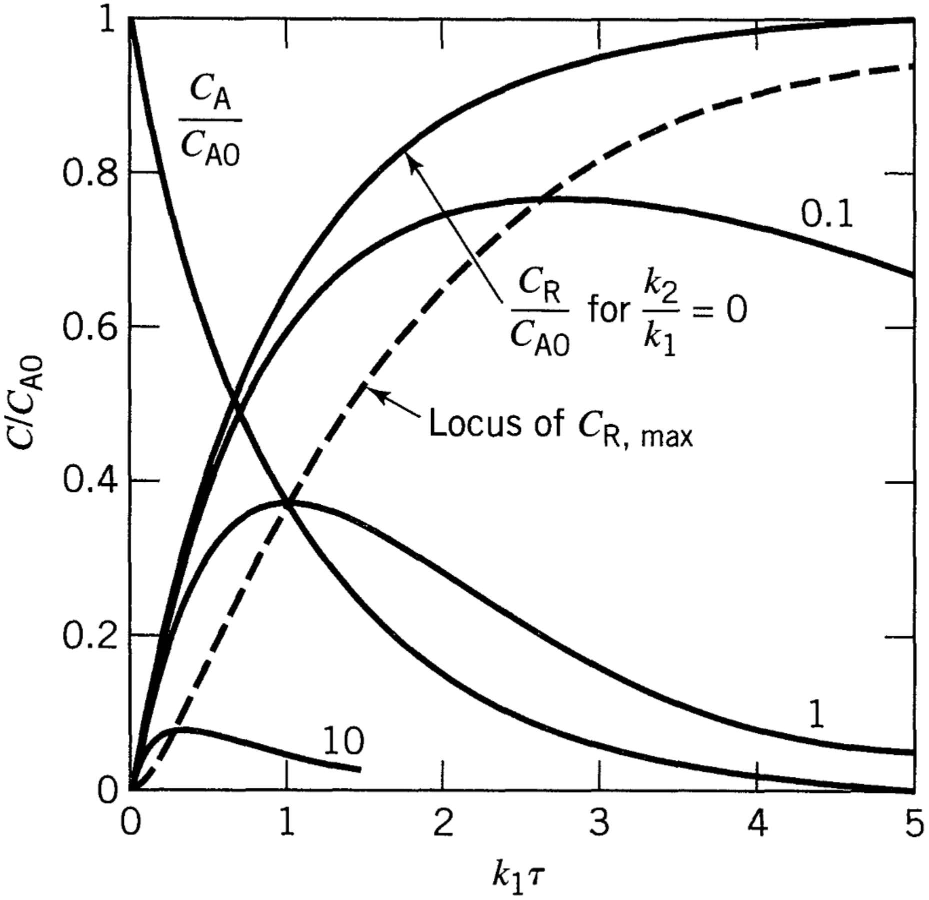
✓ **Plot using the equation of C_A, C_R and C_S**

$$\frac{C_A}{C_{A0}} = e^{-k_1\tau}$$

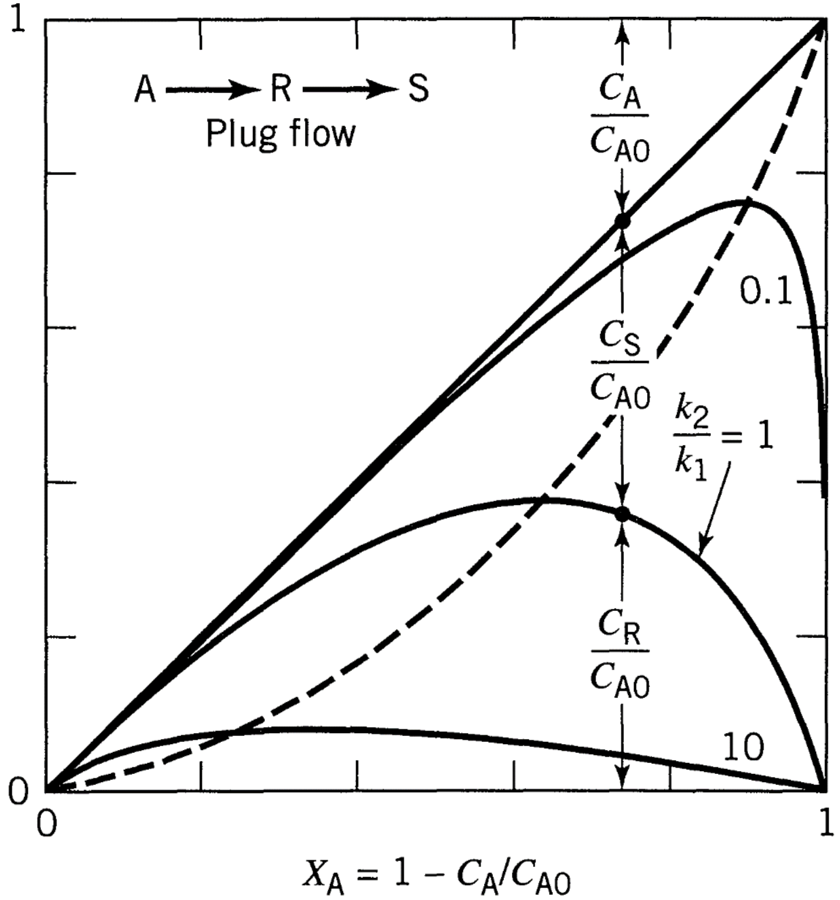
$$\frac{C_R}{C_{A0}} = \frac{k_1}{k_2 - k_1}\left(e^{-k_1\tau} - e^{-k_2\tau}\right)$$

$$C_S = C_{A0} - C_A - C_R$$

Concentration-time curves of the intermediate R



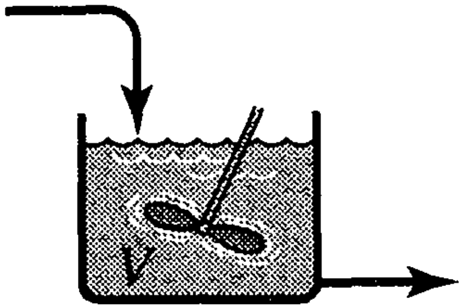
Time-independent plot, relates the concentration of all reaction components



Irreversible first order series reaction: Product distribution in Mixed Flow Reactor (CSTR)

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

v_0
C_{A0}
$C_{R0} = C_{S0} = 0$
F_{A0}
$F_{R0} = F_{S0} = 0$



v
C_A
C_R
$C_S = C_{A0} - C_A - C_R$
F_A
F_R
F_S

$$\tau_m = \frac{V}{v}$$

For constant volume (liquid)

$\vartheta_0 = \vartheta$

Rate of input=rate of output + rate of disappearance by reaction

$$F_{A0} = F_A + (-r_A)V$$

$$vC_{A0} = vC_A + k_1 C_A V$$

$$\frac{V}{v} = \tau_m$$

$$\boxed{\frac{C_A}{C_{A0}} = \frac{1}{1 + k_1 \tau_m}}$$

Cont..

$$vC_{R0} = vC_R + (-r_R)V$$

$$0 = vC_R + (-k_1C_A + k_2C_R)V$$

$$\boxed{\frac{C_R}{C_{A0}} = \frac{k_1\tau_m}{(1 + k_1\tau_m)(1 + k_2\tau_m)}}$$

$$C_A + C_R + C_S = C_{A0} = \text{constant}$$

$$\boxed{\frac{C_S}{C_{A0}} = \frac{k_1k_2\tau_m^2}{(1 + k_1\tau_m)(1 + k_2\tau_m)}}$$

Cont..

For C_R^{max}

Put $dC_R/d\tau_m = 0$ where,

$$\frac{dC_R}{d\tau_m} = 0 = \frac{C_{A0}k_1(1 + k_1\tau_m)(1 + k_2\tau_m) - C_{A0}k_1\tau_m[k_1(1 + k_2\tau_m) + (1 + k_1\tau_m)k_2]}{(1 + k_1\tau_m)^2(1 + k_2\tau_m)^2}$$

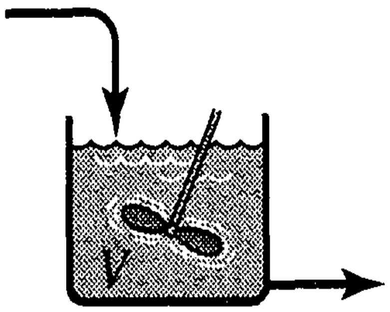
$$\boxed{\begin{gathered}\tau_{m,opt} = \frac{1}{\sqrt{k_1k_2}} \\ \frac{C_{R,max}}{C_{A0}} = \frac{1}{[(k_2/k_1)^{1/2} + 1]^2}\end{gathered}}$$

Try it to get?

Different method

v_0
C_{A0}
$C_{R0} = C_{S0} = 0$
F_{A0}
$F_{R0} = F_{S0} = 0$

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$



v
C_A
C_R
$C_S = C_{A0} - C_A - C_R$
F_A
F_R
F_S

$$\tau_m = \frac{V}{v}$$

(m for mixed flow reactor)

For CSTR

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \frac{X_A}{-r_A}$$

$$\frac{V}{F_{R0}} = \frac{\tau}{C_{R0}} = \frac{X_R}{-r_R}$$

$$\frac{V}{F_{S0}} = \frac{\tau}{C_{S0}} = \frac{X_S}{-r_S}$$

(Sign of r_R and r_S depends on what conversion expressions are used)

$$Using, X_A = \frac{C_{A0} - C_A}{C_{A0}}$$

$$Using, X_R = \frac{C_{R0} - C_R}{C_{R0}}$$

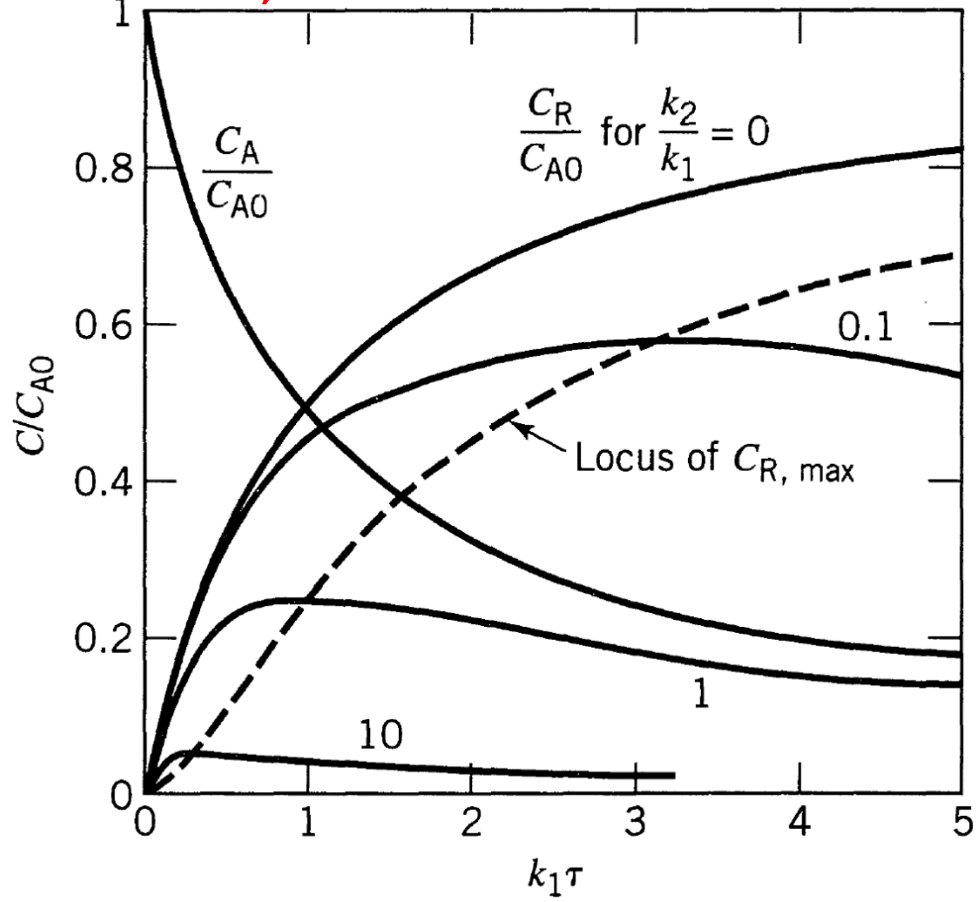
$$Using, X_S = \frac{C_{S0} - C_S}{C_{S0}}$$

Get same expressions of C_A, C_R, and Cs

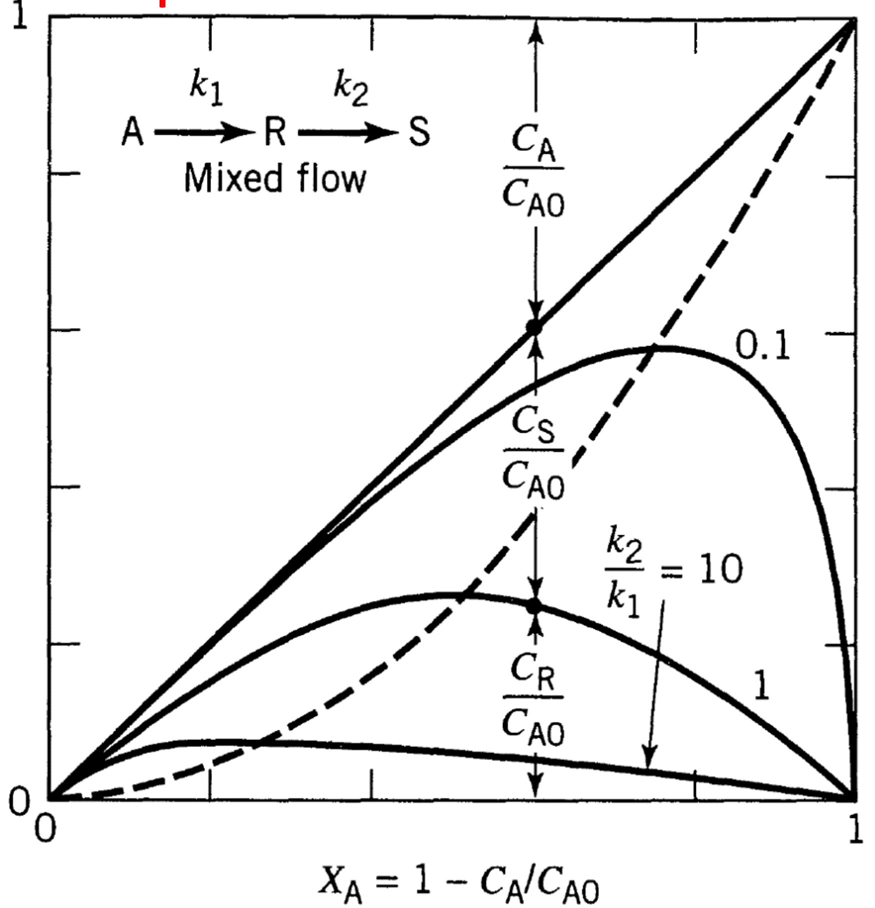
Distribution of products and reactant in a Mixed Flow Reactor (CSTR) for series reaction A→R→S

✓ **Plot using the equation of C_A, C_R and C_S**

Concentration-time curves of A , S and intermediate R

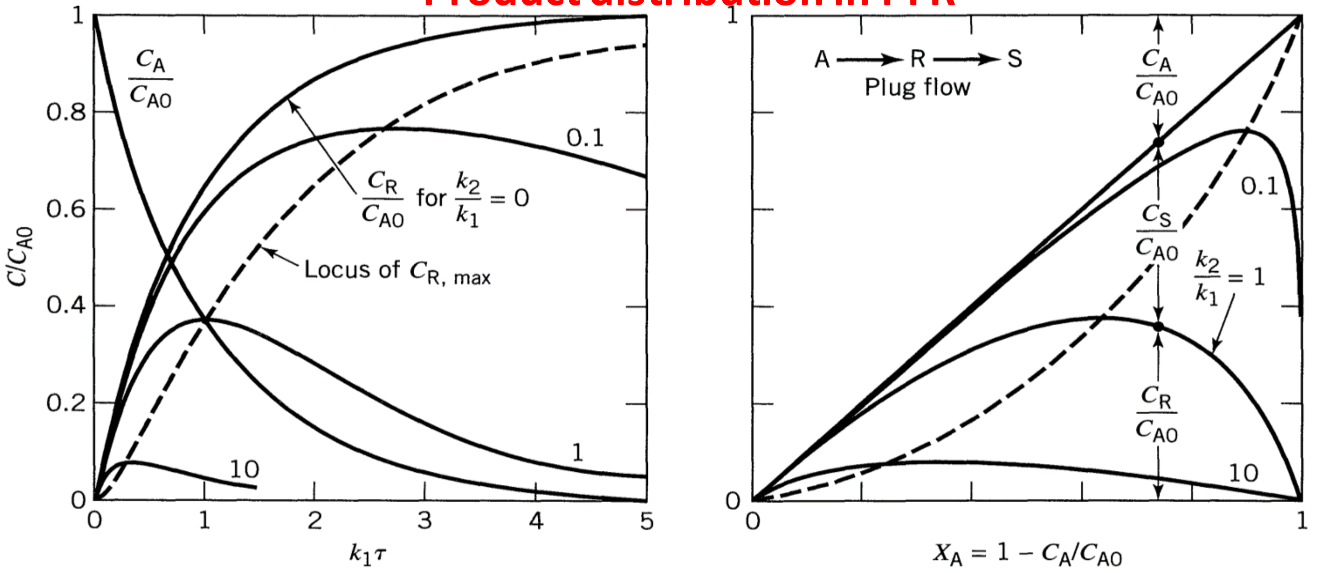


Relative concentration of all reaction components

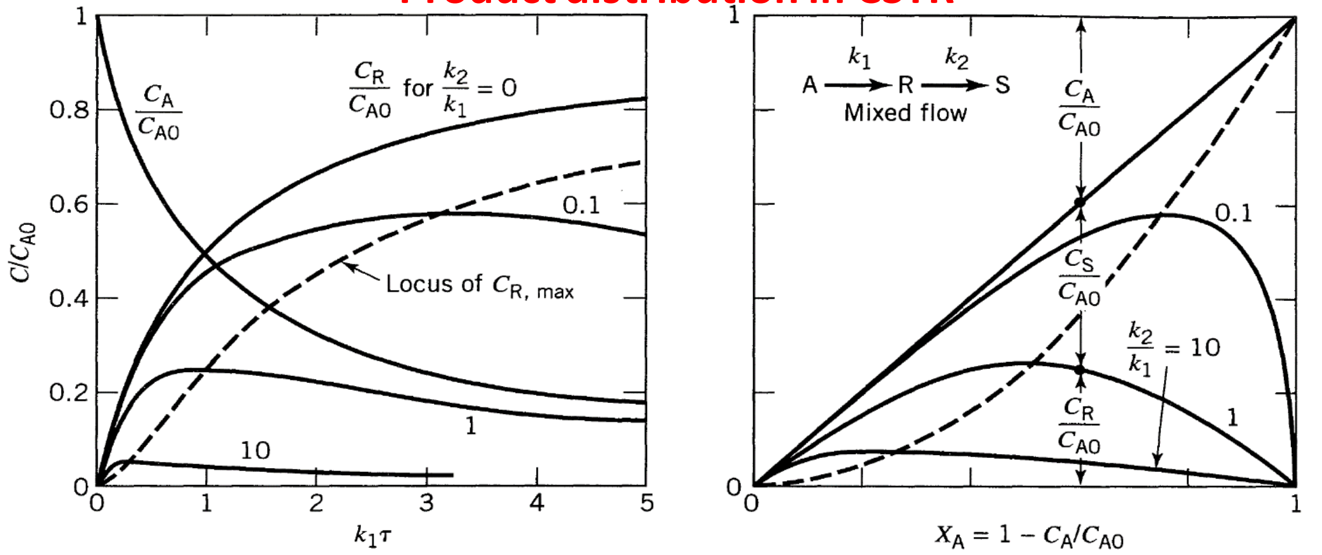


Comparison of distribution of products and reactant in a PFR and CSTR for series reaction A→R→S

Product distribution in PFR

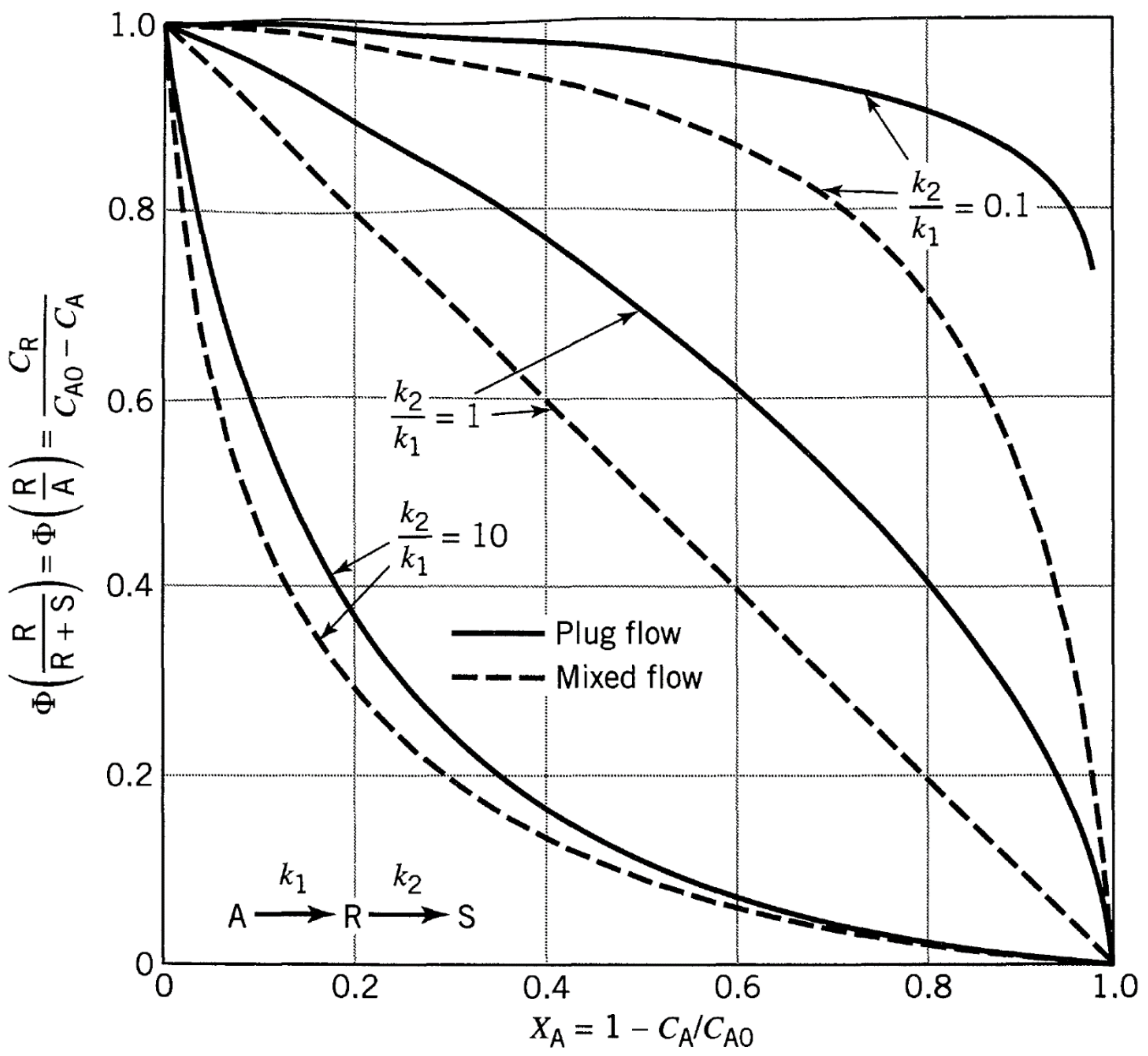


Product distribution in CSTR



- For any reaction the maximum obtainable concentration of R in a plug flow reactor is always higher than the maximum obtainable in a mixed reactor
- Except when $k_1 = k_2$ the PFR always requires a smaller time than does the CSTR to achieve the maximum concentration of R, the difference in times becoming progressively larger as k_2/k_1 departs from unity
- Such plots find most use in kinetic studies because they allow the determination of k_2/k_1 by matching the experimental points with one of the family of curves on the appropriate graph.

Fractional yield of intermediate R in CSTR and PFR



- **Fractional yield of R** is **always higher for plug flow than for mixed flow** for any conversion level.

- If for the reaction considered k_2/k_1 is much smaller than unity, we should **design for a high conversion of A (around 0.8)** and probably dispense with recycle of unused reactant.

- However, **if k_2/k_1 is greater than unity**, the **fractional yield drops** very sharply even at low conversion. Hence, to avoid obtaining unwanted S instead of R we must **design for a very small conversion of A per pass, separation of R, and recycle of unused reactant**.