

Introduction to Chemical Reactors

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3. Multiple Reactions

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Objectives and sources

- Extend the models for reactor design to chemical systems of multiple reactions (in **series**, **parallel** and their **combinations**).
- Calculate the conditions for **maximum yield** and **selectivity** of a given product.
- Identify the best reactor and its operating conditions for a given objective, e.g. maximise yield.

- Schmidt: Chapter 4

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3.1 Introduction and basic concepts

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Multiple reactions can be in

- *series*,
- *parallel*, or
- *combination of series and parallel*.

In reactors with multiple competing reactions we are interested not only in maximising the *conversion*, X , of the desired reaction, but also the *selectivity*, S_J , and/or *yield*, Y_J , of a given product.

Unfortunately, there is generally a trade-off between X and S_J (Y_J).

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Motivation

Virtually all industrial/commercial processes involve systems of multiple reactions.

In a **single reaction system** the objective is often to **increase the reaction rate** (thus *minimising the reactor volume or the residence time*). This is generally achieved **by increasing the temperature** of operation.

However, in a **multiple reaction system** the problem is to create a *reactor configuration* to

- **maximise** the production of a **desired product**, or
- **minimise** the production of **undesired ones**.

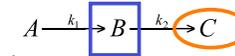
Types of multiple reactions

1. Reactions in series



Main
product

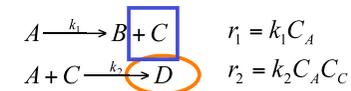
byproduct



2. Reactions in parallel



3. Complex systems of reaction: series and parallel



Selectivity (S_J)

$$S_J = \frac{\text{moles of desired product J formed}}{\text{moles of all products formed}}$$

So, for example, for a reaction where $A \rightarrow B$

$$S_J = \frac{N_J}{N_{A0} - N_A} = \frac{F_J}{F_{A0} - F_A} \rho_{\text{constant}} = \frac{C_J}{C_{A0} - C_A}$$

Yield (Y_J)

$$Y_J = \frac{\text{moles of desired product J formed}}{\text{moles of reactant fed}}$$

$$Y_J = \frac{N_J}{N_{A0}} = \frac{F_J}{F_{A0}} \rho_{\text{constant}} = \frac{C_J}{C_{A0}}$$

... and for a reaction where $A \rightarrow B$

$$Y_J = S_J X_A$$

Table 4.1 from Schmidt 2nd ed.

Process	Reaction	τ	P	T	X	S	Catalyst
fermentation	sugar \rightarrow C ₂ H ₅ OH + 2CO ₂	1 week	1 atm	35°C	100%	50%	yeast
methanol synthesis	CO + 2H ₂ \rightarrow CH ₃ OH	1 min	50	250	90	99	Cu/ZnO
steam cracking	C ₂ H ₆ \rightarrow C ₂ H ₄ + H ₂	1 sec	2	850	70	85	none
ethylene oxidation	C ₂ H ₄ + $\frac{1}{2}$ O ₂ \rightarrow C ₂ H ₄ O	5 sec	2	280	10	60-90	Ag
FCC reactor	C ₁₆ \rightarrow C ₈ + C ₈ ⁺	10 sec	2	450			zeolite
FCC regenerator	C + O ₂ \rightarrow CO ₂	1 min	2	550	100	100	none
hydrotreating	C ₂₄ + H ₂ \rightarrow 2C ₁₂	1 min	30				Co-Mo
steam reforming	CH ₄ + H ₂ O \rightarrow CO + 3H ₂	1 sec	—	250		99	Ni
NH ₃ synthesis	N ₂ + 3H ₂ \rightarrow 2NH ₃	10 sec	200	250	50	100	Fe
auto catalytic converter	CO \rightarrow CO ₂ , NO \rightarrow N ₂	0.1 sec	1	400	95		Pt-Rh-Pd
maleic anhydride	C ₄ H ₁₀ + O ₂ \rightarrow C ₄ H ₄ O ₃	10 sec	2	400			VPO
NH ₃ oxidation	NH ₃ + $\frac{5}{2}$ O ₂ \rightarrow NO + H ₂ O	10 ⁻³ sec	10	900	90	90	Pt-Rh
HCN synthesis	CH ₄ + NH ₃ + O ₂ \rightarrow HCN	10 ⁻³ sec	2	1100	70	70	Pt-Rh
steam reforming	CH ₄ + H ₂ O \rightarrow CO + 3H ₂	1 sec	—	800	90	100	Ni
cyclohexane oxidation	c-C ₆ H ₁₂ \rightarrow adipic acid	1 h	1	150	5	80	Co homog.
p-xylene oxidation	xylene \rightarrow terephthalic acid	20 min	1	150	80	99	
water-gas shift	CO + H ₂ O \rightarrow CO ₂ + H ₂	1 sec	—	250	80	100	Cu/ZnO
autothermal reform	CH ₄ + $\frac{1}{2}$ O ₂ \rightarrow CO + 2H ₂	10 ⁻³ sec	—	1000	95	95	Rh
formaldehyde	CH ₃ OH + $\frac{1}{2}$ O ₂ \rightarrow HCHO	10 ⁻² sec	—	400	98	98	Fe-Mo

Notes: All values are very approximate. Selectivities are based on carbon atoms in the major reactant.
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A notation for multiple reactions

$$\sum_{j=1}^S v_{ij} A_j = 0$$

$i = 1, 2, \dots, R$ (reactions)

$j = 1, 2, \dots, S$ (species)

v_{ij} = stoichiometric coefficient of species j in reaction i ; negative if j is a reactant; positive if j is a product

$$r = k \prod_{j=1}^S C_j^{m_j}$$

m_j = order of the reaction with respect to the j^{th} species

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The reactor design equations derived for the single reaction case are applicable to each of the species present in the multiple reactions, so we do not have to re-derive them!

All we have to do is to account for the presence of each species in all the reactions ...

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Summary of reactor design equations – multiple reactions

	differential form	algebraic form	integral form
Batch	$\frac{dC_j}{dt} = \sum_{i=1}^R v_{ij} r_i$		$t = -C_{j0} \int_0^X \frac{dX}{\sum_{i=1}^R v_{ij} r_i(X)}$
CSTR	$\frac{dC_j}{dt} = \frac{1}{\tau} (C_{j0} - C_j) + \sum_{i=1}^R v_{ij} r_i$	$C_{j0} - C_j = -\tau \sum_{i=1}^R v_{ij} r_i$	$V = \frac{-F_{j0} X}{\sum_{i=1}^R v_{ij} r_i}$
PFR	$\frac{dC_j}{d\tau} = \sum_{i=1}^R v_{ij} r_i$		$V = -F_{j0} \int_0^X \frac{dX}{\sum_{i=1}^R v_{ij} r_i(X)}$

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One design equation is created for each of the species present in the system.

We end up with a system of n simultaneous equations in n unknowns (the concentrations of the species as a function of time).

In some cases the yield/selectivity of a species is non-monotonic, i.e. it has a maximum value in the range of $X = 0.0 \dots 1.0$.

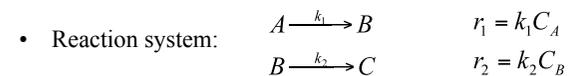
3.2 Multiple reactions in series

In the case of a PFR we get a system of simultaneous differential equations.

Let's solve a system of two 1st order reactions in series (the simplest case). The same method is applicable to more complicated systems, i.e. more than two reactions of any order.

Series reactions in a PFR

$$\frac{dC_j}{d\tau} = \sum_{i=1}^R \nu_{ij} r_i$$



• Mole Balances for PFR:

$$\begin{aligned} \frac{dC_A}{d\tau} &= -r_1 = -k_1 C_A \\ \frac{dC_B}{d\tau} &= r_1 - r_2 = k_1 C_A - k_2 C_B \\ \frac{dC_C}{d\tau} &= r_2 = k_2 C_B \end{aligned}$$

$$\text{BCs: } C_A = C_{A0} \quad ; \quad C_{B0} = C_{C0} = 0$$

Series reactions in a PFR (2)

Solve eqn. 1 (separable) $\frac{dC_A}{C_A} = -k_1 d\tau \Rightarrow C_A = C_{A0} \exp[-k_1 \tau]$

Solve eqn. 2. Subst. C_A into eqn. 2; $\frac{dC_B}{d\tau} + k_2 C_B = k_1 C_{A0} \exp[-k_1 \tau]$

not separable, use Integrating Factor $IntFact = \exp\left[\int k_2 d\tau\right] = e^{k_2 \tau}$

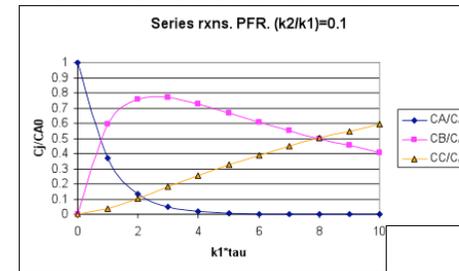
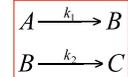
and get:

$$C_B = C_{A0} \frac{k_1}{k_2 - k_1} (\exp[-k_1 \tau] - \exp[-k_2 \tau])$$

To get C_C we could substitute C_B into eqn. 3 and solve, but we notice that $(C_{A0} - C_A) = C_B + C_C$. Hence, solve for C_C and get:

$$C_C = C_{A0} \left[1 - \frac{k_2}{k_2 - k_1} \exp[-k_1 \tau] + \frac{k_1}{k_2 - k_1} \exp[-k_2 \tau] \right]$$

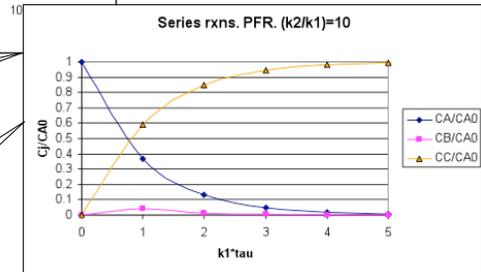
Series reactions in a PFR (3)



Dimensionless plot
 $C_A/C_{A0}, C_B/C_{A0}, C_C/C_{A0}$
vs.
 $k_1 \tau$

They have a maximum C_B

Looks like $A \rightarrow C$



Maximum yield of B in PFR (series reactions)

$$Y_B = \frac{C_B}{C_{A0}}$$

There is an optimum τ to maximise C_B

$$\frac{d}{d\tau}(C_B) = 0 = \frac{d}{d\tau} \left(C_{A0} \frac{k_1}{k_2 - k_1} (e^{-k_1 \tau} - e^{-k_2 \tau}) \right) \Rightarrow \tau_{opt} = \frac{\ln(k_2/k_1)}{k_2 - k_1}$$

substitute τ_{opt} into expression for C_B to get C_{Bmax}

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

$$Y_{Bmax} = \frac{C_{Bmax}}{C_{A0}} = \left(\frac{k_1}{k_2} \right)^{\frac{k_2}{k_2 - k_1}}$$

In the case of a CSTR operating at steady-state we get a system simultaneous algebraic equations.

Let's solve a system of two 1st order reactions in series (the simplest case). The same method is applicable to more complicated systems, i.e. more than two reactions of any order.

Series reactions in a CSTR

$$C_{j0} - C_j = -\tau \sum_{i=1}^R \nu_{ij} r_i$$

- Reaction system:

$$A \xrightarrow{k_1} B \quad r_1 = k_1 C_A$$

$$B \xrightarrow{k_2} C \quad r_2 = k_2 C_B$$

- Mole Balances for CSTR:

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

$$C_B - C_{B0} = \tau(k_1 C_A - k_2 C_B)$$

$$C_C - C_{C0} = \tau(k_2 C_B)$$

- Solve:

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

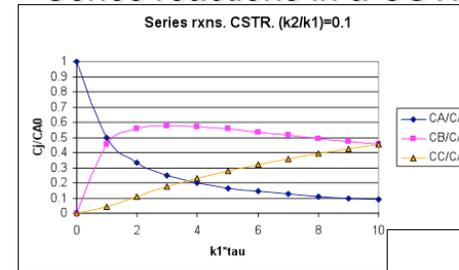
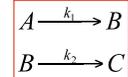
$$C_B = \frac{k_1 C_{A0} \tau}{(1 + k_1 \tau)(1 + k_2 \tau)}$$

$$C_C = \frac{k_1 k_2 C_{A0} \tau^2}{(1 + k_1 \tau)(1 + k_2 \tau)}$$

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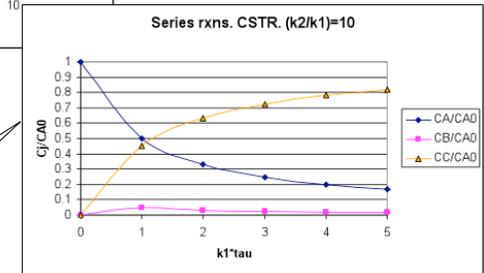
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Series reactions in a CSTR (2)



Dimensionless plot
 $C_A/C_{A0}, C_B/C_{A0}, C_C/C_{A0}$
 vs.
 $k_1 \tau$

Looks like
 $A \rightarrow C$



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Maximum yield of B in CSTR (series reactions)

$$Y_B \rho_{\text{constant}} = \frac{C_B}{C_{A0}}$$

There is an optimum τ to maximise C_B

$$\frac{d}{d\tau}(C_B) = 0 = \frac{d}{d\tau} \left(\frac{k_1 C_{A0} \tau}{(1 + k_1 \tau)(1 + k_2 \tau)} \right) \Rightarrow \tau_{\text{opt}} = \frac{1}{\sqrt{k_1 k_2}}$$

substitute τ_{opt} into expression for C_B to get $C_{B\text{max}}$

$$C_{B\text{max}} = \frac{k_1 C_{A0}}{\left(k_1^{1/2} + k_2^{1/2}\right)^2}$$

$$Y_{B\text{max}} = \frac{C_{B\text{max}}}{C_{A0}} = \frac{k_1}{\left(k_1^{1/2} + k_2^{1/2}\right)^2}$$

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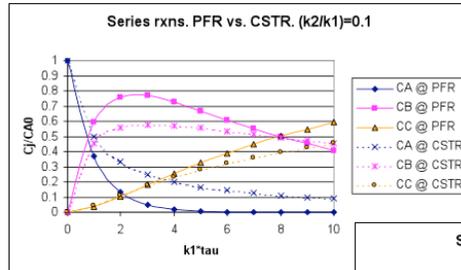
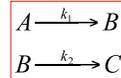
The behaviour of PFRs and CSTRs operating with multiple reactions in series is qualitatively similar.

But are PFR and CSTR identical with respect to multiple reactions?

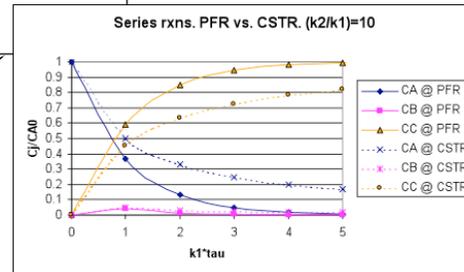
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PFR vs. CSTR for series reactions



The PFR gives higher yield than the CSTR (for positive order reactions).



The CSTR has always B present (reacting into C), whereas in a PFR initially there is only A

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PFR vs. CSTR for series reactions (2)

1. There is an *optimum residence time* in a continuous reactor or an *optimum reaction time* in a batch reactor to maximise yield of an intermediate.
2. The PFR will always give a higher maximum yield of an intermediate than a CSTR if all the series reactions obey positive-order kinetics.

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3.3 Multiple reactions in parallel

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Multiple reactions in parallel are addressed identically to reactions in series:

One design equation is created for each of the species present in the system.

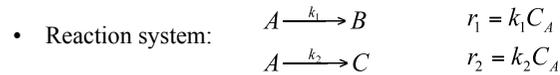
Again, we end up with a system of n simultaneous equations in n unknowns (the concentrations of the species as a function of time): PFRs result in a system of simultaneous differential equations, and steady-state CSTRs in a system of simultaneous algebraic equations.

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Parallel reactions in a PFR

$$\frac{dC_j}{d\tau} = \sum_{i=1}^R v_{ij} r_i$$



Mole Balances for PFR:

$$\frac{dC_A}{d\tau} = -r_1 - r_2 = -k_1 C_A - k_2 C_A$$

$$\frac{dC_B}{d\tau} = r_1 = k_1 C_A$$

$$\frac{dC_C}{d\tau} = r_2 = k_2 C_A$$

BCs: $C_A = C_{A0}$; $C_{B0} = C_{C0} = 0$

Parallel reactions in a PFR (2)

Solve eqn. 1 (separable) $\frac{dC_A}{C_A} = -(k_1 + k_2)d\tau \Rightarrow C_A = C_{A0} \exp[-(k_1 + k_2)\tau]$

Solve eqn. 2: subst. C_A into eqn. 2; $\frac{dC_B}{d\tau} = k_1 C_{A0} \exp[-(k_1 + k_2)\tau]$

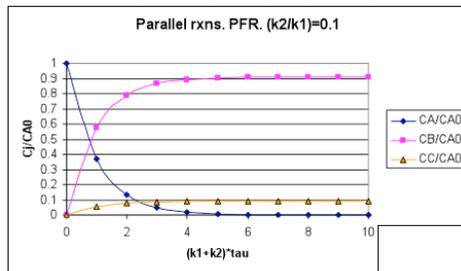
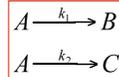
It is separable, integrate and get: $C_B = C_{A0} \frac{k_1}{k_1 + k_2} (1 - \exp[-(k_1 + k_2)\tau])$

Similarly, eqn. 3 is separable, solve and get:

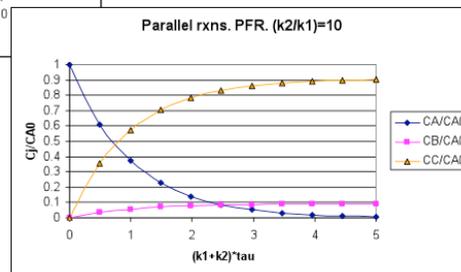
$$C_C = C_{A0} \frac{k_2}{k_1 + k_2} (1 - \exp[-(k_1 + k_2)\tau])$$

The selectivity to form B is: $S_{B \rho \text{ constant}} = \frac{C_B}{C_B + C_C} = \frac{k_1}{k_1 + k_2}$

Parallel reactions in a PFR (3)



Dimensionless plot
 $C_A/C_{A0}, C_B/C_{A0}, C_C/C_{A0}$
vs.
 $(k_1 + k_2) \tau$

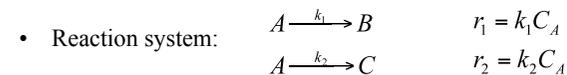


from expression
for $C_A(\tau)$

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

Parallel reactions in a CSTR

$$C_{j0} - C_j = -\tau \sum_{i=1}^R v_{ij} r_i$$



Mole Balances for CSTR:

$$C_A - C_{A0} = -\tau(k_1 + k_2)C_A$$

$$C_B - C_{B0} = \tau k_1 C_A$$

$$C_C - C_{C0} = \tau k_2 C_A$$

BCs: $C_A = C_{A0}$; $C_{B0} = C_{C0} = 0$

Solve:

$$C_A = \frac{C_{A0}}{1 + (k_1 + k_2)\tau}$$

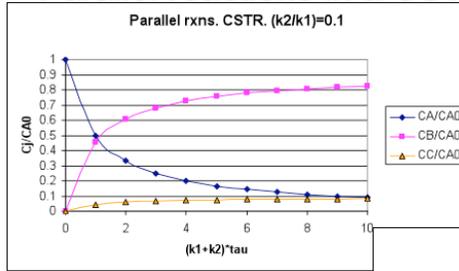
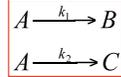
$$C_B = \frac{k_1 \tau C_{A0}}{1 + (k_1 + k_2)\tau}$$

$$C_C = \frac{k_2 \tau C_{A0}}{1 + (k_1 + k_2)\tau}$$

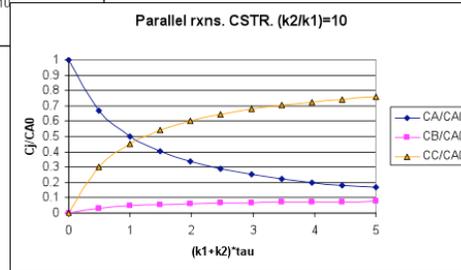
Selectivity to form B
identical to PFR case:

$$S_{B \rho \text{ constant}} = \frac{C_B}{C_B + C_C} = \frac{k_1}{k_1 + k_2}$$

Parallel reactions in a CSTR (2)



Dimensionless plot
 $C_A/C_{A0}, C_B/C_{A0}, C_C/C_{A0}$
 vs.
 $(k_1 + k_2) \tau$

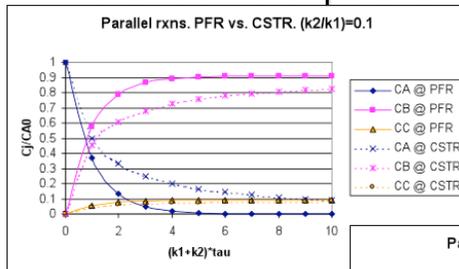
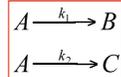


from expression
for $C_A(\tau)$

$$\tau = \frac{(C_{A0} - C_A)}{C_A(k_1 + k_2)}$$

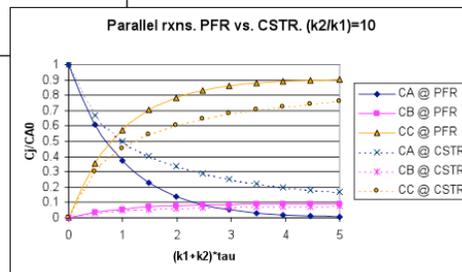
Similarly to the case of multiple reactions in series, PFRs and CSTRs are qualitatively similar but quantitatively different.

PFR vs. CSTR for parallel reactions



For parallel, irreversible,
first-order reactions:

- the τ is smaller in a PFR
- selectivity is identical



3.4 Instantaneous selectivity and yield

Instantaneous (differential) selectivity and yield

An alternative definition of selectivity and yield is in terms of the **rates of formation** of the species (rather than the concentrations or molar flowrates), i.e.

$$s_J = \frac{\text{rate of formation of product J}}{\text{rate of formation of all products}} \quad y_{J/A} = \frac{\text{rate of formation of product J}}{\text{rate of depletion of reaction A}}$$

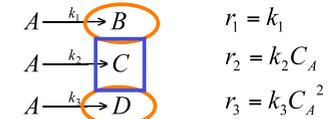
$$s_J = \frac{dC_J}{\sum_{i=1}^{\text{prods}} dC_i} \quad y_{J/A} = -\frac{dC_J}{dC_A}$$

Note: sometimes the selectivity is defined in terms of the formation of unwanted products, rather than formation of all products.

3.5 Reactor selection for systems of multiple reactions

Example: Trambouze reactions

Parallel reaction system:



Selectivity
(instantaneous):

$$s_C = \frac{dC_C}{dC_B + dC_C + dC_D} = \frac{k_2 C_A}{k_1 + k_2 C_A + k_3 C_A^2}$$

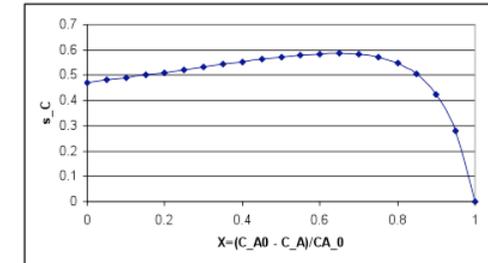
$$k_1 = 1; k_2 = 4; k_3 = 2;$$

$$C_{A0} = 2.0$$

Plotting s_C vs. X

(with $C_A = C_{A0} [1 - X]$)

$$\begin{aligned} s_{C,\max} @ X_{\max} &= 0.646 \\ C_{A,\max} &= 0.708 \\ s_{C,\max} &= 0.586 \end{aligned}$$



Choice of reactors for multiple reactions

- Series reactions
 - If an intermediate product is desired: there is an optimum τ for Y_{\max} .
PFR gives higher Y_{\max} if reactions have positive order,
CSTR gives higher Y_{\max} if reactions have negative order
 - If a final product is desired:
PFR requires shorter time and produces less intermediates (for +ve order)
- Parallel reactions
 - Reactions with same order: PFR and CSTR give equal Selectivity
- Series-parallel reactions
 - Solve mass balance equations!

Summary

For systems of multiple reactions we must solve R simultaneous mass balance equations.

Series reactions

- There is:
 - an optimum residence time in a continuous reactor or
 - an optimum reaction time in a batch reactorto maximise yield of an intermediate.
- The PFR will always give a higher maximum yield of an intermediate for positive-order kinetics.

Parallel reactions

- τ is smaller in a PFR, selectivity is identical in PFR and CSTR.