SEMESTER GASAL TAHUN AKADEMIK 2007/2008

PERANCANGAN REAKTOR

DR. Ir. I Gusti S. Budiaman, M.T.

JURUSAN TEKNIK KIMIA – FTI

UPN "VETERAN" YOGYAKARTA

2007

TUJUAN INSTRUKSIONAL KHUSUS

MAHASISWA MEMPUNYAI KEMAMPUAN MENTERJEMAHKAN DAN MEMAHAMI PERANCANGAN BERBAGAI TIPE REAKTOR MELIPUTI BENTUK REAKTOR, PROSES, KONDISI OPERASI, DAN SUSUNAN REAKTOR, SERTA PEMILIHAN TIPE REAKTOR

TUJUAN INSTRUKSIONAL UMUM

MAHASISWA MEMPUNYAI KEMAMPUAN MERANCANG BERBAGAI TIPE REAKTOR UNTUK REAKSI-REAKSI HOMOGEN DAN HETEROGEN

MATERI

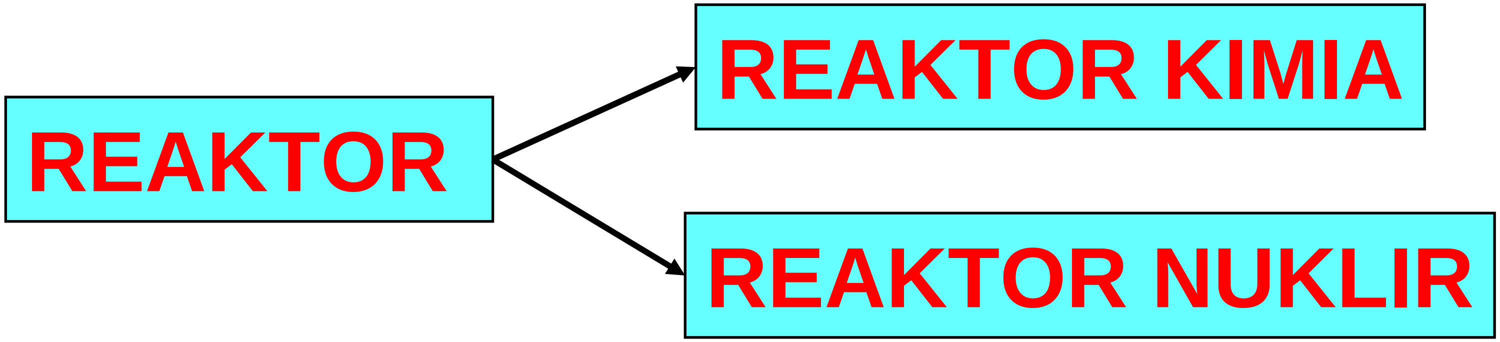
- Pendahuluan: meliputi review posisi MKA Reaktor dalam Teknik Kimia, bagaimana merancang reaktor, definisi laju reaksi, panas reaksi, konversi, yield, dan selektivitas
- Reaktor Homogen
  - Reaktor Batch (RB)
  - Reaktor Semi Batch (RSB)
  - RATB
  - RAP
- Reaktor Heterogen
  - Reaktor Fixed Bed
  - Reaktor Fluidized Bed
  - Reaktor Moving Bed
  - Reaktor Gelembung
  - Reaktor Slurry

PUSTAKA

- Fogler, H.S., 1986, “Element of Chemical Reaction Engineering”
- Levenspiel, O., 1999, “Chemical Reaction Engineering”
- Missen, R.W., Mims, C.A., and Saville, B.A., 1999, “Introduction to Chemical Reaction Engineering and Kinetics”
- Hill JR, C.G., 1977, “An Introduction to Chemical Engineering Kinetics & Reactor Design”

REAKTOR

MERUPAKAN MKA YANG TERGABUNG DALAM KELOMPOK ENGINEERING SCIENCE, MEMPELAJARI PERANCANGAN BERBAGAI TIPE REAKTOR UNTUK REAKSI-REAKSI HOMOGEN DAN HETEROGEN MELIPUTI BENTUK REAKTOR, PROSES, KONDISI OPERASI, DAN SUSUNAN REAKTOR, SERTA PEMILIHAN TIPE REAKTOR

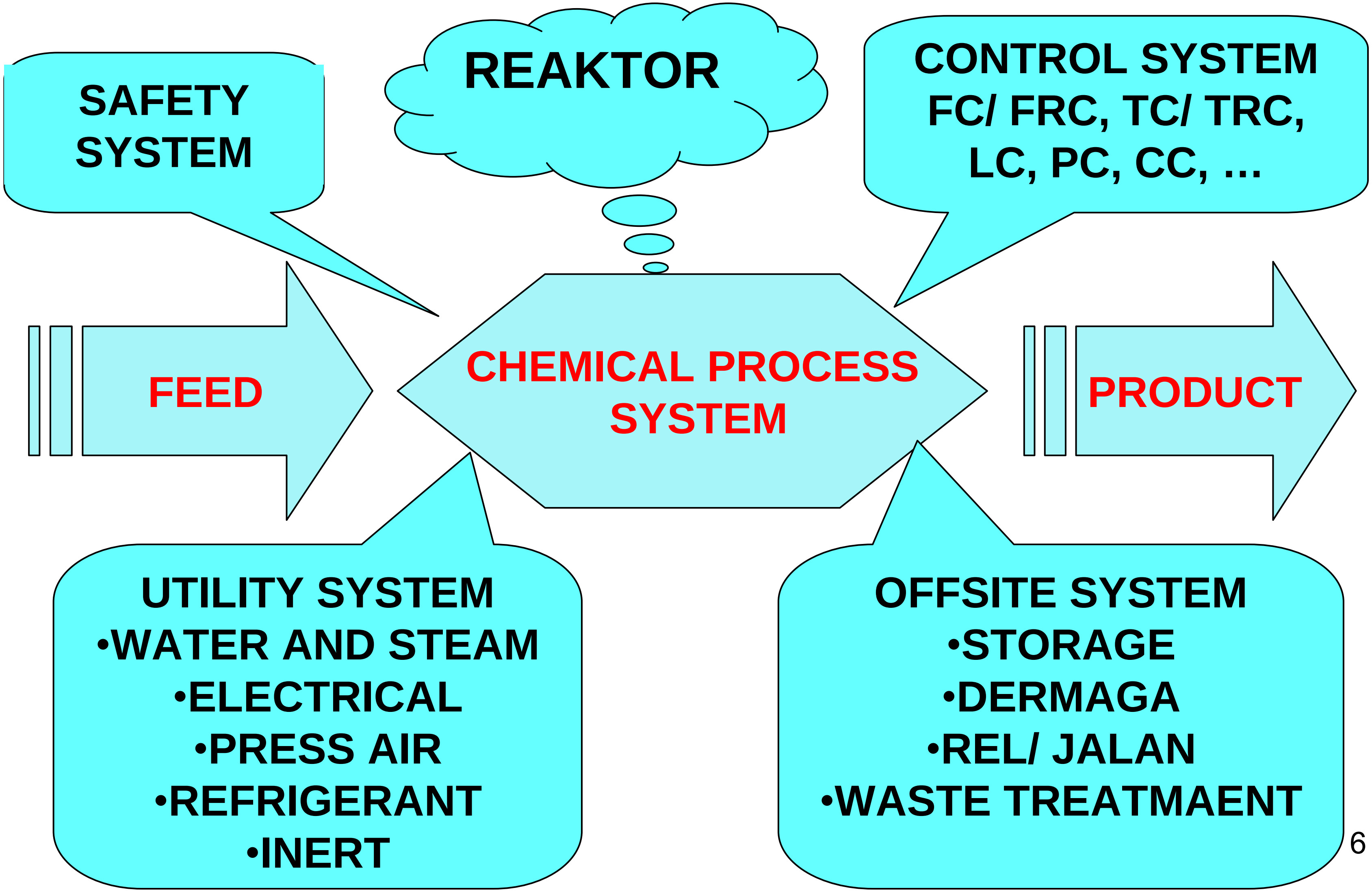


REAKTOR

REAKTOR KIMIA

REAKTOR NUKLIR

ILUSTRASI SISTEM PROSES KIMIA



REAKTOR

SAFETY SYSTEM

CONTROL SYSTEM
FC/ FRC, TC/ TRC, LC, PC, CC, …

FEED

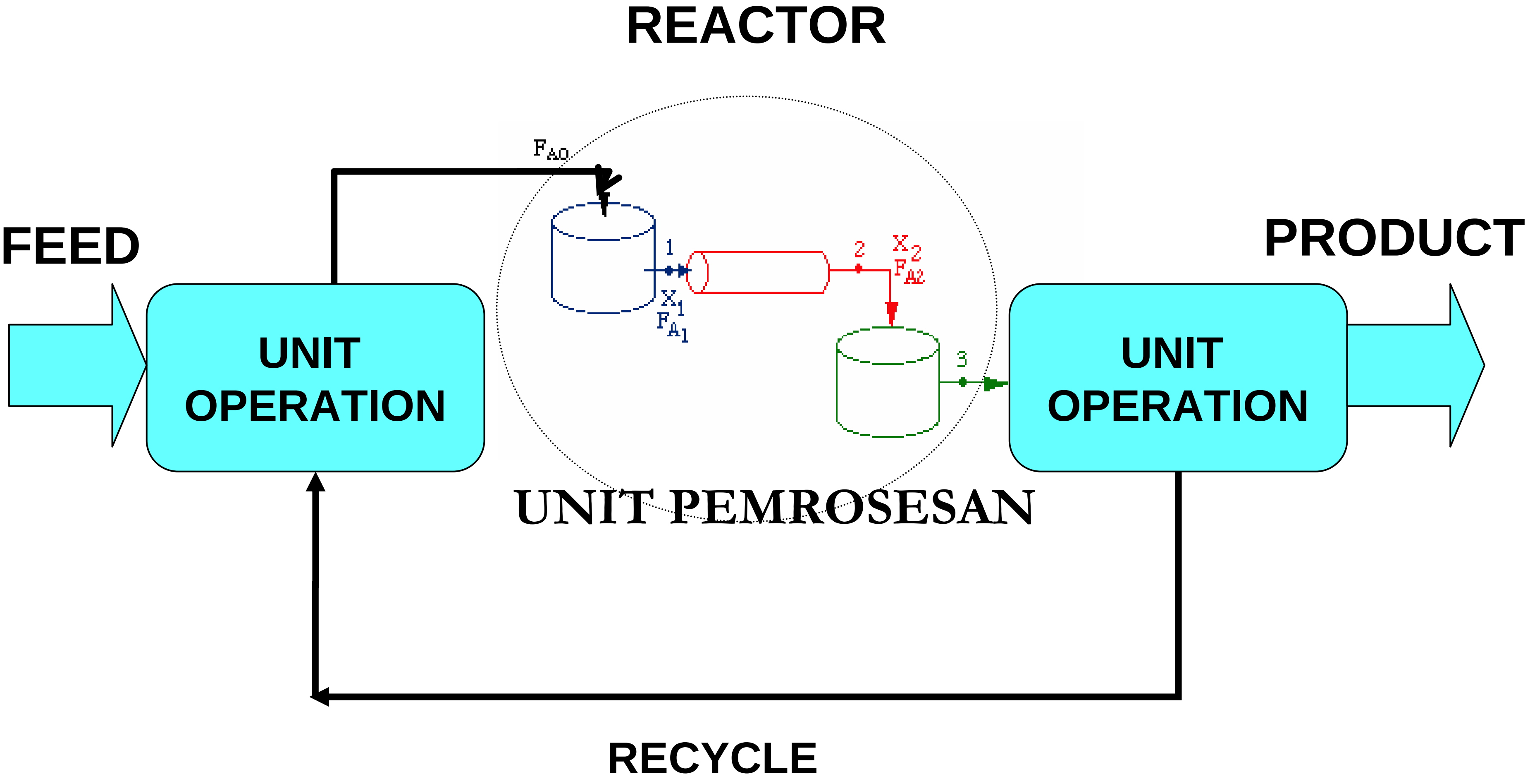
CHEMICAL PROCESS SYSTEM

PRODUCT

UTILITY SYSTEM
- WATER AND STEAM
- ELECTRICAL
- PRESS AIR
- REFRIGERANT
- INERT

OFFSITE SYSTEM
- STORAGE
- DERMAGA
- REL/ JALAN
- WASTE TREATMAENT

CHEMICAL PROCESS SYSTEM



REACTOR

FEED

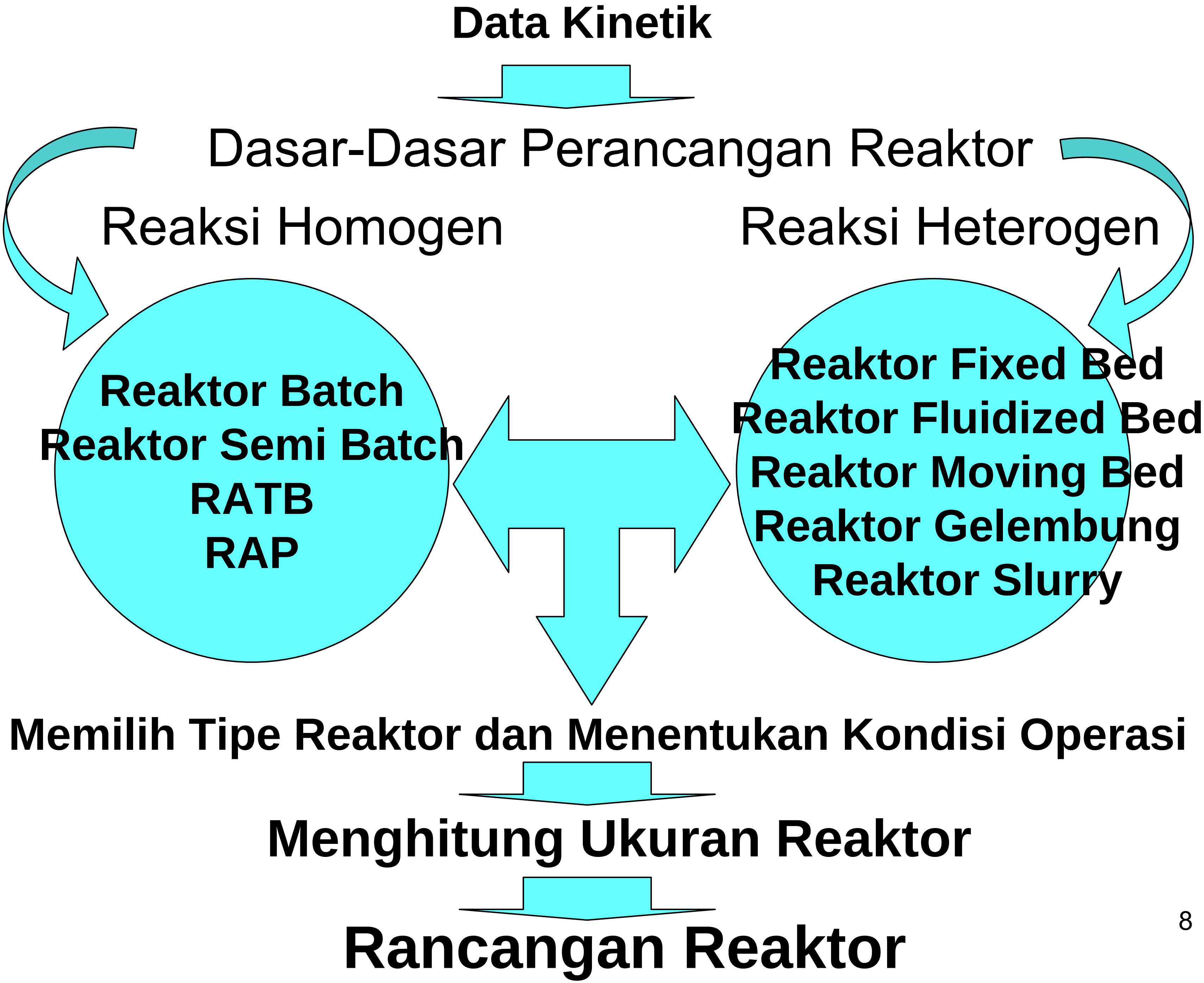
UNIT OPERATION

UNIT PEMROSESAN

UNIT OPERATION

PRODUCT

RECYCLE



Data Kinetik

Dasar-Dasar Perancangan Reaktor

Reaksi Homogen

Reaktor Batch
Reaktor Semi Batch
RATB
RAP

Reaksi Heterogen

Reaktor Fixed Bed
Reaktor Fluidized Bed
Reaktor Moving Bed
Reaktor Gelembung
Reaktor Slurry

Memilih Tipe Reaktor dan Menentukan Kondisi Operasi

Menghitung Ukuran Reaktor

Rancangan Reaktor

Membuat perancangan reaktor

Menghitung volume reaktor

Memilih tipe reaktor dan menentukan kondisi operasi

Menghitung: Reaktor batch, RATB, RAP untuk reaktor tunggal dan reaktor seri

Menghitung: Reaktor Fixed Bed, Reaktor Fluidize Bed, Reaktor Moving Bed, Reaktor Gelembung, Reaktor Slurry

Menghitung berbagai tipe reaktor homogen

Menghitung berbagai tipe reaktor heterogen

Menjelaskan dasar-dasar perancangan reaktor untuk reaksi-reaksi homogen dan heterogen

Definisi kec. reaksi, konversi, dan panas reaksi.

DEFINISI KECEPATAN REAKSI

Kecepatan reaksi ekstensif:

$$R_i = \frac{mol\ i\ terbentuk}{satuan\ waktu} = \frac{dn_i}{dt}$$

Kecepatan reaksi intensif:

1. Berdasarkan satuan volume fluida reaksi

$$r_i = \frac{mol\ i\ terbentuk}{(volume\ \ fluida)(waktu)} = \frac{1}{V}\frac{dn_i}{dt}$$

2. Berdasarkan satuan massa padatan (dalam sistem fluida-padat)

$$r_i' = \frac{mol\ i\ terbentuk}{(massa\ \ pada\,tan)(waktu)} = \frac{1}{W}\frac{dn_i}{dt}$$

Kecepatan reaksi intensif (lanjut)

3. **Berdasarkan satuan luas permukaan antar fasa (interfasial area)**

$$r_i'' = \frac{mol\ i\ terbentuk}{(luas\ \ permukaan)(waktu)} = \frac{1}{S}\frac{dn_i}{dt}$$

4. Berdasarkan satuan volume padatan (dalam sistem gas-padat):

$$r_i''' = \frac{mol\ i\ terbentuk}{(volume\ \ padatan)(waktu)} = \frac{1}{V_s}\frac{dn_i}{dt}$$

Kecepatan reaksi intensif (lanjut)

5. Berdasarkan satuan volume reaktor

$$r_i'''' = \frac{mol\ i\ terbentuk}{(volume\ reaktor)(waktu)} = \frac{1}{V_r}\frac{dn_i}{dt}$$

Catatan: Dalam sistem reaksi homogen,

volume fluida dalam reaktor = volume reaktor

atau, *V* = *Vr*

Hubungan antara kecepatan reaksi ekstensif dan intensif:

$$R_i \boxed{= V\ r_i} \boxed{= W\ r_i' = S\ r_i'' = V_s\ r_i''' = V_r\ r_i''''}$$

Konversi: $0 \leq X \leq 1$

Konversi suatu reaktan A dinyatakan dengan:

$$X_A = \frac{mol\ A\ yang\ terkonversi}{mol\ A\ awal} = \frac{mol\ A\ yang\ bereaksi}{mol\ A\ awal}$$

Reaktor Batch: $$X_A = \frac{n_{A,0} - n_A}{n_{A,0}}$$

Reaktor Alir: $$X_A = \frac{F_{A,0} - F_A}{F_{A,0}}$$

Volume tetap: $$X_A = \frac{C_{A,0} - C_A}{C_{A,0}}$$

Dengan n dalam mol, F dalam mol per waktu, C = n/V atau F/Fv pada awal dan pada akhir reaksi

Yield (Perolehan): $0 \le Y_{P/A} \le 1$

Perolehan sebuah produk P terhadap reaktan A ($Y_{P/A}$) dapat dinyatakan sebagai

$$Y_{P/A} = \frac{mol\ A\ yang\ bereaksi\ membentuk\ P}{mol\ A\ awal}$$

$$Y_{P/A} = \frac{mol\ A\ yang\ bereaksi\ membentuk\ P}{mol\ P\ yang\ terbentuk} x \frac{mol\ P\ yang\ terbentuk}{mol\ A\ awal}$$

Reaktor Batch:

$$Y_{P/A} = \frac{|\nu_A|_P}{\nu_P} \frac{n_P - n_{P0}}{n_{A0}}$$

Reaktor Alir:

$$Y_{P/A} = \frac{|\nu_A|_P}{\nu_P} \frac{F_P - F_{P0}}{F_{A0}}$$

Reaktor Volume tetap:

$$Y_{P/A} = \frac{|\nu_A|_P}{\nu_P} \frac{C_P - C_{P0}}{C_{A0}}$$

Selektivitas *(Fractional Yield)* $0 \leq S_{P/A} \leq 1$

Selektivitas *overall* sebuah produk P terhadap reaktan A ($S_{P/A}$) dapat dinyatakan sebagai:

$$S_{P/A} = \frac{mol\ A\ yang\ bereaksi\ membentuk\ P}{mol\ A\ yang\ bereaksi}$$

$$S_{P/A} = \frac{mol\ A\ yang\ bereaksi\ membentuk\ P}{mol\ P\ yang\ terbentuk} x \frac{mol\ P\ yang\ terbentuk}{mol\ A\ yang\ bereaksi}$$

Selektivitas reaktor batch: $S_{P/A} = \frac{\left|\nu_A\right|_P}{\nu_P} \frac{n_P - n_{P0}}{n_{A0} - n_A}$

Selektivitas reaktor alir: $S_{P/A} = \frac{\left|\nu_A\right|_P}{\nu_P} \frac{F_P - F_{P0}}{F_{A0} - F_A}$

Selektivitas reaktor volume tetap: $S_{P/A} = \frac{\left|\nu_A\right|_P}{\nu_P} \frac{C_P - C_{P0}}{C_{A0} - C_A}$

Hubungan antara perolehan, konversi, dan selektivitas:

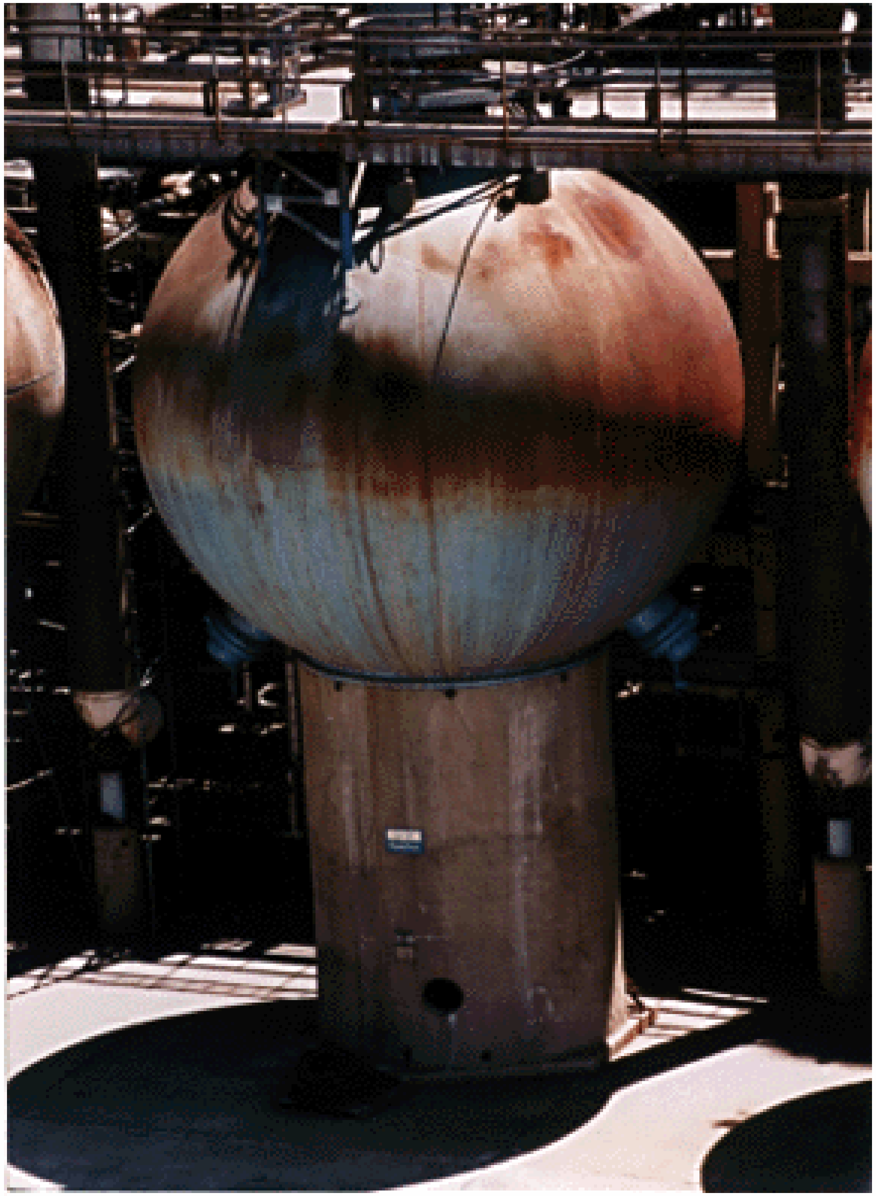
$$Y_{P/A} = X_A \cdot S_{P/A}$$

Instantaneous fractional yield sebuah produk P terhadap reaktan A ($S_{P/A}$) dapat dinyatakan sebagai:

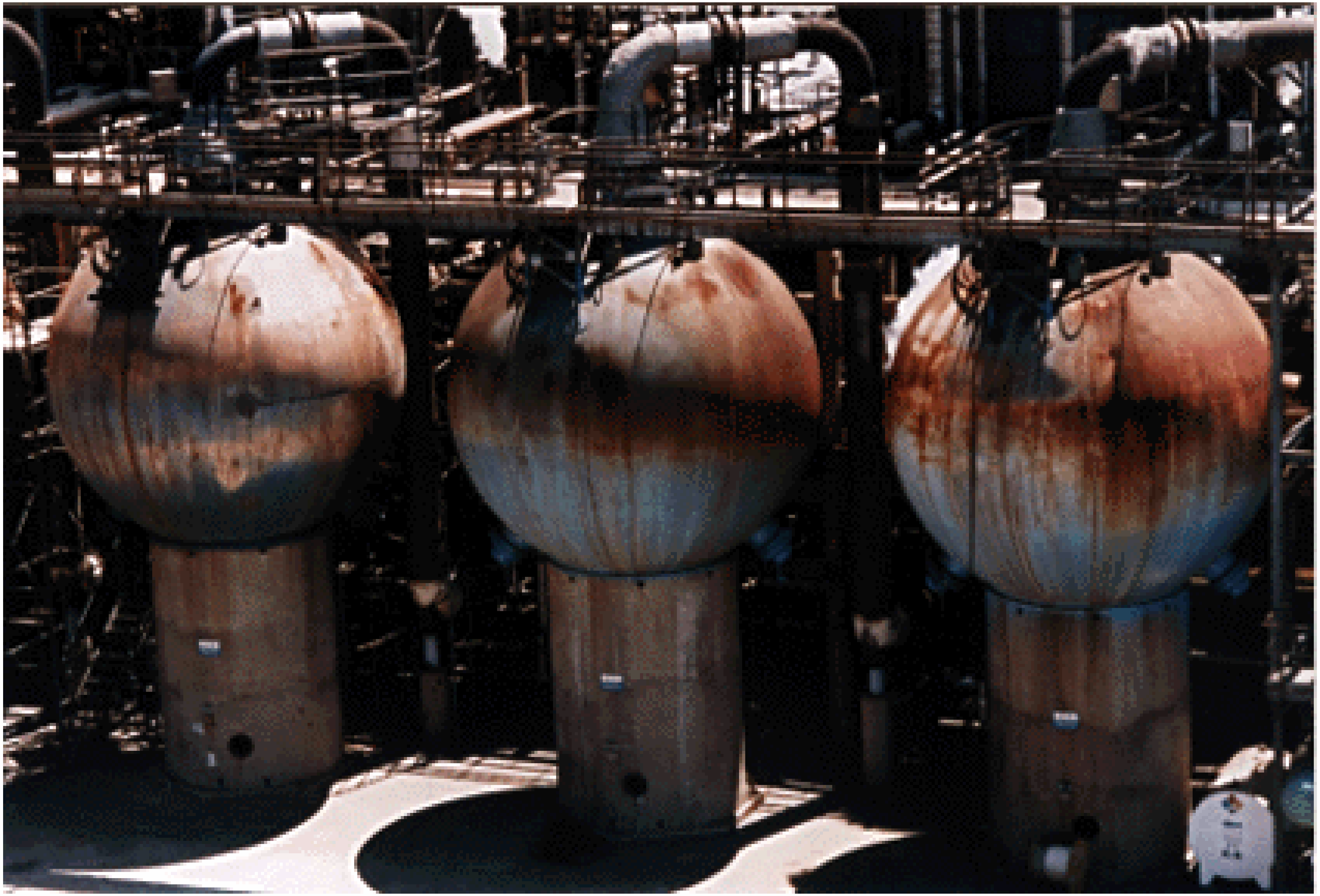
$$s_{P/A} = \frac{kecepatan\ pembentukan\ P}{kecepatan\ berkurangnya\ A} = \frac{r_P}{-r_A}$$

Reactor System Used at Amoco

Spherical Reactor



Three Spherical Reactors



Spherical Reactors Connected in Series

Hydrotreating Unit

Cutaway View of CSTR

Batch Reactor

Batch Reactor Stirring Apparatus

Pikirkan yang terbaik untuk anda

Selamat Belajar

02

Dasar-Dasar Perancangan Reaktor Untuk Reaksi Homogen Isotermal

Mahasiswa mampu menjelaskan dasar-dasar perancangan reaktor untuk reaksi homogen isotermal

- Penyusunan Persamaan neraca mole secara umum
- Aplikasi neraca mole pada tipe reaktor berbeda: Reaktor batch (RB), reaktor alir tangki berpengaduk (RATB), reaktor alir pipa (RAP), dan reaktor packed bed (RPB).
- Persamaan desain untuk reaksi tunggal RB, RATB, RAP, dan RPB
- Pembahasan contoh soal

General Mole Balance Equation

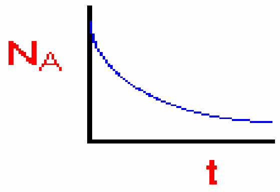
Persamaan neraca mole pada elemen volume dV

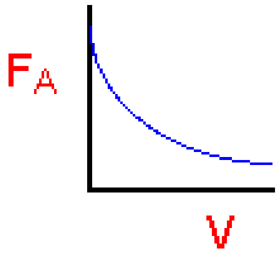
$$R_{\text{masuk}} - R_{\text{keluar}} + R_{\text{generasi}} = R_{\text{akumulasi}}$$

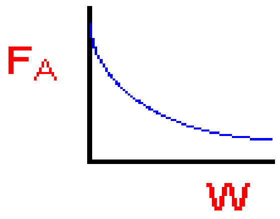
$$F_{A0} - F_A + \int_0^V r_A \, dV = \frac{dN_A}{dt}$$

Mole Balance on Different Reactor Types

Reactor Type	Differential	Algebraic	Integral
Batch	$\frac{dN_A}{dt} = r_A V$		$t = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_A V}$
CSTR		$V = \frac{F_{A0} - F_A}{-r_A}$	
PFR	$\frac{dF_A}{dV} = r_A$		$V = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A}$
PBR	$\frac{dF_A}{dW} = r'_A$		$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A}$







Case - 01

- Calculate the time to reduce the number of moles by a factor of 10 in a batch reactor for the reaction with $-r_A = k\ C_A$, when $k = 0.046\ \text{min}^{-1}$

SOLUTION

Case - 02

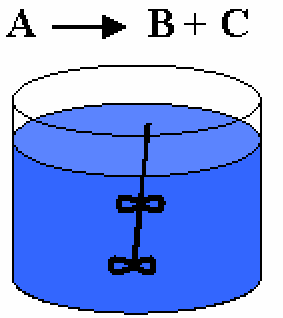
The irreversible liquid phase second order reaction is carried out in a CSTR. The entering concentration of A, CA0, is 2 molar and the exit concentration of A, CA, is 0.1 molar. The entering and exiting volumetric flow rate, vo, is constant at 3 dm^3/s. What is the corresponding reactor volume?

$$2\,A \xrightarrow{k_1} B \qquad k_1 = 0.03\ \ dm^3/mol \cdot s$$

SOLUTION

Case – 03 (CDP1-AA)

A 200-dm^3 constant-volume batch reactor is pressurized to 20 atm with a mixture of 75% A and 25% inert. The gas-phase reaction is carried out isothermally at 227 °C.



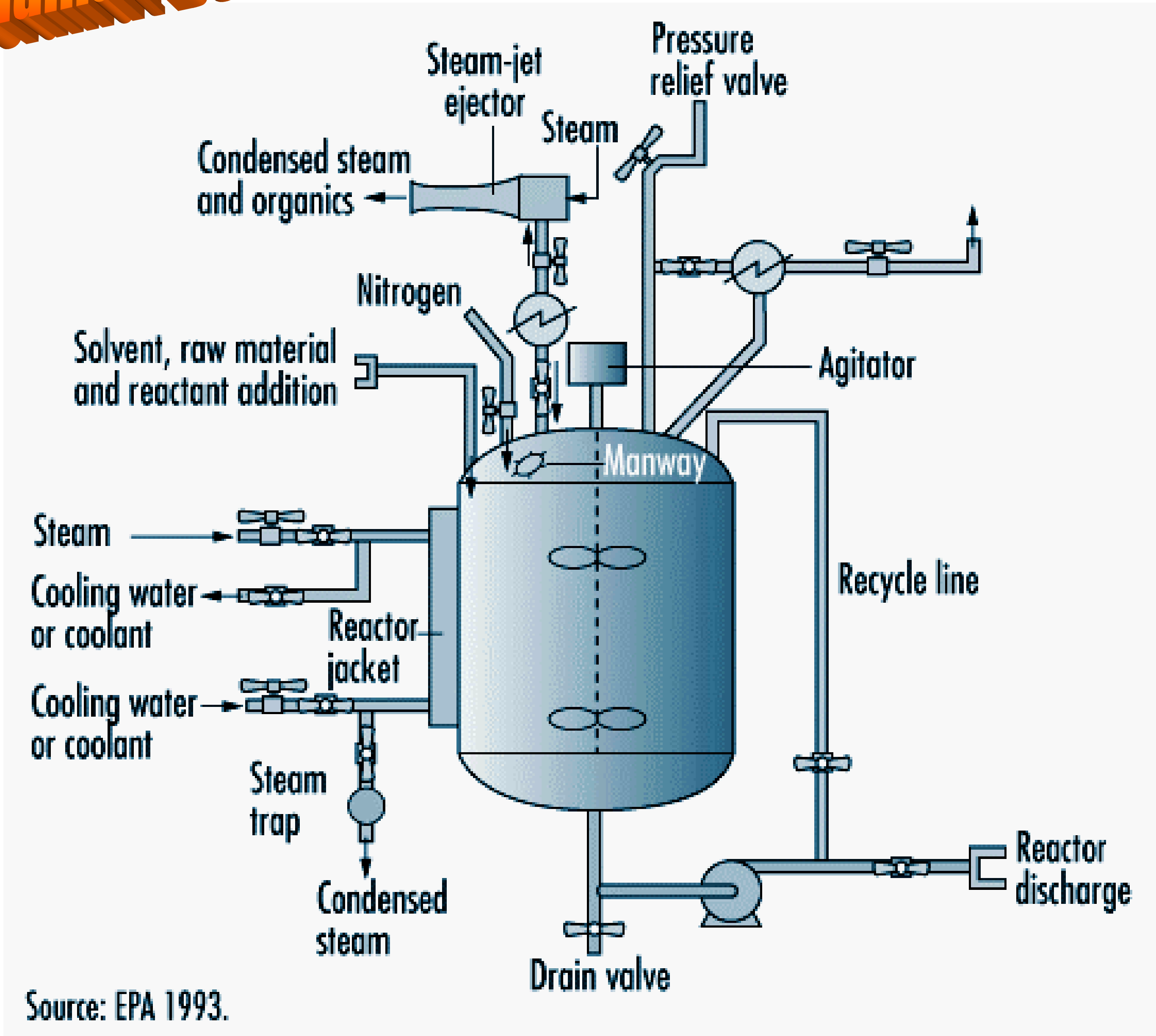
- Assuming that the ideal gas law is valid, how many moles of A are in the reactor initially? What is the initial concentration of A?
- If the reaction is first order: $-r_A = kC_A$ with $k = 0.1\frac{1}{\text{min}}$

  Calculate the time necessary to consume 99% of A.
- If the reaction is second order: $-r_A = kC_A^2$ with $k = 0.7\frac{\text{dm}^3}{\text{mol} \bullet \text{min}}$

  Calculate the time to consume 80% of A. Also calculate the pressure in the reactor at this time if the temperature is 127 °C.

SOLUTION

Selamat Belajar



Source: EPA 1993.

Solution Case - 01:

$$t = \int_{N_{AO}}^{N_A} \frac{dN_A}{r_A V} = -\int_{N_{AO}}^{N_A} \frac{dN_A}{-r_A V}$$

$$-r_A V = kC_A V = k\frac{N_A}{V}V = kN_A$$

$$t = \int_{N_A}^{N_{AO}} \frac{dN_A}{kN_A} = \frac{1}{k}\ln\frac{N_{AO}}{N_A}$$

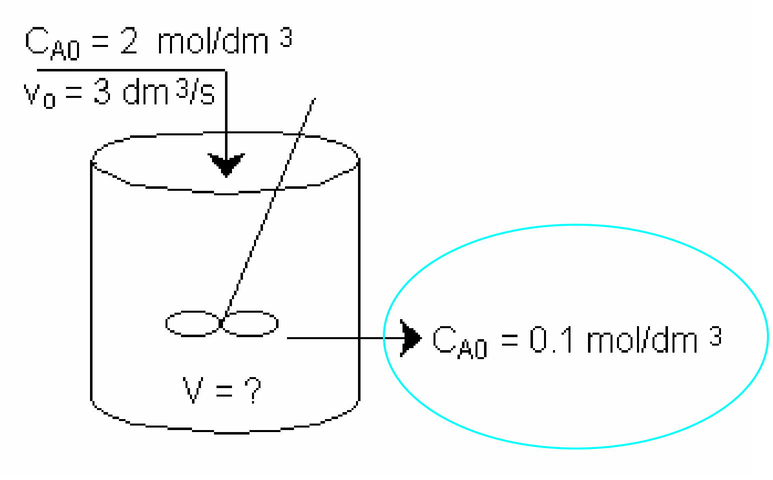
$$t = \frac{1}{0.046\text{min}^{-1}} \times \ln 10 = \frac{1}{0.046\text{min}^{-1}} \times 2.3$$

Therefore, t = 50 minutes

BACK

Solution Case - 02

BACK



Mole Balance $$V = \frac{F_{A0} - F_A}{-r_A}$$

Rate Law $$-r_A = kC_A^2$$

Combine $$V = \frac{F_{A0} - F_A}{kC_A^2}$$

$$F_{A0} = v_0 C_{A0} = \frac{3\ dm^3}{s} \bullet \frac{2\ molA}{dm^3} = \frac{6\ molA}{s}$$

$$F_A = v_0 C_A = \frac{3\ dm^3}{s} \bullet \frac{0.1\ molA}{dm^3} = \frac{0.3\ molA}{s}$$

$$V = \frac{(6 - 0.3)\frac{mol}{s}}{\left(0.03\frac{dm^3}{mol \bullet s}\right)\left(3\frac{mol}{dm^3}\right)^2} = \frac{5.7 dm^3}{0.27} = 21.11\ dm^3$$

What is wrong with this solution?

Solution Case - 03

- **How many moles of A are in the reactor initially? What is the initial concentration of A?** If we assume ideal gas behavior, then calculating the moles of A initially present in the reactor is quite simple. We insert our variables into the ideal gas equation:

$$N_{To} = \frac{P_o V}{RT} = \frac{20\ \text{atm} * 200\ \text{dm}^3}{0.082 \frac{\text{dm}^3 \bullet \text{atm}}{\text{mol} \bullet \text{K}} * 500\ \text{K}} = 97.6\text{mol}$$

Knowing the mole fraction of A (y_{Ao}) is 75%, we multiply the total number of moles (N_{To}) by the y_{Ao}:

$$N_{Ao} = y_{Ao} N_{To} = 73.2 \text{ moles of A}$$

The initial concentration of A (C_{Ao}) is just the moles of A divided by the volume:

$$C_{Ao} = \frac{N_{Ao}}{V} = \frac{73\text{mol}}{200\ \text{dm}^3} = 0.366 \frac{\text{mol}}{\text{dm}^3}$$

- **Time (t) for a 1st order reaction to consume 99% of A.** With both 1st and 2nd order reactions, we will begin with the mole balance:

$$\begin{bmatrix}\text{rate of flow of}\\ \text{species into the}\\ \text{system}\end{bmatrix} - \begin{bmatrix}\text{rate of flow of}\\ \text{species out of}\\ \text{the system}\end{bmatrix} + \begin{bmatrix}\text{rate of}\\ \text{generation of}\\ \text{species by}\\ \text{reaction in}\\ \text{system}\end{bmatrix} = \begin{bmatrix}\text{rate of}\\ \text{accumulation of}\\ \text{species within the}\\ \text{system}\end{bmatrix}$$

$$F_{Ao} \qquad - \qquad F_A \qquad + \qquad \int r_A dV \qquad = \qquad \frac{dN_A}{dt}$$

There is no flow in or out of our system, and we will assume that there is no spatial variation in the reaction rate. We are left with:

$$0 \quad - \quad 0 \quad + \quad r_A V \quad = \quad \frac{dN_A}{dt}$$

Knowing the moles per volume (N_A/V) is concentration (C_A), we then define the reaction rate as a function of concentration:

$$r_A = \frac{dC_A}{dt}$$

First Order Reaction

This is the point where the solutions for the different reaction orders diverge.

Our first order rate law is: $-r_A = kC_A$

We insert this relation into our mole balance:

$$-kC_A = \frac{dC_A}{dt}$$

and integrate:

$$-k\int_{0}^{t} dt = \int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A}$$

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

Knowing $C_A=0.01\ C_{Ao}$ and our rate constant ($k=0.1\ \text{min}^{-1}$), we can solve for the time of the reaction:

$$t = -\frac{1}{k}\ln(0.01) = \frac{4.61}{k} = 46.1\text{min}$$

BACK

03

TABEL STOIKIOMETRI

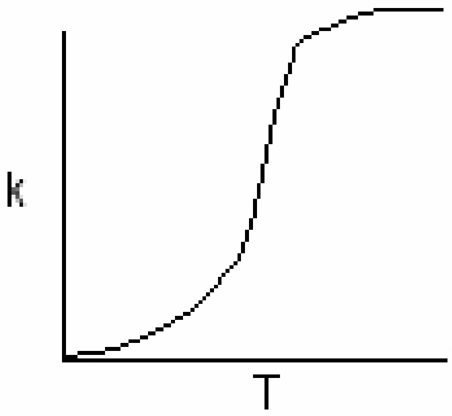
Rate Laws

- Power Law Model $-r_A = kC_A^{\alpha}C_B^{\beta}$

α order in A
β order in B
Overall Reaction Order = $\alpha+\beta$

- k is the specific reaction rate (constant) and is given by the Arrhenius Equation:

$$k = Ae^{-E/RT},$$



Where:
E = activation energy (cal/mol)
R = gas constant (cal/mol*K)
T = temperature (K)
A = frequency factor

$$T \rightarrow \infty \quad k \rightarrow A \quad A \approx 10^{13}$$

$$T \rightarrow 0 \quad k \rightarrow 0$$

Stoichiometric Tables

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

Using stoichiometry, we set up all of our equations with the amount of reactant A as our basis.

Batch System Stoichiometric Table

Species	Symbol	Initial	Change	Remaining
A	A	N_{A0}	$-N_{A0}X$	$N_A = N_{A0}(1-X)$
B	B	$N_{B0} = N_{A0}\Theta_B$	$-\frac{b}{a}N_{A0}X$	$N_B = N_{A0}\left(\Theta_B - \frac{b}{a}X\right)$
C	C	$N_{C0} = N_{A0}\Theta_C$	$+\frac{c}{a}N_{A0}X$	$N_C = N_{A0}\left(\Theta_C + \frac{c}{a}X\right)$
D	D	$N_{D0} = N_{A0}\Theta_D$	$+\frac{d}{a}N_{A0}X$	$N_D = N_{A0}\left(\Theta_D + \frac{d}{a}X\right)$
Inert	I	$N_I = N_{A0}\Theta_I$	-------	$N_I = N_{A0}\Theta_I$
		N_{T0}		$N_T = N_{T0} + \delta N_{A0}X$

Where: $\Theta_i = \frac{N_{i0}}{N_{A0}} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$ and $\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$

Concentration -- Batch System:

$$C_A = \frac{N_A}{V}$$

Constant Volume Batch:

$$V = V_0$$

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X)$$

$$C_B = \frac{N_B}{V} = \frac{N_{A0}}{V_0}\left(\Theta_B - \frac{b}{a}X\right) = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

etc.

Flow System Stoichiometric Table

Species	**Symbol**	**Reactor Feed**	**Change**	**Reactor Effluent**
A	A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	B	$F_{B0} = F_{A0}\Theta_B$	$-\frac{b}{a}F_{A0}X$	$F_B = F_{A0}\left(\Theta_B - \frac{b}{a}X\right)$
C	C	$F_{C0} = F_{A0}\Theta_C$	$+\frac{c}{a}F_{A0}X$	$F_C = F_{A0}\left(\Theta_C + \frac{c}{a}X\right)$
D	D	$F_{D0} = F_{A0}\Theta_D$	$+\frac{d}{a}F_{A0}X$	$F_D = F_{A0}\left(\Theta_D + \frac{d}{a}X\right)$
Inert	I	$F_{I0} = F_{A0}\Theta_I$	-------	$F_I = F_{A0}\Theta_I$
		F_{T0}		$F_T = F_{T0} + \delta F_{A0}X$

Where: $\Theta_i = \frac{F_{i0}}{F_{A0}} = \frac{C_{i0}\upsilon_0}{C_{A0}\upsilon_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$ and $\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$

- Concentration -- Flow System:

$$C_A = \frac{F_A}{\upsilon}$$

- **Liquid Phase Flow System:**

$$\upsilon = \upsilon_0$$

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_0} = C_{A0}(1-X)$$

$$C_B = \frac{F_B}{\upsilon} = \frac{F_{A0}}{\upsilon_0}\left(\Theta_B - \frac{b}{a}X\right) = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

etc.

- Gas Phase Flow System:
  - From the compressibility factor equation of state: $\upsilon = \upsilon_0 \left(\frac{F_T}{F_{T0}} \right) \frac{T}{T_0} \frac{P_0}{P}$
  - The total molar flowrate is: $F_T = F_{T0} + F_{A0} \delta X$

$$\upsilon = \upsilon_0 \left(1 + y_{A0} \delta X \right) \frac{T}{T_0} \frac{P_0}{P}$$

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_0 (1+\varepsilon X)} \frac{T_0}{T} \frac{P}{P_0} = C_{A0} \frac{(1-X)}{(1+\varepsilon X)} \frac{T_0}{T} \frac{P}{P_0}$$

$$C_B = \frac{F_B}{\upsilon} = \frac{F_{A0}\left(\Theta_B - \frac{b}{a} X \right)}{\upsilon_0 (1+\varepsilon X)} \frac{T_0}{T} \frac{P}{P_0} = C_{A0} \frac{\left(\Theta_B - \frac{b}{a} X \right)}{(1+\varepsilon X)} \frac{T_0}{T} \frac{P}{P_0}$$

etc.

Algorithm for Isothermal Reactor Design

Example: The elementary gas phase reaction $2A + B \rightarrow C$

takes place in a CSTR at constant temperature (500 K) and constant pressure (16.4 atm). The feed is equal molar in A and B.

<u>Mole Balance</u>

$$V = \frac{F_{A0}X}{-r_A}$$

<u>Rate Law</u>

$$-r_A = kC_A^2 C_B$$

For a gas phase system: $C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_0(1+\varepsilon X)(P_0/P)(T/T_0)}$

If the conditions are isothermal ($T = T_0$) and isobaric ($P = P_0$):

$$C_A = C_{A0}\frac{(1-X)}{(1+\varepsilon X)}\frac{T_0}{T}\frac{P}{P_0} = C_{A0}\frac{(1-X)}{(1+\varepsilon X)}$$

And if the feed is equal molar, then:

$$\varepsilon = y_{A0}\delta = 0.5\left(\frac{1}{2}-\frac{1}{2}-1\right) = -0.5$$

- This leaves us with C_A as a function of conversion alone:

$$C_A = C_{A0}\frac{(1-X)}{(1-0.5X)}$$

- Similarly for C_B:

$$C_B = C_{A0}\frac{\left(\Theta_B - \frac{1}{2}X\right)}{(1+\varepsilon X)} = C_{A0}\frac{(1-0.5X)}{(1-0.5X)} = C_{A0}$$

[Why do you suppose C_B is a constant, when B is being consumed?]

$$C_{A0} = \frac{y_{A0}P_0}{RT_0} = \frac{(0.5)(16.4\,\text{atm})}{\left(\frac{0.082\,\text{atm}\bullet\text{m}^3}{\text{kmol}\bullet\text{K}}\right)(500\text{K})} = 0.2\frac{\text{kmol}}{\text{m}^3} = 0.2\frac{\text{mol}}{\text{dm}^3}$$

Combine

$$-r_A = kC_A^2C_B = kC_{A0}^3\,\frac{(1-X)^2}{(1-0.5X)^2}$$

$$-r_A = \left(10\,\frac{\text{dm}^6}{\text{mol}^2\bullet\text{s}}\right)\left(0.2\,\frac{\text{mol}}{\text{dm}^3}\right)^3\,\frac{(1-X)^2}{(1-0.5X)^2}$$

$$-r_A = \left(0.08\,\frac{\text{mol}}{\text{dm}^3\bullet\text{s}}\right)\frac{(1-X)^2}{(1-0.5X)^2}$$

Evaluate

$$V = \frac{F_{A0}X}{-r_A} = \frac{(5\text{ mol/s})(0.9)[1-0.5\,(0.9)]^2}{\left(0.8\,\frac{\text{mol}}{\text{dm}^3\bullet\text{s}}\right)(1-0.9)^2}$$

$$\boxed{V = 1701\,\text{dm}^3}$$

Example: The elementary liquid phase reaction

$$2A \rightarrow B$$

is carried out isothermally in a CSTR. Pure A enters at a volumetric flow rate of 25 dm^3/s and at a concentration of 0.2 mol/dm^3.

What CSTR volume is necessary to achieve a 90% conversion when k = 10 dm^3/(mol*s)?

Mole Balance $$V = \frac{F_{Ao} X}{-r_a}$$

Rate Law $$-r_A = kC_A{}^2$$

Stoichiometry liquid phase (v = vo)

$$F_{Ao} = v_o C_{Ao}$$

$$F_A = vC_A = v_o C_A$$

$$C_A = \frac{F_A}{v} = \frac{F_A}{v_o} = \frac{F_{Ao}(1-X)}{v_o}$$

$$C_A = C_{Ao}(1-X)$$

Combine

$$V = \frac{v_o C_{Ao} X}{k C_{Ao}^{\ 2}(1-X)^2} = \frac{v_o X}{k C_{Ao}(1-X)^2}$$

Evaluate, at X = 0.9,

$$V = \frac{25\frac{dm^3}{s}(0.90)}{\left(10\frac{dm^3}{mol\cdot s}\right)\left(0.2\frac{mol}{dm^3}\right)(1-0.9)^2}$$

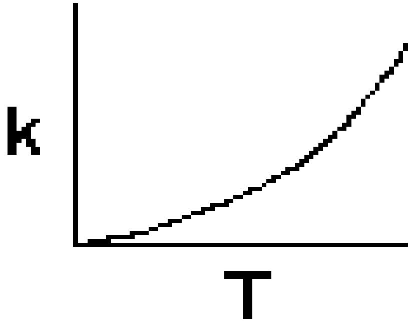
$$V = 1125\ \mathrm{dm}^3$$

Space Time

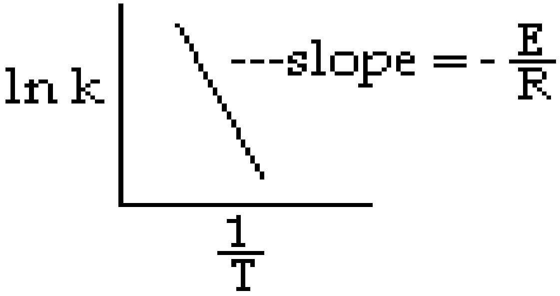
$$\tau = \frac{V}{v_o} = \frac{1125 dm^3}{25\frac{dm^3}{s}} = 45s$$

Arrhenius Equation

1.) $k = Ae^{-E/RT}$



2.) $\ln k = \ln A - \frac{E}{R}\left(\frac{1}{T}\right)$



$$k(T_2) = k(T_1)\exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

Terjadilah seperti yang engkau pikirkan!

04-05-06
Design Equations

Conversion

- The conversion of species A in a reaction is equal to the number of moles of A reacted per mole of A fed.

Batch: $X = \frac{(N_{A0} - N_A)}{N_{A0}}$

Flow: $X = \frac{(F_{A0} - F_A)}{F_{A0}}$

Design Equations

The following design equations are for single reactions only. Design equations for multiple reactions will be discussed later.

Reactor Mole Balances in Terms of Conversion

Reactor	**Differential**	**Algebraic**	**Integral**
Batch	$N_{A0}\dfrac{dX}{dt} = -r_A V$		$t = N_{A0}\displaystyle\int_0^X \dfrac{dX}{-r_A V}$ Derive
CSTR		$V = \dfrac{F_{A0}X}{-r_A}$	
PFR	$F_{A0}\dfrac{dX}{dV} = -r_A$		$V = F_{A0}\displaystyle\int_0^X \dfrac{dX}{-r_A}$ Derive
PBR	$F_{A0}\dfrac{dX}{dW} = -r'_A$		$W = F_{A0}\displaystyle\int_0^X \dfrac{dX}{-r'_A}$

REAKTOR BATCH

Chp. 12 Missen, 1999

BATCH VERSUS CONTINUOUS OPERATION

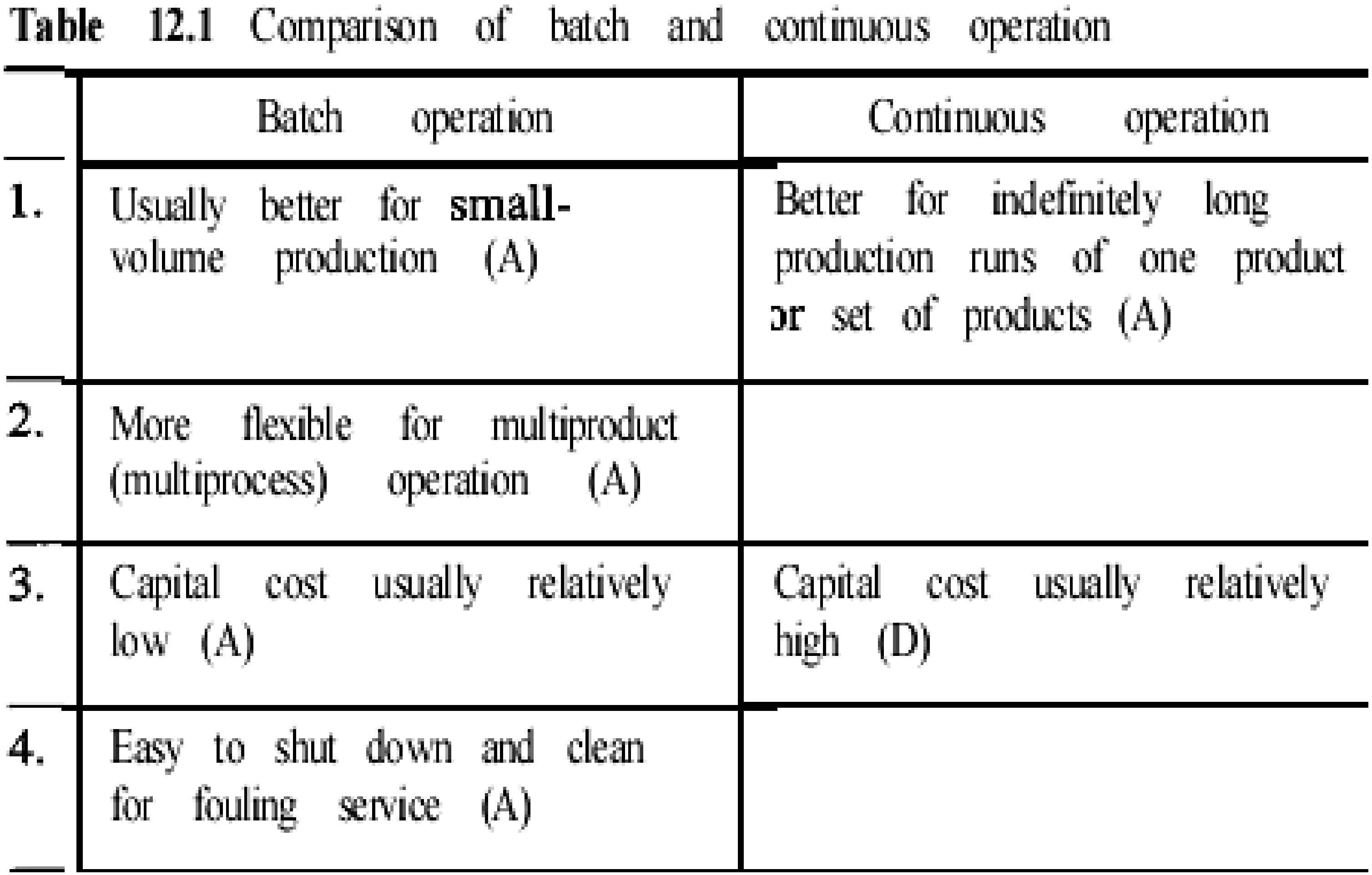


Table 12.1 Comparison of batch and continuous operation

	Batch operation	Continuous operation
1.	Usually better for **small-volume** production (A)	Better for indefinitely long production runs of one product or set of products (A)
2.	More flexible for multiproduct (multiprocess) operation (A)	
3.	Capital cost usually relatively low (A)	Capital cost usually relatively high (D)
4.	Easy to shut down and clean for fouling service (A)	

	Batch operation	Continuous operation
5.	Inherent down-time between batches (D)	No down-time except for scheduled and emergency maintenance (A); but loss of production in lengthy stoppages can be costly (D)
6.	Operating cost may be relatively high (D)	Operating cost relatively low (A)
7.	Unsteady-state operation means process control and obtaining uniformity of product more difficult (D) (but see England, 1982)	Steady-state operation means process control and obtaining uniformity of product less difficult (A)

DESIGN EQUATIONS FOR A BATCH REACTOR (BR)

Pertimbangan umum

- t adalah waktu reaksi yang diperlukan untuk mencapai konversi f_{A1} sampai f_{A2}
- A adalah limiting reactant
- Besaran yang diketahui: N_{A0}, f_{A1}, & f_{A2}
- Besaran yang tidak diketahui: t, $(-r_A)$, V, dan T
- Pertimbangkan reaksi:

$$\mathbf{A + \ldots \rightarrow \nu_C\, C + \ldots}$$

$$r_A V = \frac{dN_A}{dt} = \frac{dN_{A0}\left(1 - f_A\right)}{dt} = -\frac{N_{A0}\, df_A}{dt}$$

Waktu reaksi:

$$t = N_{A0} \int_{f_{A1}}^{f_{A2}} \frac{df_A}{-r_A V}$$

- Kecepatan reaksi

$$-r_A = f(f_A, T)$$

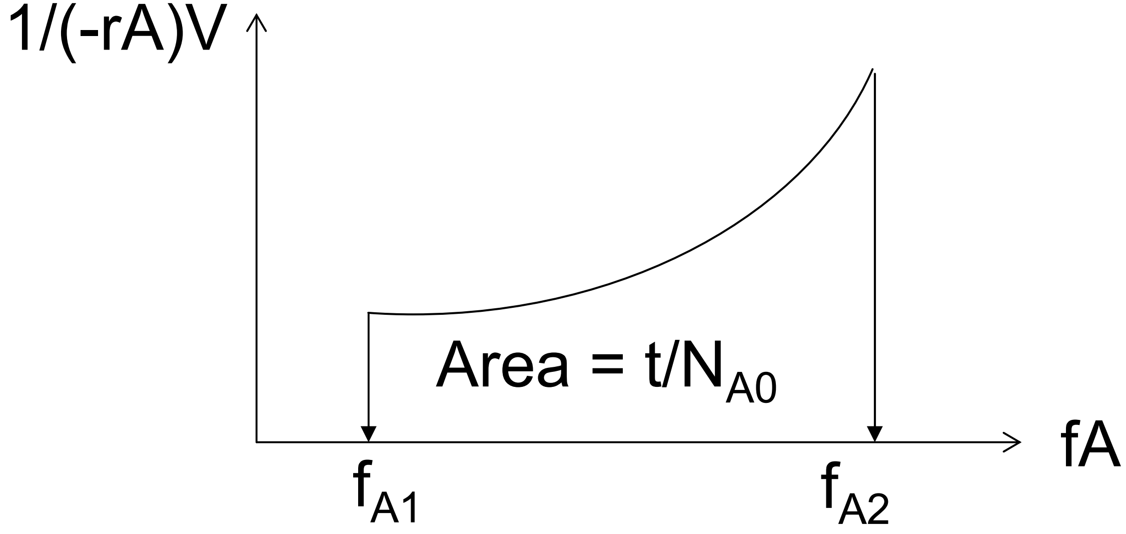
- Neraca Energi Memberikan

$$T = f(f_A, V)$$

- Persamaan keadaan

$$V = f(N_A, T, P)$$

Interpretasi nilai t/N_{A0} dapat ditentukan melalui grafik



Kecepatan produsi (pembentukan) C pada basis kontinyu

- Waktu siklus adalah total waktu per batch

  tc = t + td, t = waktu reaksi

  td = down time adalah waktu yang diperlukan untuk pengisian, pengeluaran, dan pencucian

$$\Pr(C) = \frac{mol\ C\ terbentuk}{batch} \times \frac{batch}{waktu}$$

$$\Pr(C) = \frac{N_{C2} - N_{C1}}{tc} = \frac{\Delta N_C}{t_C} = \frac{\nu_C \Delta NA}{t + td}$$

Dalam konversi XA

$$\Pr(C) = \frac{\nu_C\ N_{A0}\left(f_{A2} - f_{A1}\right)}{t + td}$$

Dalam banyak kasus
$f_{A1} = 0$ dan $f_{A2} = X_A$

NERACA ENERGI; TEMPERATUR BERUBAH

- Bentuk umum:

  R in – R Out + R gen = R acc
- Untuk RB: Panas masuk dapat dari pemenas koil/ jaket, panas keluar dapat dari pendingin koil/ jaket, dan panas generasi adalah panas yang dihasilkan atau dibutuhkan oleh reaksi

Transfer panas: R in/ R out ditunjukkan dengan pers.:

$$Q = UAc(Tc - T)_m$$

U = koef. Transfer panas keseluruhan, J $m^{-2}s^{-1}K^{-1}$ atau w m^{-2} k^{-1} → ditentukan dengan perc. Atau korelasi empiris

Ac = Luas pemanas/ pendingin koil

Tc = Suhu koil

$(Tc - T)_m$ = beda suhu rata2 DTm utk trasfer panas

Bila $Q > 0$ $(Tc > T)$ → Panas masuk

$Q < 0$ $(Tc < T)$ → panas keluar

Panas generasi:

R gen = $(-\Delta H_{RA})(-r_A)$ atau $(-\Delta U_{RA})(-r_A)V$

Bila $\Delta H_{RA} > 0$ (reaksi endotermis)
$\Delta H_{RA} > 0$ (reaksi eksotermis)

Panas akumulasi:

Racc = dH/dt = N_t Cp dT/dt = m_t Cp dT/dt

Total mole:

$$N_t = \sum_{i=1}^{n} N_i$$ (termasuk inert)

Kapasitas panas sistem pada P tetap:

$$C_P \doteq \sum_{i=1}^{N} x_i C_{Pi}$$

dengan xi = fraksi mole komponen i

Massa total sistem

$$m_t = \sum_{i=1}^{N} m_i$$

Kapasitas panas spesifik sistem:

$$c_P \doteq \sum_{i=1}^{N} w_i c_{Pi}$$

dengan wi = fraksi massa komponen i

Neraca energi RB non isotermal dan non adiabatis:

$$UA_c(T_c - T)_m + (-\Delta H_{RA})(-r_A)V = n_t C_P \frac{\mathrm{d}T}{\mathrm{d}t}$$

RB Operasi Isotermal

$$t = C_{A0} \int_{f_{A1}}^{f_{A2}} \frac{df_A}{-r_A}$$ (densitas konstan)

$$Pr(C) = \frac{\nu_C c_{A0} V(f_{A2} \quad f_{A1})}{t + t_d}$$ (densitas konstan)

Contoh 12-1 Missen

Determine the time required for 80% conversion of 7.5 mol A in a 15-L constant-volume batch reactor operating isothermally at 300 K. The reaction is first-order with respect to A, with $k_A = 0.05\ \text{min}^{-1}$ at 300 K.

Solusi

Contoh 12-2 Missen

A liquid-phase reaction between cyclopentadiene (A) and benzoquinone (B) is conducted in an isothermal batch reactor, producing an adduct (C). The reaction is first-order with respect to each reactant, with $k_A = 9.92 \text{ X } 10e^3 \text{ L mol}^{-1}\text{s}^{-1}$ at 25°C. Determine the reactor volume required to produce 175 mol C h^{-1}, if $f_A = 0.90$, $C_{A0} = C_{B0} = 0.15 \text{ mol L}^{-1}$, and the down-time td between batches is 30 min.
The reaction is $A + B \rightarrow C$.

Solusi

Densitas sistem berubah

- Berimplikasi pada volume reaktor atau sistem reaksi tidak konstan
- Untuk RB dapat dilihat pada reaktor vessel yg dilengkapi piston
- Densitas berubah biasanya fasa gas
- Densitas dapat berubah bila salah satu T, P, atau N_t (mole total) berubah

Contoh 12-3 Missen

Reaksi fasa gas A → B + C dilangsungkan dalam 10 L (mula-mula) reaktor batch isotermal pada 25 °C tekanan tetap. Reaksi orde 2 terhadap A dengan $k_A = 0{,}023\ \mathrm{L\ mol^{-1}s^{-1}}$. Tentukan waktu yang diperlukan untuk konversi 75% dari 5 mol A.

Solusi

Pengendalian Transfer Panas Untuk Menjaga Kondisi Isotermal

- Bila reaksi eksotermis atau endotermis, maka diperlukan pengendalian temperatur (T) untuk menjaga kondisi isotermal dengan memberi pendingin atau pemanas
- Tinjau reaksi: A + • • • → Produk
- Operasi isotermal → dT/dt = 0, sehingga

$$\dot{Q} = UA_c(T_c - T), = -(-\Delta H_{RA})(-r_A)V$$

Dari neraca mol reaktor batch $(-r_A) = (n_{Ao}/V)(\mathrm{d}f_A/\mathrm{d}t)$

Substitusi ke pers. Energi didapat

$$\dot{Q} = UA_c(T_c - T), = -(-\Delta H_{RA})n_{Ao}(\mathrm{d}f_A/\mathrm{d}t)$$

Bila diasumsi temperatur koil (Tc) konstan

$$T_c = T - \frac{(-\Delta H_{RA})n_{Ao}}{UA_c}\frac{\mathrm{d}f_A}{\mathrm{d}t}$$

Contoh 12-4 Missen

Tentukan Q dan Tc (sebagai fungsi waktu) yang diperlukan untuk menjaga kondisi reaktor isotermal dalam contoh 12-1, jika ΔH_{RA} = -47500 J mol^{-1}, dan UAc = 25,0 WK^{-1}. Apakah Q mewakili kecepatan penambahan panas atau pengambilan panas?

Solusi

OPERASI NON ISOTERMAL

- Adiabatis (Q = 0)
- Non Adiabatis (Q ≠ 0)

Operasi Adiabatis:

Temperatur akan naik dalam reaksi eksotermis dan turun dalam reaksi endotermis

Persamaan Neraca Energi Sistem Adiabatis, Q = 0

$$(-\Delta H_{RA})(-r_{\mathrm{A}})V = n_t C_P \frac{\mathrm{d}T}{\mathrm{d}t}$$

Substitusi (-r_A)V dari neraca massa dalam term f_A

$$(-\Delta H_{RA})n_{\mathrm{A}o} \frac{\mathrm{d}f_{\mathrm{A}}}{\mathrm{d}t} = n_t C_P \frac{\mathrm{d}T}{\mathrm{d}t}$$

Karena hubungan df_A/dt dengan dT/dt adalah implisit terhadap t, shg pers. menjadi

$$(-\Delta H_{RA}) n_{Ao} \mathrm{d} f_A = n_t C_p \mathrm{d} T$$

Di integralkan:

$$T = T_o + n_{Ao} \int_{f_{Ao}}^{f_A} \frac{(-\Delta H_{RA})}{n_t C_p} \mathrm{d} f_A$$

Bila (-ΔH$_{RA}$), Cp, dan n_t konstan

$$T = T_o + \frac{(-\Delta H_{RA}) n_{Ao}}{n_t C_p} (f_A - f_{Ao})$$

Waktu yang diperlukan untuk mencapai konversi f_A, dari pers. Neraca massa:

$$t = n_{Ao} \int_{f_{Ao}}^{f_A} \frac{\mathrm{d} f_A}{(-r_A) V}$$

Algoritma menghitung t RB Adiabatis

- Pilih harga f_A: $f_{A0} \le f_A \le f_A$ (ditentukan)
- Hitung T pada f_A dari pers. Neraca energi
- Hitung (-rA) dari persamaan kecepatan
- Hitung volume dari persamaan keadaan
- Ulangi langkah 1 s.d. 4 untuk beberapa nilai f_A
- Hitung t dari pers. Neraca massa

Contoh 12-5 Missen

Dekomposisi fasa gas A→ R + S, dilangsungkan dalam reaktor batch dengan kondisi awal T_0 = 300 K, V_0 = 0,5 m^3, dan tekanan total konstan 500 kPa. Harga Cp untuk A, R, dan S adalah 185,6; 104,7; dan 80,9 J mol^{-1} K^{-1}. Entalpi reaksi = -6280 J mol^{-1} dan reaksi orde satu terhadap A dg k_A=$10^{14}e^{-10000/T}$ h^{-1}. Tentukan f_A dan T sebagai fungsi t, bila Q = 0, fA = 0,99.

Solusi

MULTIPLE REACTIONS IN BATCH REACTORS

- Contoh-1: Menentukan kecepatan reaksi keseluruhan dari sejumlah reaksi

$$A + B \xrightarrow{k_I} C$$

$$C \xrightarrow{k_{II}} 2E$$

$$2A \xrightarrow{k_{III}/2} D$$

- Diawali dengan menentukan koefisien stoikiomeri untuk tiap komponen dari tiap reaksi

$$\begin{array}{lll} \nu_{A,I} = -1 & \nu_{A,II} = 0 & \nu_{A,III} = -2 \\ \nu_{B,I} = -1 & \nu_{B,II} = 0 & \nu_{B,III} = 0 \\ \nu_{C,I} = +1 & \nu_{C,II} = -1 & \nu_{C,III} = 0 \end{array}$$

$$\nu_{D,I} = 0 \quad \nu_{D,II} = 0 \quad \nu_{D,III} = +1$$
$$\nu_{E,I} = 0 \quad \nu_{E,II} = +2 \quad \nu_{E,III} = 0$$

- Asumsi semua reaksi elementer, shg kec reaksi dapat dinyatakan sebagai:

$$\mathscr{R}_I = k_I ab$$
$$\mathscr{R}_{II} = k_{II} c$$
$$\mathscr{R}_{III} = (k_{III}/2)a^2$$

- Menentukan kecepatan reaksi tiap komponen menggunakan rumus

$$\mathscr{R}_A = \nu_{A,I}\mathscr{R}_I + \nu_{A,II}\mathscr{R}_{II} + \nu_{A,III}\mathscr{R}_{III} + \cdots$$

atau $$\mathscr{R}_A = \sum_{Reactions} \nu_{A,I}\mathscr{R}_I = \sum_I \nu_{A,I}\mathscr{R}_I$$

Sehingga diperoleh persamaan

$$\mathscr{R}_A = -k_I ab - k_{III} a^2$$

$$\mathscr{R}_B = -k_I ab$$

$$\mathscr{R}_C = +k_I ab - k_{II} c$$

$$\mathscr{R}_D = (k_{III}/2) a^2$$

$$\mathscr{R}_E = +2k_{II} c$$

Neraca mole RB untuk N komponen dan M set reaksi:

$$\frac{d(Va)}{dt} = V\mathscr{R}_A = V(\nu_{A,I}\,\mathscr{R}_I + \nu_{A,II}\,\mathscr{R}_{II} + \nu_{A,III}\,\mathscr{R}_{III} + \cdots + M \text{ terms})$$

$$\frac{d(Vb)}{dt} = V\mathscr{R}_B = V(\nu_{B,I}\,\mathscr{R}_I + \nu_{B,II}\,\mathscr{R}_{II} + \nu_{B,III}\,\mathscr{R}_{III} + \cdots)$$

$$\frac{d(Vc)}{dt} = V\mathscr{R}_C = V(\nu_{C,I}\,\mathscr{R}_I + \nu_{C,II}\,\mathscr{R}_{II} + \nu_{C,III}\,\mathscr{R}_{III} + \cdots)$$

Diperoleh N set PD ordiner, satu untuk tiap komponen dan M set persamaan kec reaksi komponen, satu untuk tiap reaksi.

Dari N set PD ordiner harus diket N set kondisi awal

$a = a_0 \quad \text{at} \quad t = 0$ dll.

Contoh-2: Selesaikan persamaan design reaktor batch untuk set reaksi contoh-1. Asumsi sistem fasa cair dengan densiti konstan.

Penyelesaian:

Untuk densiti konstan berarti volume reaktor adl konstan shg pers design menjadi:

$$\left.\begin{aligned}
\frac{da}{dt} &= -k_I ab - k_{III} a^2 && a = a_0 \quad \text{at} \quad t = 0 \\
\frac{db}{dt} &= -k_I ab && b = b_0 \quad \text{at} \quad t = 0 \\
\frac{dc}{dt} &= +k_I ab - k_{II} c && c = c_0 \quad \text{at} \quad t = 0 \\
\frac{dd}{dt} &= (k_{III}/2) a^2 && d = d_0 \quad \text{at} \quad t = 0 \\
\frac{de}{dt} &= +2k_{II} c && e = e_0 \quad \text{at} \quad t = 0
\end{aligned}\right\}$$

Set pers ini akan sukar diselesaikan dengan cara analitis dan akan lebih mudah dg cara numeris

Contoh-3

Selesaikan persamaan design RB untuk reaksi dalam contoh-2. Digunakan k_I=0.1 mol/($m^3 \cdot$h), k_{II}=1.2 h^{-1}, k_{III}=0,06 mol/($m^3 \cdot$h). Kondisi awal adalah $a_0 = b_0 = 20$ mol/m^3. Waktu reaksi adalah 1 jam.

Selamat Belajar Belajar dan Belajar!
And...Sukses...

Selamat Belajar Belajar dan Belajar!
And...Sukses...

Derivation of Batch Reactor Design Equations

$$\frac{dN_A}{dt} = r_A V$$

$$N_A = N_{Ao} - N_{Ao}X$$

$$dN_A = 0 - N_{Ao}dX$$

$$-N_{Ao}\frac{dX}{dt} = r_A V$$

$$\boxed{N_{Ao}\frac{dX}{dt} = -r_A V}$$

$$\frac{N_{Ao}dx}{-r_A V} = dt$$

$t = 0 \quad X = 0$

$$\boxed{t = N_{Ao}\int_0^X \frac{dx}{-r_A V}}$$

Return

Derivation of PFR Reactor Design Equations

$$\frac{dF_A}{dV} = r_A$$

$$F_A = F_{Ao} - F_{Ao}X$$

$$dF_A = 0 - F_{Ao}dX$$

$$-F_{Ao}\frac{dX}{dV} = r_A$$

$$\boxed{F_{Ao}\frac{dX}{dV} = -r_A}$$

$$\frac{F_{Ao}dX}{-r_A} = dV$$

$t = 0 \quad X = 0$

$$\boxed{V = F_{Ao}\int_0^X \frac{dX}{-r_A}}$$

Return

Solusi contoh 12-1 Missen

$$c_{Ao} = n_{Ao}/V = 7.5115 = 0.5$$

$$f_{A1} = 0; \; f_{A2} = 0.80$$

$$(-r_A) = k_A c_A = k_A c_{Ao}(1 - f_A)$$

$$t = c_{Ao} \int_0^{f_A} \frac{df_A}{k_A c_{Ao}(1 - f_A)}$$

$$= \frac{-\ln(1 - f_A)}{k_A} = \frac{-\ln(0.2)}{\mathbf{0.05}} = 32.2 \text{ min}$$

Kembali

Solusi contoh 12-2 Missen

from the stoichiometry, Since $C_{A0} = C_{B0}$

$$(-r_A) = k_A c_A c_B = k_A c_A^2 = k_A c_{Ao}^2 (1 - f_A)^2$$

Then, with $f_{A1} = 0$, and $f_{A2} = f_A$,

$$t = c_{Ao} \int_0^{f_A} \frac{df_A}{k_A c_{Ao}^2 (1 - f_A)^2} = \frac{1}{k_A c_{Ao}} \frac{f_A}{1 - f_A}$$

$$= \frac{1}{\mathbf{9.92} \times 10^{-3} \times 0.15} \frac{0.9}{0.1} = \mathbf{6050s} = \mathbf{1.68}\ \text{h}$$

$$V = \frac{(t + t_d) Pr(\text{C})}{\nu_C c_{Ao} f_A} = \frac{(1.68 + 0.5)175}{1(0.15)0.9}$$

$$= \mathbf{2830}\ \text{L or } 2.83\ \text{m}^3$$

Kembali

Solusi contoh 12-3 Missen

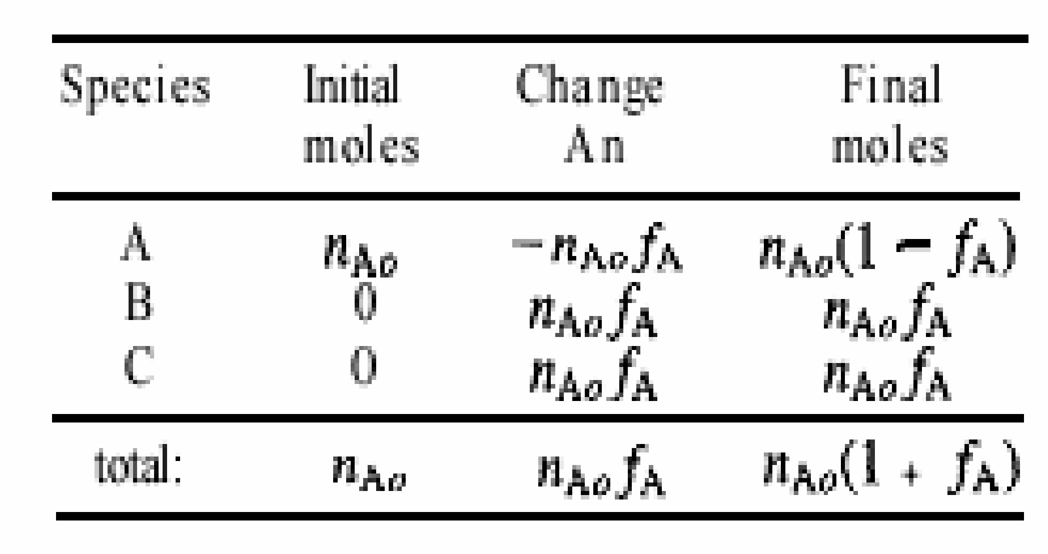
Persamaan design untuk RB

$$t = n_{Ao}\int_0^{f_A}\frac{df_A}{(-r_A)V}$$

Kecepatan reaksi

$$(-r_A) = k_A c_A^2 = k_A(n_A/V)^2 = \frac{k_A n_{Ao}^2(1-f_A)^2}{V^2}$$

Perubahan jumlah mole dan volume setelah reaksi berlangsung ditentukan menggunakan tabel stokiometri



Species	Initial moles	Change Δn	Final moles
A	n_{Ao}	$-n_{Ao}f_A$	$n_{Ao}(1-f_A)$
B	0	$n_{Ao}f_A$	$n_{Ao}f_A$
C	0	$n_{Ao}f_A$	$n_{Ao}f_A$
total:	n_{Ao}	$n_{Ao}f_A$	$n_{Ao}(1+f_A)$

Untuk gas ideal $V = n_t RT/P,$

Untuk kasus ini R, T, dan P konstan sehingga berlaku

$\frac{V}{V_o} = \frac{n_{Ao}(1 + f_A)}{n_{Ao}}$ atau $V = V_o(1 + f_A),$

Substitusi ke pers. Kecepatan reaksi dan pers desain:

$$t = \frac{V_o}{k_A n_{Ao}} \int_0^{f_A} \frac{(1 + f_A)\mathrm{d}f_A}{(1 - f_A)^2}$$

Untuk integral, ambil a = 1 – f_A → f_A = 1 – a → df_A = -da, integral menjadi:

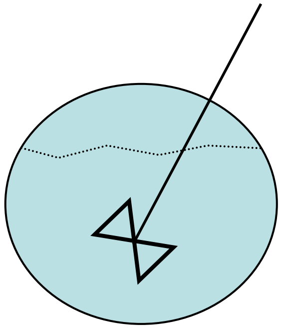
$$\int_1^{0.25} \frac{\mathbf{a - 2}}{\alpha^2}\,\mathrm{da} = \ln(0.25) + 6 = 4.61$$

Sehingga diperoleh:

$$t = 10\ \mathrm{L}\ \times 4.61/(0.023\ \mathrm{L\ mol^{-1}\ s^{-1}} \times 5.0\ \mathrm{mol}) = 400\ \mathrm{s}$$

Return

Solusi 12-4 Missen



Diketahui: n_{A0} = 7,5 mol, V = 15 L, f_{A0} =0, f_A = 0,8, k_A = 0,05 min^{-1}

Neraca mole:

$$\frac{\mathrm{d}f_A}{\mathrm{d}t} = \frac{V}{n_{Ao}}(-r_A) = \frac{V}{n_{Ao}}k_A\frac{n_{Ao}}{V}(1-f_A) = k_A(1-f_A)$$

Diintegralkan diperoleh:

$$f_A = 1 - e^{-k_A t}$$

Neraca energi untuk operasi isotermal:

$$\dot{Q} = UA_c(T_c - T), = -(-\Delta H_{RA})n_{Ao}(\mathrm{d}f_A/\mathrm{d}t)$$

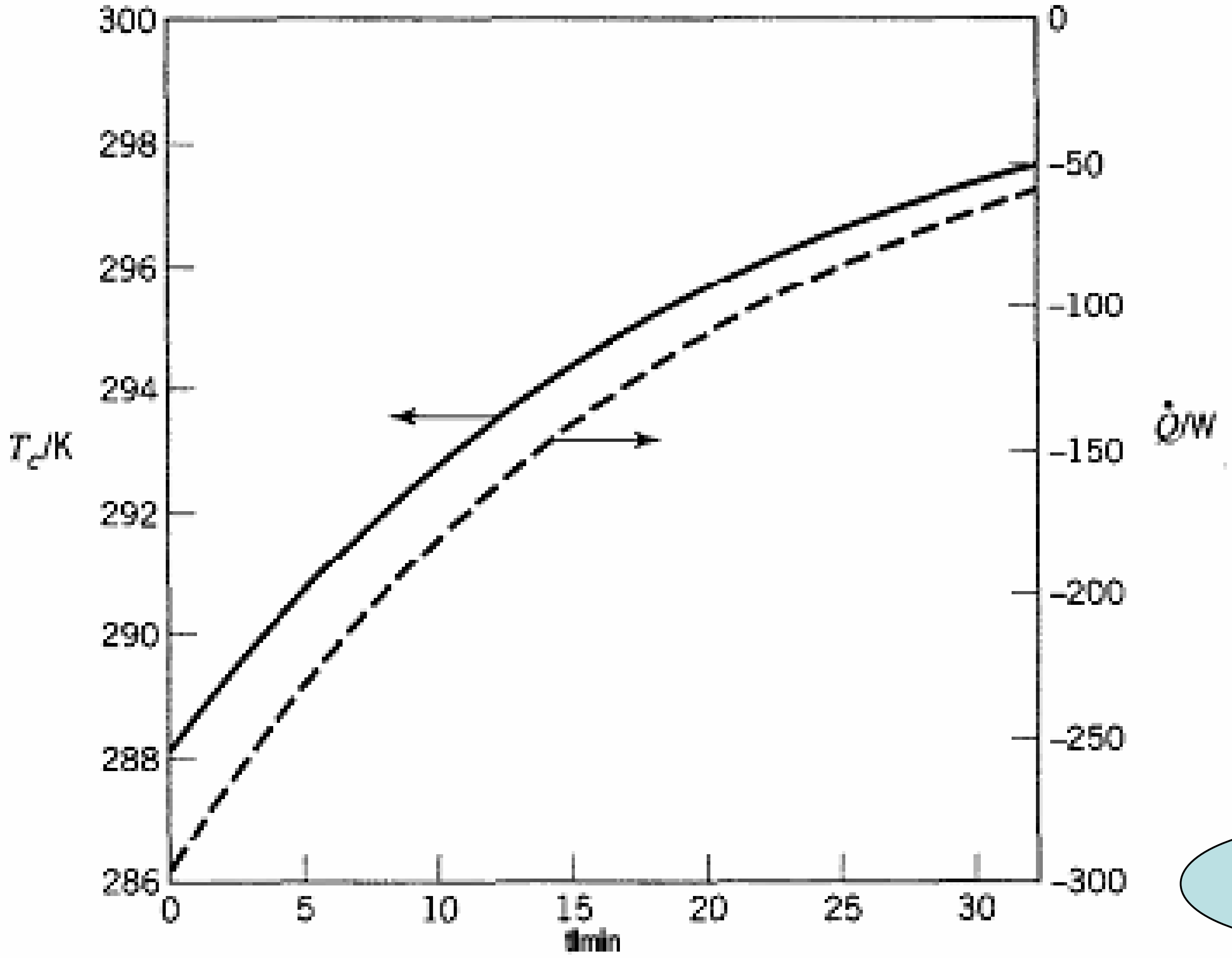
$$\dot{Q} = -(-\Delta H_{RA})n_{Ao}k_A e^{-k_A t} = -(47{,}500)7.5(0.05/60)e^{-0.05t} = -297e^{-0.05t}\ \text{J s}^{-1}\text{ or W}$$

Karena Q < 0 → panas diambil dari sistem → reaksi eksotermis

Menghitung Tc sebagai fungsi waktu, dari neraca energi

$$T_c = T - \frac{(-\Delta H_{RA})n_{Ao}}{} k_A e^{-k_A t}$$

Bu



Return

Solusi 12-5 Missen

Pers. Laju reaksi: $(-r_A) = k_A c_A = k_A n_A/V = k_A n_{Ao}(1 - f_A)/V$

Dari pers. Neraca massa:

$$t = n_{Ao}\int_0^{f_A} \frac{df_A}{(-r_A)V}$$

Substitusikan $(-r_A)$ diperoleh:

$$t = \int_0^{f_A} \frac{df_A}{k_A(1 - f_A)} \qquad \text{(A)}$$

Dengan $k_A = 10^{14} e^{-10,000/T}$ (B)

Neraca energi operasi adiabatis (Bila $-\Delta H_{RA}$, Cp, dan *nt* konstan):

$$T = T_o + \frac{(-\Delta H_{RA})n_{Ao}}{n_t C_P}(f_A - f_{Ao})$$

$$\begin{aligned} n_t C_P &= n_t \sum x_i C_{Pi} = n_t \sum (n_i/n_t) C_{Pi} \\ &= \sum n_i C_{Pi} = n_A C_{PA} + n_R C_{PR} + n_S C_{PS} \\ &= n_{Ao}(1 - f_A) C_{PA} + n_{Ao} f_A C_{PR} + n_{Ao} f_A C_{PS} \\ &= n_{Ao}\left[C_{PA} + (C_{PR} + C_{PS} - C_{PA}) f_A\right] \\ &= 185.6 n_{Ao} \end{aligned}$$

Substitusikan ke pers. Neraca enargi:

$$T = 300 + \frac{6280 n_{Ao}}{185.6 n_{Ao}} f_A = 300 + 33.8 f_A \qquad \text{(C)}$$

Pers. (A), (B), dan (C) diselesaikan secara simultan pada inkremen Δf

$$t_j = t_{j-1} + 0.5(G_j + G_{j-1})(f_{Aj} - f_{A,j-1})$$

$$G = 1/[k_A(1 - f_A)]$$

$G^* = 0,5(G_j + G_{j-1})$

f_A	C, T/K	B, kA/h^{-1}	G	G*	A, t/h^{-1}
0	300.00	0.33	3.00		0.00
0.1	303.38	0.48	2.30	2.65	0.26
0.2	306.76	0.70	1.80	2.05	0.47
0.3	310.14	0.99	1.44	1.62	0.63
0.4	313.52	1.41	1.19	1.31	0.76
0.5	316.90	1.97	1.01	1.10	0.87
0.6	320.28	2.76	0.91	0.96	0.97
0.7	323.66	3.82	0.87	0.89	1.06
0.8	327.04	5.25	0.95	0.91	1.15
0.9	330.42	7.18	1.39	1.17	1.27
0.99	333.46	9.47	10.56	5.98	1.80

Pers. A diselesaikan dengan Trapezoidal Rule rata-rata

Return

07-08-09

REAKTOR ALIR TANGKI BERPENGADUK (RATB)

Sifat-sifat mendasar pada RATB

1. Pola alir adalah bercampur sempurna (back mixed flow atau BMF)
2. Meskipun aliran melalui RATB adalah kontinyu, tapi kec volumetris aliran pada pemasukan dan pengeluaran dapat berbeda, disebabkan oleh terjadinya perubahan densiti
3. BMF meliputi pengadukan yang sempurna dalam volume reaktor, yg berimplikasi pada semua sifat-sifat sistem menjadi seragam diseluruh reaktor
4. Pengaduka yg sempurna juga mengakibatkan semua komponen dlm reaktor mempunyai kesempatan yg sama utk meninggalkan reaktor

Sifat-sifat mendasar pada RATB (Lanjut)

5. Sebagai akibat poin 4, terdapat distribusi kontinyu dari waktu tinggal
6. Sebagai akibat dari poin 4, aliran keluaran mempunyai sifat-sifat sama dengan fluida dalam reaktor
7. Sebagai akibat dari 6, terdapat satu langkah perubahan yg menjelaskan perubahan sifat-sifat dari input dan output
8. Meskipun terdapat perubahan distribusi waktu tinggal, pencampuran sempurna fluida pada tingkat mikroskopik dam makroskofik membimbing utk merata-rata sifat-sifat seluruh elemen fluida

Keuntungan dan Kerugian Menggunakan RATB

- Keuntungan
  - Relatif murah untuk dibangun
  - Mudah mengontrol pada tiap tingkat, karena tiap operasi pada keadaan tetap, permukaan perpindahan panas mudah diadakan
  - Secara umum mudah beradaptasi dg kontrol otomatis, memberikan respon cepat pada perubahan kondisi operasi (misal: kec umpan dan konsentrasi)
  - Perawatan dan pembersihan relatif mudah
  - Dengan pengadukan efisien dan viskositas tidak terlalu tinggi, dalam praktek kelakuan model dapat didekati lebih dekat untuk memprediksi unjuk kerja.

- Kerugian
  - Secara konsep dasar sangat merugikan dari kenyataan karena aliran keluar sama dengan isi vesel
  - Hal ini menyebabkan semua reaksi berlangsung pada konsentrasi yang lebih rendah (katakan reaktan A, C_A)antara keluar dan masuk
  - Secara kinetika normal r_A turun bila C_A berkurang, ini berarti diperlukan volume reaktor lebih besar untuk memperoleh konversi yg diinginkan
  - (Untuk kinetika tidak normal bisa terjadi kebalikannya, tapi ini tidak biasa, apakah contohnya dari satu situasi demikian?)

Persamaan perancangan untuk RATB

Pertimbangan secara umum:

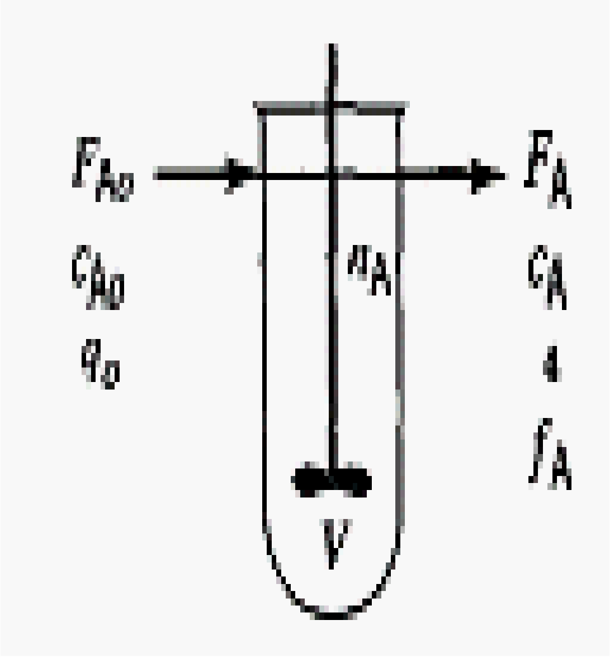
- Neraca masa
- Neraca Energi

Perancangan proses RATB secara khas dibangun untuk menentukan volume vesel yang diperlukan guna mencapai kecepatan produksi yang diinginkan

Parameter yang dicari meliputi:

- Jumlah stage yg digunakan untuk operasi optimal
- Fraksi konversi dan suhu dalam tiap stage
- Dimulai dengan mempertimbangkan neraca massa dan neraca energi untuk tiap stage

Neraca massa, volume reaktor, dan kecepatan produksi



Untuk operasi kontinyu dari RATB vesel tertutup, tinjau reaksi:

$A + \ldots \rightarrow \nu_C\, C + \ldots$

dengan kontrol volume didefinisikan sebagai volume fluida dalam reaktor

$$\begin{pmatrix} \textit{rate of} \\ \textit{input of} \\ \text{A} \textit{ by flow} \end{pmatrix} - \begin{pmatrix} \textit{rate of} \\ \textit{output of} \\ \text{A} \textit{ by flow} \end{pmatrix} - \begin{pmatrix} \textit{rate of} \\ \textit{disappearance} \\ \textit{of } \text{A} \textit{ by} \\ \textit{reaction} \end{pmatrix} = \begin{pmatrix} \textit{rate of} \\ \textit{accumulation} \\ \textit{of } \text{A} \textit{ within} \\ \textit{the control} \\ \textit{volume} \end{pmatrix} \qquad (1)$$

Secara operasional:

$$F_{A0} - F_A - (-r_A)V = dn_A/dt \qquad (2)$$

Dalam term kecepatan volumetrik:

$$c_{A0}q_0 - c_A q - (-r_A)V = dn_A/dt \qquad (3)$$

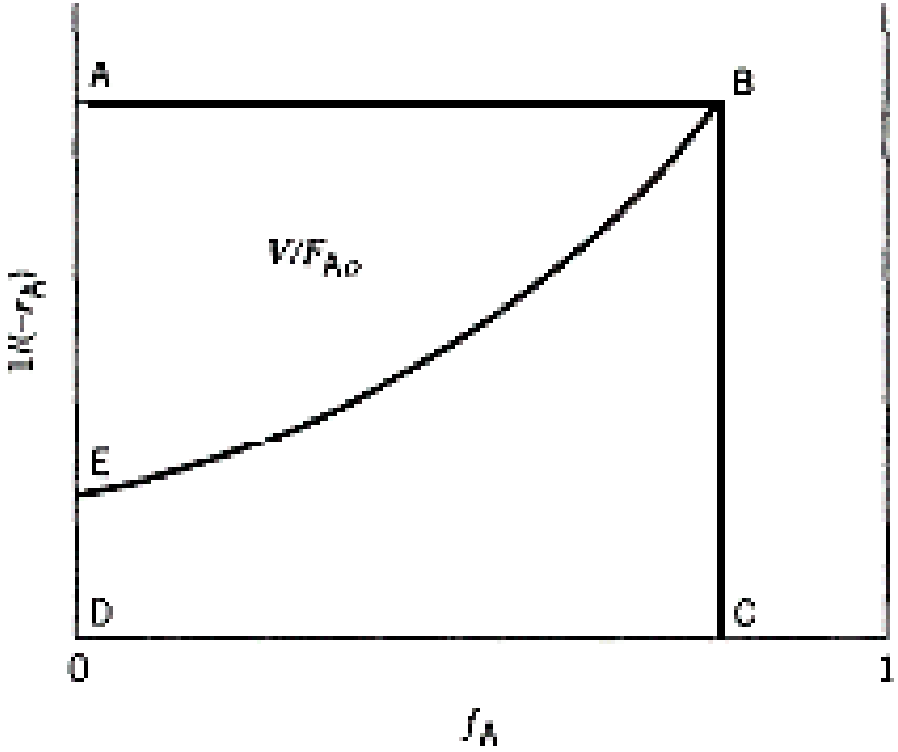
Dalam term konversi A, dengan hanya A yg tidak bereaksi dalam umpan (f_{A0} = 0):

$$F_{A0}f_A - (-r_A)V = dn_A/dt \qquad (4)$$

Untuk opersasi tunak (steady state) → $dn_A/dt = 0$

$$V = (c_{Ao}q_o - c_Aq)/(-r_A) \quad (5)$$

$$= F_{Ao}f_A/(-r_A) \quad (6)$$



Residence time: $\bar{t} = V/q$ (7)

Space time: $\tau = V/q_o$ (8)

Kecepatan produksi:

$$Pr(\mathrm{C}) = F_{\mathrm{C}} = \nu_{\mathrm{C}} F_{\mathrm{A}o} f_{\mathrm{A}} = c_{\mathrm{C}} q \qquad (9)$$

Neraca Energi

- Untuk reaktor alir kontinyu seperti RATB, neraca energi adalah neraca entalpi (H), bila kita mengabaikan perbedaan energi kinetik dan energi potensial dalam aliran, dan kerja shaft antara pemasukan dan pengeluaran
- Akan tetapi, dalam perbandingannya dengan BR, kesetimbangan harus meliputi entalpi masuk dan keluar oleh aliran
- Dalam hal berbagai transfer panas dari atau menuju kontrol volume, dan pembentukan atau pelepasan entalpi oleh reaksi dalam kontrol volume.
- Selanjutnya persamaan energi (entalpi) dinyatakan sbg:

$$\begin{pmatrix}\text{rate of}\\ \text{input of}\\ \text{enthalpy by}\\ \text{flow, heat}\\ \text{transfer or}\\ \text{reaction}\end{pmatrix} - \begin{pmatrix}\text{rate of}\\ \text{output}\\ \text{of enthalpy by}\\ \text{flow, heat}\\ \text{transfer or}\\ \text{reaction}\end{pmatrix} = \begin{pmatrix}\text{rate of}\\ \text{accumulation}\\ \text{of enthalpy}\\ \text{within control}\\ \text{volume}\end{pmatrix}$$

$$\Big|_{T_{ref}}^{T_o} \dot{m}_o c_{Po} \mathrm{d}T - \Big|_{T_{ref}}^{T} \dot{m} c_P \mathrm{d}T + UA_c(T_c - T), + (-\Delta H_{RA})(-r_A)V = \mathrm{d}H/\mathrm{d}t \qquad (10)$$

$$= \mathrm{d}(m_t c_P T)/\mathrm{d}t$$

Untuk operasi tunak $m = m_0$

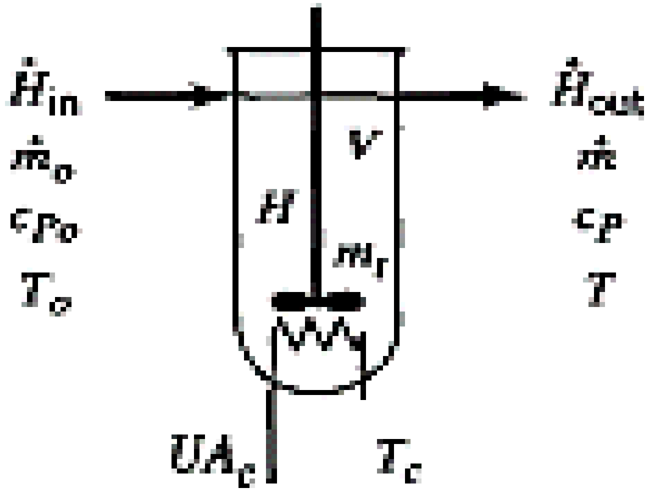
$$\dot{m} c_P (T_o - T) + UA_c(T_c - T) + (-\Delta H_{RA})(-r_A)V = 0 \qquad (11)$$

Substitusi $F_{A0}\, f_A$ untuk $(-r_A)V$

$$\dot{m} c_p (T_o - T) + UA_c(T_c - T) + (-\Delta H_{RA}) F_{Ao} f_A = 0 \qquad (12)$$

Hubungan f_A denga suhu

$$f_{\mathrm{A}} = -\frac{\dot{m}c_p T_o + UA_c T_c}{(-\Delta H_{RA})F_{Ao}} + \left[\frac{\dot{m}c_p + UA_c}{(-\Delta H_{RA})F_{Ao}}\right]T \qquad (13)$$



Sistem densiti konstan

Untuk sistem densiti konstan, beberapa hasil penyederhanaan antara lain:

Pertama, tanpa memperhatikan tipe reaktor, fraksi konversi limiting reactant, f_A, dapat dinyatakan dalam konsentrasi molar

$$f_A = (c_{Ao} - c_A)/c_{Ao} \qquad \text{(constant density)} \qquad (14)$$

Kedua, untuk aliran reaktor seperti RATB, *mean residence time* sama dengan *space time,* karena

$q = q_0$

$$\bar{t} = \tau \qquad \text{(constant density)} \qquad (15)$$

Ketiga, untuk RATB, term akumulasi dalam persamaan neraca massa menjadi:

$$dn_A/dt = V\,dc_A/dt \qquad \text{(constant density)} \qquad (16)$$

Terakhir, untuk RATB, persamaan neraca massa keadaan tunak dapat disederhanakan menjadi:

$$V = (c_{Ao} - c_A)q/(-r_A) \qquad \text{(constant density)} \qquad (17)$$

Operasi keadaan tunak pada temperatur T

Untuk operasi keadaan tunak, term akumulasi dalam pers neraca massa dihilangkan

$$dn_A/dt = 0 \qquad \text{(steady-state)}$$

Atau, untuk densiti konstan

$$dc_A/dt = 0 \qquad \text{(steady-state, constant density)}$$

Bila T tertentu, V dapat dihitung dari pers neraca massa tanpa melibatkan neraca energi

Contoh 1.

For the liquid-phase reaction A + B → products at 20°C suppose 40% conversion of A is desired in steady-state operation. The reaction is pseudo-first-order with respect to A, with k_A = 0.0257 h^{-1} at 20°C. The total volumetric flow rate is 1.8 $m^3 h^{-1}$, and the inlet molar flow rates of A and B are F_{AO} and F_{BO} mol h^{-1}, respectively. Determine the vessel volume required, if, for safety, it can only be filled to 75% capacity.

Contoh 2.

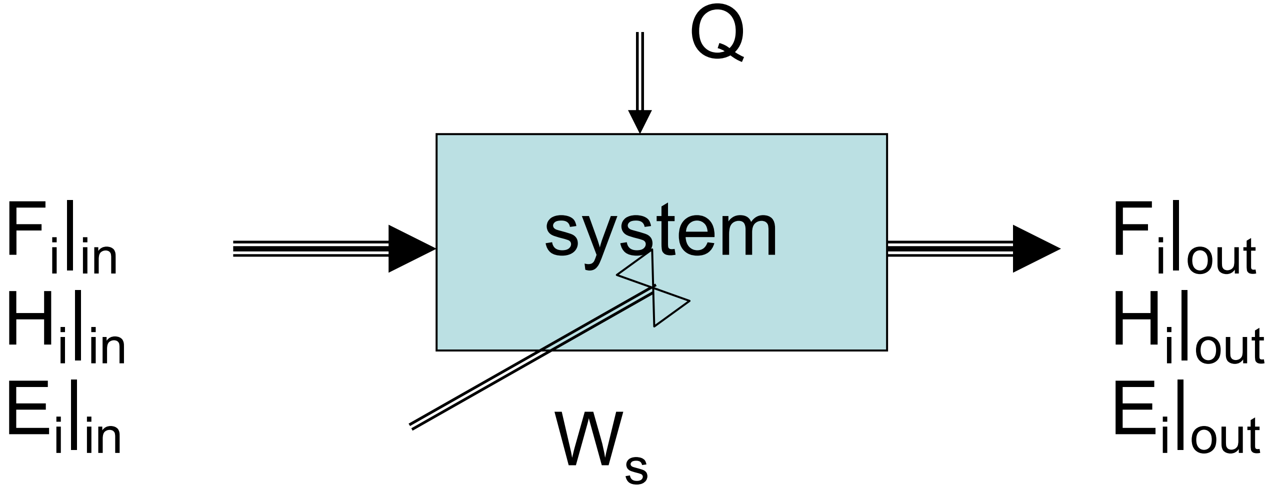
A liquid-phase reaction A → B is to be conducted in a CSTR at steady-state at 163°C. The temperature of the feed is 20°C and 90% conversion of A is required. Determine the volume of a CSTR to produce 130 kg B h^{-1}, and calculate the heat load (Q) for the process. Does this represent addition or removal of heat from the system?

Data: $M_A = M_B = 200$ g mol^{-1}; cp = 2.0 J $g^{-1}K^{-1}$; $\rho = 0.95$ g cm^{-3}; $\Delta H_{RA} = -87$ kJ mol^{-1}; $k_A = 0.80$ h^{-1} at 163°C

Contoh 3

Consider the startup of a CSTR for the liquid-phase reaction A → products. The reactor is initially filled with feed when steady flow of feed (q) is begun. Determine the time (t) required to achieve 99% of the steady-state value of fA. Data: V = 8000 L; q = 2 L $s\text{-}^{1}$; C_{Ao} = 1.5 mol L^{-1}; k_A = 1.5 x $l0^{-4}$ s^{-1}.

TINJAU ULANG NERACA ENERGI SISTEM ALIR



Neraca Energi

$$R_{in} - R_{out} + R_{gen} = R_{acc}$$

$$\dot{Q} - \dot{W} + \sum_{i=1}^{n} F_i E_i \Big|_{in} - \sum_{i=1}^{n} F_i E_i \Big|_{out} = \left(\frac{dE}{dt} \right)_{System} \qquad (8\text{-}1)$$

E_i = Energy of component i

$$\dot{W} = \dot{W}_s - \underbrace{\sum_{i=1}^{n} F_i PV_i \Big|_{in} + \sum_{i=1}^{n} F_i PV_i \Big|_{out}}_{} \qquad (8\text{-}2)$$

Work do to flow velocity

For chemical reactor K_i, P_i, and “other” energy are neglected so that:

$$E_i = U_i \qquad (8\text{-}3)$$

and

$$H_i = U_i + PV_i \qquad (8\text{-}4)$$

Combined the eq. 8-4, 8-3, 8-2, and 8-1 be result,

$$\dot{Q} - \dot{W}_s + \sum_{i=1}^{n} F_i H_i \Big|_{in} - \sum_{i=1}^{n} F_i H_i \Big|_{out} = \left(\frac{dE}{dt} \right)_{System} \qquad (8\text{-}5)$$

General Energy Balance:

$$\boxed{\dot{Q} - \dot{W}_s + \sum F_{i0} H_{i0} - \sum F_i H_i = \frac{dE_{system}}{dt}}$$

For steady state operation:

$$\boxed{\dot{Q} - \dot{W}_s + \sum F_{i0} H_{i0} - \sum F_i H_i = 0}$$

We need to put the above equation into a form that we can easily use to relate X and T in order to size reactors. To achieve this goal, we write the molar flow rates in terms of conversion and the enthalpies as a function of temperature. We now will "dissect" both Fi and Hi.

Flow Rates, Fi

For the generalized reaction:

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

$$F_A = F_{A0}(1 - X), \quad F_B = F_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

In general,

$$F_i = F_{A0}(\Theta_i + \upsilon_i X)$$

$$\upsilon_A = -1, \quad \upsilon_B = -\frac{b}{a}, \quad \upsilon_C = \frac{c}{a}, \quad \upsilon_D = \frac{d}{a}$$

Enthalpies, Hi

Assuming no phase change:

$$H_i = H_i^\circ(T_R) + \int_{T_R}^{T} C_{Pi}\,dT$$

$$\sum \upsilon_i H_i = \Delta H_R(T) = \Delta H_R^\circ(T_R) + \int_{T_R}^{T} \Delta C_P\,dT$$

$$\boxed{\Delta H_{RX} = \frac{d}{a}H_D + \frac{c}{a}H_C - \frac{b}{a}H_B - H_A}$$

$$C_{Pi} = \alpha_i + \beta_i T + \chi_i T^2$$

$$\Delta C_P = \frac{d}{a}C_{PD} + \frac{c}{a}C_{PC} - \frac{b}{a}C_{PB} - C_{PA}$$

Mean heat capacities:

$$\hat{C}_{Pi} = \frac{\int_{T_R}^{T} C_{Pi}\,dT}{(T - T_R)}$$

$$\tilde{C}_{Pi} = \frac{\int_{T_{io}}^{T} C_{Pi}\,dT}{(T - T_{io})}$$

$$\boxed{H_i = H_i^{\circ}(T_R) + \hat{C}_{Pi}(T - T_R)}$$

$$\boxed{\Delta H_R(T) = \Delta H_R^{\circ}(T_R) + \Delta\hat{C}_P(T - T_R)}$$

$$\boxed{\sum \upsilon_i \hat{C}_{Pi} = \Delta\hat{C}_P = \frac{d}{a}\hat{C}_{PD} + \frac{c}{a}\hat{C}_{PC} - \frac{b}{a}\hat{C}_{PB} - \hat{C}_{PA}}$$

Self Test

Calculate ΔH°_{Rx} , ΔC_P , and $\Delta H_{RX}(400)$

for the reaction, $A \rightarrow 2B + C$

There are inerts **I** present in the system.

Additional Information:

$$H_A^{\circ}(298) = -100 \text{ kcal/mol A} \qquad \tilde{C}_{P_A} = 80 \text{ cal/mol °C}$$

$$H_B^{\circ}(298) = -40 \text{ kcal/mol B} \qquad \tilde{C}_{P_B} = 20 \text{ cal/mol/°C}$$

$$H_C^{\circ}(298) = -30 \text{ kcal/mol C} \qquad \tilde{C}_{P_C} = 30 \text{ cal/mol °C}$$

$$H_I^{\circ}(298) = -100 \text{ kcal/mol I} \qquad \tilde{C}_{P_I} = 190 \text{ cal/mol °C}$$

Solution

$$\Delta H_{Rx}^{\circ}(298) = H_C^{\circ} + 2H_B^{\circ} - H_A^{\circ} = (-30) + 2(-40) - (-100) = -10 \frac{\text{kcal}}{\text{mole A}}$$

$$\Delta \hat{C}_P = \tilde{C}_{P_C} + 2\tilde{C}_{P_B} - \tilde{C}_{P_A} = 30 + 2(20) - 80 = -10 \frac{\text{cal}}{\text{mol °C}}$$

$$\Delta H_{Rx}(T) = \Delta H_{Rx}^{\circ}(298) + \Delta C_P (T - T_R)$$

$$= -10 \frac{\text{kcal}}{\text{mole} \quad \text{A}} + (-10)(T - 298)$$

$$\Delta H_R(400) = -10 \frac{\text{kcal}}{\text{mole} \quad \text{A}} - 10(400 - 298) = -10,000 - (10)(102)$$

$$= -11,200 \frac{\text{cal}}{\text{mole} \quad \text{A}}$$

Note: The inerts do not come into these claculations of ΔH_{Rx}° or $\Delta \hat{C}_P$.

Energy Balance with "dissected" enthalpies:

$$\boxed{\dot{Q} - \dot{W}_S - F_{A0}\int_{T_R}^{T}\sum \Theta_i C_{Pi}\,dT - F_{A0}X\left[\Delta H_R^\circ(T_R) + \int_{T_R}^{T}\Delta C_P\,dT\right] = 0}$$

For constant or mean heat capacities:

$$\boxed{\dot{Q} - \dot{W}_S - F_{A0}X\left[\Delta H_R^\circ(T_R) + \Delta\hat{C}_P(T - T_R)\right] = F_{A0}\sum \Theta_i \tilde{C}_{Pi}(T - T_{i0})}$$

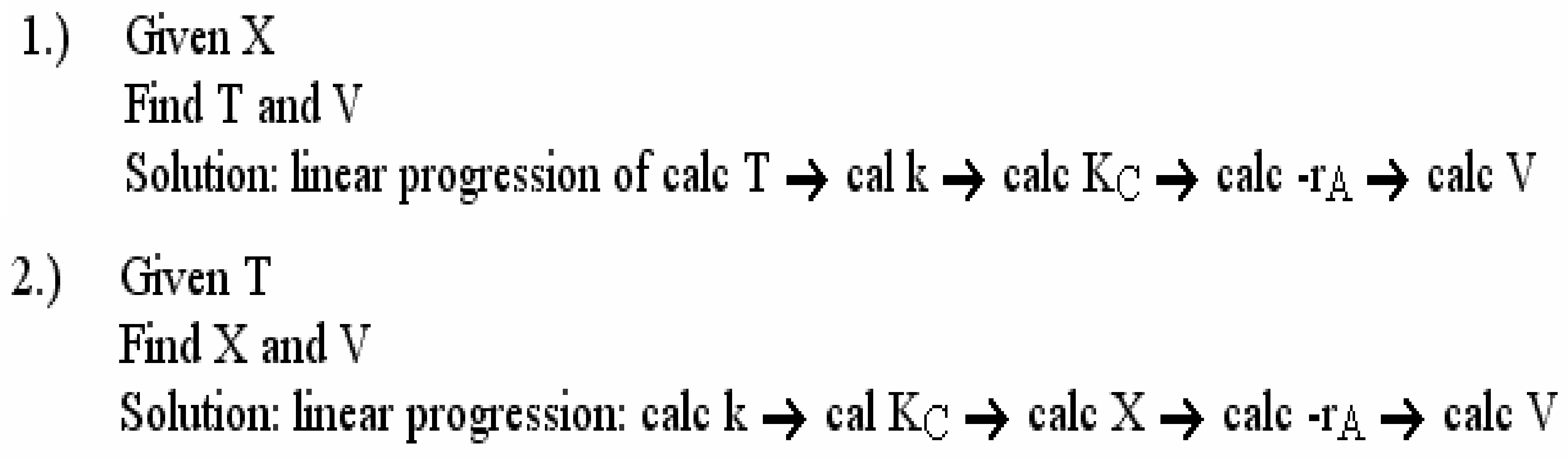
Adiabatic Energy Balance:

$$T = T_0 - \frac{X\left[\Delta H_R^\circ(T_R) + \Delta\hat{C}_P(T_0 - T_R)\right]}{\sum \Theta_i \tilde{C}_{Pi} + X\Delta\hat{C}_P} = T_0 - \frac{X\left[\Delta H_R(T_0)\right]}{\sum \Theta_i \tilde{C}_{Pi} + X\Delta\hat{C}_P}$$

Adiabatic Energy Balance for variable heat capacities:

$$X=\frac{\sum\Theta_i\alpha_i(T_0-T)+\frac{1}{2}\sum\Theta_i\beta_i\left(T_0^2-T^2\right)+\frac{1}{3}\sum\Theta_i\chi_i\left(T_0^3-T^3\right)}{\Delta H_R(T_R)+\Delta\alpha(T-T_R)+\frac{1}{2}\Delta\beta\left(T^2-T_R^2\right)+\frac{1}{3}\Delta\chi\left(T^3-T_R^3\right)}$$

CSTR Algorithm (Section 8.3 Fogler)



1.) Given X

Find T and V

Solution: linear progression of calc T → cal k → calc K_C → calc $-r_A$ → calc V

2.) Given T

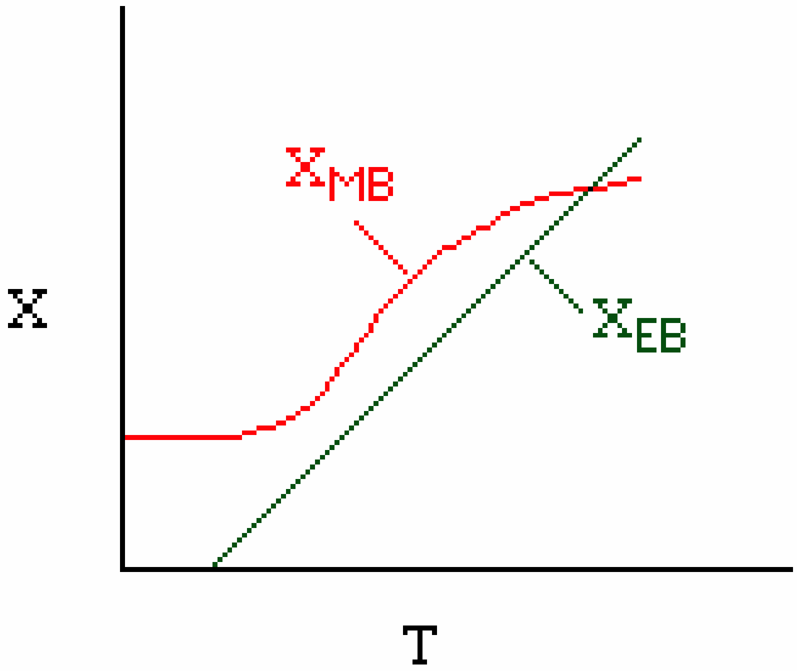
Find X and V

Solution: linear progression: calc k → cal K_C → calc X → calc $-r_A$ → calc V

3.) Given V

Find X

Solution: plot X_{EB} vs. T and X_{MB} vs. T on the same graph:



Self Test

For and adiabatic reaction with $\dot{W}_s$ and $\Delta C_P=0$, sketch conversion as a function of temperature.

Solution

$$\dot{Q} - \dot{W}_s - F_{A0}X\left[\Delta H^\circ_{Rx}(T_R) + \Delta\hat{C}_p(T - T_R)\right] = F_{A0}\sum\theta_i C_{P_i}(T - T_0)$$

$$\dot{Q} = 0, W_s = 0, \Delta\hat{C}_p = 0 \quad \therefore \Delta H_{Rx} = \Delta H^\circ_{Rx}$$

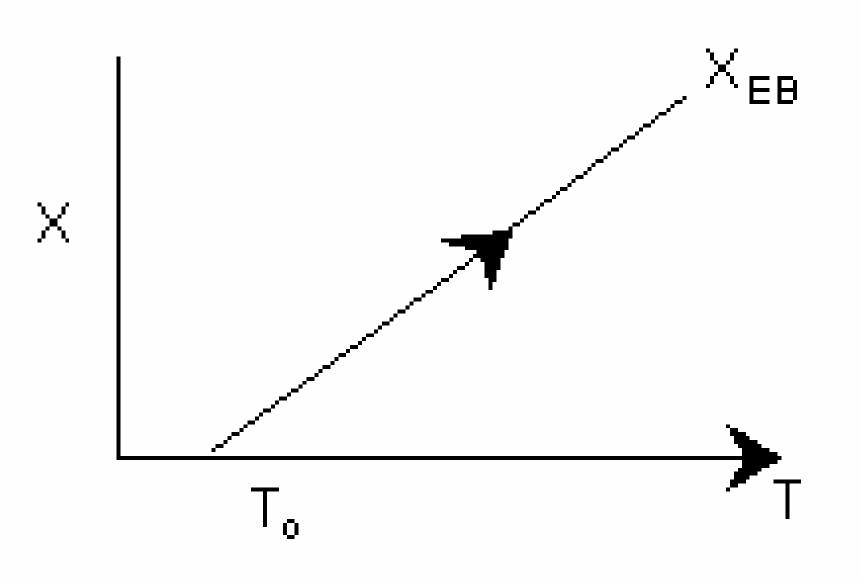
$$X\left[-\Delta H_{Rx}(T_R)\right] = \left(\sum\theta_i C_{P_i}\right)(T - T_0)$$

$$X_{EB} = \frac{\left[\sum\theta_i C_{P_i}\right]}{\left[-\Delta H_{Rx}\right]}\left[T - T_0\right]$$

A. For an exothermic reaction, ΔH_{RX} is negative (-), X_{EB} increases with increasing T.

[e.g., ΔH_{RX}= -100 kJ/mole A]

$$X_{EB} = \frac{\left(\sum \theta_i C_{P_i}\right)\left(T - T_0\right)}{+\left[\text{a positive number}\quad\right]}$$

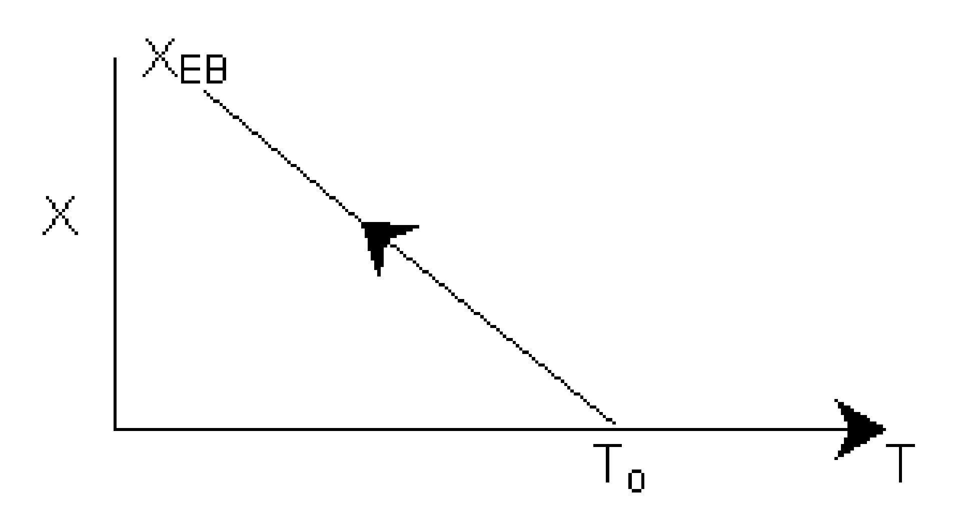


B. <u>For an endothermic reaction,</u> ΔH_{RX} is positive (+),

X_{EB} increases with decreasing T.

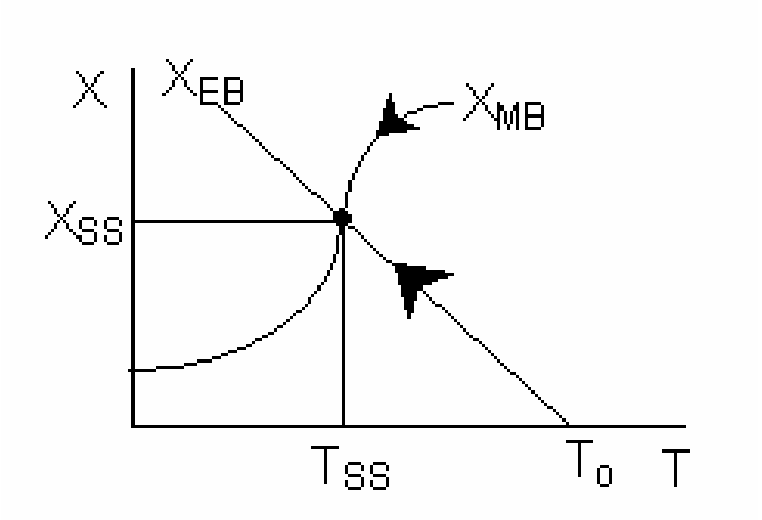
[e.g., ΔH_{RX}= +100 kJ/mole A]

$$X = \frac{\left[\sum \theta_i C_{P_i}\right]\left[T - T_0\right]}{-\left[\Delta H_{Rx}\right]} = \frac{\left[\sum \theta_i C_{P_i}\right]\left[T - T_0\right]}{\left[a\ negative\ number\right]}$$



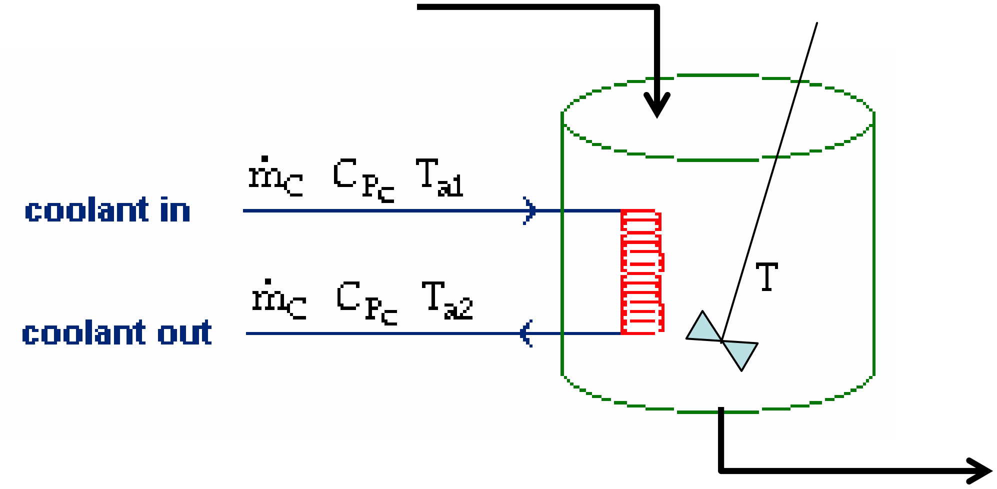
For a first orde

$$X_{MB} = \frac{\tau k}{1+\tau k} = \frac{\tau A e^{-E/RT}}{1+\tau A e^{-E/RT}}$$



Both the mole and energy balances are satisfied when $X_{MB}=X_{EB}$. The steady state temperature and conversion are T_{SS} and X_{SS}, respectively, for an entering temperature T_O.

Evaluating the Heat Exchange Term, Q



Energy transferred between the reactor and the coolant:

$$\dot{Q} = \dot{m}_C C_{P_C} \left(T_{a1} - T_{a2} \right)$$

Assuming the temperature inside the CSTR, T, is spatially uniform:

Manipulating the Energy Exchange Term

Combining:

$$\dot{Q} = \dot{m}_C C_{Pc}\left(T_{a1} - T_{a2}\right) = UA\,\frac{\left(T_{a1} - T_{a2}\right)}{\ln\left(\dfrac{T_{a1} - T}{T_{a2} - T}\right)}$$

$$\ln\left(\frac{T_{a1} - T}{T_{a2} - T}\right) = \frac{UA}{\dot{m}C_{Pc}}\,\frac{\left(T_{a1} - T_{a2}\right)}{\left(T_{a1} - T_{a2}\right)} = \frac{UA}{\dot{m}C_{Pc}}$$

$$\left(\frac{T_{a1} - T}{T_{a2} - T}\right) = \exp\left(\frac{UA}{\dot{m}C_{Pc}}\right)$$

$$\left(T_{a1} - T\right)\exp\left(-\frac{UA}{\dot{m}C_{Pc}}\right) = \left(T_{a2} - T\right)$$

$$T_{a2} = T + \left(T_{a1} - T\right)\exp\left(-\frac{UA}{\dot{m}C_{Pc}}\right)$$

$$\dot{Q} = \dot{m}_C C_{Pc}\left(T_{a1} - T_{a2}\right) = \dot{m}_C C_{Pc}\left[T_{a1} - T - \left(T_{a1} - T\right)\exp\left(-\frac{UA}{\dot{m}C_{Pc}}\right)\right]$$

$$\dot{Q} = \dot{m}_C C_{Pc}\left[(T_{a1} - T) - (T_{a1} - T)\exp\left(-\frac{UA}{\dot{m}C_{Pc}}\right)\right]$$

$$\dot{Q} = \dot{m}_C C_{Pc}(T_{a1} - T)\left[1 - \exp\left(-\frac{UA}{\dot{m}C_{Pc}}\right)\right]$$

At high coolant flow rates the exponential term will be small, so we can expand the exponential term as a Taylor Series, where the terms of second order or greater are neglected, then:

$$\dot{Q} = \dot{m}_C C_{Pc}(T_{a1} - T)\left[1 - \exp\left(-\frac{UA}{\dot{m}C_{Pc}}\right)\right]$$

$$\dot{Q} = \dot{m}_C C_{Pc}\left(T_{a1} - T\right)\left[1 - \left(1 - \frac{UA}{\dot{m} C_{Pc}}\right)\right] = \dot{m}_C C_{Pc}\left(T_{a1} - T\right)\left(\frac{UA}{\dot{m} C_{Pc}}\right)$$

$$\dot{Q} = UA\left(T_{a1} - T\right)$$

Since the coolant flow rate is high, $T_{a1} \cong T_{a2} \cong T_a$:

$$\dot{Q} = UA\left(T_a - T\right)$$

Reversible Reactions (Chp8 Fogler, Appendix C)

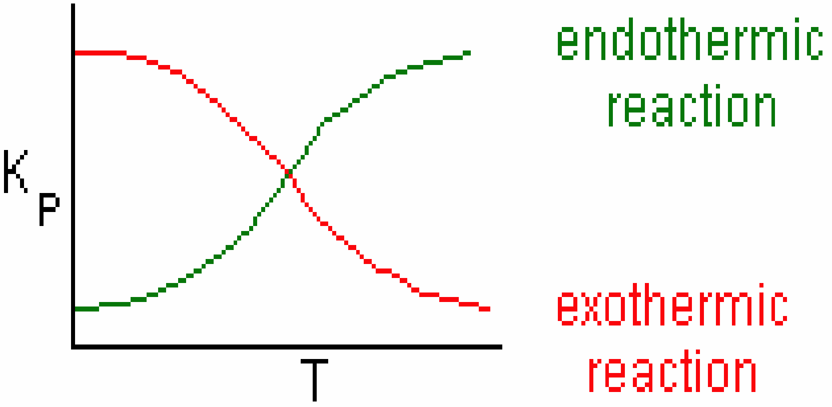
For Ideal gases, K_C and K_P are related by

$$K_P = K_C(RT)^{\delta}$$

$$\delta = \Sigma \nu_i$$

$$K_C = \frac{K_P}{(RT)^{\delta}}$$

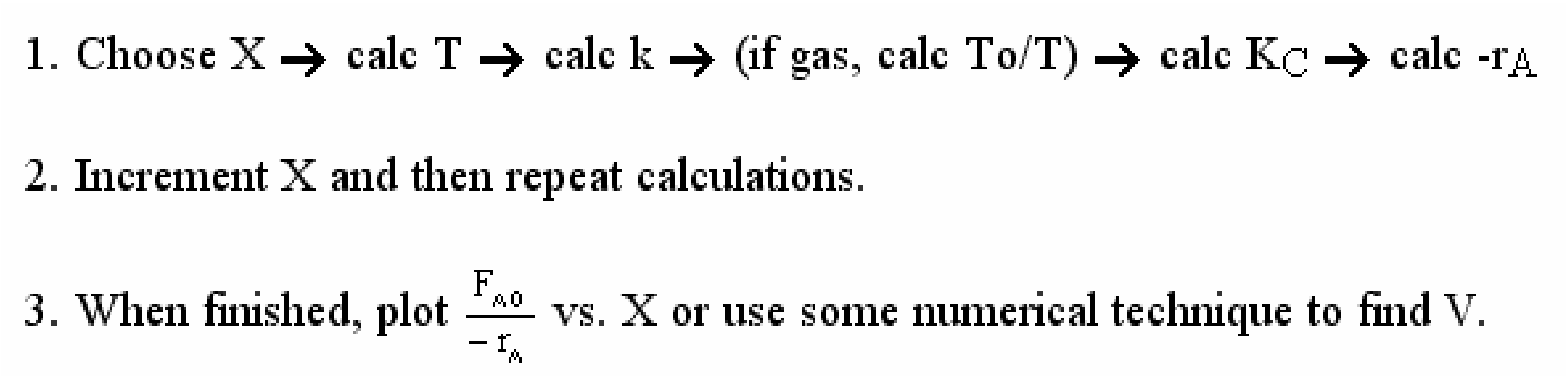
$$\frac{d\ln K_P}{dT} = \frac{\Delta H_R(T)}{RT^2} = \frac{\Delta H_R^o(T_R) + \Delta\hat{C}_P(T - T_R)}{RT^2}$$



For the special case of $\Delta\hat{C}_P = 0$:

$$\boxed{K_P(T_2) = K_P(T_1)\exp\left[\frac{\Delta H_R^o(T_R)}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]}$$

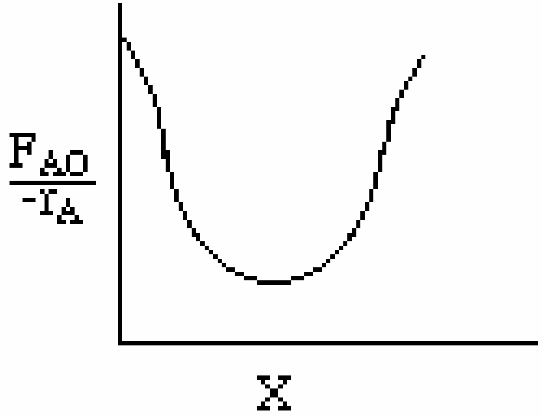
Algorithm for Adiabatic Reactions:



1. Choose X → calc T → calc k → (if gas, calc To/T) → calc K_C → calc $-r_A$

2. Increment X and then repeat calculations.

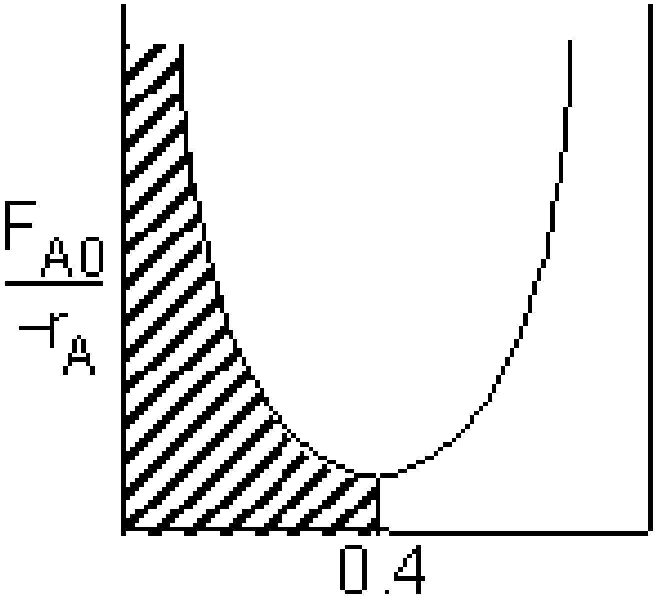
3. When finished, plot $\frac{F_{A0}}{-r_A}$ vs. X or use some numerical technique to find V.



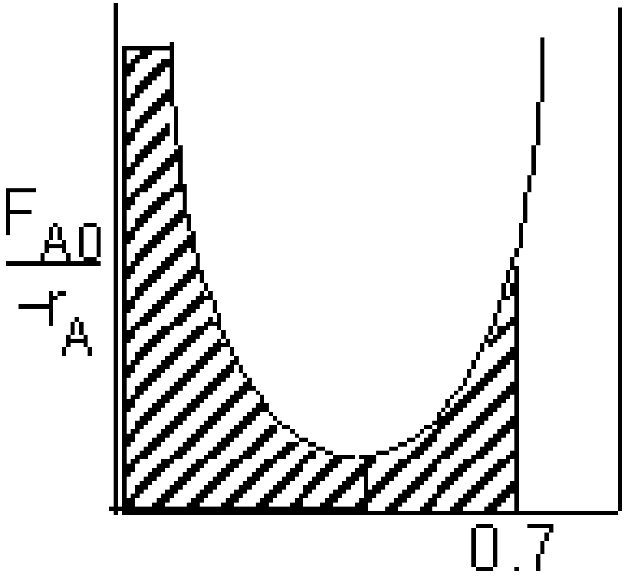
Levenspiel Plot for an exothermal, adiabatic reaction.

PFR  (The shaded area in the plot is the volume.)

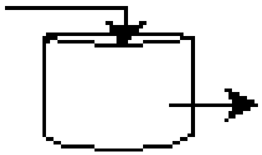
For an exit conversion of 40%



For an exit conersion of 70%

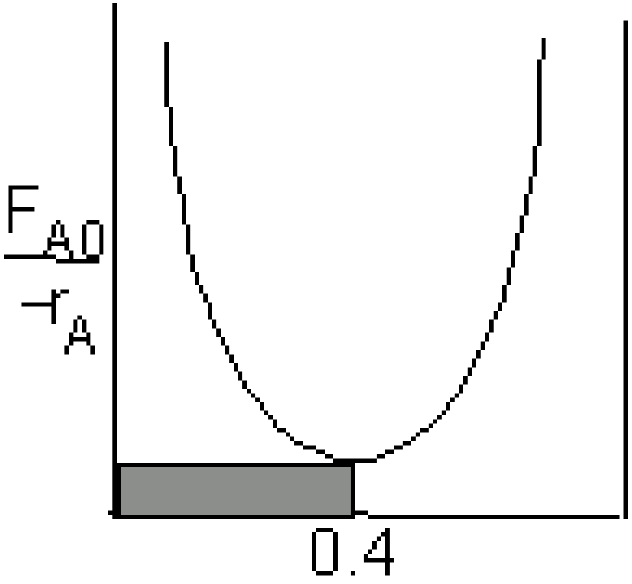


CSTR

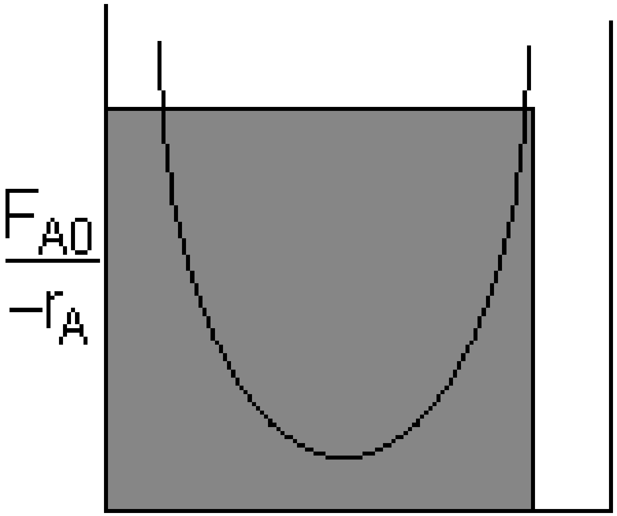


Shaded area is the reactor volume.

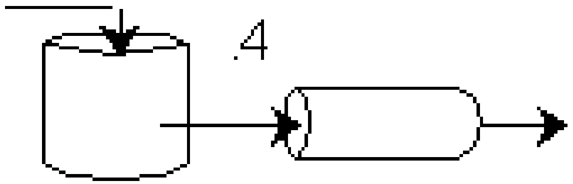
For an exit conversion of 40%

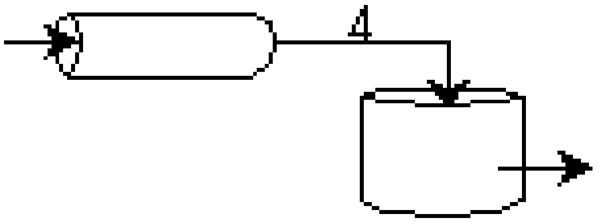


For an exit conersion of 70%

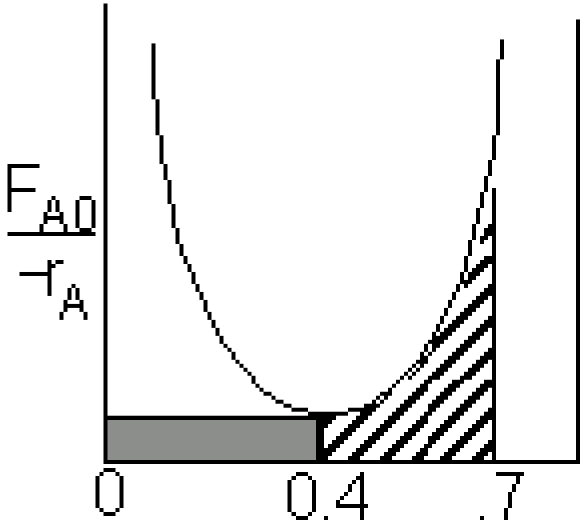


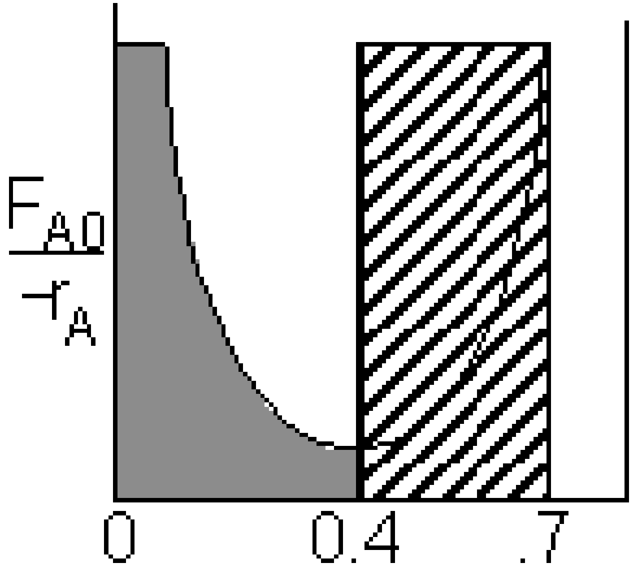
CSTR+PFR





For an intermediate conversion of 40% and exit conversion of 70%





Example: Exothermic, Reversible Reaction

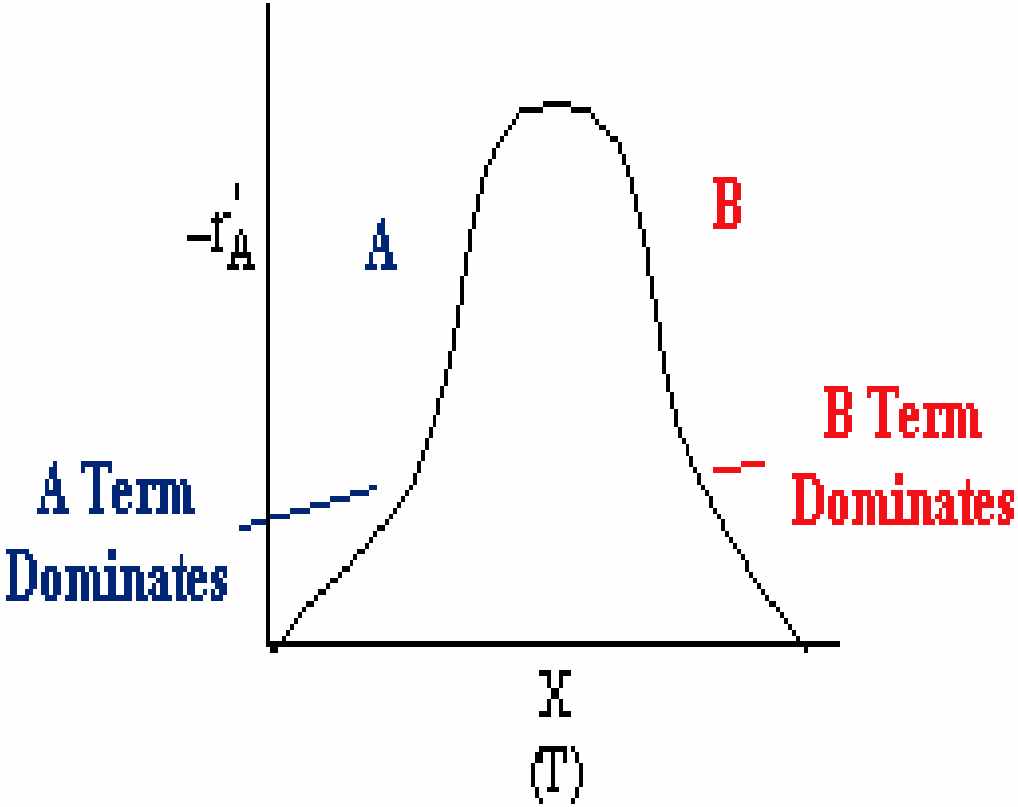
Why is there a maximum in the rate of reaction with respect to conversion (and hence, with respect to temperature and reactor volume) for an adiabatic reactor?

Rate Law:

$$-r_A' = k\left[C_A C_B - \frac{C_C^2}{K_C}\right]$$

$$-r_A' = \underbrace{\left[A\exp\left(-\frac{E}{RT}\right)\right]}_{\mathbf{A}}\underbrace{\left[C_{A0}^2\left((1-X)(2-X)-\frac{4X^2}{K_C}\right)\left(\frac{T_0}{T}y\right)^2\right]}_{\mathbf{B}}$$

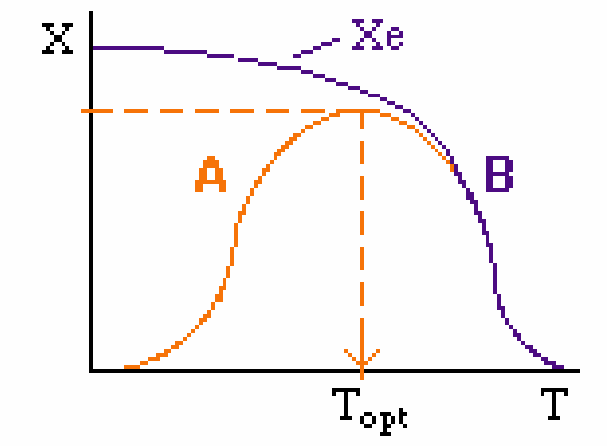
$$T = T_0 - \frac{X\Delta H_{RX}}{\Sigma\Theta_i C_{Pi} + X\Delta C_P}$$



A ↑ with ↑ T

B ↓ with ↑ X & ↑ T

Reactor Inlet Temperature and Inter stage Cooling



Optimum Inlet Temperature:

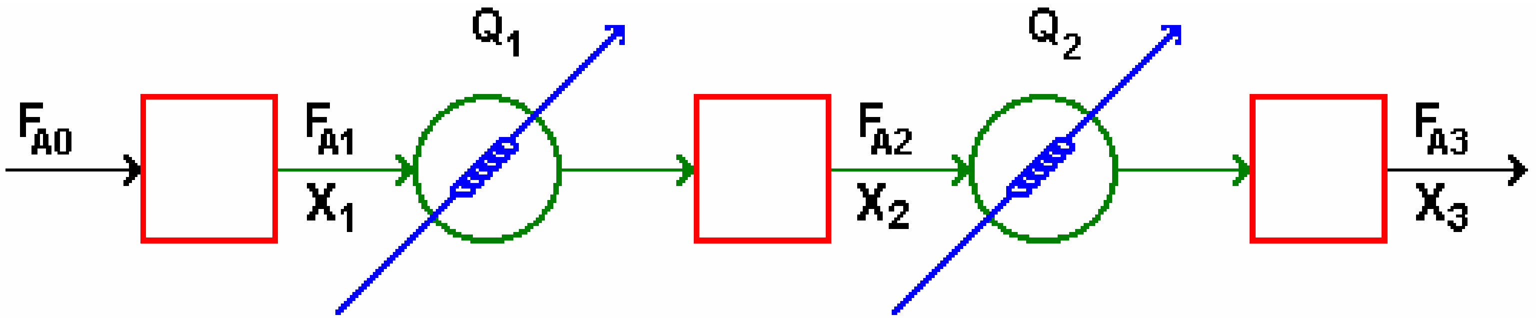
Fixed Volume Exothermic Reactor

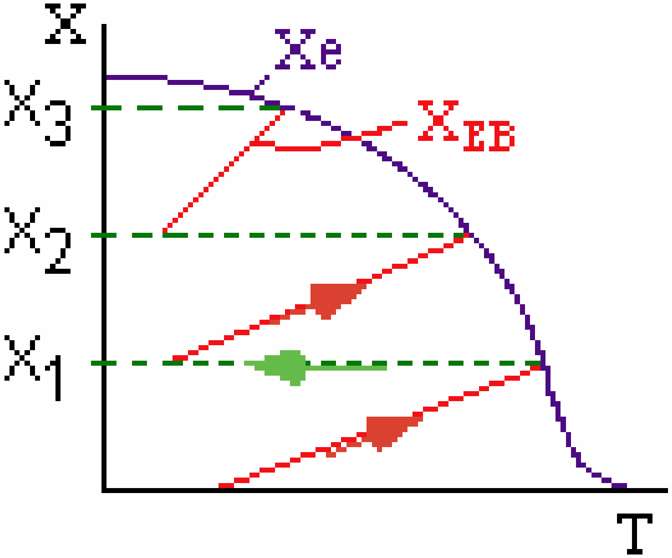
$$A + B \leftrightarrow 2C$$

Curve A: Reaction rate slow, conversion dictated by rate of reaction and reactor volume. As temperature increases rate increases and therefore conversion increases.

Curve B: Reaction rate very rapid. Virtual equilibrium reached in reaction conversion dictated by equilibrium conversion.

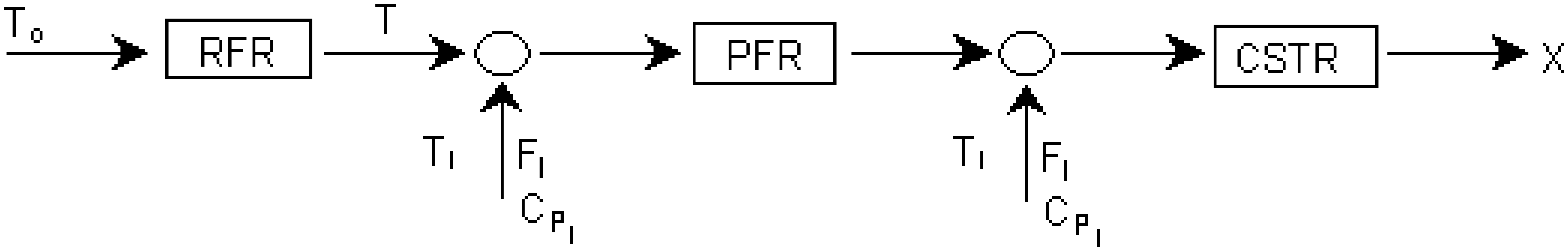
Interstage Cooling:





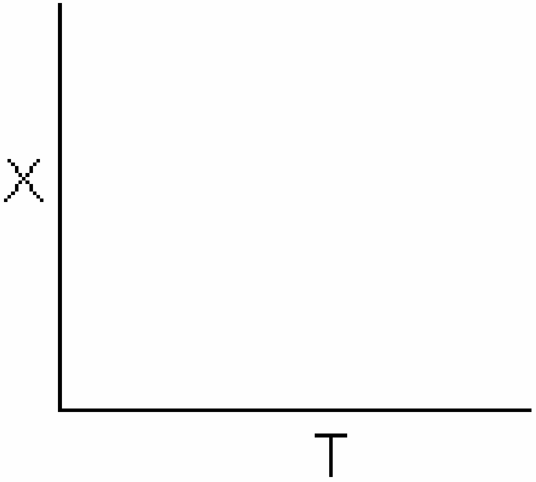
Self Test

An inert **I** is injected at the points shown below:



Sketch the conversion-temperature trajectory for an endothermic reaction.

$$A \rightleftarrows B$$

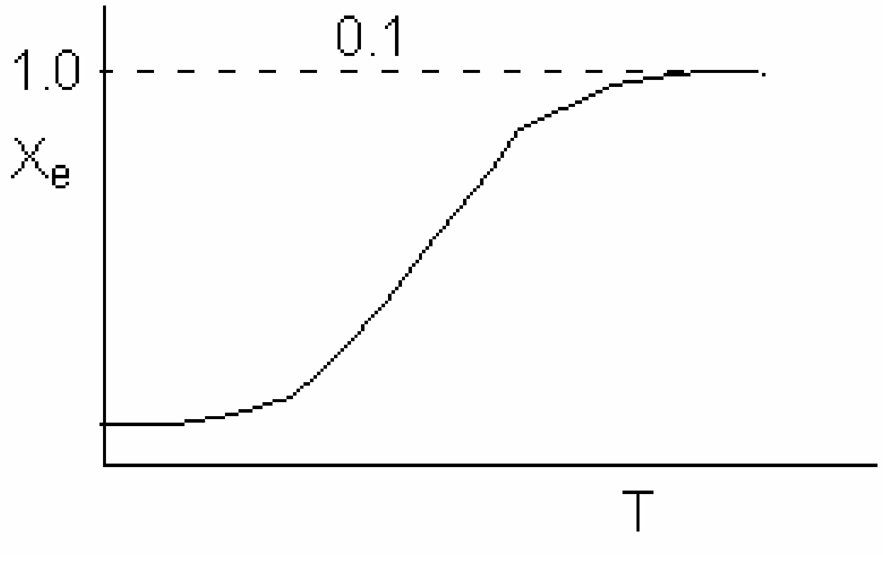


Solution

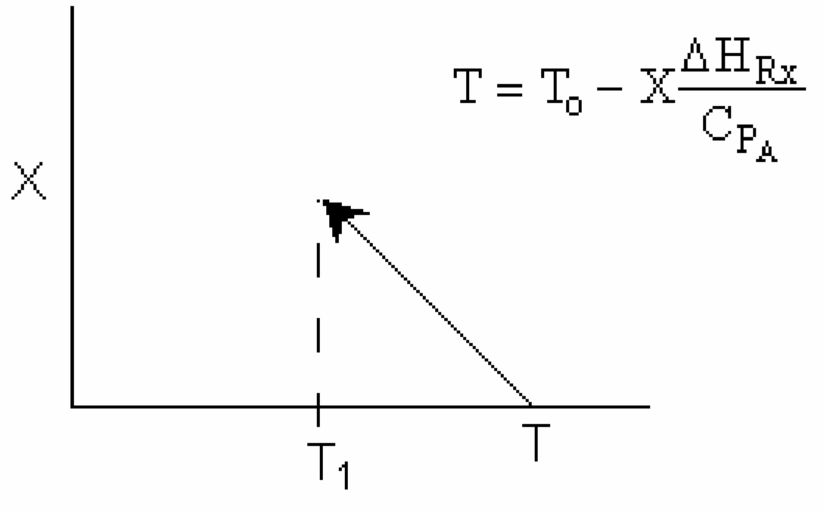
For an endothermic reaction, the equilibrium conversion increases with increasing T.

For $\frac{\Delta H^\circ_{Rx}}{R} = +10000\ K^{-1}$ and K_{eq}=.1 and T_2

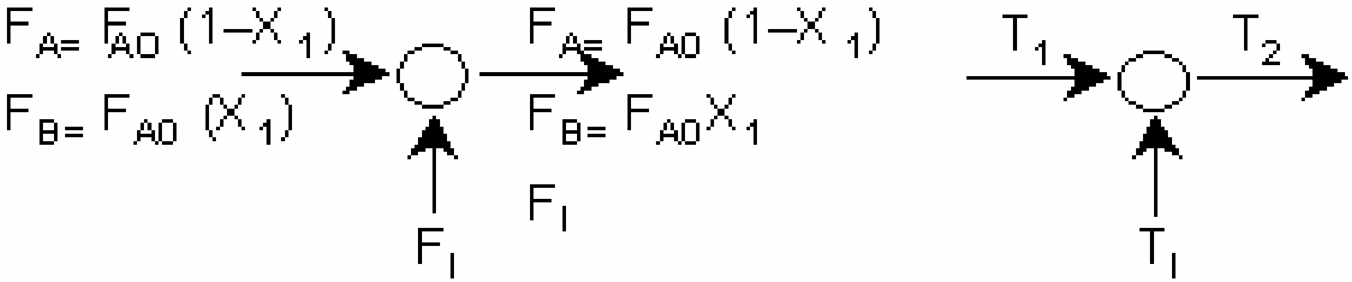
$$K_{eq} = \exp\left[10000\right]\left[\frac{1}{T_2} - \frac{1}{T}\right]$$



From the energy balance we know the temperature decreases with increasing conversion.



$$T = T_o - X\frac{\Delta H_{Rx}}{C_{P_A}}$$

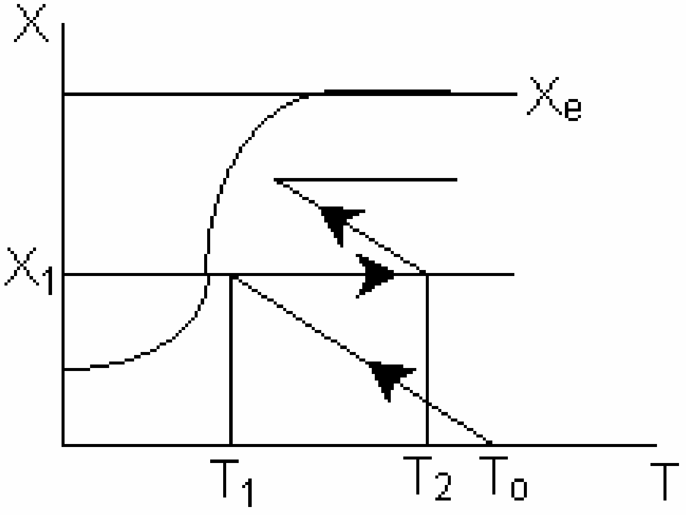


Energy Balance around junction:

$$F_A C_{P_A}(T_1 - T_R) + F_B C_{P_B}(T_1 - T_R) + F_I C_{P_I}(T_I - T_R)$$
$$= F_A C_{P_A}(T_2 - T_R) + F_B C_{P_B}(T_2 - T_R) + F_I C_{P_I}(T_2 - T_R)$$

Solving T2

$$T_2 = T_R + \frac{F_{A0} C_{P_A}(1 - X_1)(T_1 - T_R) + F_{A0} C_{P_B} X_1 (T - T_R) + F_I C_{P_I}(T_I - T_R)}{F_{A0} C_P (1 - X_1) + F_{A0} C_{P_B} X_1 + F_I C_{P_I}}$$

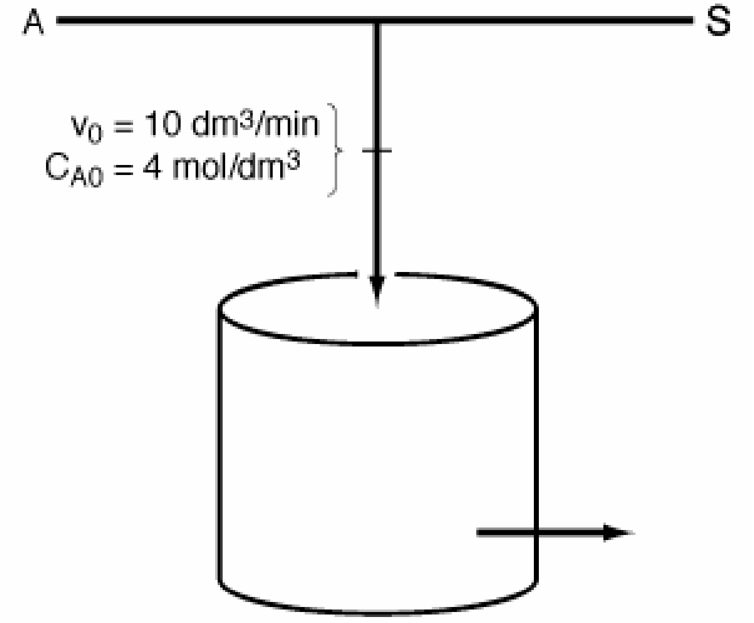


Example CD8-2
Second Order Reaction Carried Out Adiabatically in a CSTR

The acid-catalyzed irreversible liquid-phase reaction

$$A \longrightarrow B$$

is carried out adiabatically in a CSTR.



The reaction is second order in A. The feed, which is equimolar in a solvent (which contains the catalyst) and A, enters the reactor at a total volumetric flowrate of 10 dm^3/min with the concentration of A being 4M. The entering temperature is 300 K.

a) What CSTR reactor volume is necessary to achieve 80% conversion?
b) What conversion can be achieved in a 1000 dm^3 CSTR? What is the new exit temperature?
c) How would your answers to part (b) change, if the entering temperature of the feed were 280 K?

Additional Information:

$$\Delta H_{Rx}(300\ \text{K}) = -3300\ \text{cal/mol}\cdot{}^{\circ}\text{C}$$

$$C_{P_A} = 15\ \text{cal/mol}\cdot{}^{\circ}\text{C}$$

$$C_{P_B} = 15\ \text{cal/mol}\cdot{}^{\circ}\text{C}$$

$$C_{P_S} = 18\ \text{cal/mol}\cdot{}^{\circ}\text{C}$$

$$k(300\ \text{K}) = 0.0005\ \text{dm}^3/\text{mol}\cdot\text{min}$$

$$E = 15{,}000\ \text{cal/mol}$$

Example CD8-2 Solution, Part A Second Order Reaction Carried Out Adiabatically in a CSTR

(a) We will solve part (a) by using the nonisothermal reactor design algorithm discussed in Chapter 8.

1. CSTR Design Equation: $V = \frac{F_{A0}X}{-r_A}$

2. Rate Law: $-r_A = kC_A^2$

3. Stoichiometry: liquid, $\upsilon = \upsilon_0$

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

4. Combine:

$$V = \frac{F_{A0}X}{kC_A^2} = \frac{C_{A0}\upsilon_0 X}{k[C_{A0}(1-X)]^2}$$

$$V = \frac{\upsilon_0 X}{kC_{A0}(1-X)^2}$$

Given conversion (X), you must first determine the reaction temperature (T), and then you can calculate the reactor volume (V).

5. Determine T:

$$T = \frac{X[-\Delta H_{Rx}(T_R)] + \sum \Theta_i \tilde{C}_{P_i} T_0 + X\Delta\hat{C}_P T_R}{\sum \Theta_i \tilde{C}_{P_i} + X\Delta\hat{C}_P}$$

For this problem:

$$\Delta\hat{C}_P = C_{P_B} - C_{P_A} = (15-15)\text{cal/mol} \cdot {}^\circ\text{C} = 0$$

which leaves us with: $T = \dfrac{X\left[-\Delta H_{Rx}(T_R)\right] + \sum \Theta_i \tilde{C}_{P_i} T_0}{\sum \Theta_i \tilde{C}_{P_i}}$

After some rearranging we are left with:

$$T = T_0 + \frac{X\left[-\Delta H_{Rx}(T_R)\right]}{\sum \Theta_i \tilde{C}_{P_i}}$$

Substituting for known values and solving for T:

$$T = 300\,\mathrm{K} + \frac{(0.8)\left[-(-3300\,\mathrm{cal/mol})\right]}{\left[(15+18)(\mathrm{cal/mol\cdot {}^\circ C})\right]}$$

$$T = 380\,\mathrm{K}$$

6. Solve for the Rate Constant (k) at T = 380 K:

$$k(T) = k(T_1)\exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

$$k(380\,K) = \left(0.0005\,\frac{dm^3}{mol\cdot min}\right)\exp\left[\frac{\left(15{,}000\,\frac{cal}{mol}\right)}{\left(1.987\,\frac{cal}{mol\cdot K}\right)}\left(\frac{1}{300K} - \frac{1}{380K}\right)\right]$$

$$k = 0.1\ dm^3/mol\cdot min$$

7. Calculate the CSTR Reactor Volume (V):

Recall that: $V = \dfrac{\upsilon_0 X}{kC_{A0}(1-X)^2}$

Substituting for known values and solving for V:

$$V = \frac{\left(10\,\frac{dm^3}{min}\right)(0.8)}{\left(0.1\frac{dm^3}{mol\cdot min}\right)\left(4\,\frac{mol}{dm^3}\right)(1-0.8)^2}$$

$$\boxed{V = 500\,dm^3}$$

Example CD8-2 Solution, Part B
Second Order Reaction Carried Out Adiabatically in a CSTR

(b) For part (b) we will again use the nonisothermal reactor design algorithm discussed in Chapter 8. The first four steps of the algorithm we used in part (a) apply to our solution to part (b). It is at step number 5, where the algorithm changes.

NOTE: We will find it more convenient to work with this equation in terms of space time, rather than volume:

Space time is defined as: $\tau = \frac{V}{\upsilon_0}$

After some rearranging: $\frac{V}{\upsilon_0} = \frac{1}{kC_{A0}} \frac{X}{(1-X)^2}$

Substituting: $\tau = \frac{1}{kC_{A0}} \frac{X}{(1-X)^2}$

Given reactor volume (V), you must solve the energy balance and the mole balance simultaneously for conversion (X), since it is a function of temperature (T).

5. Solve the Energy Balance for X_{EB} as a function of T:

From the adiabatic energy balance (as applied to CSTRs):

$$X_{EB} = \frac{\sum \Theta_i \tilde{C}_{P_i}\left(T - T_0\right)}{-\Delta H_{Rx}\left(T_R\right)}$$

$$X_{EB} = \frac{\left(C_{P_A} + C_{P_S}\right)\left(T - T_0\right)}{-\Delta H_{Rx}\left(T_R\right)}$$

6. Solve the Mole Balance for X_{MB} as a function of T:

We'll rearrange our combined equation from step 4 to give us:

$$\tau k C_{A0} = \frac{X}{(1-X)^2}$$

Rearranging gives:

$$\tau k C_{A0} - 2\tau k C_{A0} X + \tau k C_{A0} X^2 = X$$

$$\tau k C_{A0} - (2\tau k C_{A0} + 1)X + \tau k C_{A0} X^2 = 0$$

Solving for X gives us:

$$X = \frac{(2\tau k C_{A0} + 1) - \sqrt{(2\tau k C_{A0} + 1)^2 - 4(\tau k C_{A0})^2}}{2(\tau k C_{A0})}$$

$$X = \frac{(2\tau k C_{A0} + 1) - \sqrt{4(\tau k C_{A0})^2 + 4\tau k C_{A0} + 1 - 4(\tau k C_{A0})^2}}{2(\tau k C_{A0})}$$

After some final rearranging we get:

$$X_{MB} = \frac{(2\tau k C_{A0} + 1) - \sqrt{4\tau k C_{A0} + 1}}{2(\tau k C_{A0})}$$

Let's simplify a little more, by introducing the Damköhler Number, Da:

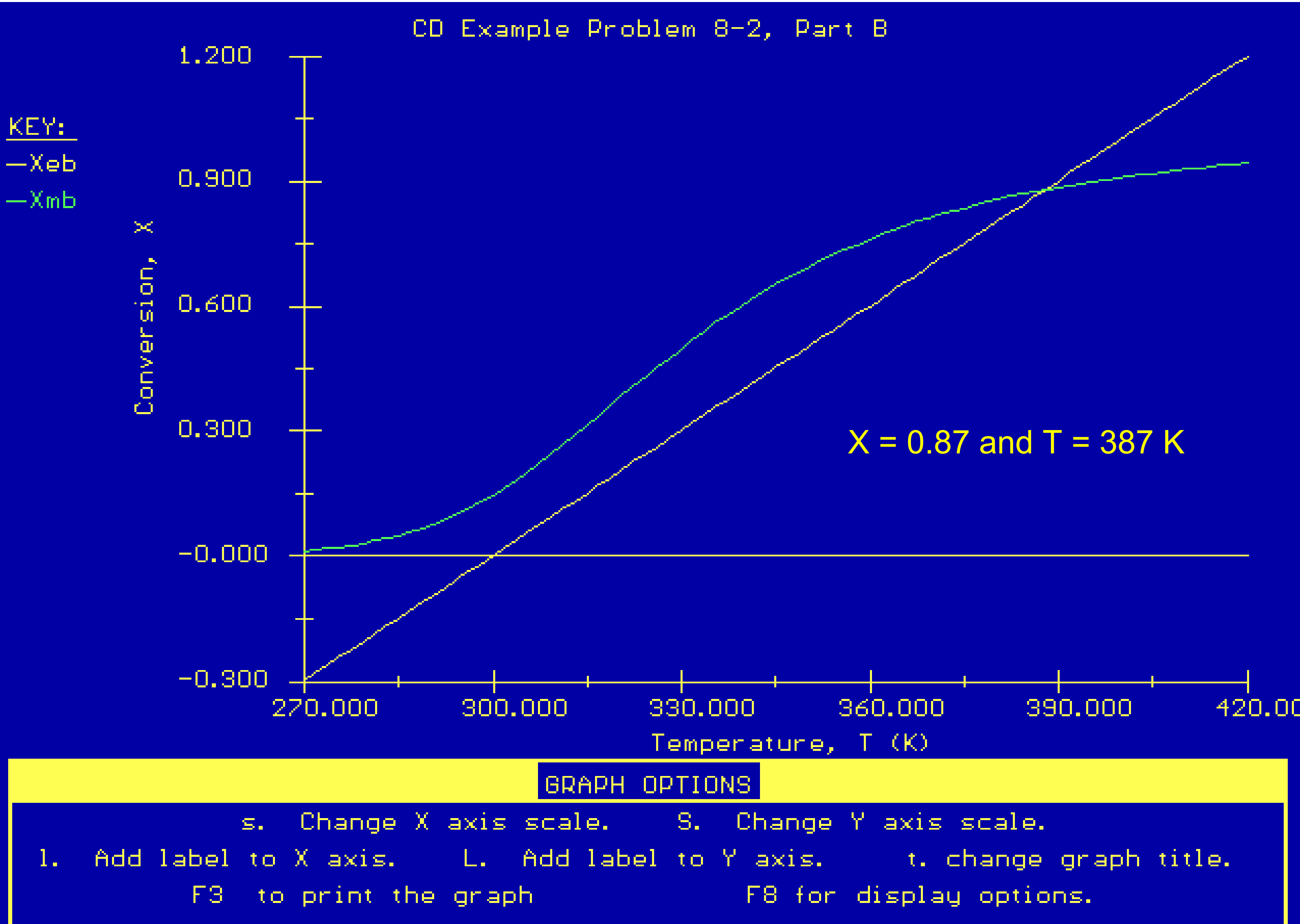
$$Da = \tau k C_{A0}$$

We then have:

$$X_{MB} = \frac{(2Da+1) - \sqrt{4Da+1}}{2(Da)}$$

7. Plot X_{EB} and X_{MB}:

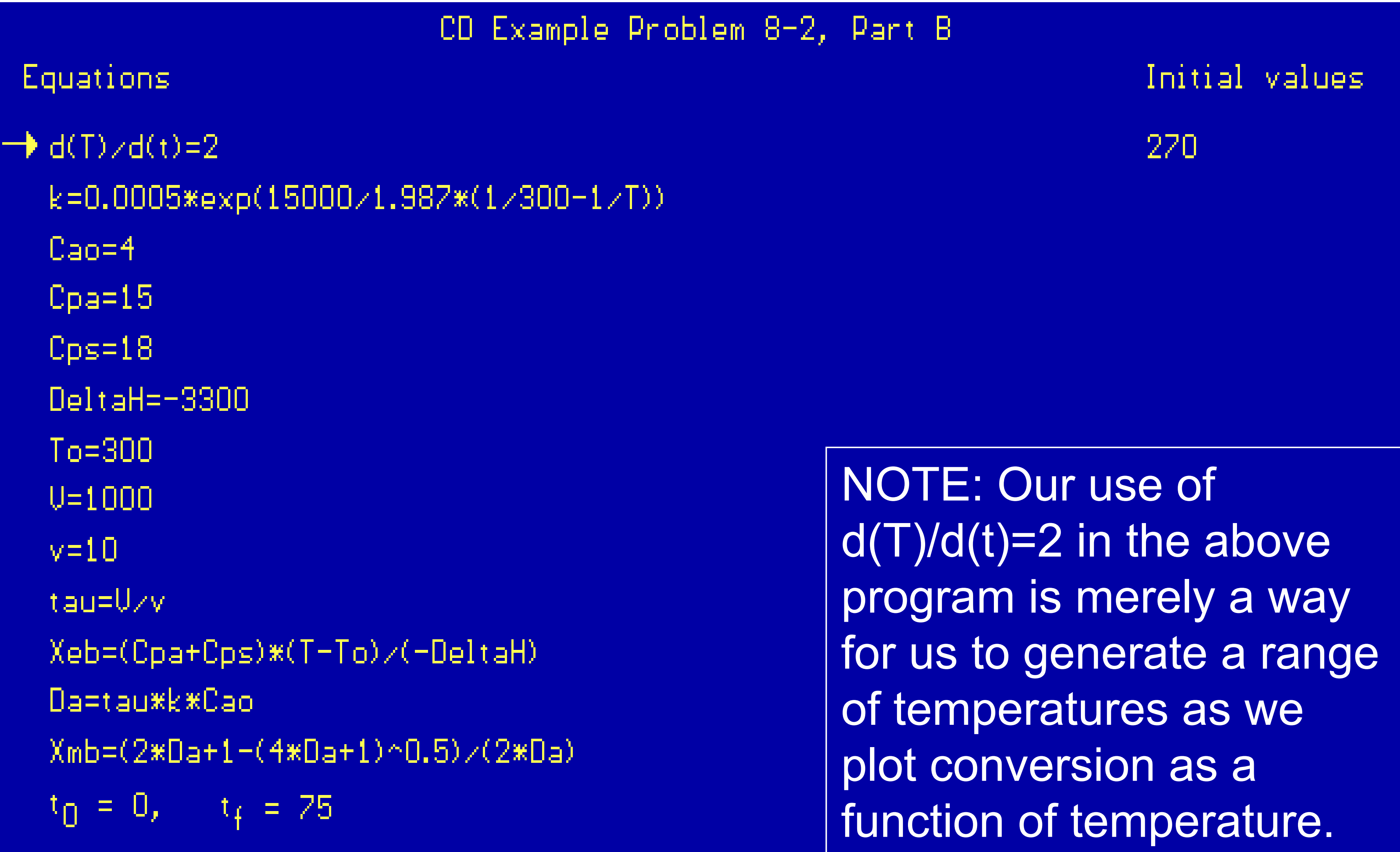
You want to plot XEB and XMB on the same graph (as functions of T) to see where they intersect. This will tell you where your steady-state point is. To accomplish this, we will use Polymath (but you could use a spreadsheet).



CD Example Problem 8-2, Part B

X = 0.87 and T = 387 K

Our corresponding Polymath program looks like this:



```
                         CD Example Problem 8-2, Part B
Equations                                                          Initial values

→ d(T)/d(t)=2                                                      270
  k=0.0005*exp(15000/1.987*(1/300-1/T))
  Cao=4
  Cpa=15
  Cps=18
  DeltaH=-3300
  To=300
  V=1000
  v=10
  tau=V/v
  Xeb=(Cpa+Cps)*(T-To)/(-DeltaH)
  Da=tau*k*Cao
  Xmb=(2*Da+1-(4*Da+1)^0.5)/(2*Da)
  t0 = 0,    tf = 75
```

NOTE: Our use of d(T)/d(t)=2 in the above program is merely a way for us to generate a range of temperatures as we plot conversion as a function of temperature.

Example CD8-2 Solution, Part C Second Order Reaction Carried Out Adiabatically in a CSTR

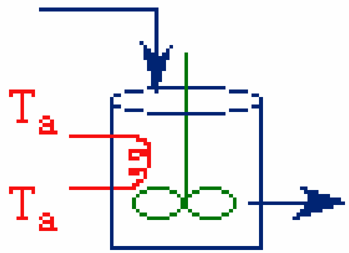
(c) For part (c) we will simply modify the Polymath program we used in part (b), setting our initial temperature to 280 K. All other equations remain unchanged.

7. Plot X_{EB} and X_{MB}:

We see that our conversion would be about 0.75, at a temperature of 355 K.

Multiple Steady States

$$\dot{Q} - \dot{W}_S - F_{A0}\sum \Theta_i \tilde{C}_{Pi}(T - T_0) + (r_A V)(\Delta H_R(T)) = 0$$



$$\dot{W}_S \cong 0$$

$$UA(T_A - T) - F_{A0}\overbrace{\sum \Theta_i \hat{C}_{Pi}}^{C_{P0}}(T - T_0) + (r_A V)(\Delta H_R(T)) = 0$$

Factor F_{A0} C_{P0} and then divide by F_{A0}

$$-C_{P0}\left[(T - T_0) + \frac{UA}{F_{A0}C_{P0}}(T - T_A)\right] + \left[\frac{(r_A V)(\Delta H_R)}{F_{A0}}\right] = 0$$

$$\boxed{\kappa = \frac{UA}{F_{A0}C_{P0}}, \quad T_C = \frac{T_0 + \kappa T_A}{1+\kappa}}$$

$$\left[\frac{(r_A V)(\Delta H_R(T))}{F_{A0}}\right] - \left[C_{P0}(1+\kappa)(T - T_C)\right] = 0$$

For a CSTR: $F_{A0}X = -r_A V$

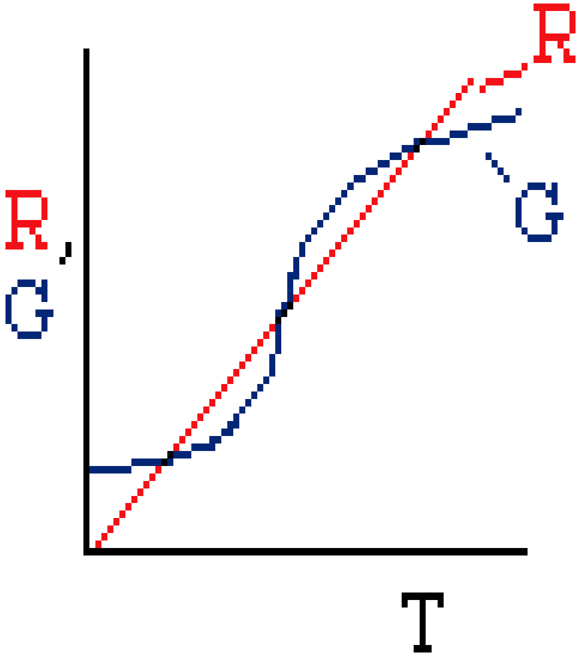
$$\left[X(-\Delta H_R(T))\right] - \left[C_{P0}(1+\kappa)(T - T_C)\right] = 0$$

$$G(T) - R(T) = 0$$

where

$$\boxed{G(T) = \left(\frac{-r_A V}{F_{A0}}\right)(-\Delta H_R(T)) = X(-\Delta H_R(T))}$$

$$\boxed{R(T) = C_{P0}(1+\kappa)(T - T_C)}$$



R > G: Temp. will decrease

R < G: Temp. will increase

Self Test

Can there be multiple steady states (MSS) for a irreversible first order endothermic reaction?

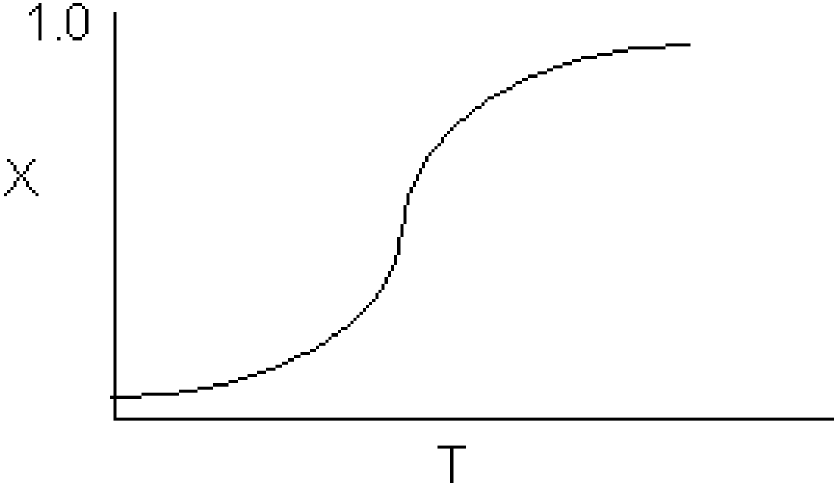
Solution

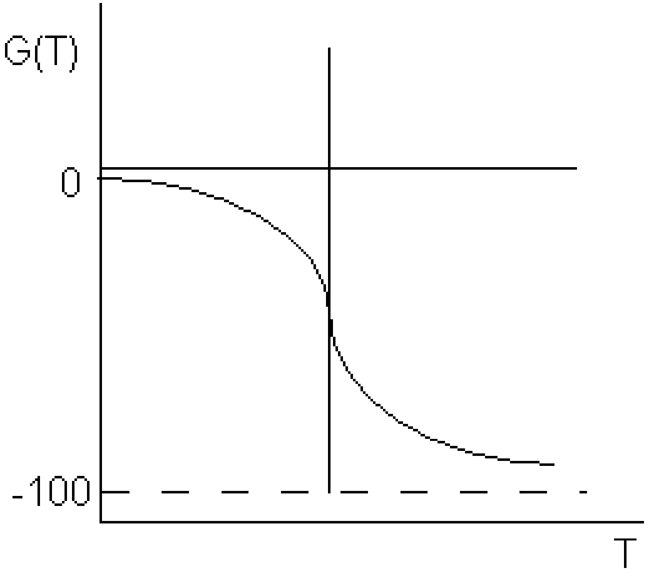
$$G(T) = (X)(-\Delta H_{Rx})$$

For an endothermic reaction H_{RX} is positive, (e.g., H_{RX}=+100 kJ/mole)

$$G(T) = -100 \quad X$$

$$X = \frac{\tau k}{1+\tau k} = \frac{\tau A e^{-E/RT}}{1+\tau A e^{-E/RT}}$$



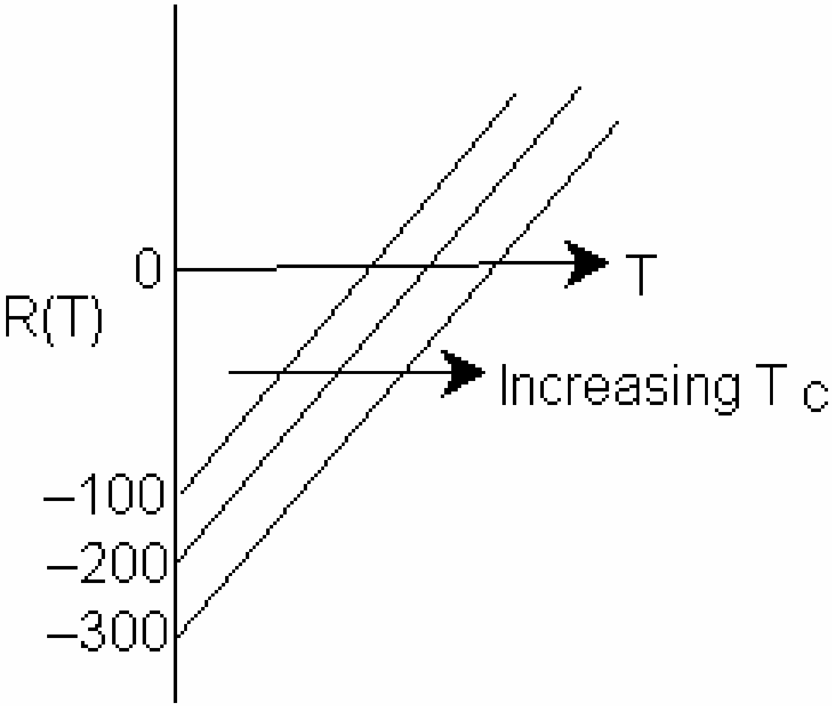


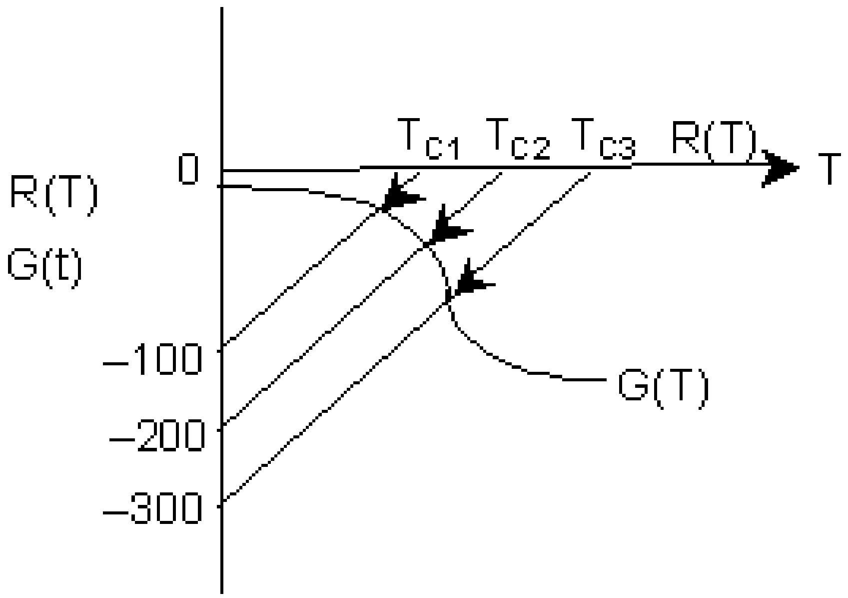
$$G = -\Delta H_{RX}$$

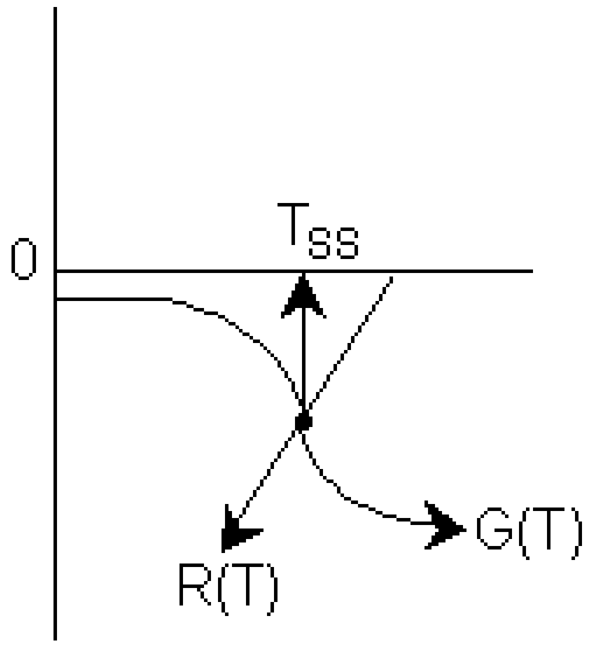
$$G = -100\frac{\tau A e^{-E/RT}}{1+\tau A e^{-E/RT}}$$

$$R(T) = C_{P_0}(1+K)(T-T_C)$$

$$T_C = \frac{T_o + \kappa T_a}{1+\kappa}$$







There are no multiple steady states for an endothermic, irreversible first order reactor. The steady state reactor temperature is T_S. Will a *reversible* endothermic first order reaction have M_{SS}?

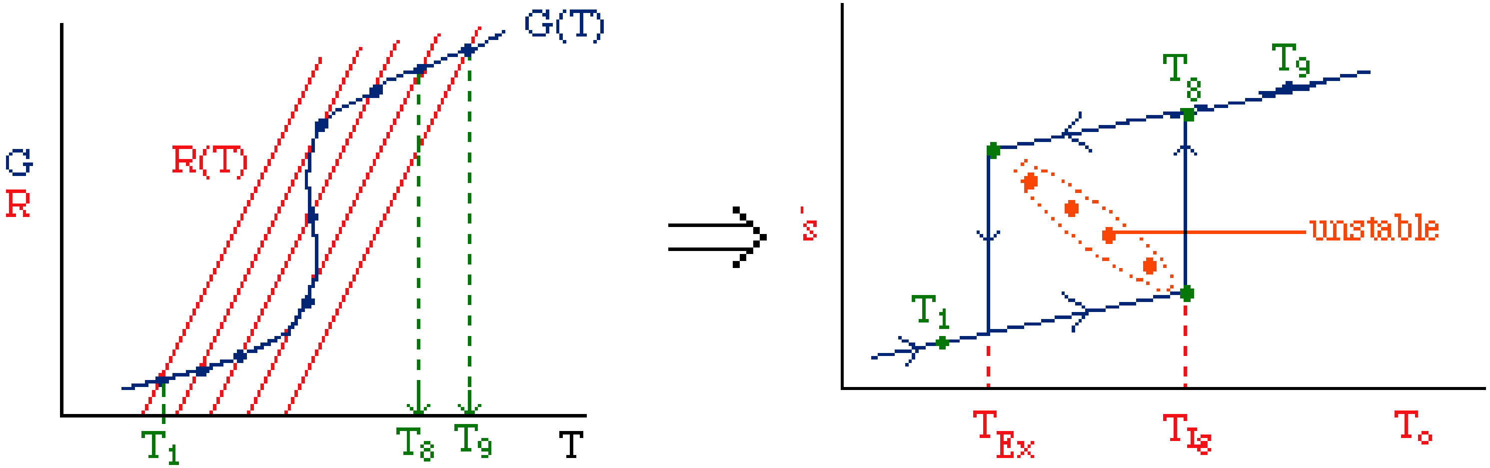
Now we need to find X. We do this by combining the mole balance, rate law, Arrhenius Equation, and stoichiometry.

For the first-order, irreversible reaction A → B, we have:

$$X = \frac{\tau k}{1+\tau k} \qquad \text{where} \qquad \tau k = \left(\frac{V}{v_0}\right) A e^{-E/RT}$$

At steady state:

$$\underbrace{\frac{\tau k}{1+\tau k}(-\Delta H_R)}_{G(T)} = \underbrace{C_{P0}(1+\kappa)\ (T-T_C)}_{R(T)}$$



Unsteady State CSTR

Balance on a system volume that is well-mixed:

$$\dot{Q} - \dot{W}_S + \Sigma F_{io}H_{io} - \Sigma F_i H_i = \frac{dE_{sys}}{dt} = \frac{d\Sigma N_i E_i}{dt} = \frac{d\Sigma N_i H_i}{dt} = \Sigma H_i \frac{dN_i}{dt} + \Sigma N_i \frac{dH_i}{dt}$$

$$F_{io} - F_i + r_i V = \frac{dN_i}{dt} \qquad \frac{dH_i}{dt} = C_{P_i}\frac{dT}{dt}$$

$$\dot{Q} - \dot{W}_S + \Sigma F_{io}H_{io} - \Sigma F_i H_i = \Sigma H_i (F_{io} - F_i + r_i V) + \Sigma N_i C_{P_i}\frac{dT}{dt} = \Sigma H_i F_{io} - \Sigma H_i F_i + \Sigma r_i V H_i + \Sigma N_i C_{P_i}\frac{dT}{dt}$$

$$r_i = \nu_i(-r_A)$$

$$\dot{Q} - \dot{W}_S + \Sigma F_{io}(H_{io} - H_o) = -r_A V \Sigma \nu_i H_i + \Sigma N_i C_{P_i}\frac{dT}{dt}$$

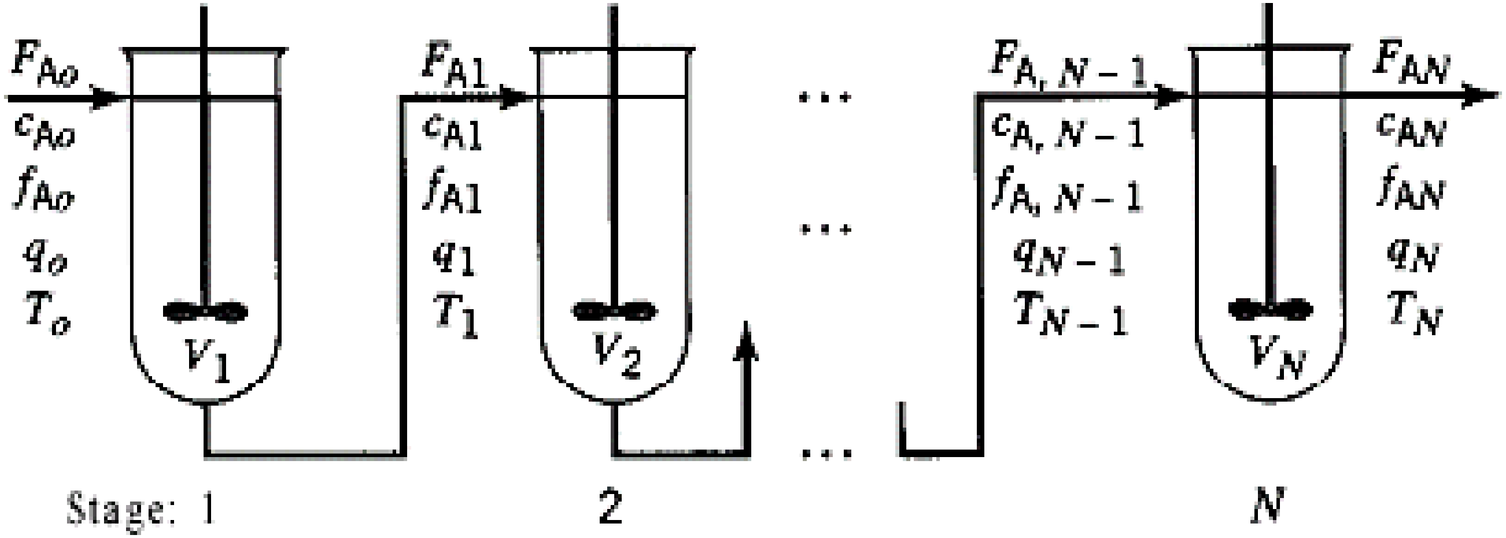
$$\boxed{\dot{Q} - \dot{W}_S + (r_A V)[\Delta H_R(T)] = \Sigma F_{io}(H_i - H_{io}) + \Sigma N_i C_{P_i}\frac{dT}{dt}}$$

$$\boxed{\dot{Q} - W_S - F_{A0}\Sigma \Theta_i \tilde{C}_{P_i}(T - T_o) + (r_A V)[\Delta H_R(T)] = \Sigma N_i C_{P_i}\frac{dT}{dt}}$$

RATB Bertingkat (Multistage)

- RATB bertingkat terdiri atas 2 atau lebih reaktor tangki berpengaduk yang disusun seri
- Keuntungan RATB bertingkat dua atau lebih, untuk mencapai hasil yg sama? ukuran/ volume reaktor lebih kecil dibandingkan RATB tunggal
- Kerugian utama RATB bertingkat beroperasi pada konsentrasi yang lebih rendah diantara pemasukan dan pengeluaran
- Untuk RATB tunggal, berarti bahwa beroperasi pada konsentrasi dalam sistem serendah mungkin, dan untuk kinetika normal, diperlukan volume reaktor semakin besar
- Bila 2 tangki (beroperasi pd T sama) disusun seri, yang kedua beroperasi pada konsentrasi sama spt tangki tunggal diatas, tapi yg pertama beroperasi pada konsentrasi lebih tinggi, jadi volume total kedua tangki lebih kecil daripada tangki tunggal

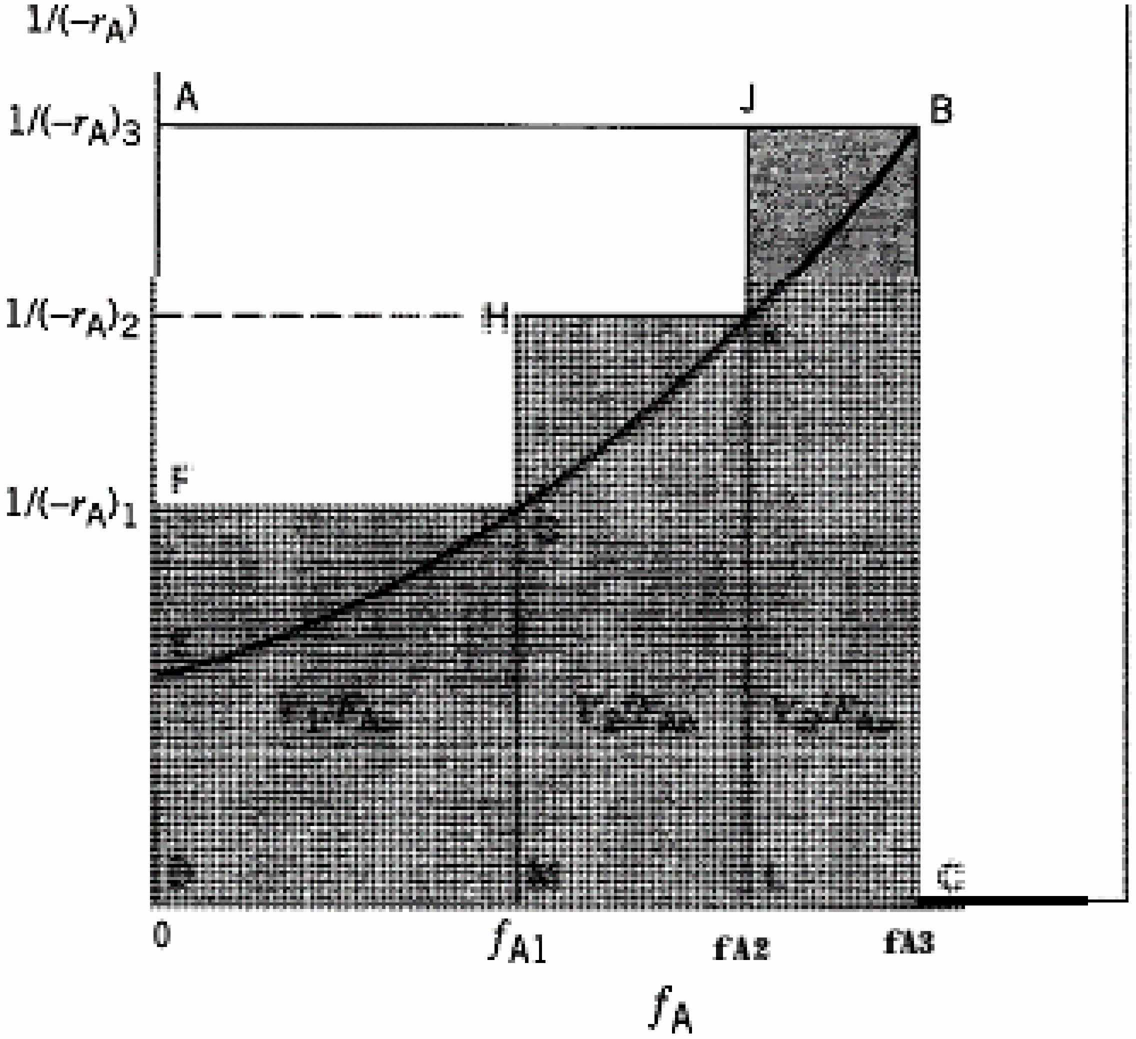
Rangkaian RATB bertingkat N



Pers neraca massa pada RATB ke i

$$V_i = F_{Ao}(f_{Ai} - f_{A,i-1})/(-r_A)_i \qquad (14.4\text{-}1)$$

Grafik ilustrasi operasi 3 RATB seri



Penyelesaian pers 14.4-1 untuk mencari V (diberi f_A) atau mencari f_A (diberi V) dapat dilakukan secara grafik atau secara analitis. Cara grafik dapat digunakan untuk mencari f_A, atau bila bentuk analitis $(-r_A)$ tidak diketahui

Penyelesaian grafis untuk N = 2

Untuk stage 1: $(-r_{\mathrm{A}})_1 = (F_{\mathrm{A}o}/V_1)f_{\mathrm{A}1}$

Untuk stage 2: $(-r_{\mathrm{A}})_2 = (F_{\mathrm{A}o}/V_2)(f_{\mathrm{A}2} - f_{\mathrm{A}1})$

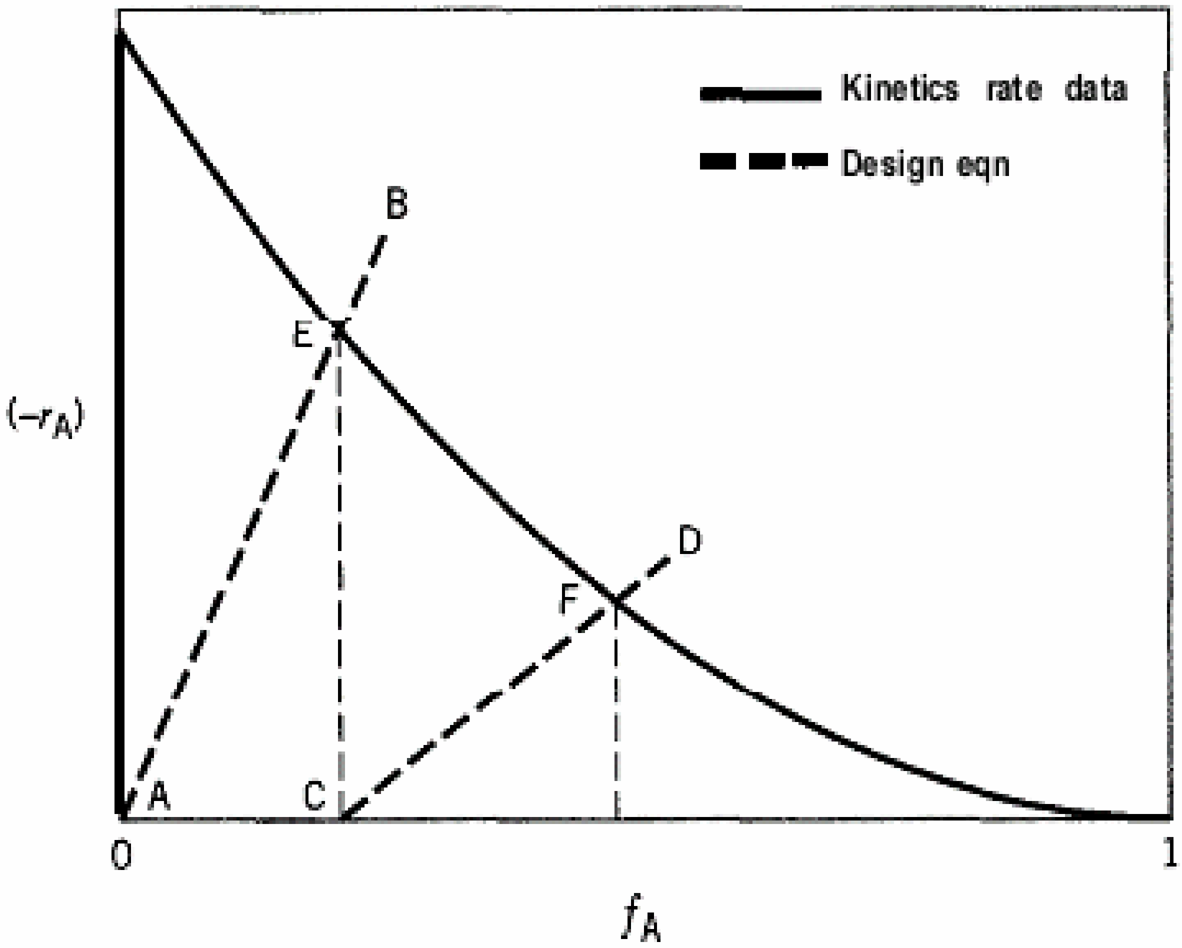


Figure 14.11 Basis for graphical solution for multistage CSTR (for A + … → products)

Example 14-9

A three-stage CSTR is used for the reaction A → products. The reaction occurs in aqueous solution, and is second-order with respect to A, with k_A = 0.040 L mol^{-1} min^{-1}. The inlet concentration of A and the inlet volumetric flow rate are 1.5 mol L^{-1} and 2.5 L min^{-1}, respectively. Determine the fractional conversion (f_A) obtained at the outlet, if V_1 = 10 L, V_2 = 20 L, and V_3 = 50 L, (a) analytically, and (b) graphically.

Solusi

Untuk stage 1 dari persamaan kecepatan

$$(-r_A)_1 = k_A c_{A1}^2 = k_A c_{Ao}^2 (1 - f_{A1})^2$$

Karena densitas konstan

$$(-r_A)_1 = (F_{Ao}/V_1)(f_{A1} - 0)$$

Lakukan pengaturan sehingga diperoleh pers kwadrat

$$f_{A1}^2 - \left(\frac{F_{Ao}}{k_A c_{Ao}^2 V_1} + 2\right) f_{A1} + 1 = 0$$

Atau dengan memasukkan bilangan numerik

$$f_{A1}^2 - 6.167 f_{A1} + 1 = 0$$

- Diperoleh $f_{A1} = 0.167$
- Similarly, for stages 2 and 3, we obtain $f_{A2} = 0.362$, and $f_{A3} = 0.577$, which is the outlet fractional conversion from the three-stage CSTR.

Penyelesaian cara grafis sbb

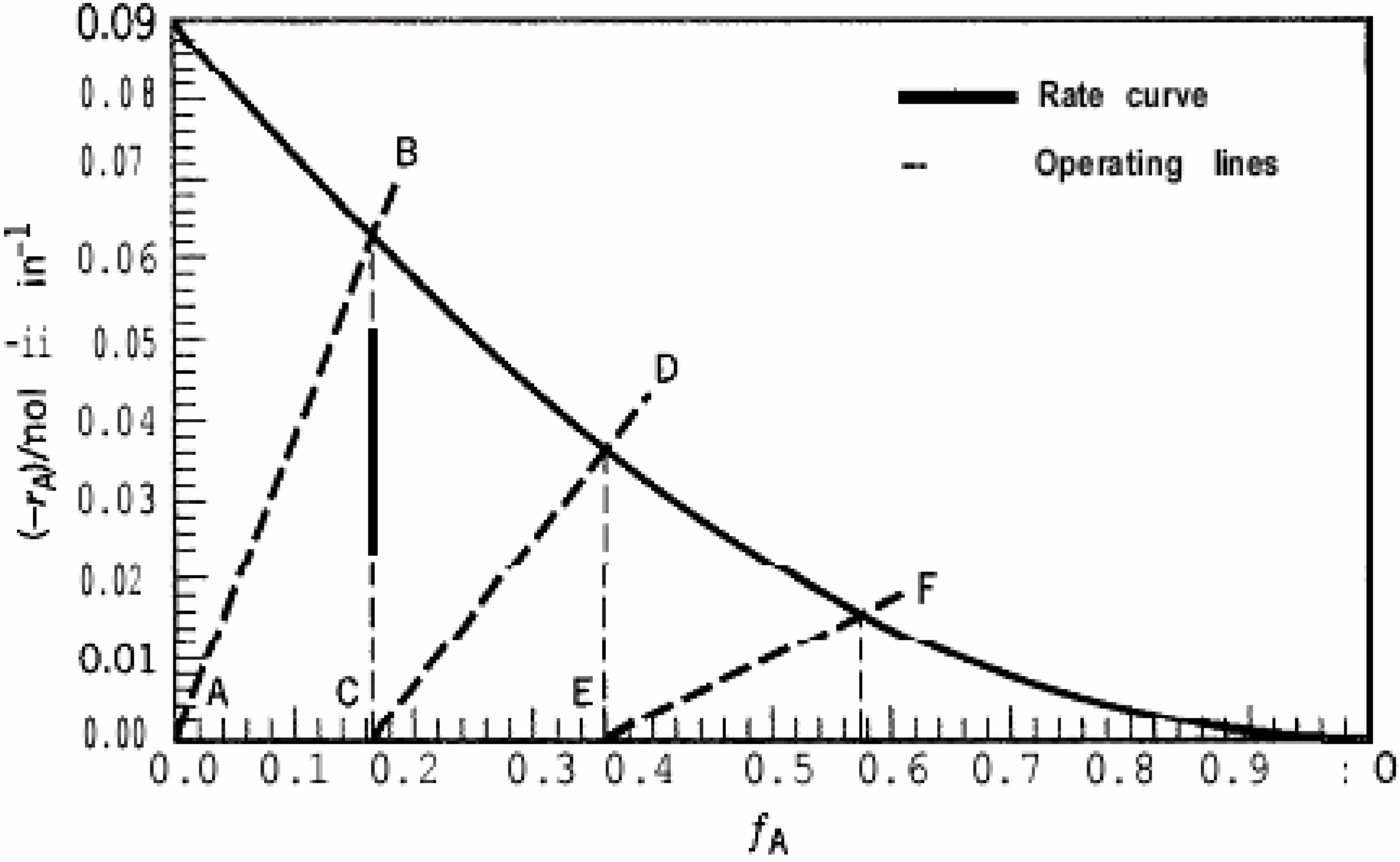


Figure. 14.12 Graphical solution of Example 14-9

(b) The graphical solution is shown in Figure 14.12. The curve for (- r_A) from the rate law is first drawn. Then the operating line AB is constructed with slope $F_{A0}/V_1 = c_{A0}q_0/V_1 =$ 0.375 mol $L^{-1}min^{-1}$ to intersect the rate curve at f_{A1} = 0.167; similarly, the lines CD and EF, with corresponding slopes 0.1875 and 0.075, respectively, are constructed to intersect 0.36 and f_{A3} = 0.58, respectively. These are the same the rate curve at the values f_{A2} = values as obtained in part (a).

Optimal Operation

The following example illustrates a simple case of optimal operation of a multistage CSTR to minimize the total volume. We continue to assume a constant-density system with isothermal operation

Exp. 14-10

Consider the liquid-phase reaction A + . . . → products taking place in a two-stage CSTR. If the reaction is first-order, and both stages are at the same T, how are the sizes of the two stages related to minimize the total volume V for a given feed rate (F_{Ao}) and outlet conversion (f_{A2})?

Solusi

From the material balance, equation 14.4-1, the total volume is

$$V = V_1 + V_2 = F_{Ao}\left[\frac{f_{A1} - 0}{(-r_A)_1} + \frac{f_{A2} - f_{A1}}{(-r_A)_2}\right] \qquad \text{A}$$

From the rate law,

$$(-r_A)_1 = k_A c_{Ao}(1 - f_{A1}) \qquad \text{B}$$

$$(-r_A)_2 = k_A c_{Ao}(1 - f_{A2}) \qquad \text{C}$$

Substituting (B) and (C) in (A), we obtain

$$V = \frac{F_{Ao}}{k_A c_{Ao}}\left(\frac{f_{A1}}{1 - f_{A1}} + \frac{f_{A2} - f_{A1}}{1 - f_{A2}}\right) \qquad \text{D}$$

$$\left(\frac{\partial V}{\partial f_{A1}}\right)_{f_{A2},T} = 0 \qquad \text{E}$$

From (E) and (D), we obtain

$$\frac{\partial V}{\partial f_{A1}} = \frac{F_{Ao}}{k_A c_{Ao}}\left[\frac{1}{(1-f_{A1})^2} - \frac{1}{1-f_{A2}}\right] = 0$$

from which $f_{A2} = f_{A1}(2 - f_{A1})$

If we substitute this result into the material balance for stage 2 (contained in the last term in (D)), we have

$$V_2 = \frac{F_{Ao}}{k_A c_{Ao}}\left(\frac{f_{A2} - f_{A1}}{1 - f_{A2}}\right) = \frac{F_{Ao}}{k_A c_{Ao}}\left(\frac{f_{A1}}{1 - f_{A1}}\right) = V_1$$

- That is, for a first-order reaction, the two stages must be of equal size to minimize V.
- The proof can be extended to an N-stage CSTR. For other orders of reaction, this result is approximately correct. The conclusion is that tanks in series should all be the same size, which accords with ease of fabrication.
- Although, for other orders of reaction, equal-sized vessels do not correspond to the minimum volume, the difference in total volume is sufficiently small that there is usually no economic benefit to constructing different-sized vessels once fabrication costs are considered.

Example 11

A reactor system is to be designed for 85% conversion of A (fA) in a second-order liquid phase reaction, A → products; $k_A = 0.075$ L mol^{-1} min^{-1}, $q_0 = 25$ L min^{-1}, and $C_{A0} = 0.040$ mol L^{-1}. The design options are:

(a) two equal-sized stirred tanks in series;

(b) two stirred tanks in series to provide a minimum total volume.

The cost of a vessel is \$290, but a 10% discount applies if both vessels are the same size and geometry. Which option leads to the lower capital cost?

Solusi

Case (a). From the material-balance equation 14.4-1 applied to each of the two vessels 1 and 2,

$$V_1 = F_{Ao} f_{A1}/k_A c_{A1}^2 = F_{Ao} f_{A1}/k_A c_{Ao}^2 (1 - f_{A1})^2 \qquad \text{(A)}$$

$$V_2 = F_{Ao}(f_{A2} - f_{A1})/k_A c_{Ao}^2 (1 - f_{A2})^2 \qquad \text{(B)}$$

Equating V_1 and V_2 from (A) and (B), and simplifying, we obtain

$$(f_{A2} - f_{A1})/(1 - f_{A2})^2 = f_{A1}/(1 - f_{A1})^2$$

This is a cubic equation for f_{A1} in terms of f_{A2}:

$$f_{A1}^3 - (2 + f_{A2})f_{A1}^2 + (2 + f_{A2}^2)f_{A1} - f_{A2} = 0$$

$$f_{A1}^3 - 2.85 f_{A1}^2 + 2.7225 f_{A1} - 0.85 = 0$$

- This equation has one positive real root, f_{A1} =0.69, which can be obtained by trial.
- This corresponds to $V_1 = V_2 = 5.95 \times 10^4$ L (from equation (A) or (B)) and a total capital cost of 0.9(290)(5.95 X 104)2/1000 = $31,000 (with the 10% discount taken into account)

Case (b). The total volume is obtained from equations (A) and (B):

$$V = V_1 + V_2 = \frac{F_{Ao} f_{A1}}{k_A c_{Ao}^2 (1 - f_{A1})^2} + \frac{F_{Ao}(f_{A2} - f_{A1})}{k_A c_{Ao}^2 (1 - f_{A2})^2}$$

For minimum V,

$$\left(\frac{\partial V}{\partial f_{A1}}\right)_{f_{A2}} = \frac{F_{Ao}}{k_A c_{Ao}^2}\left[\frac{1 + f_{A1}}{(1 - f_{A1})^3} - \frac{1}{(1 - f_{A2})^2}\right] = 0$$

This also results in a cubic equation for f_{A1}, which, with the value f_{A2} = 0.85 inserted, becomes

$$f_{A1}^3 - 3f_{A1}^2 + 3.0225 f_{A1} - 0.9775 = 0$$

Solution by trial yields one positive real root: f_{A1} = 0.665. This leads to V_1 = 4.95 X I0^4 L, V_2= 6.84 X I0^4 L, and a capital cost of \$34,200.

Conclusion:

The lower capital cost is obtained for case (a) (two equal-sized vessels), in spite of the fact that the total volume is slightly larger (11.9 X l0^{4} L versus 11.8 X 10^{4} L).

10-11-12-13

Plug Flow Reactors (PFR/ RAP)

Reaktor Alir Pipa (RAP), atau Plug Flow Reactors (PFR)

- Pada bab ini dipelajari analisis unjuk kerja dan perancangan RAP
- Seperti RATB, RAP selalu dioperasikan secara kontinyu pada keadaan tunak, selain daripada periode startup dan shutdown
- Tidak seperti RATB yg digunakan terutama untuk reaksi2 fasa cair, RAP dapat digunakan untuk reaksi2 fasa cair dan fasa gas.

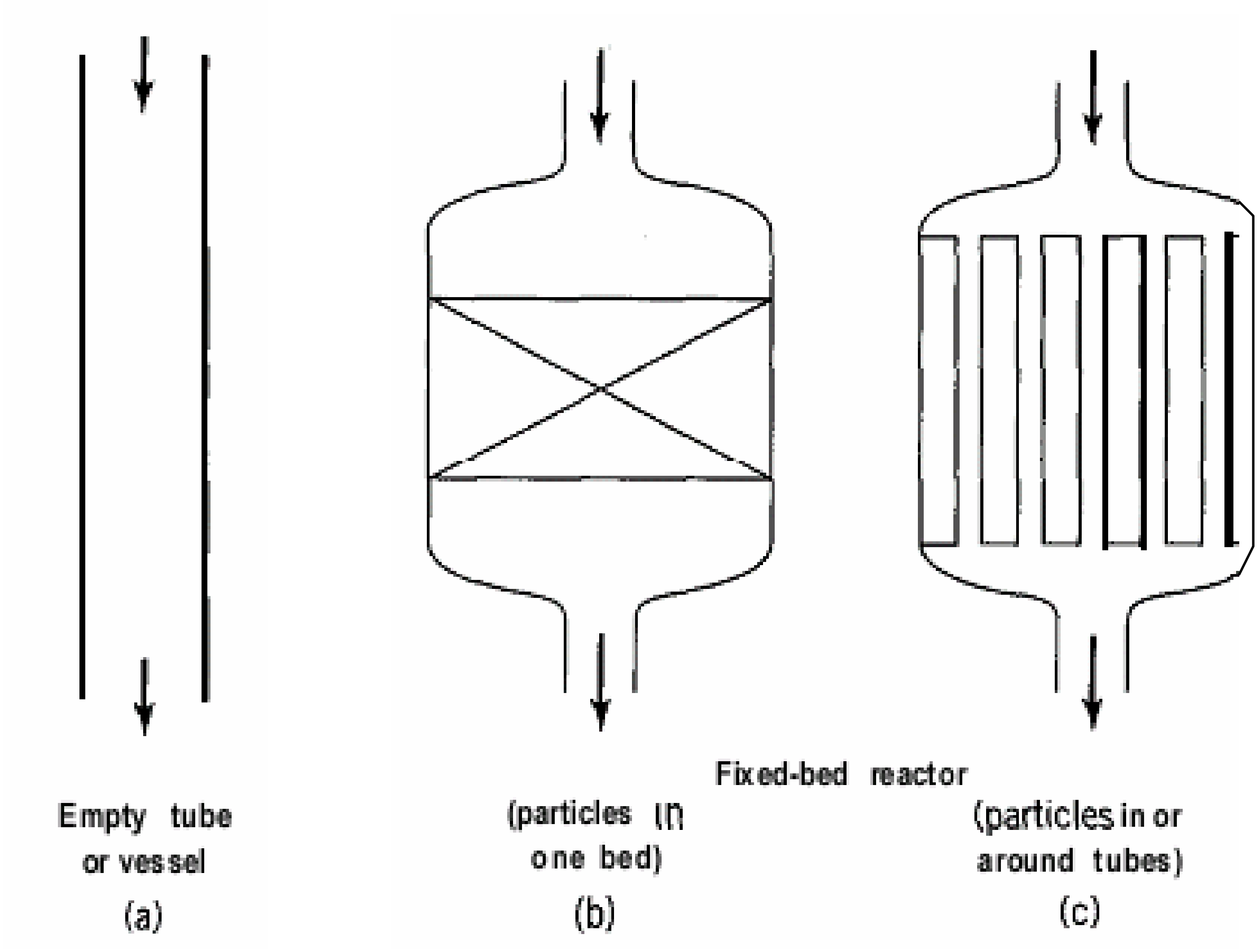
Ciri-ciri utama RAP

1. Pola aliran adalah PF, dan RAP adalah vesel tertutup
2. Kecepatan aliran volumetris dapat bervariasi secara kontinyu kearah aliran sebab perubahan densitas
3. Setiap elemen fluida mrp sistem tertutup (dibandingkan RATB); yaitu, tidak ada pencampuran kearah axial, meskipun terjadi pencampuran sempurna searah radial (dalam vesel silinder)
4. Sebagai konsequensi dari (3) sifat2 fluida dapat berubah secara kontinyu kearah radial, tapi konstan secara radial (pada posisi axial tertentu)
5. Setiap elemen fluida mempunyai residence time yg sama seperti yg lain (dibandingkan RATB)

Kegunaan RAP

- Model RAP seringkali digunakan untuk sebuah reaktor yg mana sistem reaksi (gas atau cair) mengalir pada kecepatan relatif tinggi (Re>>, sampai mendekati PF) melalui suatu vesel kosong atau vesel yg berisi katalis padat yg di packed
- Disini tidak ada peralatan seperti pengaduk, untuk menghasilkan backmixing
- Reaktor dapat digunakan dalam operasi skala besar untuk produksi komersial, atau di laboratorium atau operasi skala pilot untuk mendapatkan data perancangan

Ilustrasi contoh RAP skematik



Persamaan perancangan untuk RAP

Tinjau reaksi: A + … → ν_cC

Neraca Massa:

$$\frac{dV}{df_A} - \frac{F_{Ao}}{(-r_A)} = 0 \qquad (15.2\text{-}1)$$

Untuk mendapatkan volume:

$$V = F_{Ao} \int df_A/(-r_A) \qquad (15.2\text{-}2)$$

Pers 2 dinyatakan dalam space time $\tau = V/q_0$

$$\tau = c_{Ao} \int df_A/(-r_A) \qquad (15.2\text{-}3)$$

karena $c_{Ao} = F_{Ao}/q_o$

Bila pers (1) dituliskan kembali dalam gradien f_A terhadap perubahan posisi x dalam RAP

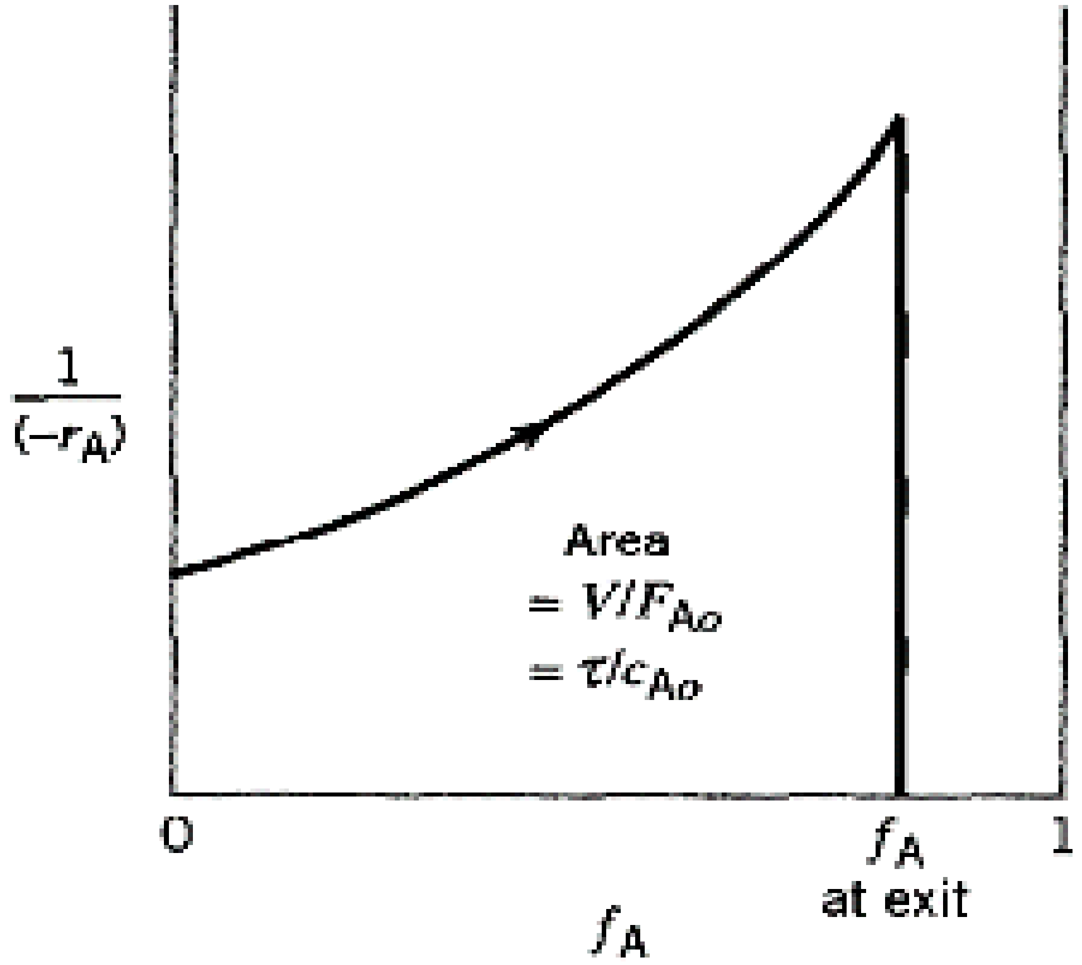
Asumsi reaktor berbentuk silinder dg jari-jari R.

Volume reaktor dari pemasukan sampai posisi x adalah:

$$V(x) = \pi R^2 x, \text{ or } dV = \pi R^2 dx$$

Substitusi dV ke pers (1) diperoleh

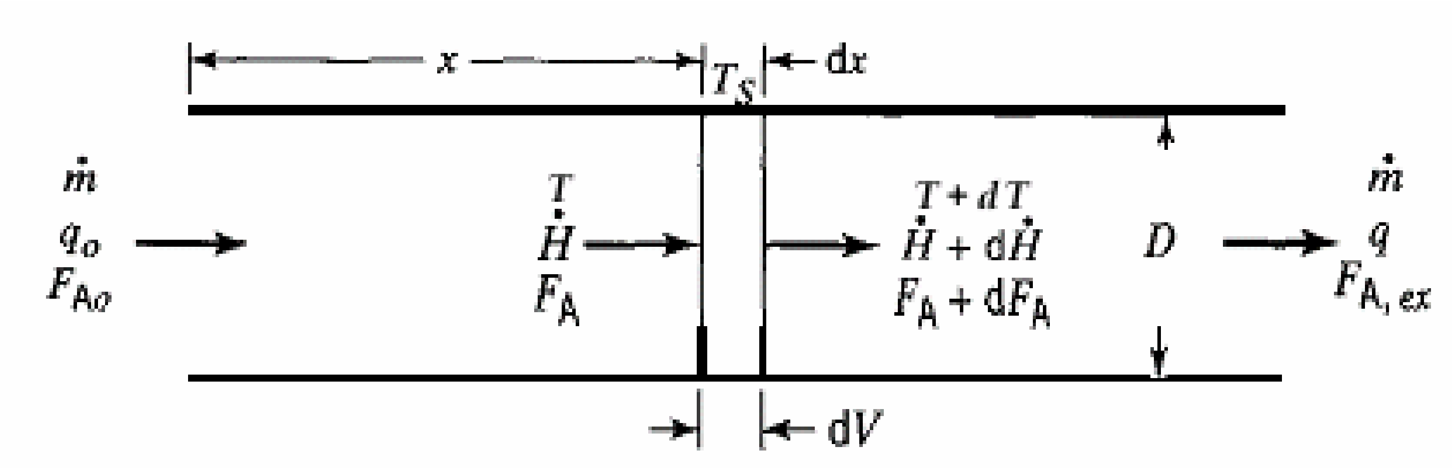
$$\frac{df_A}{dx} - \frac{\pi R^2(-r_A)}{F_{Ao}} = 0 \qquad (15.2\text{-}4)$$



Gambar: Interpretasi pers (2) atau (3) secara grafik

Neraca Energi

- Pengembangan neraca energi untuk RAP, kita pertimbangkan hanya operasi keadaan tunak, jadi kecepatan akumulasi diabaikan.
- Kecepatan entalpi masuk dan keluar oleh (1) aliran, (2) transfer panas, (3) reaksi mungkin dikembangkan atas dasar diferensial kontrol volume dV seperti gambar berikut:



1) Kecepatan entalpi masuk oleh aliran – kecepatan entalpi keluar oleh aliran

$$= \dot{H} - (\dot{H} + \mathrm{d}\dot{H}) = -\mathrm{d}\dot{H} = -\dot{m}c_p\mathrm{d}T$$

2) Kecepatan transfer panas ke (atau dari) kontrol volume

$$= \delta\dot{Q} = U(T_S - T)\mathrm{d}A_p$$

Dengan U adalah koef perpindahan panas keseluruhan, T_S adalah temperatur sekitar diluar pipa pada titik tinjauan, dan dA adalah perubahan luas bidang transfer panas

3) Kecepatan entalpi masuk/ terbentuk (atau keluar/ terserap) oleh reaksi

$$= (-\Delta H_{RA})(-r_A)dV$$

Jadi persamaan neraca energi keseluruhan (1), (2), dan (3) menjadi:

$$-\dot{m}c_P dT + U(T_S - T)dA_p + (-\Delta H_{RA})(-r_A)dV = 0 \qquad (15.2\text{-}5)$$

Persamaan (5) mungkin lebih sesuai ditransformasi ke hubungan T dan f_A, karena

$$dA_p = \pi D dx \qquad (15.2\text{-}6)$$

dan $$dV = (\pi D^2/4)dx \qquad (15.2\text{-}7)$$

dengan D adalah diameter pipa atau vesel, substitusi (6) ke (7):

$$dA_p = (4/D)dV \qquad (15.2\text{-}8)$$

Jika digunak pers (1) dan –(8) untuk mengeliminasi dV dan dAp dari pers (5), didapatkan

$$\dot{m}c_p dT = \left[(-\Delta H_{RA}) + \frac{4U(T_S - T)}{D(-r_A)}\right. F_{Ao} df_A \qquad (15.2\text{-}9)$$

Secara alternatif, pers (5) dapat ditransformasi ke temperatur sebagai fungsi x (panjang reaktor), gunakan pers (6) dan (7) untuk eliminasi dAp dan dV

$$\dot{m} c_P \mathrm{d}T = [(-\Delta H_{RA})(-r_A)(D/4) + U(T_S - T)]\pi D \mathrm{d}x \qquad (15.2\text{-}10)$$

Untuk kondisi adiabatis pers (9) dan (10) dapat disederhanakan dg menghapus term U ($\delta Q = 0$)

Neraca Momentum; Operasi Nonisobarik

- Sebagai Rule of Thumb, untuk fluida kompresibel, jika perbedaan tekanan antara pemasukan dan pengeluaran lebih besar dp 10 sampai 15%, perubahan tekanan seperti ini mempengaruhi konversi, dan harus dipertimbangkan jika merancang reaktor.
- Dalam situasi ini, perubahan tekanan disepanjang reaktor harus ditentukan secara simultas dengan perubahan fA dan perubahan T
- Dapat ditentukan dengan pers Fanning atau Darcy untuk aliran dalam pipa silinder dapat digunakan (Knudsen and Katz, 1958, p. 80)

$$-\frac{\mathrm{d}P}{\mathrm{d}x} = \frac{2\rho u^2 f}{D} = \frac{32\rho q^2 f}{\pi^2 D^5} \qquad (15.2\text{-}11)$$

Dengan P adl tekanan, x adl posisi axial dlm reaktor, ρ adl densitas fluida, u adl kecepatan linier, f adl faktor friksi Fanning, D adl diameter reaktor, dan q adl laju alir volumetrik; ρ, u, dan q dapat bervariasi dengan posisi

Nilai f dapat ditentukan melalui grafik utk pipa smooth atau dari korelasi. Korelasi yg digunakan untuk aliran turbulen dalam pipa smooth dan untuk bilangan Re antara 3000 dan 3000.000

$$f = 0.00140 + 0.125(\mathrm{Re})^{-0.32} \qquad (15.2\text{-}12)$$

1. Isothermal Operation

- For a constant-density system, since

$$f_A = (c_{Ao} - c_A)/c_{Ao} \qquad 14.3\text{-}12$$

then

$$df_A = -(1/c_{Ao})dc_A \qquad 15.2\text{-}13$$

The residence time t and the space time τ are equal.

$$t = \int dV/q = V/q_o = \tau \quad \text{(constant density)} \qquad 15.2\text{-}14$$

and

$$dt = dV/q_o = d\tau \qquad 15.2\text{-}15$$

The analogy follows if we consider an element of fluid (of arbitrary size) flowing through a PFR as a closed system, that is, as a batch of fluid. Elapsed time (t) in a BR is equivalent to residence time (t) or space time (τ) in a PFR for a constant-density system. For dV from equation 15 and for dfA from 13, we obtain, since $F_{Ao} = c_{Ao}q_o$,

$$\frac{dc_A}{dt} + (-r_A) = 0 \qquad 15.2\text{-}16$$

we may similarly write equation 2 as

$$V/q_o = -\int dc_A/(-r_A) = \tau \qquad 15.2\text{-}17$$

A graphical interpretation of this result is given in Figure 15.4.

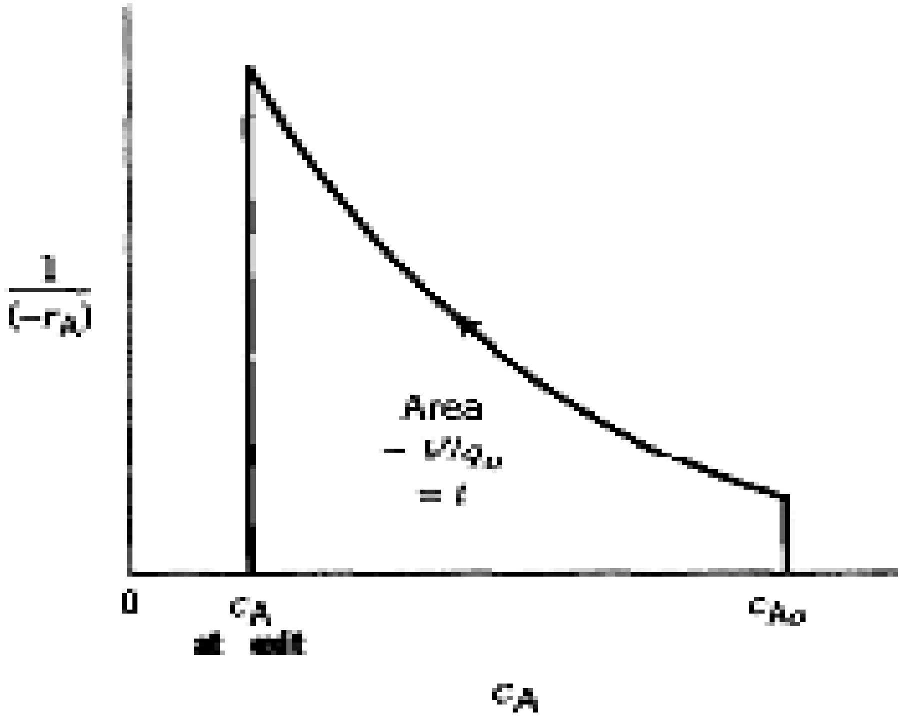


Figure 15.4 Graphical interpretation of equation 15.2-17 (constant-density system)

Example 15-2

A liquid-phase double-replacement reaction between bromine cyanide (A) and methyl-amine takes place in a PFR at 10°C and 101 kPa. The reaction is first-order with respect to each reactant, with $k_A = 2.22$ L mol^{-1} s^{-1}. If the residence or space time is 4 s, and the inlet concentration of each reactant is 0.10 mol L^{-1}, determine the concentration of bromine cyanide at the outlet of the reactor.

SOLUTION

The reaction is:

$$BrCN(A) + CH_3NH_2(B) \rightarrow NH_2CN(C) + CH_3Br(D)$$

Since this is a liquid-phase reaction, we assume density is constant. Also, since the inlet concentrations of A and B are equal, and their stoichiometric coefficients are also equal, at all points, $c_A = c_B$. Therefore, the rate law may be written as

$$(-r_A) = k_A c_A^2$$

From equations 16 and (A), $-\mathrm{d}c_A/\mathrm{d}t = k_A c_A^2$

which integrates to $$k_A t = \frac{1}{c_A} - \frac{1}{c_{Ao}}$$

On insertion of the numerical values given for k_A, t, and c_{AO}, we obtain

$$c_A = 0.053 \text{ mol L}^{-1}$$

EXAMPLE 15-3

A gas-phase reaction between methane (A) and sulfur (B) is conducted at 600°C and 101 kPa in a PFR, to produce carbon disulfide and hydrogen sulfide. The reaction is first-order with respect to each reactant, with $k_B = 12\ m^3\ mole^{-1}\ h^{-1}$ (based upon the disappearance of sulfur). The inlet molar flow rates of methane and sulfur are 23.8 and 47.6 mol h^{-1}, respectively. Determine the volume (V) required to achieve 18% conversion of methane, and the resulting residence or space time.

Solution

Reaction:

$$CH_4 + 2\,S_2 \rightarrow CS_2 + 2\,H_2S$$

Although this is a gas-phase reaction, since there is no change in T, P, or total molar flow rate, density is constant. Furthermore, since the reactants are introduced in the stoichiometric ratio, neither is limiting, and we may work in terms of B (sulphur), since k, is given, with fB(= fA) = 0.18. It also follows that cA = cB/2 at all points. The rate law may then be written as

$$(-r_B) = k_B c_A c_B = k_B c_B^2/2 \qquad \text{(A)}$$

From the material-balance equation 17 and (A),

$$v = -q_o \int_{c_{Bo}}^{c_B} \mathrm{d}c_B/(-r_B) = -q_o \int_{c_{Bo}}^{c_B} \frac{\mathrm{d}c_B}{k_B c_B^2/2} = \frac{2q_o}{k_B}\left(\frac{1}{c_B} - \frac{1}{c_{Bo}}\right) \qquad \text{(B)}$$

Since $F_{Bo} = c_{BO}q_O$, and, for constant-density, $c_B = c_{B0}(l - fB)$, equation (B) may be written as

$$V = \frac{2q_o^2}{k_B F_{Bo}}\left(\frac{f_B}{1 - f_B}\right) \qquad \text{(C)}$$

To obtain q_0 in equation (C), we assume ideal-gas behavior; thus,

$$q_o = (F_{Ao} + F_{Bo})RT/P = 71.4(8.314)873/101,000 = 5.13\ \text{m}^3\ \text{h}^{-1}$$

From equation (C),

$$V = \frac{2(5.13)^2 0.18}{12(47.6)0.82} = 0.020\ \text{m}^3$$

From equation 14, we solve for T:

$$t = \tau = V/q_o = 0.020/5.13 = 0.00390\ \text{h} = 14.0\ \text{s}$$

2. Non isothermal Operation

To characterize the performance of a PFR subject to an axial gradient in temperature, the material and energy balances must be solved simultaneously. This may require numerical integration using a software package such as E-Z Solve. Example 15-4 illustrates the development of equations and the resulting profile for f_A, with respect to position (x) for a constant-density reaction.

EXAMPLE 15-4

A liquid-phase reaction A + B → 2C is conducted in a non isothermal multi tubular PFR. The reactor tubes (7 m long, 2 cm in diameter) are surrounded by a coolant which maintains a constant wall temperature. The reaction is pseudo-first-order with respect to A, with $k_A = 4.03 \times l0^5 e^{-5624/T}$, s^{-1}. The mass flow rate is constant at 0.06 kg s^{-1}, the density is constant at 1.025 g cm^3, and the temperature at the inlet of the reactor (T_0) is 350 K.

(a) Develop expressions for dfA/dx and dT/dx.

(b) Plot $f_A(x)$ profiles for the following wall temperatures (T_S): 350 K, 365 K, 400 K, and 425 K.

Data: $C_{A0} = 0.50$ mol L^{-1}; cp = 4.2 J g^{-1} K^{-1};
$\Delta H_{RA} = -210$ kJ mol^{-1}; U = 1.59 kW m^{-2} K^{-1}.

Solution

(a) The rate law is

$$(-r_A) = k_A c_A = k_A c_{Ao}(1 - f_A) \qquad \text{(A)}$$

where k_A is given in Arrhenius form above. Substitution of equation (A) in the material-balance equation 15.2-4, $(F_{Ao}/\pi r^2)\mathrm{d}f_A/\mathrm{d}x,$

results in (with $R = D/2$ and $F_{A0}/C_{A0} = q_0$):

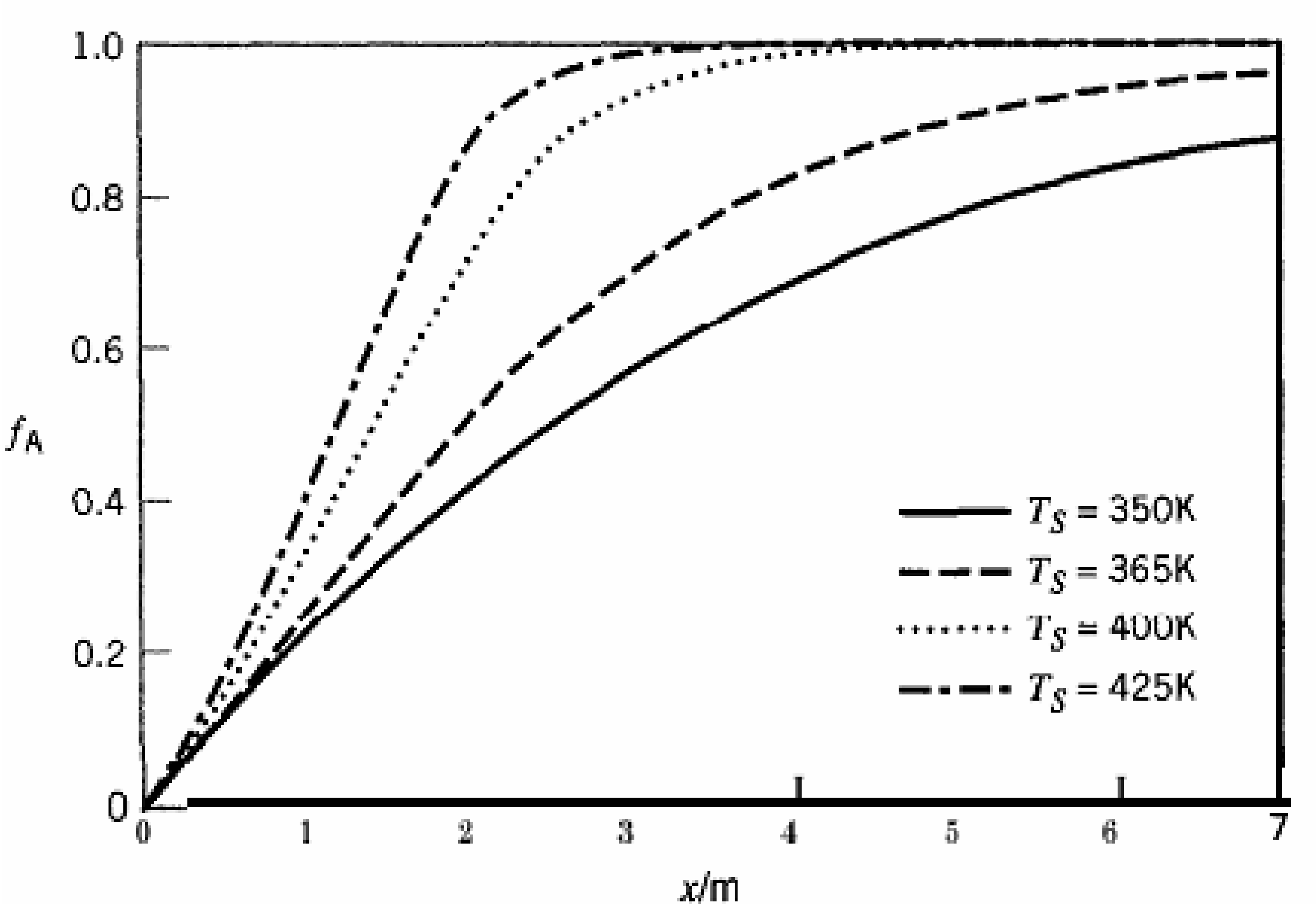


Figure 15.5 Effect of wall temperature (Ts) on conversion in a non-isothermal PFR (Example 15-4)

3. Variable-Density System

- When the density of the **reacting system is not constant through a PFR**,
- The general forms of performance **equations of Section 15.2.1 must be used**.
- The effects of continuously varying density are usually **significant only for a gas-phase reaction**.
- Change in density may result from any one, or a combination, of: **change in total moles (of gas flowing), change in T , and change in P** .
- We illustrate these effects by examples in the following sections.

Isothermal, Isobaric Operation

Example 15.6

Consider the gas-phase decomposition of ethane (A) to ethylene at 750°C and 101 kPa (assume both constant) in a PFR. If the reaction is first-order with kA = 0.534 s^{-1} (Froment and Bischoff, 1990, p. 351), and τ is 1 s, calculate fA. For comparison, repeat the calculation on the assumption that density is constant. (In both cases, assume the reaction is irreversible.)

Solution

The reaction is C2H6(A) → C2H4(B) + H2(C). Since the rate law is

$$\tau = c_{Ao}\int \frac{\mathrm{d}f_A}{(-r_A)} = \frac{1}{k_A q_o}\int_0^{f_A} \frac{q\,\mathrm{d}f_A}{1-f_A} \qquad \text{(A)}$$

Stoichiometric table is used to relate q and q_0. The resulting expression is

$$q = q_0\,(1+f_A)$$

With this result, equation (A) becomes

$$\tau = \frac{1}{k_A}\int_0^{f_A} \frac{(1+f_A)\,\mathrm{d}f_A}{1-f_A} \qquad \text{(B)}$$

The integral in this expression may be evaluated analytically with the substitution z = 1 - f_A. The result is

$$-f_A - 2\ln(1 - f_A) = k_A\tau = 0.534 \qquad \text{(C)}$$

Solution of equation (C) leads to fA = 0.361

If the change in density is ignored, integration of equation 15.2-17, with $(-r_A) = k_A C_A = k_A C_{Ao}(1 - f_A)$, leads to

$$\ln(1 - f_A) = -k_A\tau$$

from which

$$f_A = 0.414$$

Nonisothermal, Isobaric Operation

Example 15.7

A gas-phase reaction between butadiene (A) and ethene (B) is conducted in a PFR, producing cyclohexene (C). The feed contains equimolar amounts of each reactant at 525°C (T_0) and a total pressure of 101 kPa. The enthalpy of reaction is - 115 k.I (mol A)$^{-1}$, and the reaction is first-order with respect to each reactant, with $k_A = 32{,}000\ e^{-13{,}850}/T\ m^3\ mol^{-1}\ S^{-1}$. Assuming the process is adiabatic and isobaric, determine the space time required for 25% conversion of butadiene.

Data: $C_{PA} = 150\ J\ mol^{-1}\ K^{-1}$; $C_{PB} = 80\ J\ mol^{-1}\ K^{-1}$; $Cpc = 250\ J\ mol^{-1}\ K^{-1}$

Solution

The reaction is C4H6(A) + C2H4(B) → C6H10 (C). Since the molar ratio of A to B in the feed is 1: 1, and the ratio of the stoichiometric coefficients is also 1: 1, CA = CB throughout the reaction. Combining the material-balance equation (15.2-2) with the rate law, we obtain

$$V = F_{Ao}\int \frac{\mathrm{d}f_A}{(-r_A)} = F_{Ao}\int \frac{\mathrm{d}f_A}{k_A c_A c_B} = F_{Ao}\int \frac{\mathrm{d}f_A}{k_A c_A^2}$$

$$= F_{Ao}\int \frac{\mathrm{d}f_A}{k_A (F_A/q)^2} = \frac{1}{F_{Ao}}\int_0^{f_A} \frac{q^2\,\mathrm{d}f_A}{k_A(1-f_A)^2} \qquad \text{(A)}$$

Since kA depends on T, it remains inside the integral, and we must relate T to fA. Since the density (and hence q) changes during the reaction (because of changes in temperature and total moles), we relate q to fA and T with the aid of a stoichiometric table and the ideal-gas equation of state.

Species	Initial moles	Change	Final moles
A	F_{Ao}	$-f_A F_{Ao}$	$F_{Ao}(1 - f_A)$
B	F_{Ao}	$-f_A F_{Ao}$	$F_{Ao}(1 - f_A)$
C	0	$f_A F_{Ao}$	$F_{Ao} f_A)$
total	$2F_{Ao}$		$F_t = F_{Ao}(2 - f_A)$

Since at any point in the reactor, $q = F_t RT/P$, and the process is isobaric, 4 is related to the inlet flow rate q_0 by

$$\frac{q}{q_o} = \frac{F_{Ao}(2 - f_A)T}{2F_{Ao}T_o}$$

That is,

$$q = q_o(1 - 0.5 f_A)T/T_o$$

Substitution of equation (B) into (A) to eliminate q results in

$$\tau = \frac{V}{q_o} = \frac{1}{c_{Ao}T_o^2}\int_0^{f_A} \frac{(1-0.5f_A)^2T^2}{k_A(1-f_A)^2}\,\mathrm{d}f_A \tag{C}$$

To relate fA and T, we require the energy balance (15.2-9)

$$\dot{m}c_P\,\mathrm{d}T \equiv F_tC_P\,\mathrm{d}T = (-\Delta H_{RA})F_{Ao}\,\mathrm{d}f_A \tag{D}$$

$$\begin{aligned} F_tC_P &= F_AC_{PA} + F_BC_{PB} + F_CC_{PC} \\ &\equiv F_{Ao}(1-f_A)C_{PA} + F_{Ao}(1-f_A)C_{PB} + F_{Ao}f_AC_{PC} \\ &= F_{Ao}[(C_{PA}+C_{PB}) + (C_{PC}-C_{PA}-C_{PB})f_A] \end{aligned} \tag{E}$$

Substituting equation (E) in (D), and integrating on the assumption that $(-\Delta H_{RA})$ is constant, we obtain

$$T = T_o + (-\Delta H_{RA})\int_0^{f_A} \frac{\mathrm{d}f_A}{(C_{PA}+C_{PB}) + (C_{PC}-C_{PA}-C_{PB})f_A} \tag{F}$$

$$
\begin{aligned}
T &= 798 + 115{,}000 \int_0^{f_A} \frac{\mathrm{d}f_A}{230 + 20 f_A} \\
&= 798 + \frac{115{,}000}{20}\left[\ln(230 + 20\, f_A) \quad \ln 230\right] \\
&= 798 + 5750[\ln(230 + 20\, f_A) - 5.4381
\end{aligned}
\qquad \text{(G)}
$$

RECYCLE OPERATION OF A PFR

In a chemical process, the use of recycle, that is, the return of a portion of an outlet stream to an inlet to join with fresh feed, may have the following purposes:

(1) to conserve feedstock when it is not completely converted to desired products, and/or

(2) to improve the performance of a piece of equipment such as a reactor.

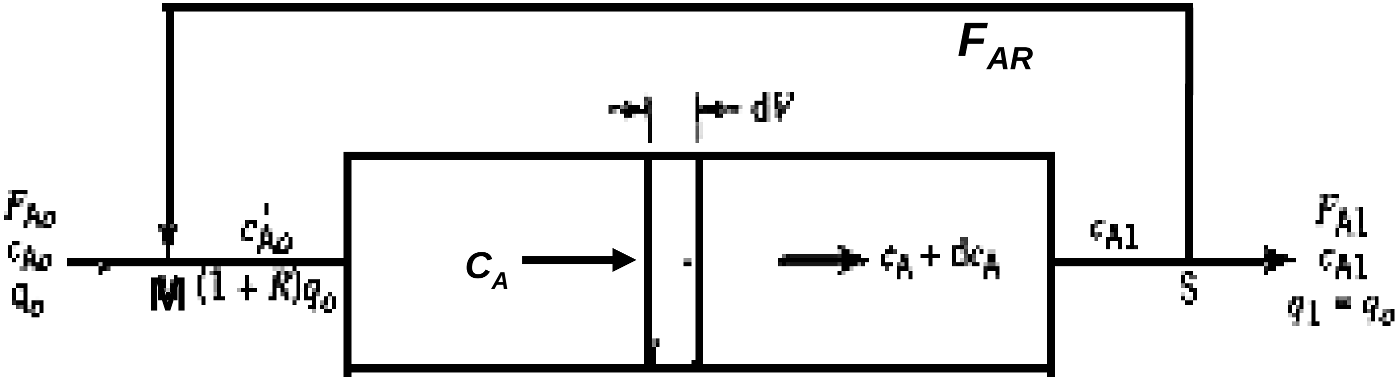


Figure 15.6 Flow diagram and terminology for recycle PFR (constant density)

$$R = \frac{\text{molar flow rate of A in recycle stream}}{\text{molar flow rate of A in product stream}} = \frac{F_{AR}}{F_{A1}} = \frac{c_{A1}q_R}{c_{A1}q_1} = \frac{q_R}{q_1} = \frac{\text{volumetric flow rate of recycle stream}}{\text{volumetric flow rate of product stream}} \tag{15.3-1}$$

where subscript R refers to recycle and subscript 1 to the vessel outlet. Equation 15.3-1 is applicable to both constant-density and variable-density systems

R may vary from 0 (no recycle) to a very large value (virtually complete recycle).

Thus, as shown quantitatively below, we expect that a recycle PFR may vary in performance between that of a PFR with no recycle and that of a CSTR (complete recycle), depending on the value of R

Constant-Density System

$$R = q_R/q_o \qquad \text{(constant density)} \tag{15.3-2}$$

Material balance for A around M:

$$q_o c_{Ao} + R q_o c_{A1} = (1 + R) q_o c'_{Ao}$$

$$c'_{Ao} = \frac{c_{Ao} + R c_{A1}}{1 + R} \tag{15.3-3}$$

material balance for A around the differential control volume dV

$$(1+R)q_o c_A = (1+R)q_o(c_A + dc_A) + (-r_A)dV$$

$$V/q_o = \tau = -(1+R)\int_{c'_{Ao}}^{c_{A1}} \frac{dc_A}{(-r_A)} \qquad (15.3\text{-}4)$$

$$\begin{aligned}(1+R)c'_{Ao} &= c_{Ao} + Rc_{A1} && \textbf{(from 15.3-3)}\\ &= c_{Ao} + Rc_{A1} + Rc_{Ao} - Rc_{Ao}\\ &= (1+R)c_{Ao} + R(c_{A1} - c_{Ao})\end{aligned}$$

Therefore,

$$\frac{c_{Ao} - c'_{Ao}}{c_{Ao} - c_{A1}} = \frac{R}{1+R} \qquad (15.3\text{-}5)$$

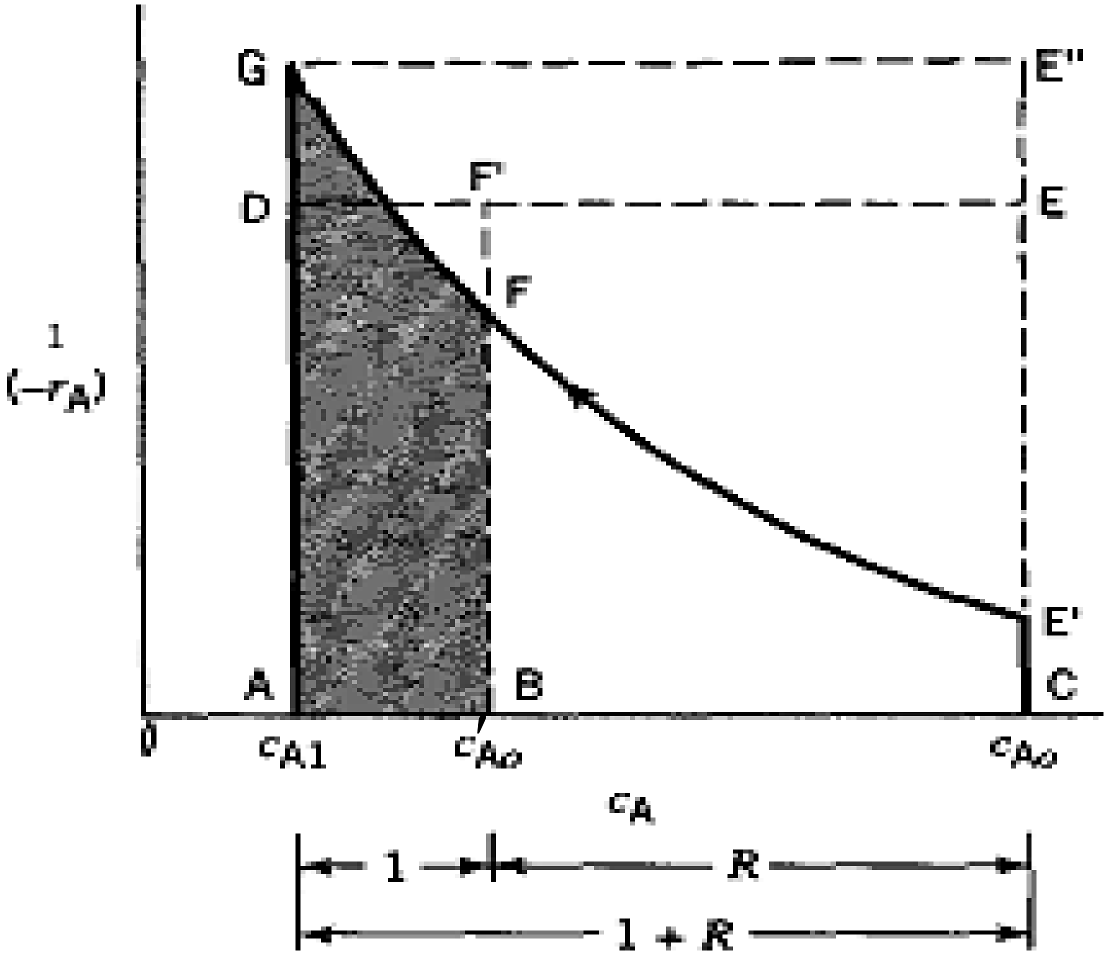


Figure 15.7 Graphical interpretation of equation 15.3-4 for recycle PFR (constant density)

Example 15-9

(a) For the liquid-phase autocatalytic reaction $A + \ldots \rightarrow B + \ldots$ taking place isothermally at steady-state in a recycle PFR, derive an expression for the optimal value of the recycle ratio, R_{opt}, that minimizes the volume or space time of the reactor. The rate law is $(-r_A) = k_A c_A c_B$.

(b) Express the minimum volume or space time of the reactor in terms of R_{opt}.

Variable-Density System

- For the reaction A + . . . → products taking place in a recycle PFR

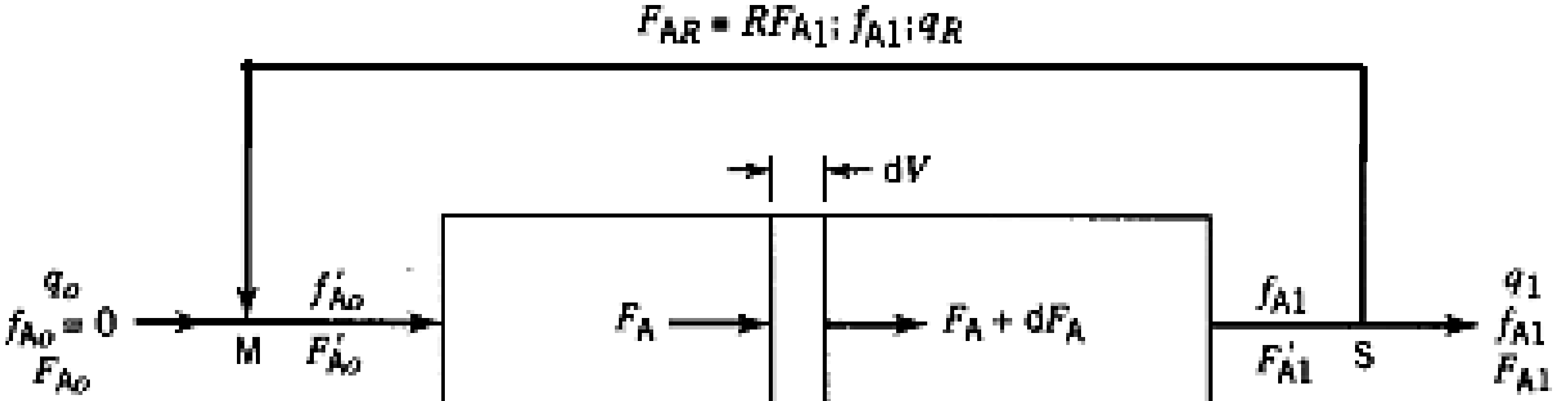


Figure 15.9 Flow diagram and terminology for recycle PFR (constant or variable density)

From a material balance for A around the mixing point M, the molar flow rate of A entering the reactor is

$$F'_{Ao} = F_{Ao} + RF_{A1} \qquad (15.3\text{-}8)$$

At the exit from the system at S, or at the exit from the reactor,

$$f_{A1} = \frac{F_{Ao} - F_{A1}}{F_{Ao}} = \frac{(1+R)F_{Ao} - (1+R)F_{A1}}{(1+R)F_{Ao}}$$

$$= \frac{(1+R)F_{Ao} - F'_{A1}}{(1+R)F_{Ao}}$$

where $F'_{A1} = (1 + R)F_{A1}$

Correspondingly, at the inlet of the reactor

$$f'_{Ao} = \frac{(1+R)F_{Ao} - F'_{Ao}}{(1+R)F_{Ao}} = \frac{(1+R)F_{Ao} - (F_{Ao} + RF_{A1})}{(1+R)F_{Ao}}$$

$$= \frac{R}{1+R}\frac{F_{Ao} - F_{A1}}{F_{Ao}} = \frac{R}{1+R} f_{A1} \qquad (15.3\text{-}9)$$

and at any point in the reactor,

$$f_A = \frac{(1+R)F_{Ao} - F_A}{(1+R)F_{Ao}} \qquad (15.3\text{-}10)$$

Equating molar flow input and output, for steady-state operation, we have

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

$$dV = -\frac{dF_A}{(-r_A)} = (1 + R)F_{Ao}\frac{df_A}{(-r_A)}$$

from equation 15.3-10. Therefore,

$$V = (1 + R)F_{Ao}\int_{f'_{Ao}}^{f_{A1}} \frac{df_A}{(-r_A)} \qquad (15.3\text{-}11)$$

That is, as R → 0, V is that for a PFR without recycle; as R → ∞, V is that for a CSTR

14

CONTINUOUS MULTIPHASE REACTORS

DEFINISI

Reaktor heterogen atau reaktor multifasa adalah reaktor yang digunakan untuk mereaksikan komponen-komponen lebih dari satu fasa dan minimal terdapat 2 fasa

Tipe Reaksi Heterogen

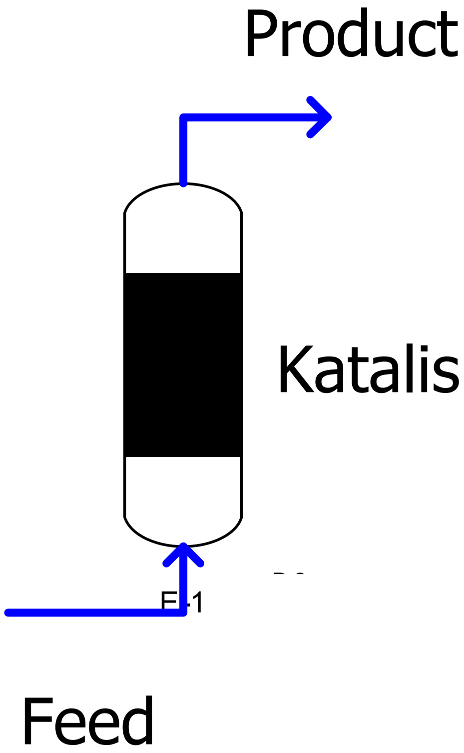
- Reaksi katalitik gas-padat → Cracking HC (katalis Si-Al)
- Reaksi non katalitik gas-padat → Pembuatan batubara
- Reaksi cair-padat → Pembuatan asetilin dari CaS2 dan air
- Reaksi padat-padat → Pembuatan semen, kalsium karbida dari batu kapur dan karbon
- Reaksi gas-cair → Hidrogenasi minyak

Tipe Reaktor Heterogen

- Reactor fixed bed
  - Submerge fixed bed reactor with upward gas bubbling
- Trickle bed reactor
- Reactor moving bed
  - Stirred slurry reactor
  - Bubbling slurry columns
  - Fluidized slurry reactor
  - Co current up flow reactors with fluidized pellets

Gambaran Reaktor Heterogen

Fixed bed:


Product

Katalis

Feed

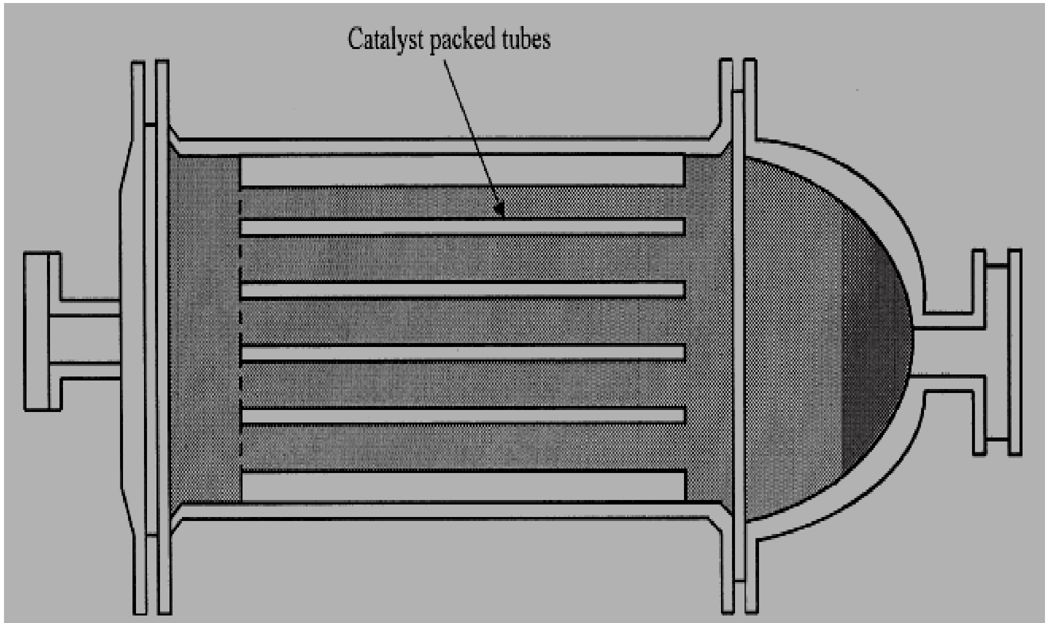
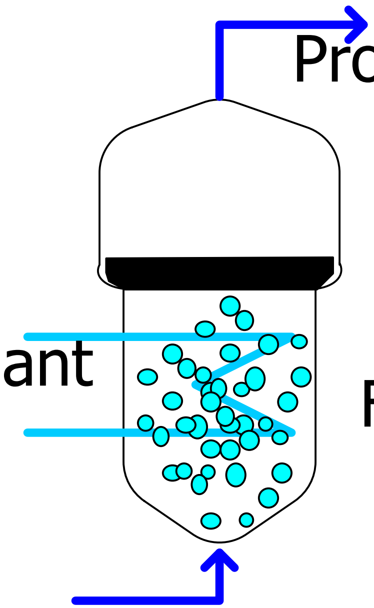


Figure 4-9. Longitudinal catalytic fixed-bed reactor.

Fluidize bed:



Product

Coolant

Fluidized bed

Reactant Gas

P-12

E-6

Fluid Catalytic Cracking Unit

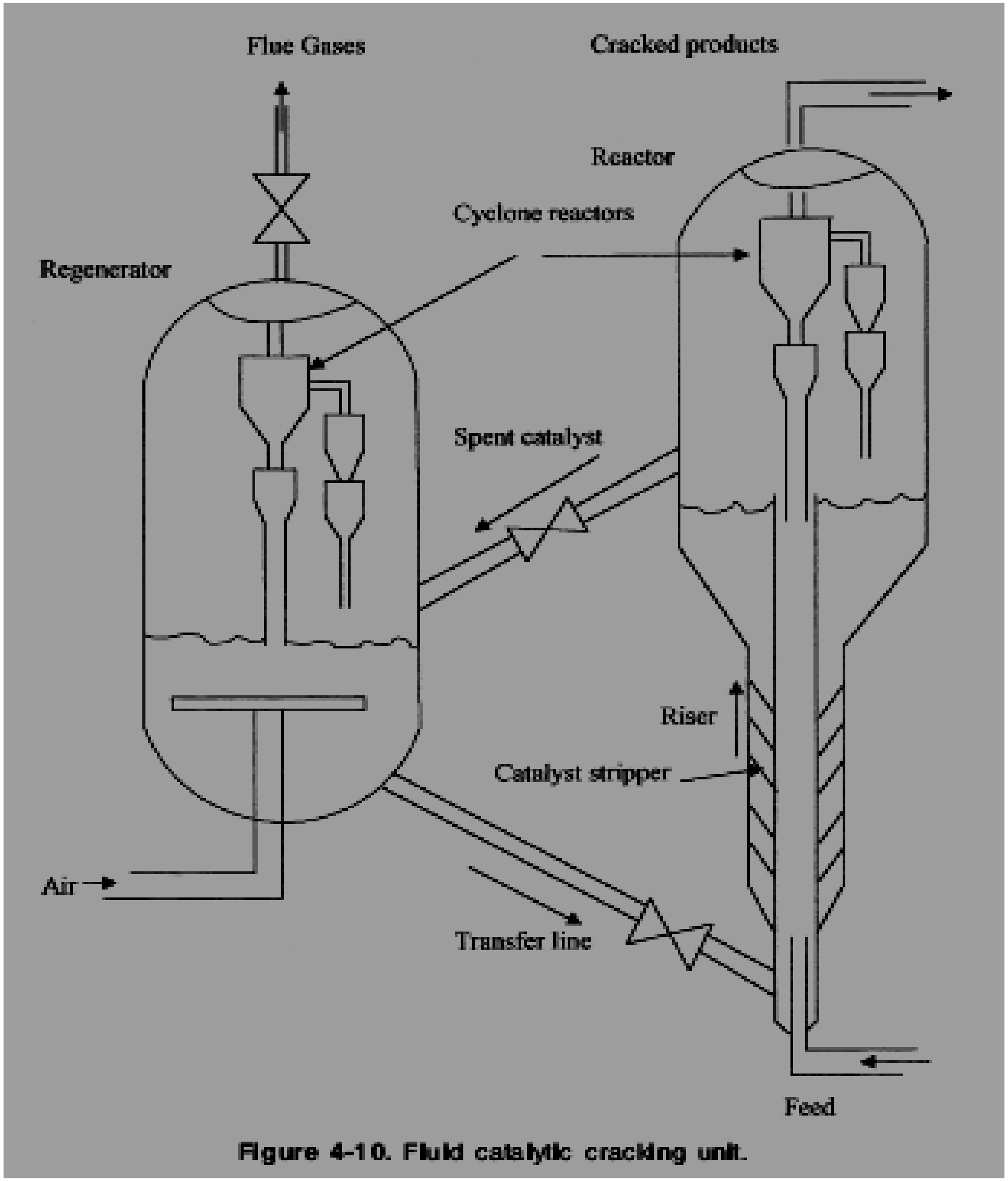


Figure 4-10. Fluid catalytic cracking unit.

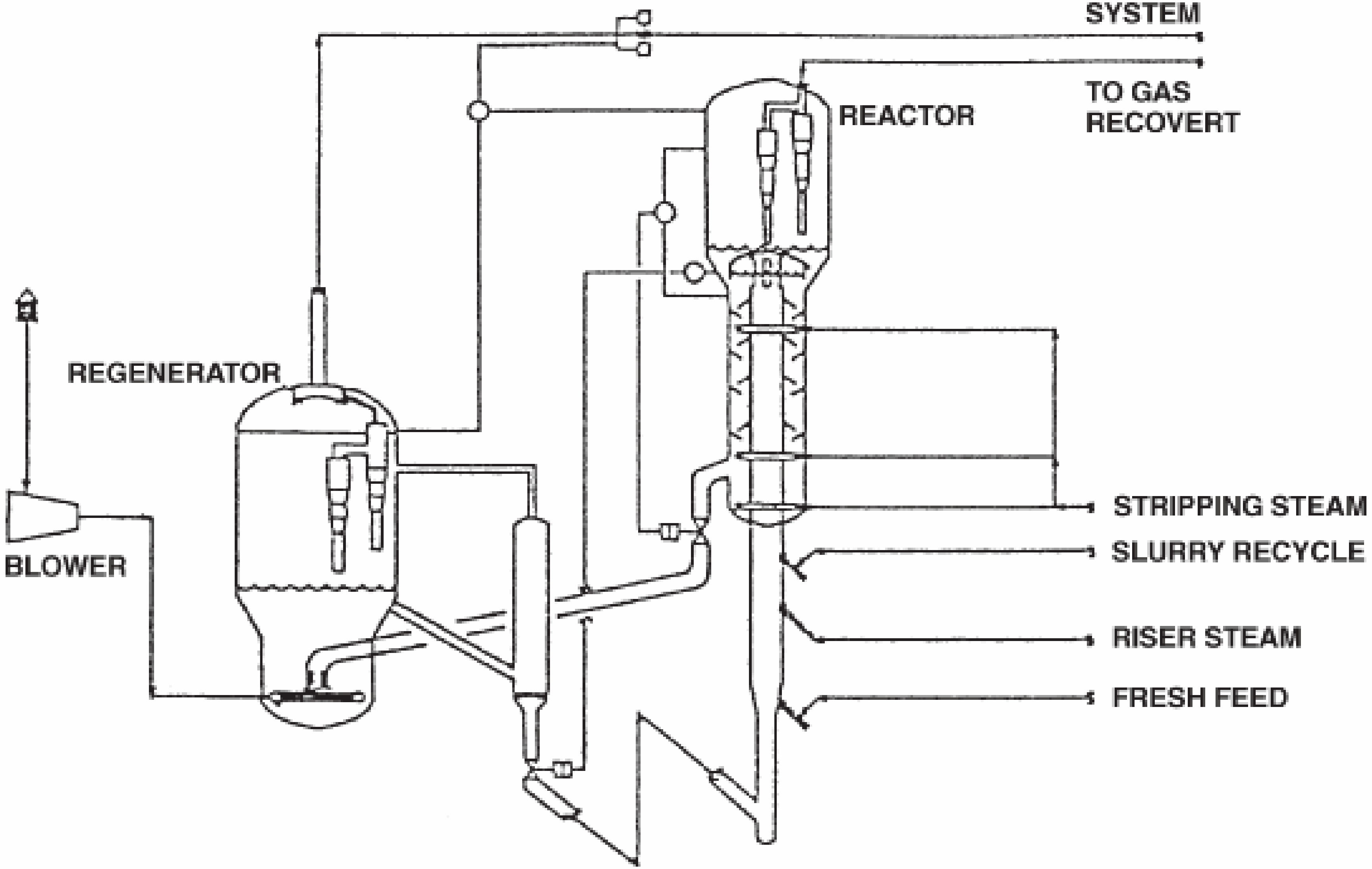


Figure 4-11. Deep catalytic cracking process flow diagram. *(Courtesy of Stone & Webster Engineering Corporation, © 1977 Stone & Webster Engineering Corporation.)*

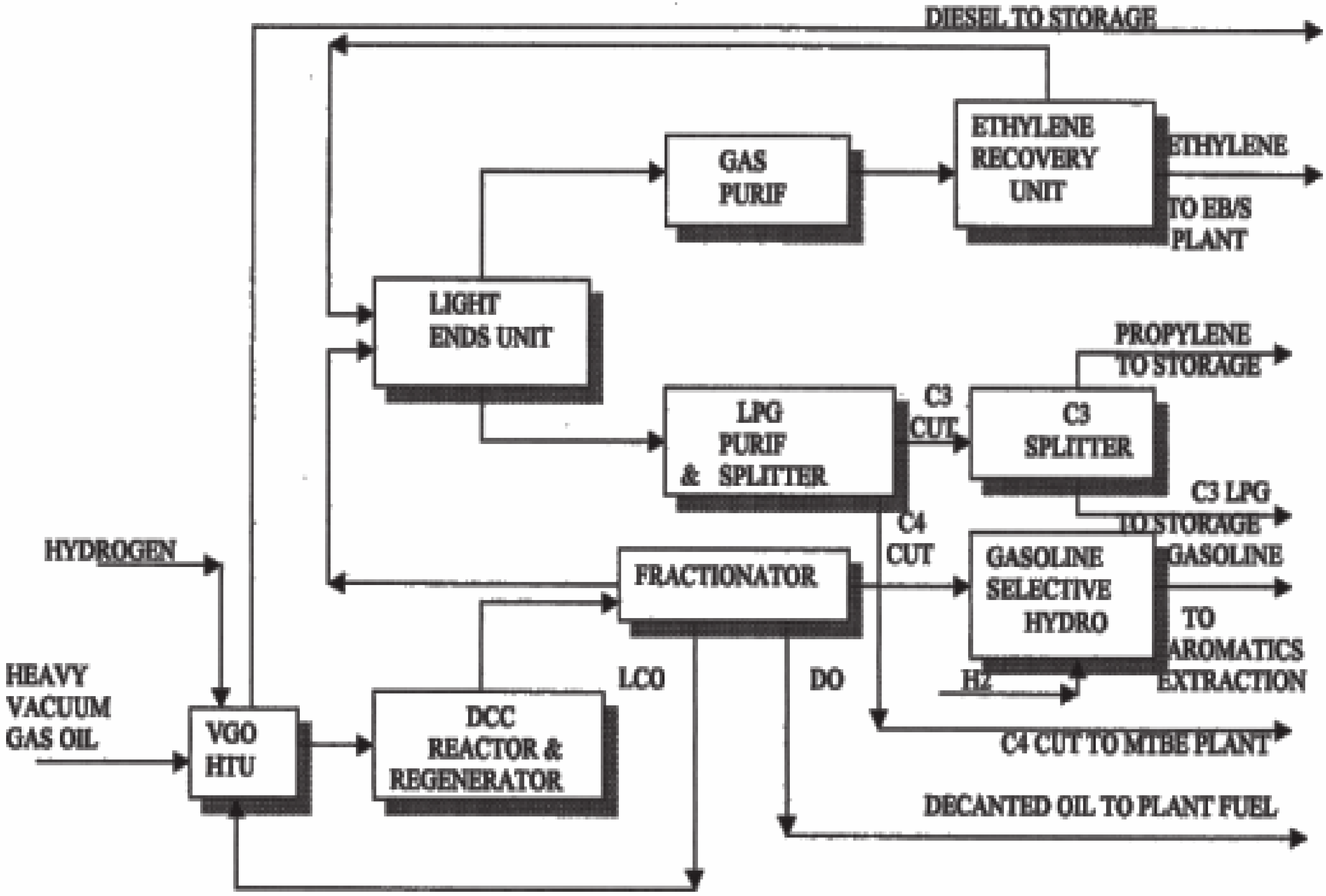


Figure 4-12. DCC plant petrochemicals integration. *(Courtesy of Stone & Webster Engineering Corporation, © 1977 Stone & Webster Engineering Corporation.)*

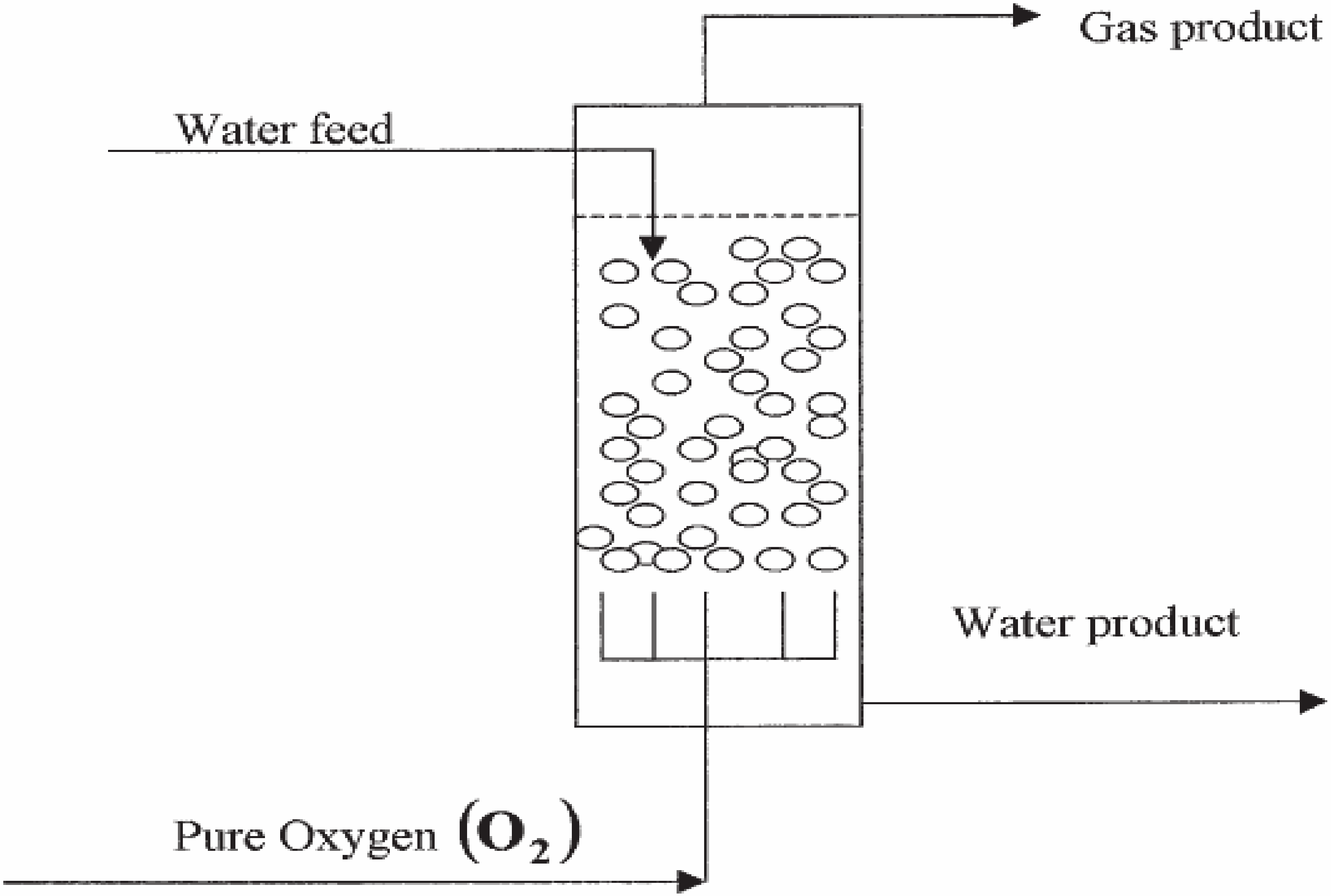


Figure 4-14. A two-phase tubular flow reactor (e.g., gas-liquid bubble reactor for oxidation of pollutants in water). *(Source: J. M. Smith,* Chemical Engineering Kinetics, *3rd ed., McGraw-Hill, Inc. 1981.)*

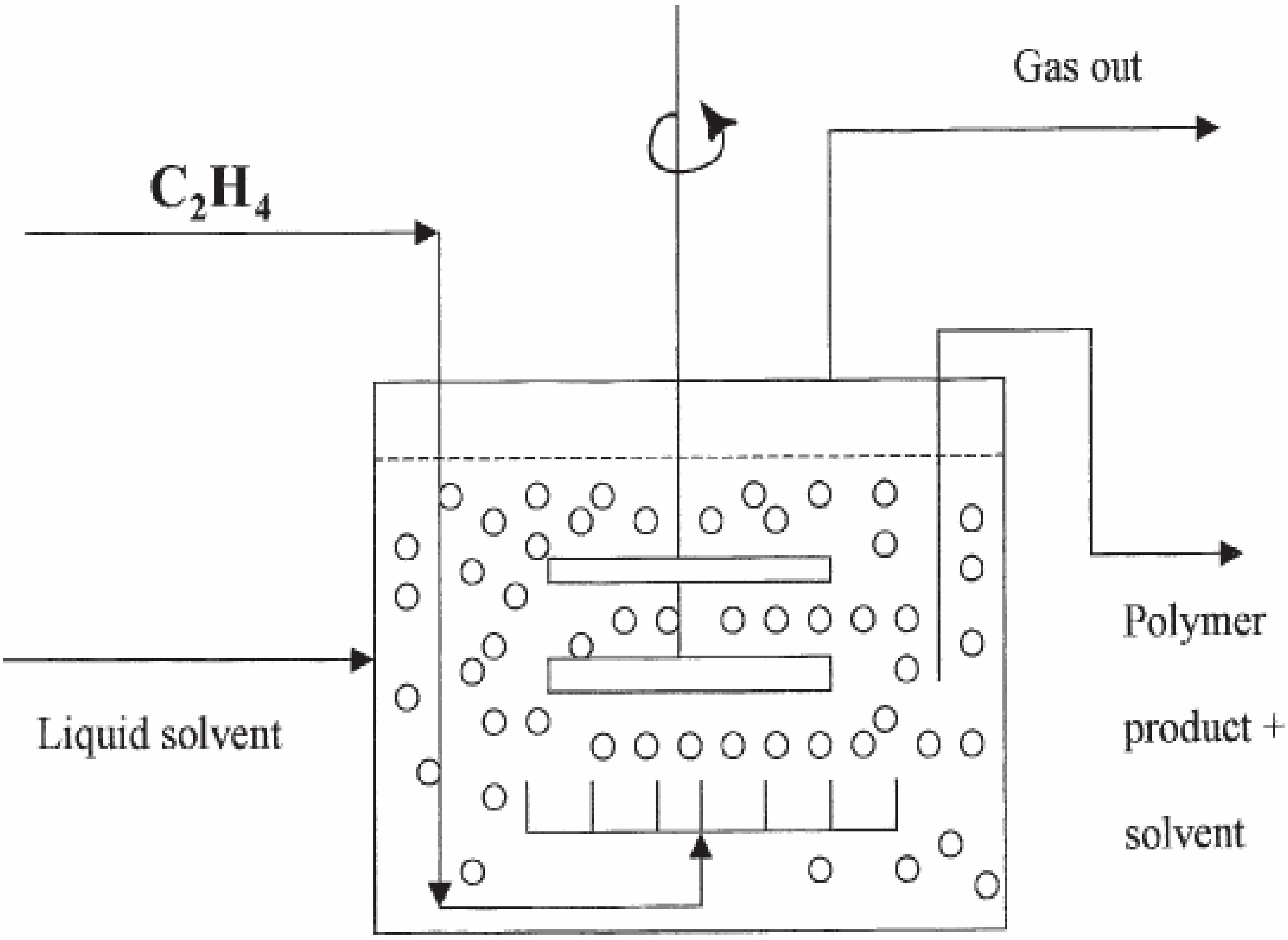


Figure 4-15. A slurry-type reactor (e.g., for C_2H_4 polymerization). *(Source: J. M. Smith*, Chemical Engineering Kinetics, *3rd ed., McGraw-Hill, Inc., 1981.)*

Trickle bed reactor (tubular reactor)

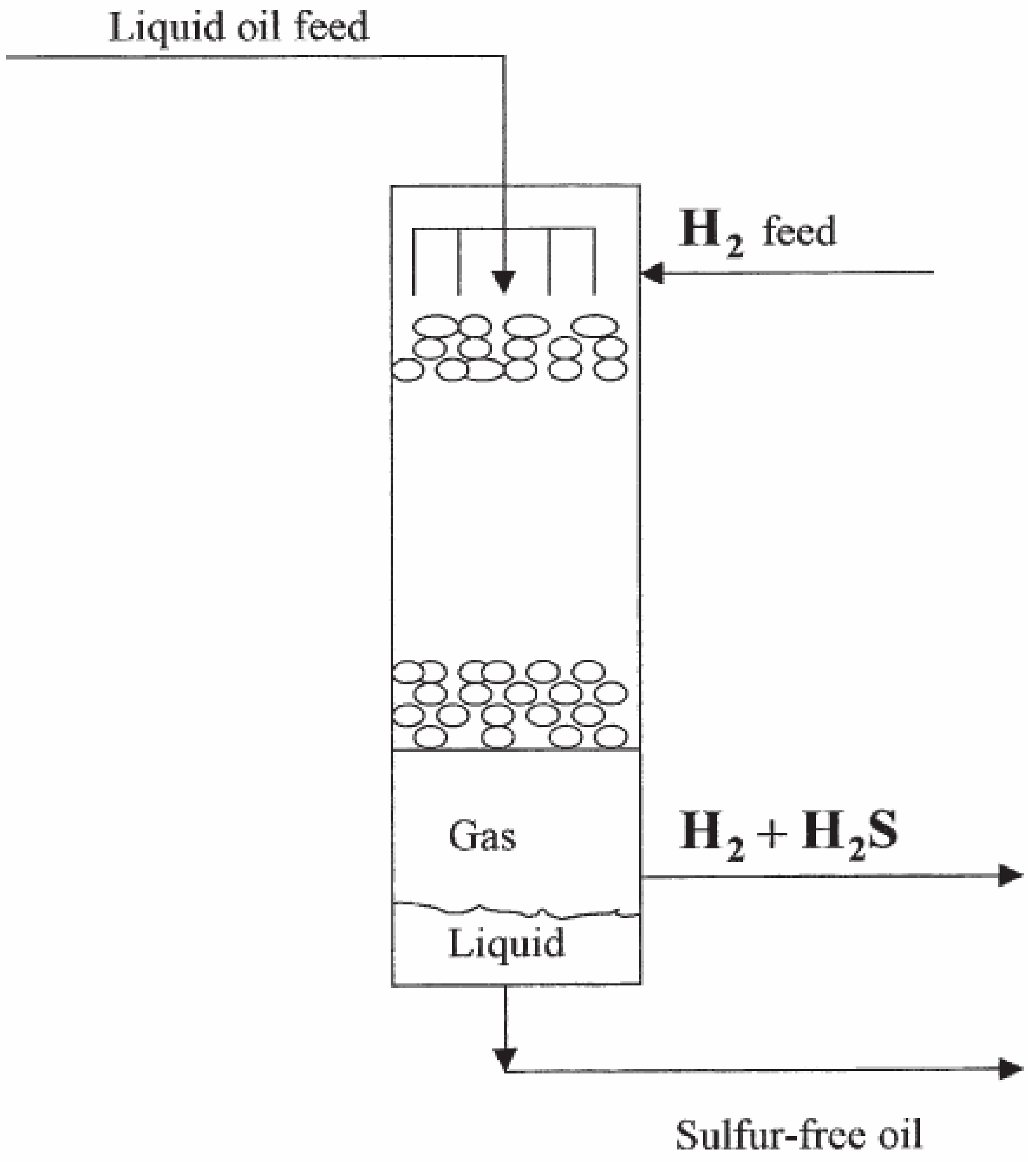


Figure 4-16. Trickle-bed (tubular reactor) for hydrodesulfurization. *(Source: J. M. Smith,* Chemical Engineering Kinetics, *3rd ed., McGraw-Hill, Inc., 1981.)*

Reaktor Diferensial

- Reaktor diferensial digunakan untuk mengevaluasi kecepatan reaksi sebagai fungsi konsentrasi pada sistem heterogen
- Dilaksanakan dalam reaktor tabung yg berisi katalis dengan jumlah kecil
- Konversi yg dihasilkan sangat kecil karena jumlah katalis yg digunakan juga kecil
- Konsentrasi reaktan keluar reaktor hampir sama dengan konsentrasi umpan
- Reaktor semacam ini tidak diminati apabila deaktivasi katalis sangat cepat
- Pers. Desain: $V = F_{A0} X/-r_A$

Model reaktor diferensial

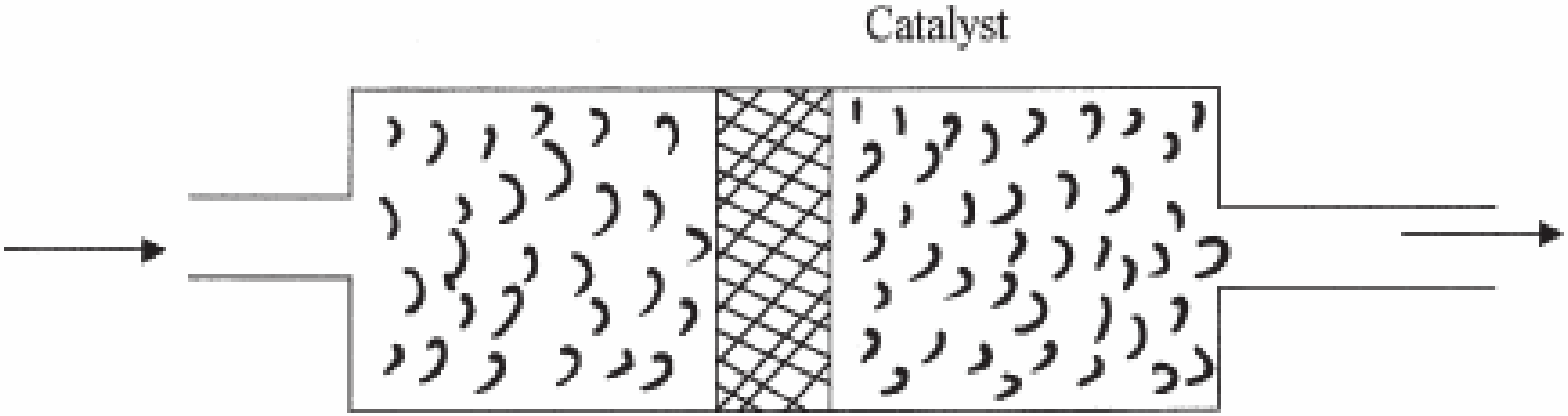
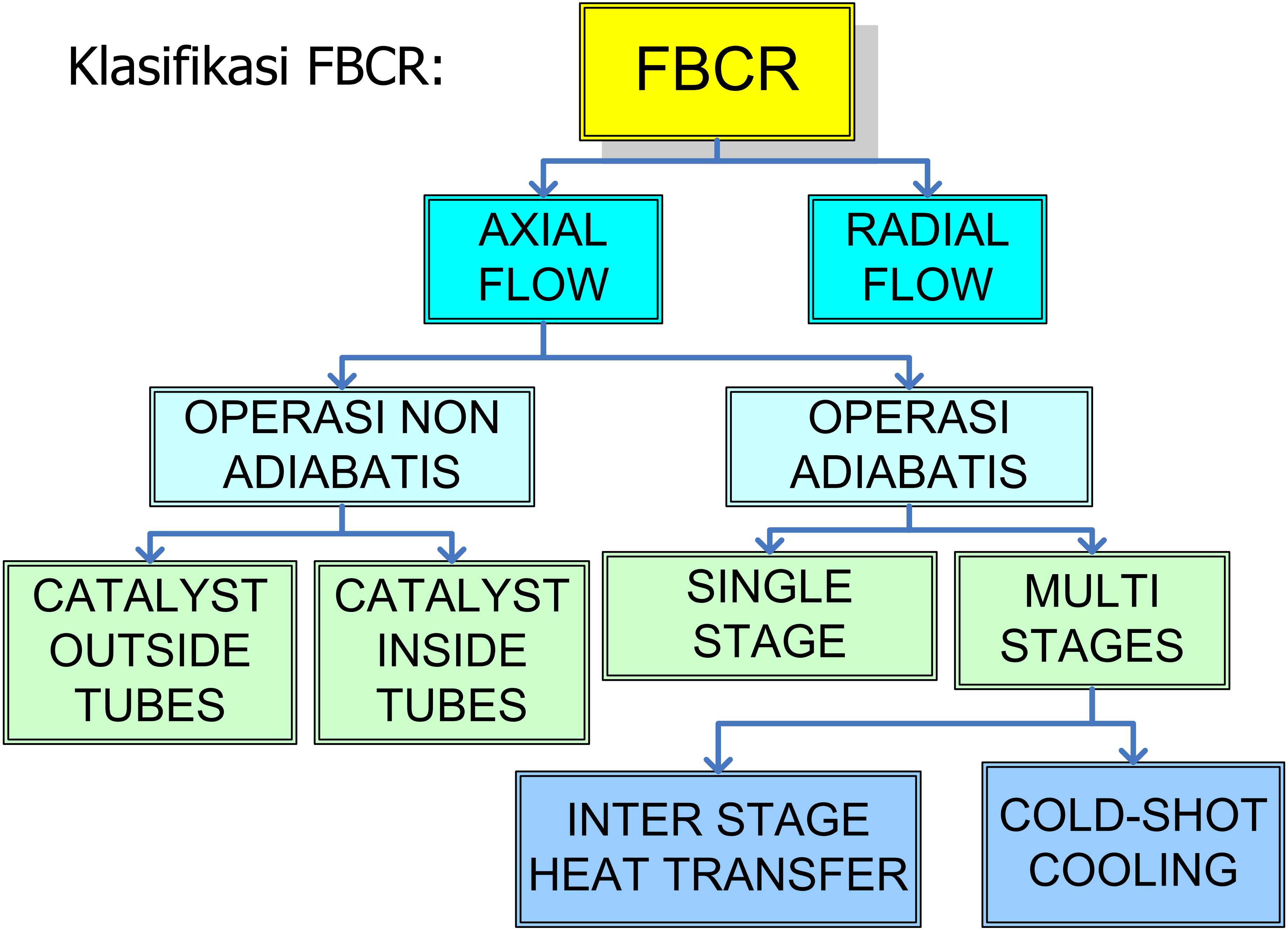


Figure 4-17. Differential reactor. *(Source: V. W. Weekman, "Laboratory Reactors and Their Limitations,"* AIChEJ, *Vol. 20, p. 833, 1974. Used with permission of the AIChEJ.)*

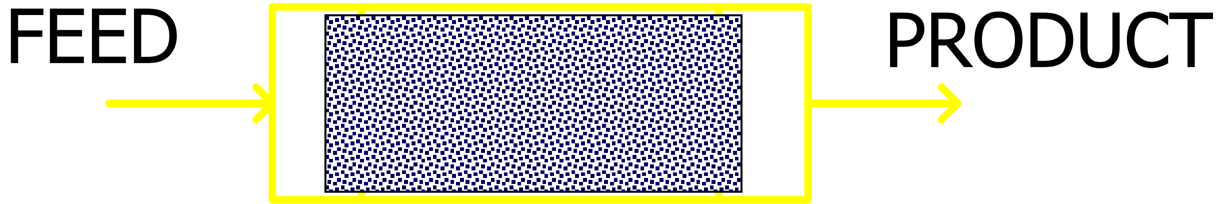
15-16-17
Fixed-Bed Catalytic Reactors (FBCR)

Klasifikasi FBCR:



- FBCR
  - AXIAL FLOW
    - OPERASI NON ADIABATIS
      - CATALYST OUTSIDE TUBES
      - CATALYST INSIDE TUBES
    - OPERASI ADIABATIS
      - SINGLE STAGE
      - MULTI STAGES
        - INTER STAGE HEAT TRANSFER
        - COLD-SHOT COOLING
  - RADIAL FLOW

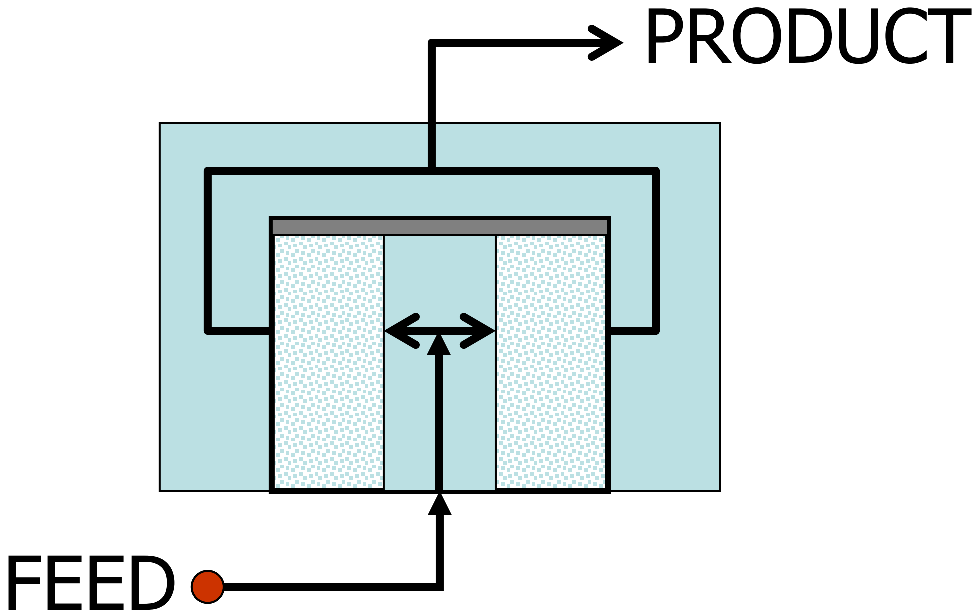
AXIAL FLOW:



FEED

PRODUCT

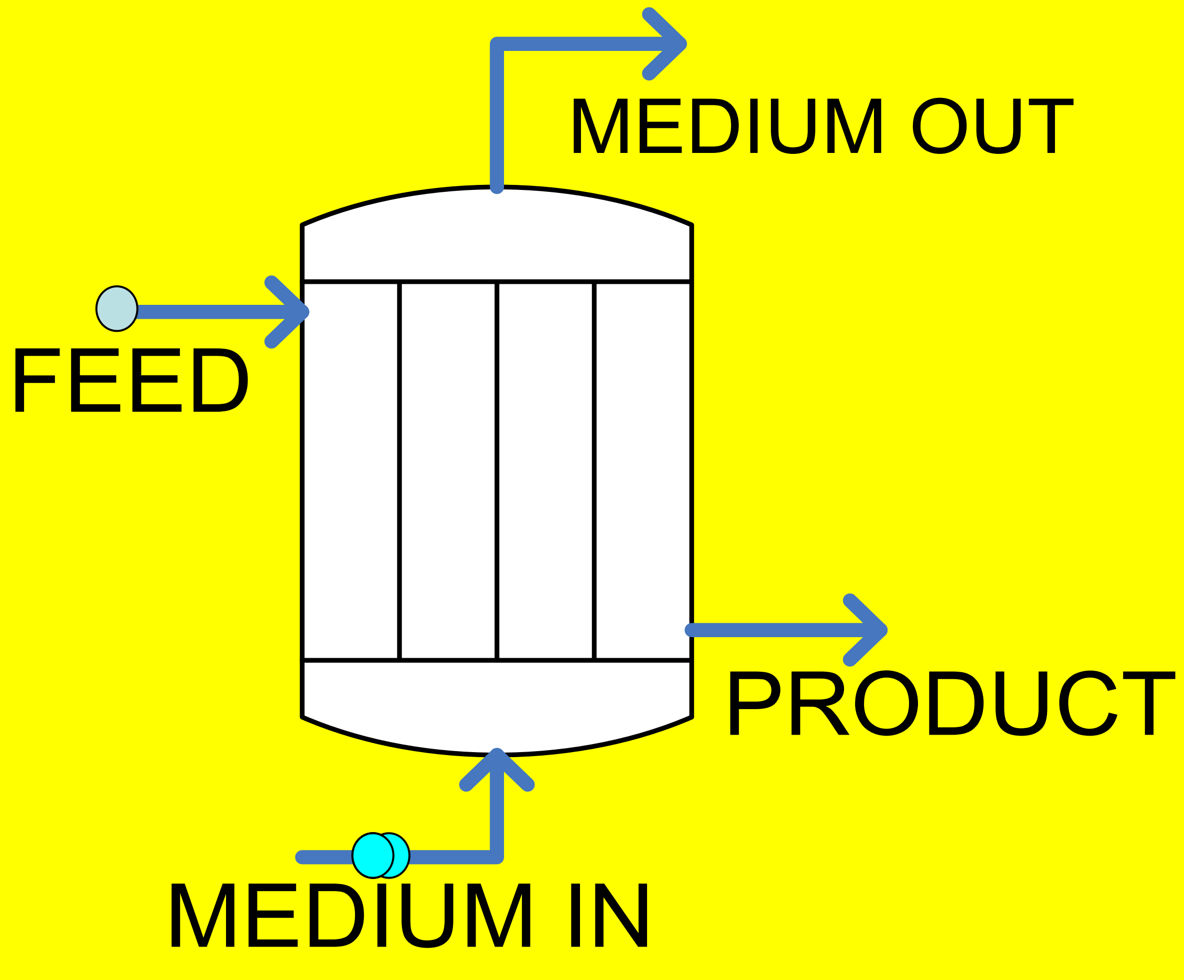
RADIAL FLOW:



PRODUCT

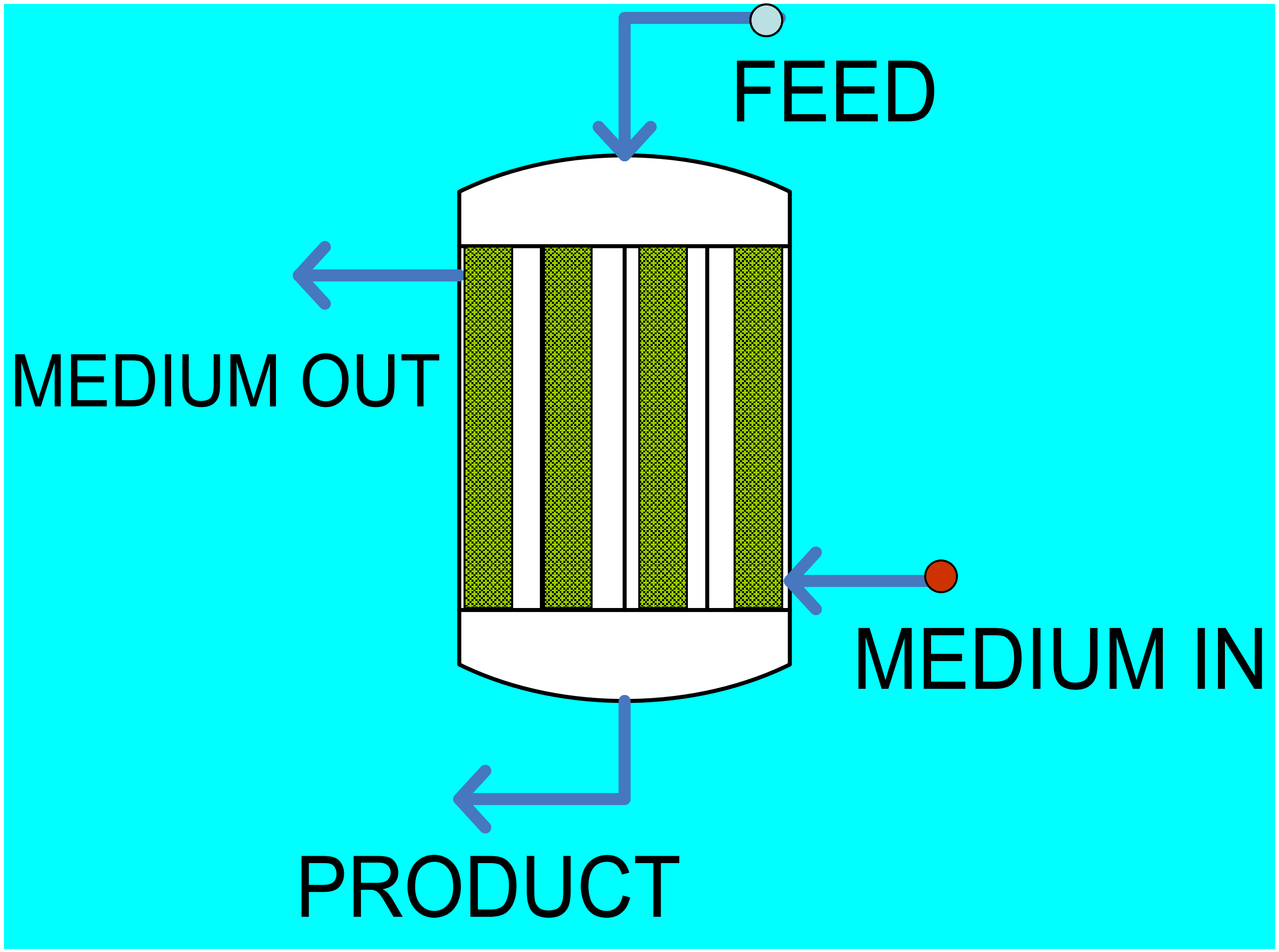
FEED

CATALYST OUTSIDE TUBES



CATALYST OUTSIDE TUBES

CATALYST INSIDE TUBES



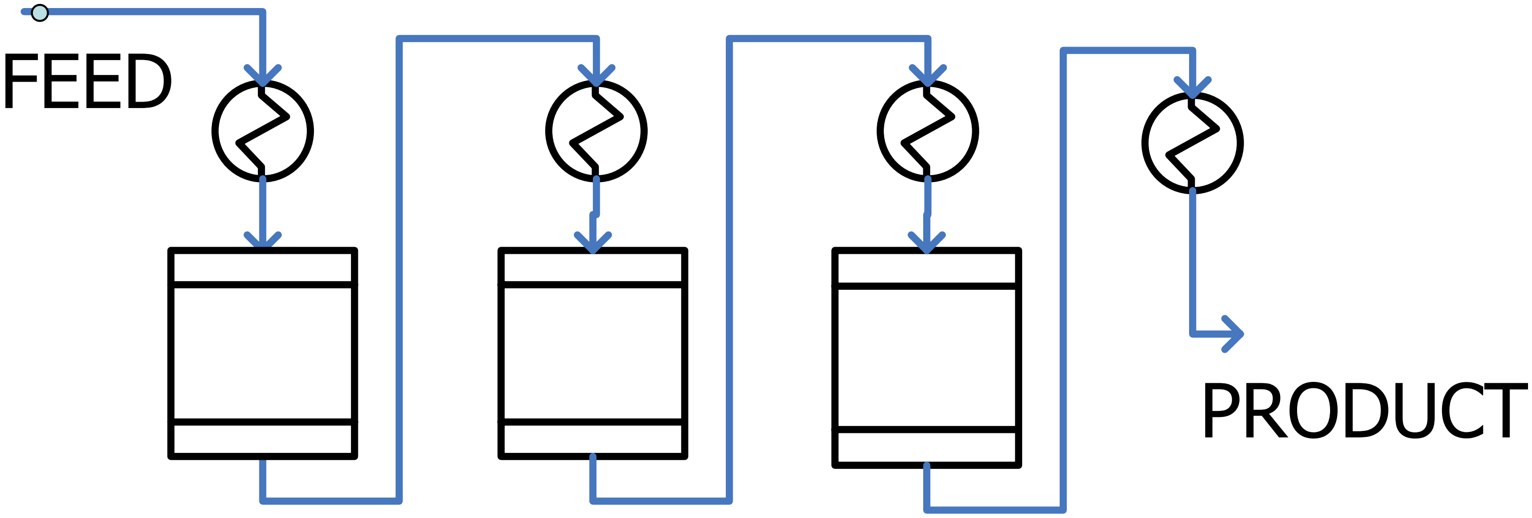
FEED

MEDIUM OUT

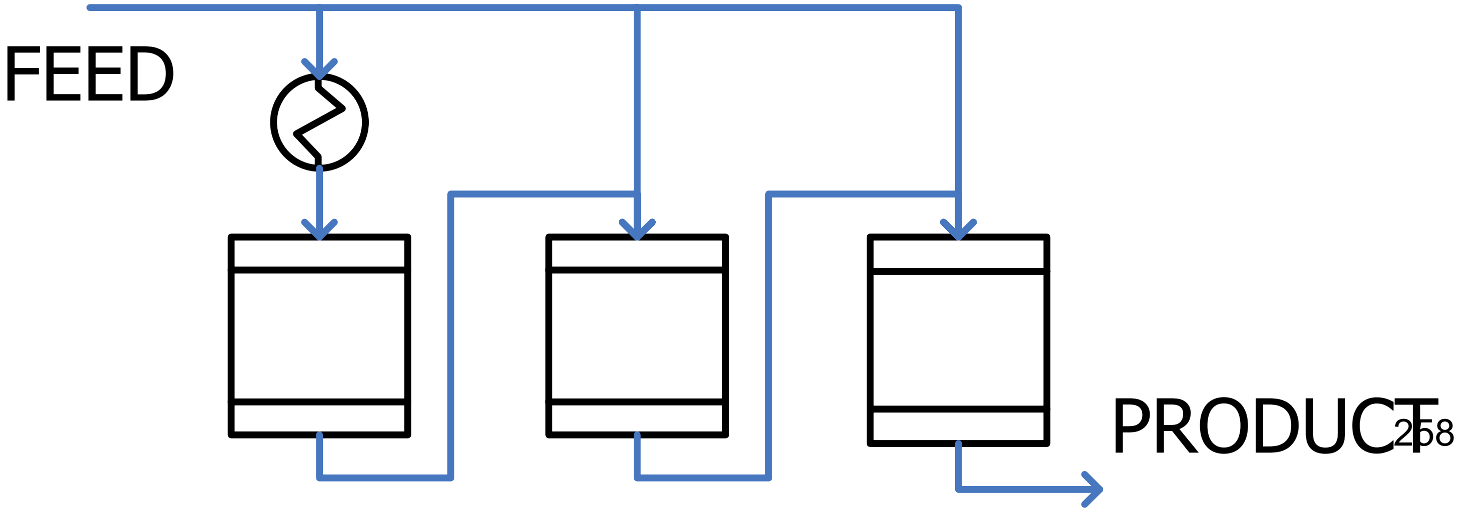
MEDIUM IN

PRODUCT

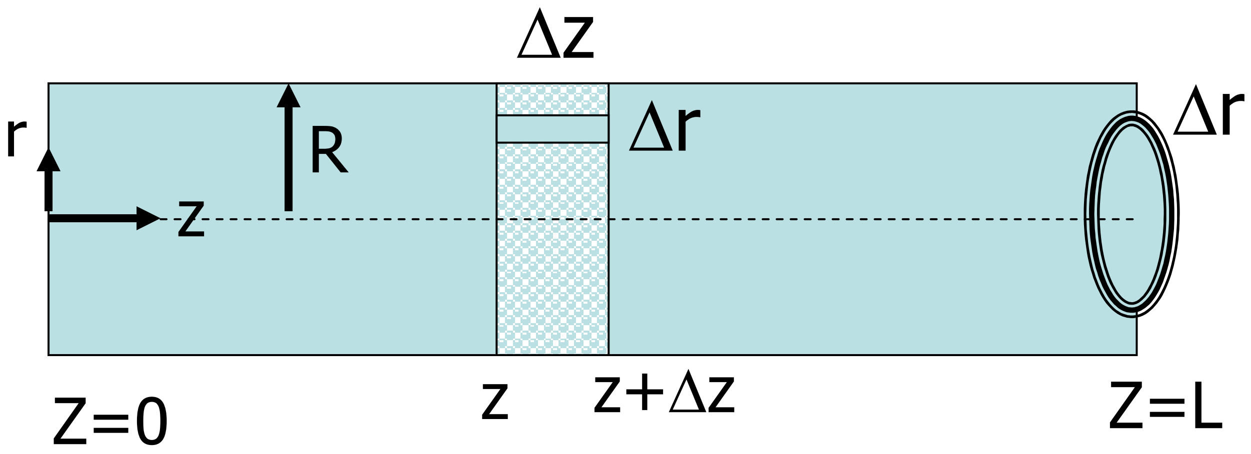
INTER STAGE HEAT TRANSFER:



COLD SHOT COOLING:



Fixed bed (Integral) reactor



Neraca mol pada elemen volume $2 \pi r \Delta r \Delta z$

$$R_{in} - R_{out} + R_{generation} = R_{acc}$$

$$\begin{bmatrix} Laju\, masuk \\ karena\, aliran \end{bmatrix} - \begin{bmatrix} Laju\, keluar \\ karena\, aliran \end{bmatrix} + \begin{bmatrix} Laju\, masuk \\ karena\, difusi \end{bmatrix} - \begin{bmatrix} Laju\, keluar \\ karena\, difusi \end{bmatrix} + \begin{bmatrix} Laju \\ generasi \end{bmatrix} = \begin{bmatrix} Laju \\ akumulasi \end{bmatrix}$$

$$u \cdot C \cdot 2\pi r \cdot \Delta r\Big|_z - u \cdot C \cdot 2\pi r \cdot \Delta r\Big|_{z+\Delta z} + 2\pi r \cdot \Delta z\left(-D_{er}\frac{\partial C}{\partial r}\right)\Bigg|_r$$

$$+ 2\pi r \cdot \Delta r\left(-D_{ez}\frac{\partial C}{\partial z}\right)\Bigg|_z - 2\pi r \cdot \Delta z\left(-D_{er}\frac{\partial C}{\partial r}\right)\Bigg|_{r+\Delta r}$$

$$- 2\pi r \cdot \Delta r\left(-D_{ez}\frac{\partial C}{\partial z}\right)\Bigg|_{z+\Delta z} + r_{i,V}\left(2\pi r \cdot \Delta r \cdot \Delta z\right)\rho_B$$

$$= \left(2\pi r \cdot \Delta r \cdot \Delta z\right)\left(\frac{\Delta C}{\Delta t}\right)$$

Lakukan penyederhanaan dan ambil limit delta → 0

Untuk komp. Umpan A, persamaan menjadi:

$$-\frac{\partial}{\partial z}\left(u\cdot C_A\right)-\frac{1}{r}\frac{\partial}{\partial r}\left[r\cdot\left(-D_{er}\frac{\partial C_A}{\partial r}\right)\right]-\frac{\partial}{\partial z}\left(-D_{ez}\frac{\partial C_A}{\partial z}\right)+r_A\rho_B=\frac{\partial C_A}{\partial t}$$

Keadaan ajeg → akumulasi = 0

$$-\frac{\partial}{\partial z}\left(u\cdot C_A\right)+D_{er}\left(\frac{1}{r}\frac{\partial C_A}{\partial r}+\frac{\partial^2 C_A}{\partial r^2}\right)+D_{ez}\frac{\partial^2 C_A}{\partial z^2}+r_A\rho_B=0 \qquad 21.4\text{-}1$$

(Model pseudo homogen 2 arah z dan r)

Bila difusi arah axial dan radial diabaikan, didapat:

$$-\frac{\partial}{\partial z}\left(u\cdot C_A\right)+r_A\rho_B=0 \qquad 21.5\text{-}1$$

Dengan u = laju linier, $-u\frac{\partial C_A}{\partial z} - C_A\frac{\partial u}{\partial z} + r_A\rho_B = 0$

Asumsi u konstan sepanjang z dan misal Ac = luas penampang reaktor:

$$-uA_c\frac{\partial C_A}{\partial z} + A_c r_A \rho_B = 0,$$

$$note: F_A = uA_c C_A \Rightarrow \; dF_A = uA_c dC_A$$

$$-\frac{dF_A}{dz} = -r_A A_c \rho_B ,\, F_A = F_{A0}\left(1 - x\right)$$

$$\frac{F_{A0}dx}{-r_A} = A_c\rho_B dz = dW,\, sehingga: \; W = \int_0^x \frac{F_{A0}dx}{-r_A} \quad \text{21.5-4}$$

Neraca energi:
Penjabaran identik Neraca mol

$$u \cdot 2\pi r \Delta r \rho c_p \left(T - T_R\right)\Big|_z - u \cdot 2\pi r \Delta r \rho c_p \left(T - T_R\right)_{z+\Delta z} + 2\pi r \cdot \Delta z \left(-k_{er} \frac{\partial T}{\partial r}\right)\Bigg|_r$$

$$+ 2\pi r \cdot \Delta r \left(-k_{ez} \frac{\partial T}{\partial z}\right)\Bigg|_z - 2\pi r \cdot \Delta z \left(-k_{er} \frac{\partial T}{\partial r}\right)\Bigg|_{r+\Delta r}$$

$$- 2\pi r \cdot \Delta r \left(-k_{ez} \frac{\partial T}{\partial z}\right)\Bigg|_{z+\Delta z} + r_{i,V} \left(2\pi r \Delta r \Delta z\right) \rho_B \left(\Delta H_{RT}\right)$$

$$= \left(2\pi r \Delta r \Delta z\right)\left(\varepsilon \rho c_p + (1-\varepsilon)\rho_s c_{ps}\right)\left(\frac{\Delta T}{\Delta t}\right)$$

Pers. Dibagi elemen volume, ambil limit Δ → 0:

Diperoleh persamaan:

$$-\frac{\partial}{\partial z}\left(u\rho c_p T\right)-\frac{1}{r}\frac{\partial}{\partial r}\left(r\cdot -k_{er}\frac{\partial T}{\partial r}\right)-\frac{\partial}{\partial z}\left(-k_{ez}\frac{\partial T}{\partial z}\right)+r_A\rho_B\Delta H_{RT}$$

$$=\left(\varepsilon\rho c_p+\left(1-\varepsilon\right)\rho_s c_{ps}\right)\frac{\partial T}{\partial t}$$

$$-\frac{\partial}{\partial z}\left(u\rho c_p T\right)+\frac{1}{r}k_{er}\frac{\partial T}{\partial r}+k_{er}\frac{\partial^2 T}{\partial r^2}+k_{ez}\frac{\partial^2 T}{\partial z^2}+r_A\rho_B\Delta H_{RT}$$

$$=\left(\varepsilon\rho c_p+\left(1-\varepsilon\right)\rho_s c_{ps}\right)\frac{\partial T}{\partial t}$$

Keterangan:
k_{er}, k_{ez} = konduktivitas termal arah radial dan axial,
ϕ= porositas, ΔH_{RT} = panas reaksi pada suhu T,
ρ = densitas, c_p = kapasitas panas

Pada keadaan steady-state dan *u* = konstan

$$-u\rho c_p \frac{\partial T}{\partial z} + \frac{1}{r}k_{er}\frac{\partial T}{\partial r} + k_{er}\frac{\partial^2 T}{\partial r^2} + k_{ez}\frac{\partial^2 T}{\partial z^2} + r_A \rho_B \Delta H_{RT} = 0$$

dengan, $u\rho$ = G

$$k_{er}\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) + k_{ez}\frac{\partial^2 T}{\partial z^2} - Gc_p\frac{\partial T}{\partial z} + r_A\rho_B\Delta H_{RT} = 0$$

21.4-2

Kondisi batas untuk vesel tertutup:

Pada z = 0

$$u\left(C_{A0} - C_A\right) = -D_{ez}\frac{dC_A}{dz} \qquad 21.4\text{-}3$$

$$Gc_p\left(T_0 - T\right) = -k_{ez}\frac{dT}{dz} \qquad 21.4\text{-}4$$

Pada z = L $$\frac{dC_A}{dz} = \frac{dT}{dz} = 0$$ 21.4-5

Pada r = 0 $$\frac{\partial C_A}{\partial r} = \frac{\partial T}{\partial r} = 0$$ 21.4-6

Pada r = R $$\frac{\partial C_A}{\partial r} = 0$$ 21.4-7

$$k_{er}\left(\frac{\partial T}{\partial r}\right)_{r=R} = U\left(T_{r=R} - T_s\right)$$ 21.4-8

T_s = temperatur sekeliling

Pertimbangan karakteristik partikel dan katalis

- Komposisi kimia → aktivitas katalis
- Sifat-sifat fisika → ukuran, bentuk, densitas, dan porositas/ rongga
- Bentuk katalis → silinder, bola, dan plat: ukuran kecil beberapa mm
- Volume bed: untuk vesel silinder $$V = \frac{\pi}{4} D^2 L$$
- Densitas bulk, ρ_B = w/V, w = massa total bed
- Rongga katalis, ε_B

$$\varepsilon_B = \frac{V - Volume\ partikel}{V} = \frac{V - V\rho_B / \rho_p}{V} = 1 - \frac{\rho_B}{\rho_p}$$

$$\rho_B = \rho_p (1 - \varepsilon_B) = \rho_s (1 - \varepsilon_p)(1 - \varepsilon_B)$$

Interaksi Fluid-partikel; Pressure Drop (-ΔP)

Bila fluida mengalir melalui partikel katalis, interaksi antara fluida dan partikel menjadi friksi pressure drop. Dari neraca momentum diperoleh pers. Berikut:

$$\frac{dP}{dz} + \frac{fu^2 \rho_f}{d_p^{'}} = 0$$

Dengan:

z = koordinat arah aliran (sepanjang bed)
f = faktor friksi
u = kecepatan linier superfisial
ρ_f = densitas fluida

d’$_p$ = diameter partikel efektif
= 6 x volume partikel/luas permukaan luar partikel

$$d'_p = 6\frac{V_p}{A_p}$$

Untuk partikel bola: $d'_p = d_p$

Untuk partikel padat silinder:

$$d'_p = 3d_p/\left(2 + d_p/L_p\right) or\ 1{,}5d_p, if\ d_p/L_p << 2$$

Dengan L_p = panjang partikel

Untuk faktor friksi dapat digunakan pers Ergun (1952)

$$f = \left\{1{,}75 + 150\left(1-\varepsilon_B\right)/R'_e\right\}\left(1-\varepsilon_B\right)/\varepsilon_B^3$$

$\dot{m}$

$$R'_e = \frac{d'_p u \rho_f}{\mu_f} = \frac{d'_p G}{\mu_f}$$

$$G = \frac{\dot{m}}{A_c} = \frac{4\dot{m}}{\pi D^2}$$

G = fluks massa, $\dot{m}$ = laju alir massa, D = diameter bed

Alternatif, menentukan D (atau L) untuk beda tekanan yang diperkenankan:

$$D^6 - \beta\kappa D^2 - \kappa = 0$$

$$\beta = \frac{150}{4(1.75)}\frac{\pi\mu_f(1-\epsilon_B)}{d'_p\dot{m}} = \frac{67.32\mu_f(1-\epsilon_B)}{d'_p\dot{m}}$$

$$\kappa = \frac{64\alpha\dot{m}^2 W}{\pi^3\rho_f d'_p(-\Delta P)\rho_B}$$ dan $$\alpha = 1.75(1-\epsilon_B)/\epsilon_B^3$$

Example 21-2

The feed to the first stage of a sulfur dioxide converter is at 100 kPa and 700 K, and contains 9.5 mol % SO_2, 11.5% O_2, and 79% N_2. The feed rate of SO_2 is 7.25 kg s^{-1}. The mass of catalyst (W) is 6000 kg, the bed voidage (ε_B) is 0.45, the bulk density of the bed (ρ_B) is 500 kg m^{-3}, and the effective particle diameter (d'_P) is 15 mm; the fluid viscosity (μ_f) is 3.8×10^{-5} kg m^{-1} s^{-1}. The allowable pressure drop ($-\Delta P$) is 7.5 kPa.

(a) Calculate the bed diameter (D) and the bed depth (L) in m, assuming that the fluid density and viscosity are constant.

(b) How sensitive are these dimensions to the allowable ($-\Delta P$)? Consider values of ($-\Delta P$) from 2.5 to 15 kPa.

SOLUTION

(a) We need to determine the total mass flow rate, *m*, and the fluid density, ρ_f.

$$\dot{m} = \dot{m}_{SO_2} + \dot{m}_{O_2} + \dot{m}_{N_2} = \dot{m}_{SO_2} + x_{O_2}F_tM_{O_2} + x_{N_2}F_tM_{N_2}$$

where χ is mole fraction, F_t is total molar flow rate, and M is molar mass.

$$F_t = \dot{m}_{SO_2}/x_{SO_2}M_{SO_2} = 7.25/[0.095(64.1)] = 1.191 \text{ kmol s}^{-1}$$

$$\dot{m} = 7.25 + 0.115(1.191)32.0 + 0.79(1.191)28.0 = 38.0 \text{ kg s}^{-1}$$

Assuming ideal-gas behavior, we have

$$\begin{aligned}\rho_f &= PM_{av}/RT = P(\dot{m}/F_t)/RT \\ &= 100000(38.0)/1191(8.3145)700 = 0.548 \text{ kg m}^{-3}\end{aligned}$$

We can now calculate α, β, and κ

$$\alpha = 1.75(1 - \epsilon_B)/\epsilon_B^3 = 1.75(1 - 0.45)/0.45^3 = 10.56$$

$$\beta = \frac{67.32\mu_f(1 - \epsilon_B)}{d_p' \dot{m}} = \frac{67.32(3.8 \times 10^{-5})(1 - 0.45)}{0.015(38.0)} = 2,47 \times 10^{-3}\ \mathrm{m}^{-2}$$

$$\kappa = \frac{64\alpha \dot{m}^2 W}{\pi^3 \rho_f d_p'(-\Delta P)\rho_B} = \frac{64(10.56)(38.0)^2 6000}{(3.142)^3 0.548(0.015)7500(500)} = 6135\ \mathrm{m}^6$$

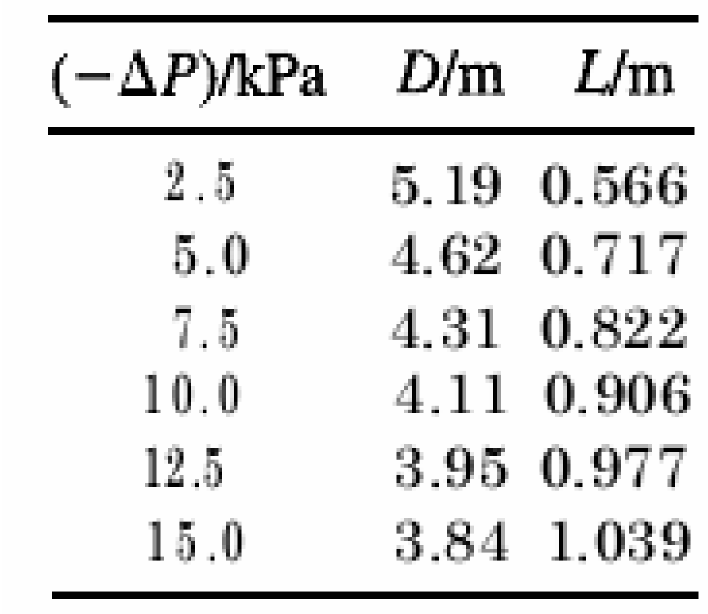
$$D^6 - 15.13D^2 - 6135 = 0$$

Solving for D by trial, we obtain: D = 4.31 m

The bed depth (L) can be calculated from equations

$$L = \frac{4W}{\rho_B \pi D^2} = \frac{4(6000)}{500(3.142)4.31^2} = 0.82\ \mathrm{m}$$

(b) The procedure described in (a) is repeated for values of (-ΔP) in increments of 2.5 kPa within the range 2.5 to 15 kPa, with results for D and L given in the following table:



$(-\Delta P)$/kPa	D/m	L/m
2.5	5.19	0.566
5.0	4.62	0.717
7.5	4.31	0.822
10.0	4.11	0.906
12.5	3.95	0.977
15.0	3.84	1.039

As expected, D decreases and L increases as (-ΔP) increases. For a given amount of catalyst, a reduced pressure drop (and operating power cost) can be obtained by reducing the bed depth at the expense of increasing the bed diameter (and vessel cost).

Example 21-3

For the dehydrogenation of ethyl benzene at equilibrium,

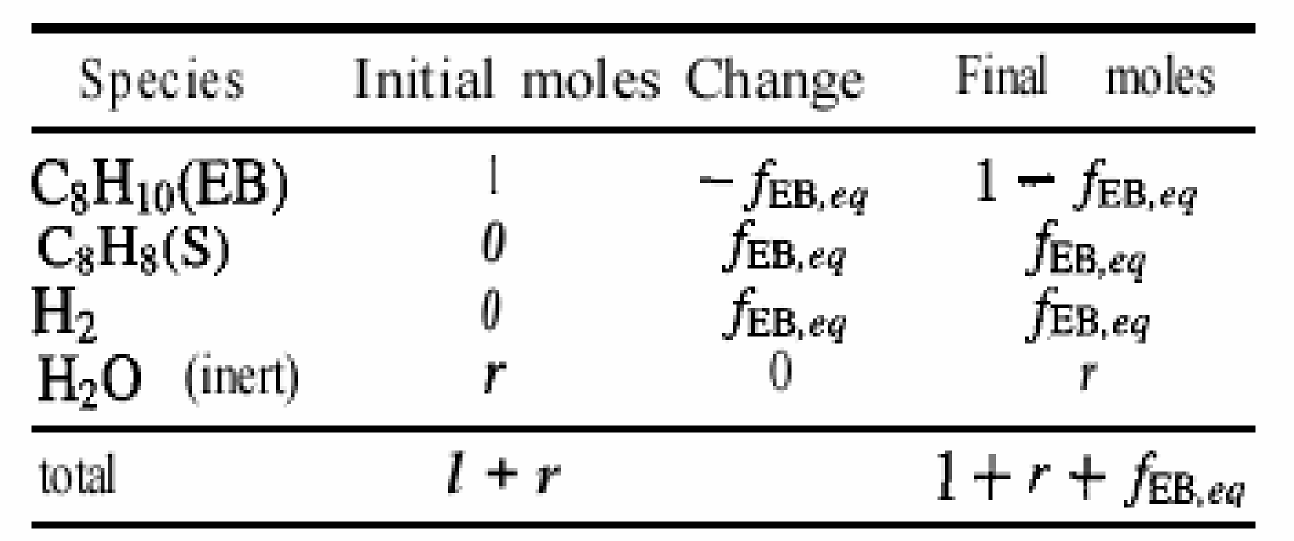
$$C_8H_{10}\,(EB) \leftrightharpoons C_8H_8\,(S) + H_2,$$

calculate and plot $f_{EB,eq}(T)$, at P = 0.14 MPa, with an initial molar ratio of inert gas (steam, H_2O) to EB of r = 15 (these conditions are also indicative of commercial operations). Assume ideal-gas behavior, with

$$Kp = 8.2 \text{ X } 10^5 \exp(-15{,}20O/T) \text{ MPa.}$$

Solution

Stoichiometric table:



Species	Initial moles	Change	Final moles
$C_8H_{10}(EB)$	1	$-f_{EB,eq}$	$1 - f_{EB,eq}$
$C_8H_8(S)$	0	$f_{EB,eq}$	$f_{EB,eq}$
H_2	0	$f_{EB,eq}$	$f_{EB,eq}$
H_2O (inert)	r	0	r
total	$1 + r$		$1 + r + f_{EB,eq}$

Applying the definition of partial pressure for each species,

$p_i = x_i P$, *we* have

$$K_p = \frac{p_S p_{H_2}}{p_{EB}} = \frac{f_{EB,eq}^2 P^2 \quad (1 + r + f_{EB,eq})}{(1 + r + f_{EB,eq})^2 \, (1 - f_{EB,eq}) P}$$

On solution for $f_{EB,eq}$, this becomes

$$f_{EB,eq} = \frac{r}{2(1 + P/K_p)} \left[\left(1 + \frac{4(1+r)(1+P/K_p)}{r^2} \right)^{1/2} - 1 \right]$$

For $P = 0.14$ MPa and $r = 15$,

$$f_{EB,eq} = \frac{7.5}{1 + 0.14/K_p} [(1 + (0.2844)(1 + 0.14/K_p)^{1/2} - 1]$$

$$K_p = 8.2 \times 10^5 \exp(-15,200/T)$$

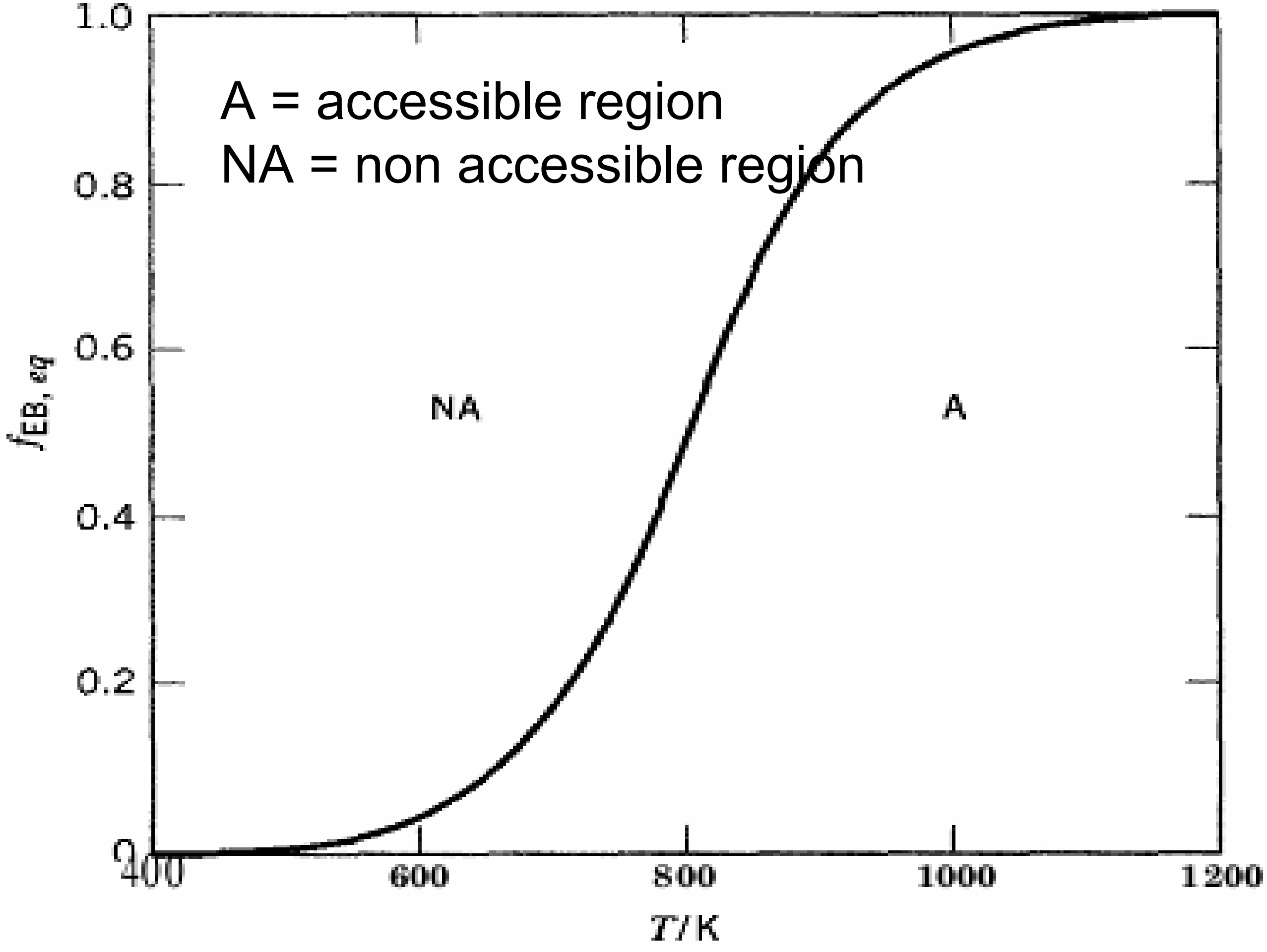
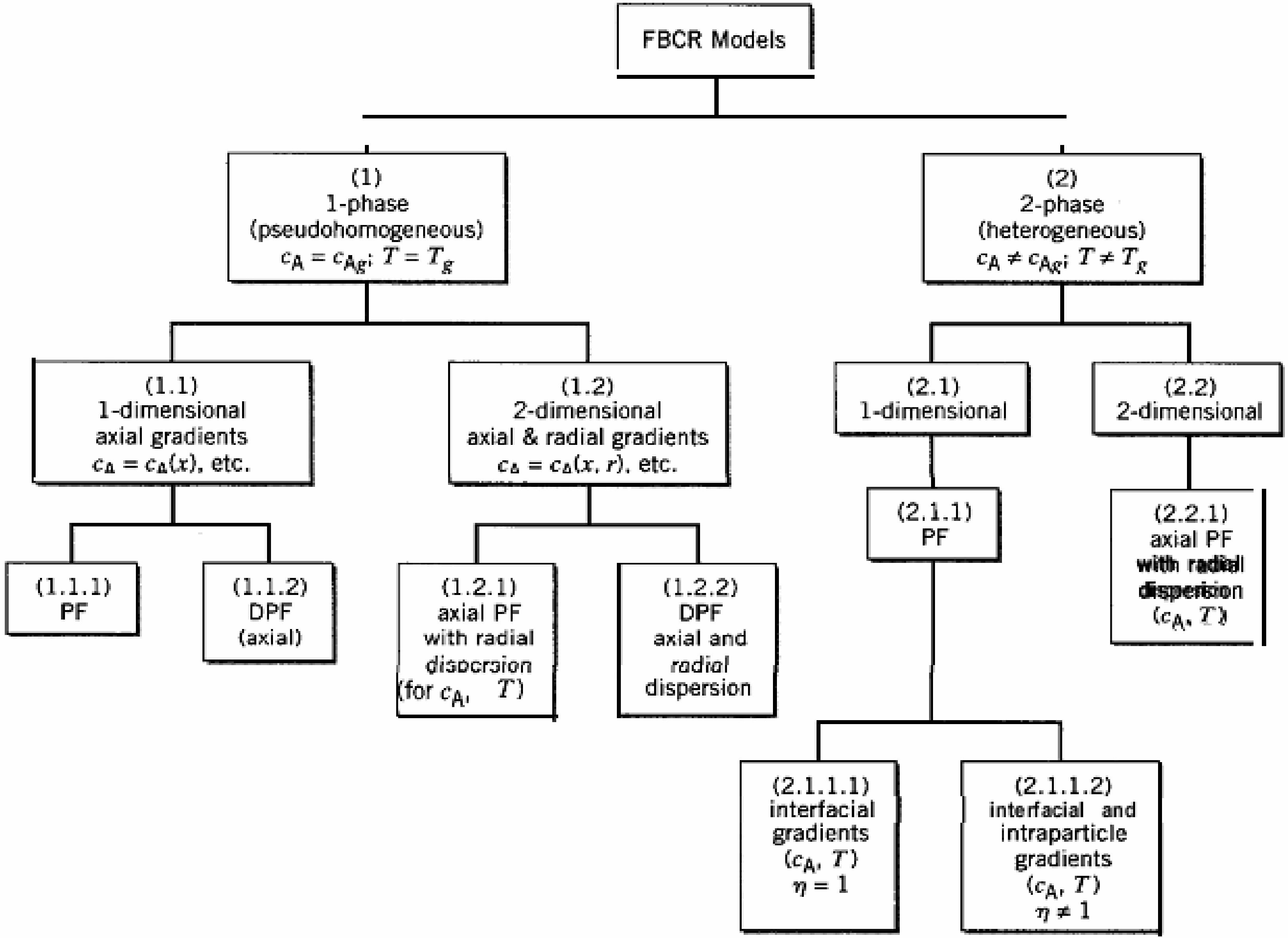


Figure 21.3 $f_{EB,eq}$ versus T for C_8H_{10} (EB) $\rightleftharpoons C_8H_8 + H_2$; P = 0.14 MPa; r = 15 (based on data from Stull et al., 1969)

A CLASSIFICATION OF REACTOR MODELS



FBCR Models

(1)
1-phase
(pseudohomogeneous)
$c_A = c_{Ag}$; $T = T_g$

(2)
2-phase
(heterogeneous)
$c_A \neq c_{Ag}$; $T \neq T_g$

(1.1)
1-dimensional
axial gradients
$c_A = c_A(x)$, etc.

(1.2)
2-dimensional
axial & radial gradients
$c_A = c_A(x, r)$, etc.

(2.1)
1-dimensional

(2.2)
2-dimensional

(1.1.1)
PF

(1.1.2)
DPF
(axial)

(1.2.1)
axial PF
with radial
dispersion
(for c_A, T)

(1.2.2)
DPF
axial and
radial
dispersion

(2.1.1)
PF

(2.2.1)
axial PF
with radial
dispersion
(c_A, T)

(2.1.1.1)
interfacial
gradients
(c_A, T)
$\eta = 1$

(2.1.1.2)
interfacial and
intraparticle
gradients
(c_A, T)
$\eta \neq 1$

Optimal Single-Stage Operation

- The amount of catalyst is a minimum, W_{min}, if $(-r_A)$ is the maximum rate at conversion, f_A.
- For an exothermic, reversible reaction, this means operating non adiabatically and non isothermally on the locus of maximum rates, subject to any limitation imposed by T_{max}
- For an endothermic, reversible reaction, it means operating isothermally at the highest feasible value of T.
- The reaction paths (f_A versus T) for the two cases are shown schematically in Figure 21.7

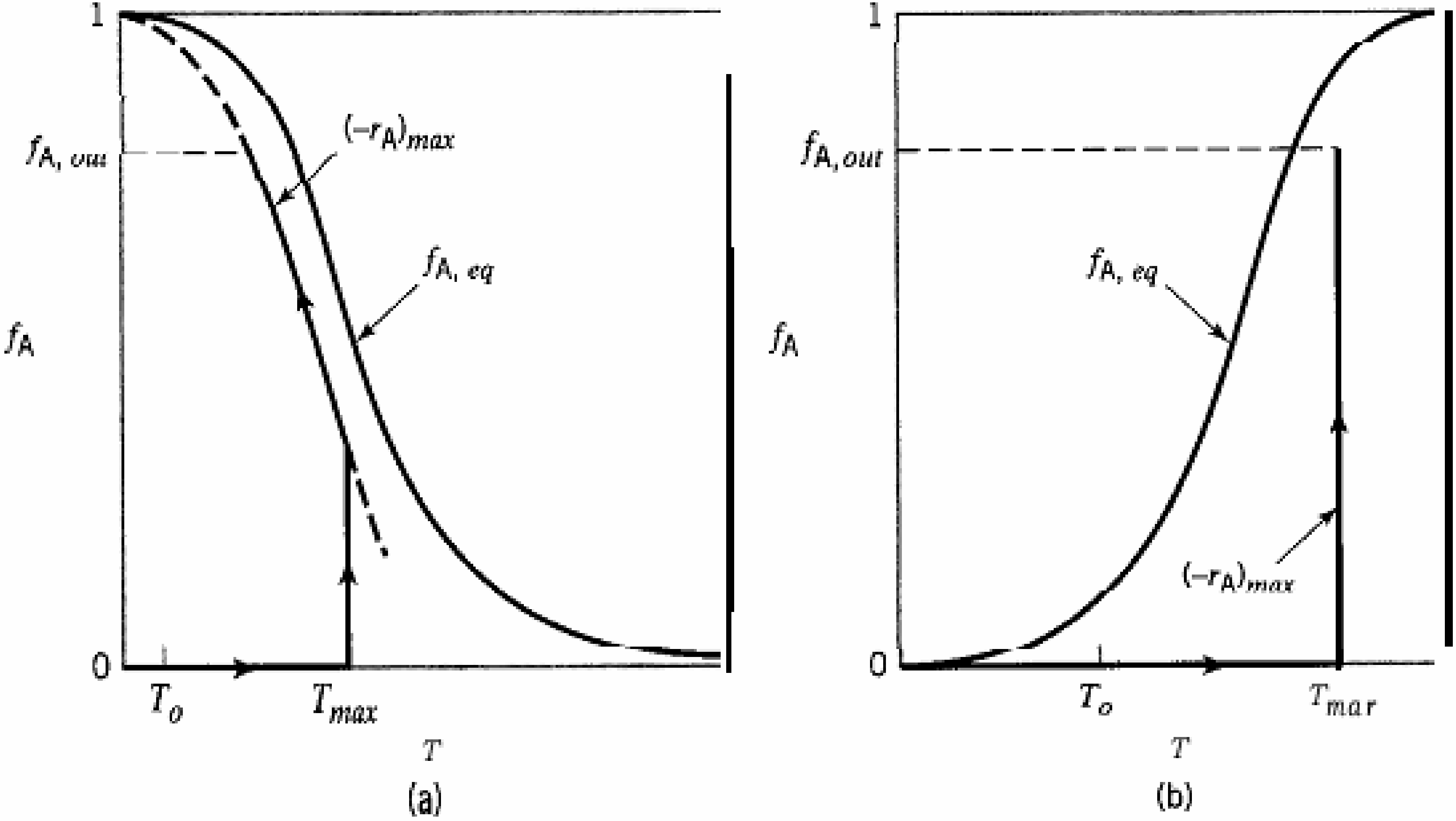


Figure 21.7 Path for W_{min} in FBCR: (a) **exothermic** reaction (nonadiabatic, **nonisothermal** operation), (b) endothermic reaction (isothermal)

Adiabatic Operation

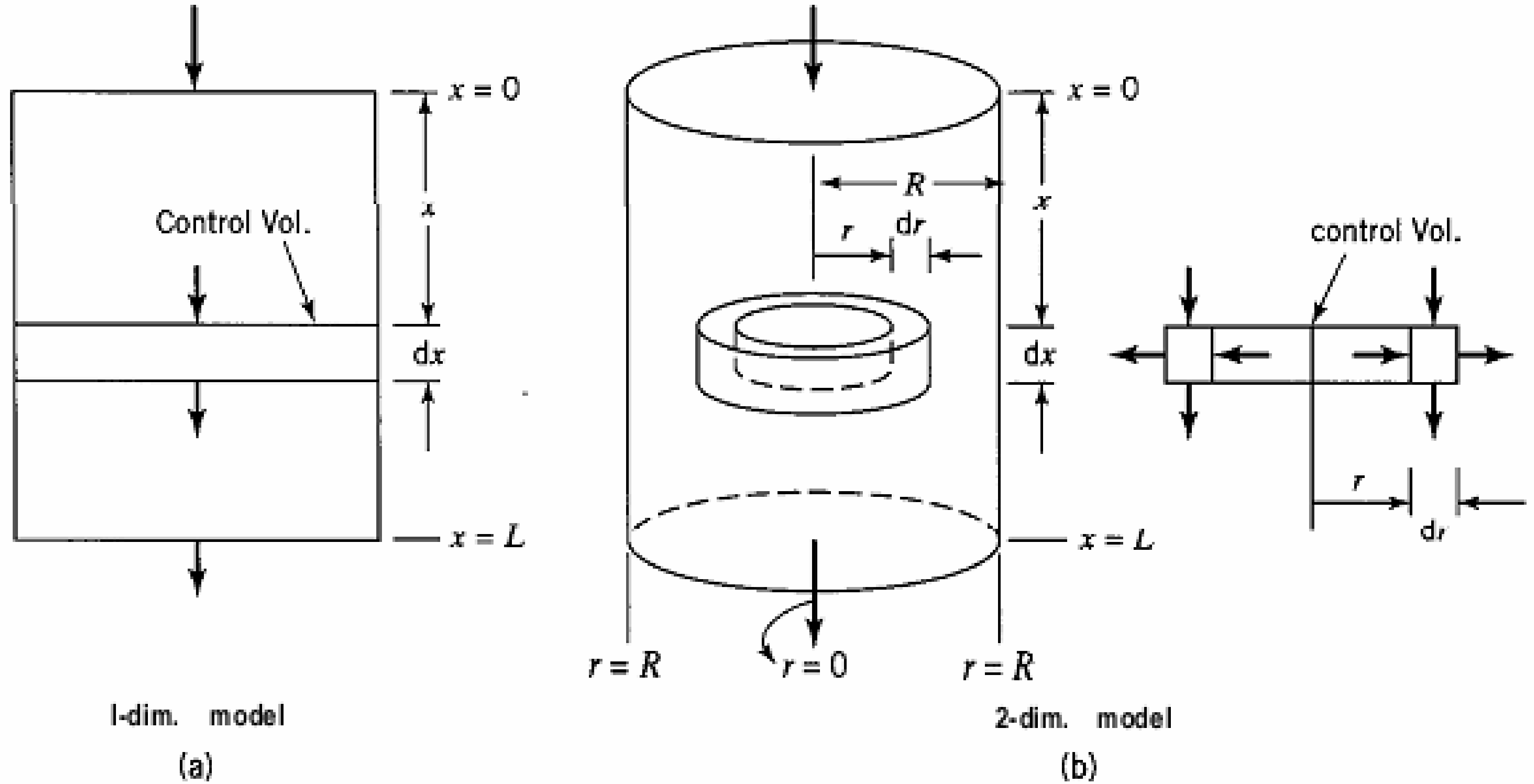


Figure 21.6 Control volumes for (a) one- and (b) two-dimensional models

Adiabatic Operation

Multistage Operation with Inter-stage Heat Transfer

- For one-dimensional plug flow, with $k_{ex} = k_{er} = 0$ and $T = T(x)$, general equation reduces to:

$$Gc_P \frac{dT}{dx} - \rho_B(-r_A)(-\Delta H_{RA}) = 0 \qquad 21.5\text{-}6$$

The one required boundary condition can be chosen as

$$T = T_0 \qquad \text{at } x = 0 \qquad 21.5\text{-}7$$

of a PFR. Since

$$G = \dot{m}/\pi r^2 \qquad 21.3\text{-}9$$

and

$$dx = dV/\pi r^2 = dW/\rho_B \pi r^2 = F_{Ao} df_A/(-r_A)\rho_B \pi r^2$$

substituting for G and dx, and rearranging, we obtain

$$\mathrm{d}f_{\mathrm{A}} = \frac{mc_p}{(-\Delta H_{R\mathrm{A}})F_{\mathrm{A}o}}\mathrm{d}T \qquad 21.5\text{-}8$$

On integration, with $f_A = 0$ at T_O, and the coefficient of dT constant, this becomes

$$f_{\mathrm{A}} = \frac{mc_p}{(-\Delta H_{R\mathrm{A}})F_{\mathrm{A}o}}(T - T_o) \qquad 21.5\text{-}9$$

Integration of equation from the inlet to the outlet of the i^{th} stage of a multistage arrangement, again with the coefficient of dT constant, results in

$$\Delta f_{\mathrm{A}i} = f_{\mathrm{A}i} - f_{\mathrm{A},i-1} = \frac{mc_p}{(-\Delta H_{R\mathrm{A}})F_{\mathrm{A}o}}(T_i - T_{i-1}) \qquad 21.5\text{-}9a$$

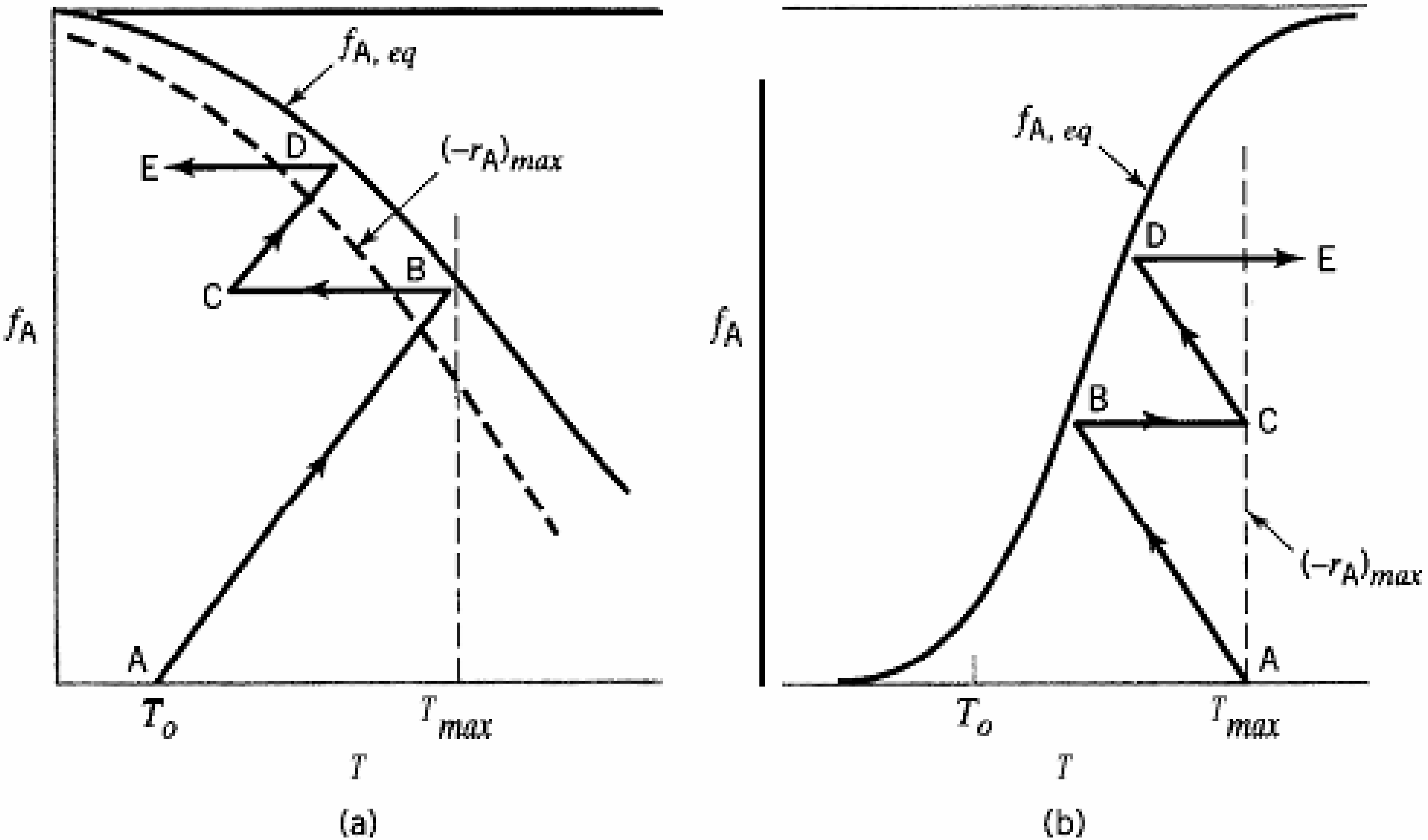


Figure 21.8 Operating lines (AB and CD) from energy equation 21.58 for two-stage (adiabatic) FBCR: (a) exothermic reversible reaction; (b) endothermic reversible reaction

Example 21-5

Reaction: $EB \leftrightarrow S + H_2$

From the data given below, calculate (a) the amount of catalyst, W, for $f_{EB} = 0.40$, and (b) the bed diameter D and bed depth L.

Data:

F_{EB0} = 11 mol s^{-1}; T_0 = 922; P_0 = 0.24 MPa;
allowable $(-\Delta P)$ = 8.1 kPa; F_{H2O} = 165 mol s^{-1};
ΔH_{REB} = 126 kJ mol^{-1}; c_p = 2.4 J g^{-1} K^{-1}; ε_B = 0.50;
$\mu_f = 2 \times 10^{-5}$ Pas; Asume ρ_B = 500 kg m^{-3} and the particles are cylindrical with d_p = 4.7 mm;
Rate law: $(-r_{EB}) = k_{EB}(P_{EB} - P_S P_{H2}/K_p)$;
$k_{EB} = 3.46 \times x10^4 \exp(-10,980/T)$ mol $(kgcat)^{-1}$ $s^{-1}MPa^{-1}$ with T in K; $Kp = 8.2 \times 10^5 \exp(-15200/T)$,MPa

SOLUTION

Mol balance EB: $W = \int_0^{0.4} F_{EBo}\,df_{EB}/(-r_{EB})$ (A)

Energy balance: $T = T_o + [(-\Delta H_{REB})F_{EBo}/\dot{m}c_P]f_{EB}$ (B)

$$(-r_{EB}) = k_{EB}(p_{EB} - p_S p_{H_2}/K_p) \quad \text{(C)}$$

$$k_{EB} = 3.46 \text{ X } 10^4 \exp(-10,980/T) \quad \text{(D)}$$

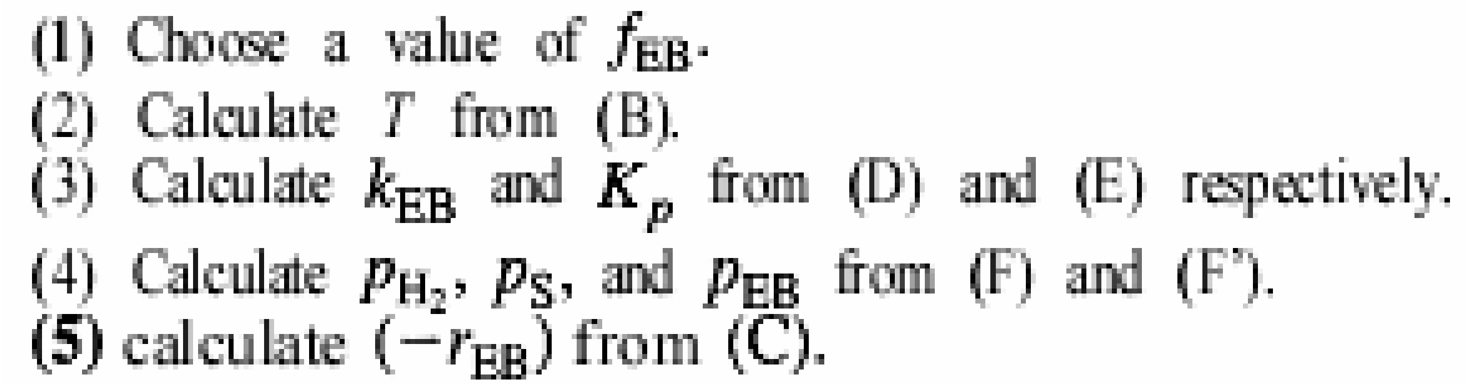
$$K_p = 8.2 \text{ X} 10^5 \exp(-15,200/T) \quad \text{(E)}$$

Species	Initial moles	Change	Final moles
EB	F_{EBo}	$-F_{EBo}f_{EB}$	$F_{EBo}(1 - f_{EB})$
S	0	$+F_{EBo}f_{EB}$	$F_{EBo}f_{EB}$
H_2	0	$+F_{EBo}f_{EB}$	$F_{EBo}f_{EB}$
H_2O	$15F_{EBo}$	0	$15F_{EBo}$
total			$F_{EBo}(16 + f_{EB})$

$$P_{H_2} = P_S = \left[f_{EB} / (16 + f_{EB}) \right] P_0 \qquad \text{(F)}$$

$$P_{EB} = \left[(1 - f_{EB}) / (16 + f_{EB}) \right] P_0 \qquad \text{(F')}$$

Where P_0, is the inlet pressure, and the small pressure drop is ignored for this purpose, since it is only 6% of P_0 These equations, (A) to (F'), may be solved using the following algorithm:



(1) Choose a value of f_{EB}.
(2) Calculate T from (B).
(3) Calculate k_{EB} and K_p from (D) and (E) respectively.
(4) Calculate p_{H_2}, p_S, and p_{EB} from (F) and (F').
(5) calculate $(-r_{EB})$ from (C).

(6) Calculate W from (A)

Results are given in the following table for a step-size of 0.1. The estimated amount of catalyst is W = 2768 kg, D = 1.99 m; L = 1.74 m

Optimal Multistage Operation with Inter-stage Cooling

- In this section, we consider one type of optimization for adiabatic multistage operation with inter-cooling for a single, reversible, exothermic reaction:
  - The minimum amount of catalyst, W_{min}, required for a specified outlet conversion.
  - The existence of an optimum is indicated by the the degree of approach to equilibrium conversion (f_{eq})
  - A close approach to equilibrium results in a relatively small number of stages (N), but a relatively large W per stage,
  - since reaction rate goes to zero at equilibrium; conversely, a more “distant” approach leads to a smaller W per stage,
  - since operation is closer to the locus of maximum rates, but a larger N. Similarly, a large extent of cooling (lower T at the inlet to a stage) results in a smaller N, but a larger W per stage,

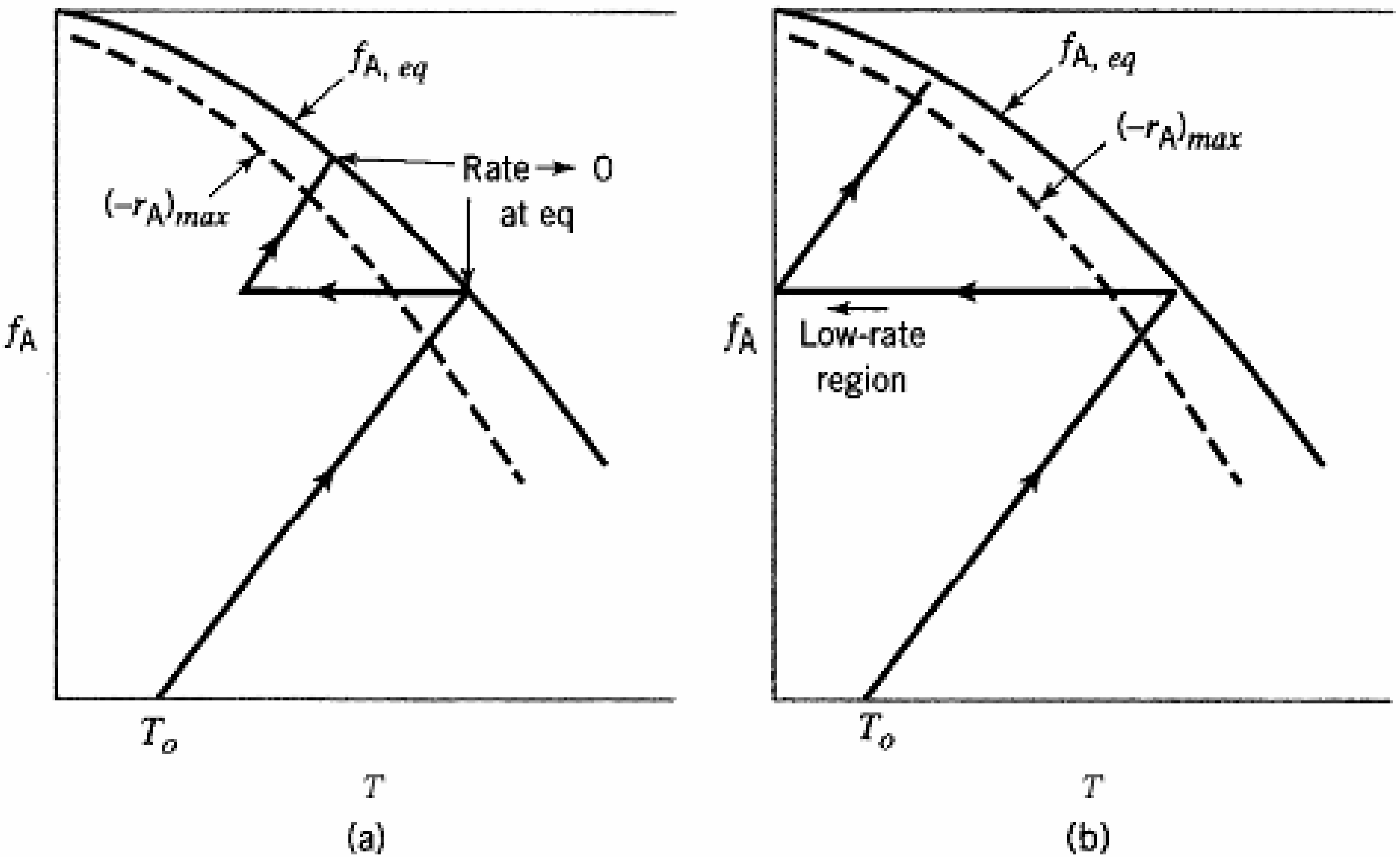


Figure 21.9 Extreme cases for FBCR, both requiring relatively large W(catalyst): (a) approach to equilibrium; (b) extent of interstage cooling

Optimization has been considered by Chartrand and Crowe (1969) for an SO_2 converter in a plant in Hamilton, Ontario, as it existed then.

1. W_{min} for specified N, $f_{N,out}$

   For an N-stage reactor, there are 2N - 1 decisions to make to determine W_{min}: N values of $T_{i,in}$ and N - 1 values of $f_{i,out}$ where sub i refers to the i^{th} stage.

   Two criteria provided (Konocki, 1956; Horn, 1961) for these are:

$$(-r_A)_{i,out} = (-r_A)_{i+1,in} \qquad (21.5\text{-}10)$$

And

$$\left[\int_{f_{A,in}}^{f_{A,out}} \frac{1}{(-r_A)} \frac{\partial(-r_A)}{\partial T} \mathrm{d} f_A\right]_i = 0 \qquad (21.5\text{-}11)$$

(2) $W_{\min}$ for specified f_{out}

- A more general case than (1) is that in which f_{out} is specified but N is not.
- This amounts to a two-dimensional search in which the procedure and criteria in case (1) constitute an inner loop in an outer-loop search for the appropriate value of N.
- Since N is a small integer, this usually entails only a small number of outer-loop iterations.

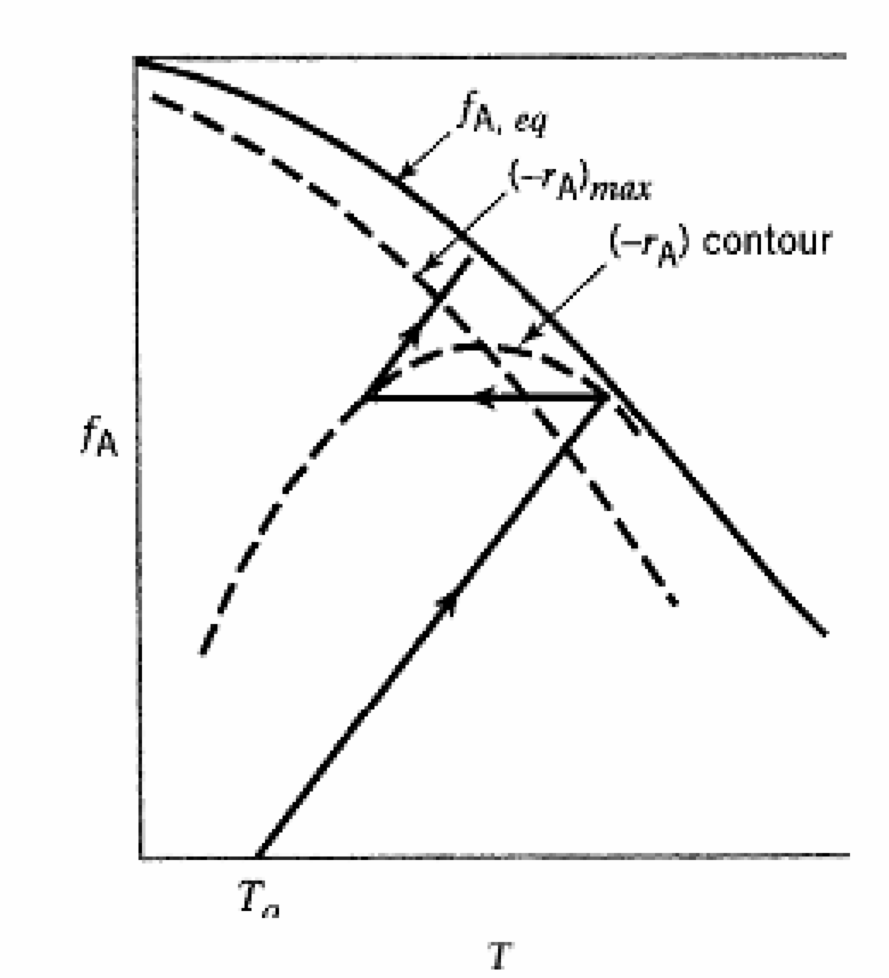
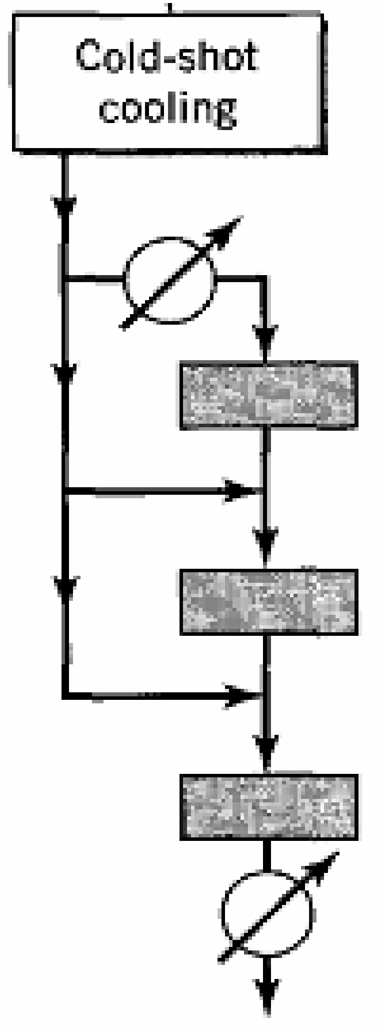


Figure 21.10 Graphical illustration of criterion 21.5-10 and its consequences & for determination of W_{min}.

Multistage Operation with Cold-Shot Cooling

- An alternative way to adjust the temperature between stages is through “cold-shot” (or “quench”) cooling.
- In adiabatic operation of a multistage FBCR for an exothermic, reversible reaction with cold-shot cooling
- T is reduced by the mixing of cold feed with the stream leaving each stage (except the last).
- This requires that the original feed be divided into appropriate portions.
- Inter-stage heat exchangers are not used, but a pre-heater and an after-cooler may be required.



- A flow diagram indicating notation is shown in Figure 21.11 for a three-stage FBCR in which the reaction A ↔ products takes place.
- The feed enters at T_0 and m kg s^{-1} or, in terms of A, at F_{AO} and $f_{AO} = 0$.
- The feed is split at S_1 so that a fraction r_1 enters stage 1 after passing through the pre-heater E_1, where the temperature is raised from T_0 to T_{01}
- A subsequent split occurs at S_2 so that a feed fraction r_2 mixes with the effluent from stage 1 at M_1 and the resulting stream enters stage 2.
- The remainder of the original feed mixes with the effluent from stage 2 at M_2 and the resulting stream enters stage 3.

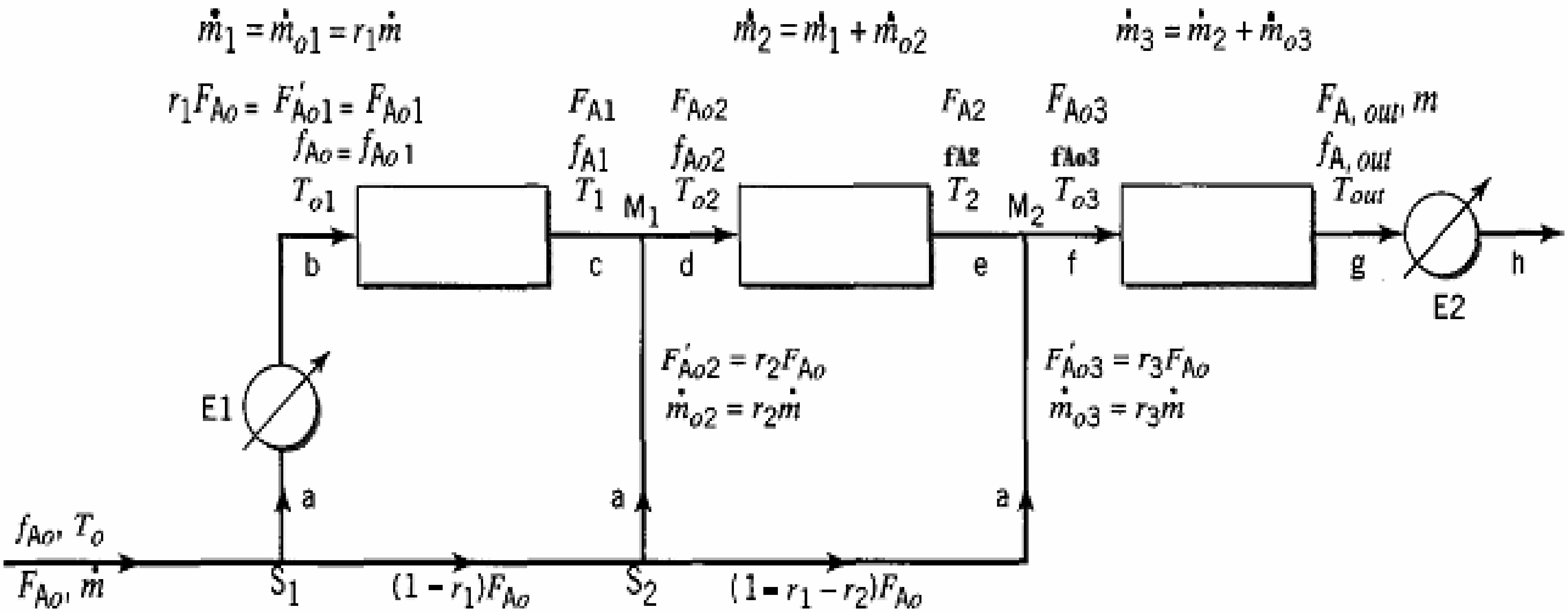


Figure 21.11 Flow diagram and notation for three-stage FBCR with cold-shot cooling

The fraction of the original feed entering any stage *i* is defined by

$$r_i = \dot{m}_{oi}/\dot{m} = F'_{Aoi}/F_{Ao}$$

Where m_{0i} and F'_{Aoi} are the portions of the feed, in specific mass and molar terms, respectively, entering stage *i*, such that

$$\sum \dot{m}_{oi} = \dot{m}$$

and

$$\sum_i F'_{Aoi} = F_{Ao}$$

It follows that

$$\sum_i r_i = 1$$

for i = 2, around M_1,

$$F_{Ao2} = F_{A1} + F'_{Ao2} = F_{A1} + r_2 F_{Ao} \qquad 21.5\text{-}15$$

Since

$$f_{Ao2} = \frac{F'_{Ao1} + F'_{Ao2} - F_{Ao2}}{F'_{Ao1} + F'_{Ao2}} = \frac{(r_1 + r_2)F_{Ao} - F_{Ao2}}{(r_1 + r_2)F_{Ao}} \qquad 21.5\text{-}16$$

and

$$f_{A1} = \frac{F'_{Ao1} - F_{A1}}{F'_{Ao1}} = \frac{r_1 F_{Ao} - F_{A1}}{r_1 F_{Ao}} \qquad 21.5\text{-}17$$

Substitution of 21.5-16 and 21.5-17 in 21.5-15 to eliminate F_{A02} and F_{A1}, respectively, results in

$$(r_1 + r_2)F_{Ao}(1 - f_{Ao2}) = r_1 F_{Ao}(1 - f_{A1}) + r_2 F_{Ao}$$

from which

$$f_{Ao2} = \frac{r_1}{r_1 + r_2} f_{A1} \qquad 21.5\text{-}18$$

Similarly, for $i = 3$, around M_2

$$f_{Ao3} = \frac{r_1 + r_2}{r_1 + r_2 + r_3} f_{A2} = (r_1 + r_2) f_{A2} \qquad 21.5\text{-}18a$$

since $r_1 + r_2 + r_3 = 1$ for a three-stage reactor.

In general, for the ith stage (beyond the first, for which $f_{A01} = f_{AO}$) of an N–stage reactor,

$$\boxed{f_{Aoi} = \left(\sum_{k=1}^{i-1} r_k \Big/ \sum_{k=1}^{i} r_k \right) f_{A,i-1} \qquad (i = 2, \ldots, N)} \qquad 21.5\text{-}19$$

If we assume c_p is constant for the relatively small temperature changes involved on mixing (and ignore any compositional effect), an enthalpy balance around M_1 is

$$\dot{m}_1 c_P(T_1 - T_{ref}) + \dot{m}_{o2} c_P(T_o - T_{ref}) = (\dot{m}_1 + \dot{m}_{o2}) c_P(T_{o2} - T_{ref})$$

Setting the reference temperature, T_{ref}, equal to T_0, and substituting for $m_1 = m_{01}$ and m_{02} from equation 21.5-12, we obtain, after cancelling c_p,

$$r_1 \dot{m}(T_1 - T_o) = (r_1 + r_2)\dot{m}(T_{o2} - T_o)$$

From which

$$T_{o2} = T_o + \frac{r_1}{r_1 + r_2}(T_1 - T_o) \qquad 21.5\text{-}20$$

In general, for stage i (beyond the first) in an N-stage reactor,

$$T_{oi} = T_o + \left(\sum_{k=1}^{i-1} r_k \Big/ \sum_{k=1}^{i} r_k \right)(T_{i-1} - T_o) \quad (i = 2, 3, \ldots, N) \qquad 21.5\text{-}21$$

The operating lines for an FBCR with cold-shot cooling are shown schematically and graphically on a plot of f_A versus T in Figure 21.12, which corresponds to Figure 21.8 (a) for multistage adiabatic operation with inter-stage cooling.

In accordance with equation 21.5-18 (with $f_{AO} = 0$):

$$\frac{ac}{ad} = \frac{f_{A1}}{f_{Ao2}} = \frac{r_1 + r_2}{r_1} \qquad 21.5\text{-}22$$

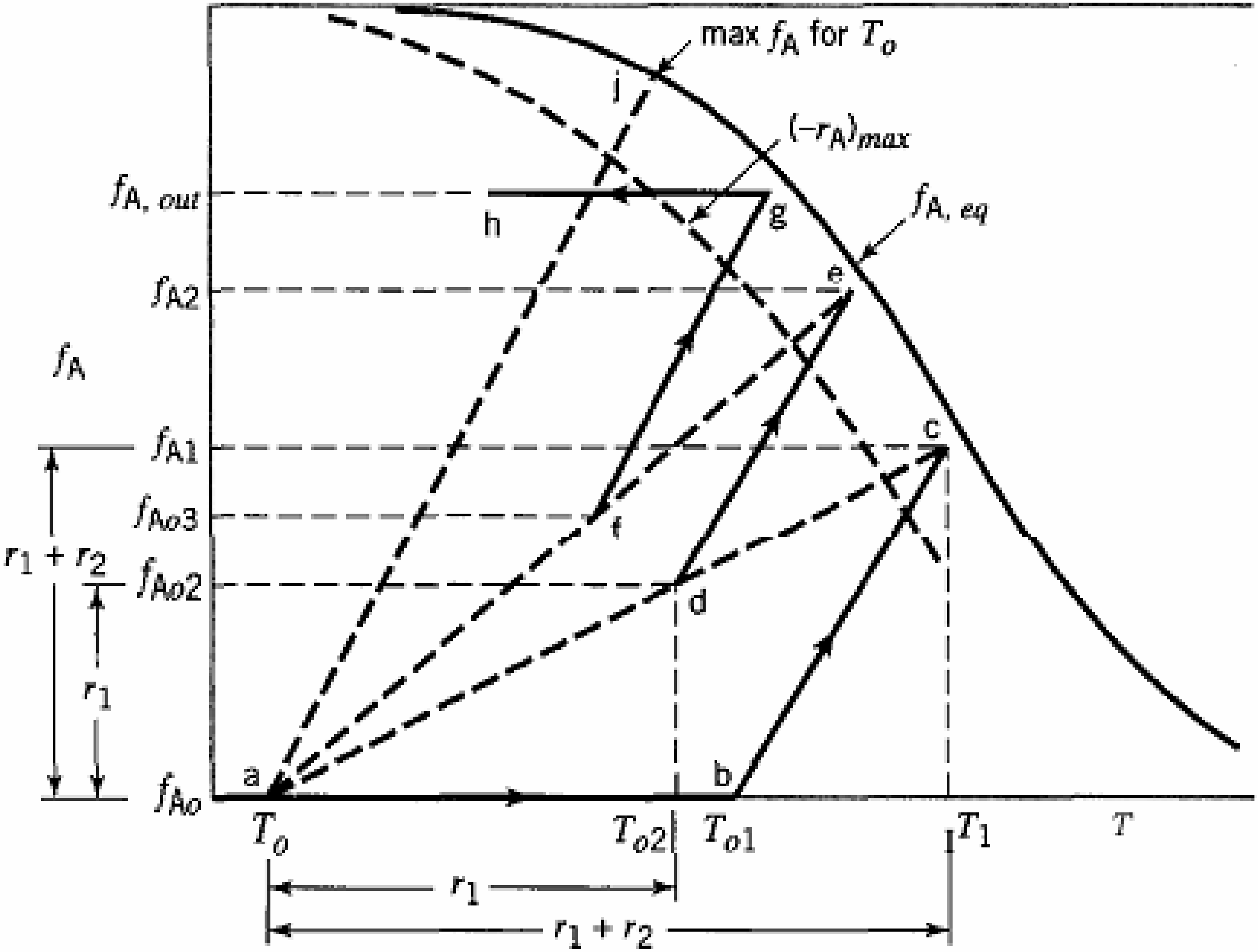


Figure 21.12 Conversion-temperature diagram showing operating lines for cold-shot cooling operation of **FBCR** for exothermic, reversible reaction

Calculations for a FBCR with Cold-Shot Cooling

The calculations for an N-stage FBCR with cold-shot cooling for a reversible, exothermic reaction may involve several types of problems: the design problem of determining N and the amount and distribution of catalyst (W_i, $i = 1,2, . . . , N$) for a specified feed rate and composition and fractional conversion (f_A),

In general, for an N-stage reactor, there are 2N degrees of freedom or free parameters from among r_i and T_i (or f_{Ai}), This number may be reduced to N + 1 if a criterion such as a constant degree of approach to equilibrium, ΔT, is used for each stage, where

Calculations for a FBCR with Cold-Shot Cooling:

- The calculations for an N-stage FBCR with cold-shot cooling for a reversible, exothermic reaction may involve several types of problems: the design problem of determining N and the amount and distribution of catalyst (W_i, $i = 1,2, . . . , N$) for a specified feed rate and composition and fractional conversion (f_A),
- In general, for an N-stage reactor, there are 2N degrees of freedom or free parameters from among r_i and T_i (or f_{Ai}), This number may be reduced to N + 1 if a criterion such as a constant degree of approach to equilibrium, ΔT, is used for each stage, where

$$\Delta T = T_{i,eq}(f_{\mathrm{A}i,eq}) - T_i \qquad 21.5\text{-}23$$

The steps in an algorithm are as follows:

(1) Calculate the operating line slope from equation 21.5-8
(2) Choose ΔT
(3) Calculate T_0 from an integrated form of 21.5-8:

$$\mathrm{d}f_{\mathrm{A}} = \frac{mc_p}{(-\Delta H_{R\mathrm{A}})F_{\mathrm{A}o}}\mathrm{d}T$$

$$f_{\mathrm{A},out} \equiv f_{\mathrm{A}N} = f_{\mathrm{A}o} + \frac{mc_p}{(-\Delta H_{R\mathrm{A}})F_{\mathrm{A}o}}(T_{out} - T_o)$$

Where,

$$T_{out} \equiv T_N = T_{N,eq}(f_{\mathrm{A}N,eq}) - \Delta T$$

$$f_{\mathrm{A}N,eq} = f_{\mathrm{A}N} + (\mathrm{d}f_{\mathrm{A}}/\mathrm{d}T)\Delta T$$

and $f_{A0} = 0$, usually.

4) Choose or and T_{o1}.

5) Calculate W_l by simultaneous solution of equation 21.5-4, with the rate law incorporated, and -8. In equation 21.5-4, F_{AO} is replaced by r_1F_{Ao}, and the limits of integration are f_{Ao} and f_{A1}, where f_{A1} is

$$f_{A1} = f_{A1,eq} - (\mathrm{d}f_A/\mathrm{d}T)\Delta T$$

and $f_{A1,eq}$ is obtained from the intersection of the operating line and $f_{A,eq}(T)$, that is, by the simultaneous solution of

$$f_A = f_{Ao} + (\mathrm{d}f_A/\mathrm{d}T)(T - T_{o1})$$

and

$$f_A = f_{A,eq}(T)$$

6) Calculate T_1, corresponding to f_{A1}) $T = T_1$

7) Choose r_2.

8) Calculate f_{Ao2} from equation 21.5-19.

9) Calculate T_{02}, from equation 21.5-21.

10) Calculate W_2 as in step (5) for W_1. The inlet conditions are $F_{A,in}=(r_1+r_2)(1-f_{Ao2})F_{Ao}$, f_{Ao2} and T_{o2}. The outlet conditions are f_{A2} and T_2, which are calculated as in steps (5) and (6) for f_{A1} and T_1, respectively, with subscript 1 replaced by 2, and subscript 0 by 1.

11) Repeat steps (7) to (10) by advancing the subscript to N until $f_{AN} \geq$ specified $f_{A,out}$. It may be appropriate to adjust r_i so that $f_{AN} = f_{A,out}$.

Example 21-6

For an FBCR operated with cold-shot cooling for the reaction A_g products, determine, from the information given below,

(a) the maximum possible fractional conversion (f_A);

(b) the fractional conversion at the outlet of a three-stage reactor.

The feed is split such that 40% enters stage 1 and 30% enters stage 2. The feed entering stage 1 is preheated from 375°C (T_0) to 450°C (T_{01}). The equilibrium temperature-fractional conversion relation is

$$T_{eq} = \frac{11835}{\ln\left[\frac{7.825\times 10^{4} f_{A,eq}}{1-f_{A,eq}}\left(\frac{1-0.0475 f_{A,eq}}{0.115-0.0475 f_{A,eq}}\right)^{1/2}\right]} \qquad \text{(A)}$$

For each stage, the outlet temperature, T_i, is to be 25°C lower than the equilibrium temperature (i.e., in equation 21.5-23, $\Delta T = 25°C$).

Other data: $m = 10$ kg s^{-1}; $F_{Ao} = 62$ $mols^{-1}$;

$c_p = 1.1$ $Jg^{-1}K^{-1}$;$\Delta H_{RA} = -85$ kJ mol^{-1}.

Solution

(a) The maximum possible conversion is obtained by applying the criterion for degree of approach to equilibrium (ΔT = 25°C) to the intersection of the operating line aj (Figure 21.12) drawn from (f_{AO}, T_o) with

$$\text{slope} = \frac{mc_P}{(-\Delta H_{RA} F_{Ao})} = \frac{10(1.1)}{85(62)} = 2.09 \times 10^{-3}\,\text{K}^{-1}$$

Simultaneous solution of equation (A) and the equation for the operating line with this slope gives the coordinates of the intersection at point j:

$$f_{A,eq} = 0.579; \quad T_{eq} = 925\ \text{K}$$

Thus, at the outlet point h (Figure 21.12), T_{out} = (925 - 25) = 900 K, and

$$f_{A.out} = (\text{slope})(T_{out} - T_o) = 2.09\ \text{x}10^{-3}(900 - 648) = 0.527$$

That is, the maximum possible fractional conversion for these conditions, regardless of the number of stages, is 0.527.

(b) We proceed by treating the three stages in order to obtain f_{A1}, f_{A2}, and f_{A3}. The procedure is described in detail for stage 1, and the results are summarized in Table 21.1. For stage 1, the equation of the operating line bc (Figure 2 1.12) through b (f_{Ao1}, T_{01}) with the slope calculated in (a) is

$$f_A = f_{Ao1} + 2.09\ \text{x}10^{-3}(T - T_{o1}) \tag{B}$$

where f_{Ao1} = 0 and T_{01}= 723 K. Solving equations (A) and (B) simultaneously for the intersection of the operating line and the equilibrium line, we obtain

$$f_{A1,eq} = 0.485 \text{ and } T_{1,eq} = 955 \text{ K}$$

Thus, $$T_1 = 955 - 25 = 930 \text{ K}$$

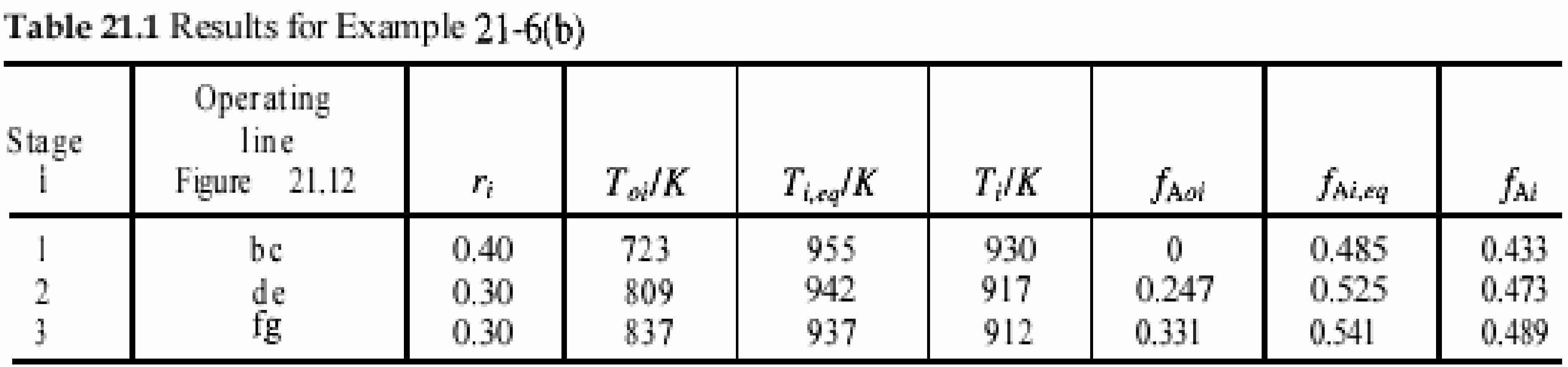


Table 21.1 Results for Example 21-6(b)

Stage i	Operating line Figure 21.12	r_i	T_{oi}/K	$T_{i,eq}/K$	T_i/K	f_{Aoi}	$f_{Ai,eq}$	f_{Ai}
1	bc	0.40	723	955	930	0	0.485	0.433
2	de	0.30	809	942	917	0.247	0.525	0.473
3	fg	0.30	837	937	912	0.331	0.541	0.489

Substitution for T = T_1 = 930, in (B) gives

$$f_A = f_{A1} = \mathbf{0.433}$$

For stage 2, we calculate f_{Ao2} from equation 21.5-18,

$$f_{Ao2} = [r_1/(r_1 + r_2)]f_{A1} = [0.4/(0.4 + 0.3)]0.433 = \mathbf{0.247}$$

and T_{02} from equation 21.5-20,

$$\begin{aligned} T_{o2} &= T_o + [r_1/(r_1 + r_2)](T_1 - T_o) \\ &= \mathbf{648} + [0.4/(0.4 + 0.3)](930 - \mathbf{648}) = \mathbf{809}\ \mathrm{K} \end{aligned}$$

Non Adiabatic Operation

- Multi-tubular Reactor; Catalyst Inside Tubes

We assume all tubes behave in the same way as a set of reactors in parallel, and apply the continuity and energy equations to a single tube. The number of tubes, N_t, must be determined as part of the design, to establish the diameter, D, of the vessel.

For a single tube, the continuity equation, 21.5-4, may be written

$$W' = F'_{Ao} \, \mathrm{d}f_A/[-r_A(T, f_A)] \qquad 21.5\text{-}29$$

Where $W' = W/N_t$, the amount of catalyst per tube, and $F'_{Ao} = F_{Ao}/N_t$, the feed rate per tube. Assume k_{ex} and $k_{er} = 0$

$$Gc_p \frac{dT}{dx} - \rho_B(-r_A)(-\Delta H_{RA}) + \delta\dot{Q} = 0$$

heat transfer through the wall: $\delta\dot{Q} = U(T_S - T)\mathrm{d}A'_p/\mathrm{d}V'$,

where A'_p is the (peripheral) heat transfer surface area per tube, and V' is the volume enclosed per tube (the rate of heat transfer is referred to unit volume, through dV',

$$\mathrm{d}A'_p = \pi d_t \mathrm{d}x$$

$$\mathrm{d}V' = \pi d_t^2 \mathrm{d}x/4 = \mathrm{d}W'/\rho_B$$

$$G' = G/N_t = 4\dot{m}'/\pi d_t^2$$

and

$$(-r_A)\mathrm{d}W = F'_{Ao}\mathrm{d}f_A$$

$$m'c_p dT = \left[\left(-\Delta H_{RA}\right) + \frac{4U\left(T_S - T\right)}{\rho_B\left(-r_A\right)dt} \right] F'_{Ao} df_A$$

A procedure or algorithm such as the following could be used:

1) Choose a value of N_t.
2) Calculate m' and F'_{Ao}
3) Calculate W' from equations 21.5-29 and -30.
4) Calculate $L_t = 4W'/p_B \pi d_t^2$.
5) Calculate ($-\Delta P$) from equation 21.3-5, and compare with the allowable ($-\Delta P$)
6) Adjust N_t based on the result in (5), and repeat steps (2) to (5) until the ($-\Delta P$) criterion is satisfied.

The value of N_t, together with d, and standard triangular or square pitch for tubes in a shell-and-tube arrangement, determines the diameter, D, of the vessel (shell)

Multitubular Reactor; Catalyst Outside Tubes

- The catalyst may be placed outside the tubes (Figure 11.5(a)).
- The result is to have a fixed bed of diameter D, say, with N_t holes, each of diameter d_t.

$$dA_p = N_t \pi d_t dx,$$

$$dV = (\pi/4)(D^2 - N_t d_t^2)dx = dW/\rho_B$$

$$(-r_A)dW = F_{Ao} df_A,$$

$$\dot{m} c_p dT = \left[\left(-\Delta H_{RA}\right) + \frac{4 N_t d_t U \left(T_S - T\right)}{\rho_B \left(-r_A\right)\left(D^2 - N_t d_t^2\right)} \right] F_{Ao} df_A \qquad 21.5\text{-}31$$

The typical problem outlined in the previous section may be solved in this case in a similar manner:

1) Choose a value of N_t, which implies a value of D.
2) Calculate W by numerical solution of equations 21.5-4 and -31.
3) Calculate value of L (i.e., L_t).
4) Calculate $(-\Delta P)$ and compare with allowable $(-\Delta P)$
5) Adjust value of N_t from result in (4), and repeat steps (2) to (4) until the $(-\Delta P)$ criterion in satisfied.

HETEROGENEOUS, ONE-DIMENSIONAL, PLUG-FLOW MODEL

- the treatment is based on the pseudo-homogeneous assumption for the catalyst + fluid system
- In this section, we consider the local gradients in concentration and temperature that may exist both within a catalyst particle and in the surrounding gas film.
- The system is then “heterogeneous.” We retain the assumptions of one-dimensional, plug-flow behavior, and a simple reaction of the form

$$A_g + \ldots \xrightarrow{cat(s)} product$$

$$\frac{\mathrm{d}(uc_A)}{\mathrm{d}x} + \rho_B(-r_A)_{obs} = 0 \qquad 21.6\text{-}1$$

and

$$Gc_P \frac{\mathrm{d}T}{\mathrm{d}x} - \rho_B(-r_\mathrm{A})_{obs}(-\Delta H_{R\mathrm{A}}) = 0 \qquad 21.6\text{-}2$$

where, in terms of η,

$$(-r_\mathrm{A})_{obs} = \eta(-r_\mathrm{A})_{int} \qquad 21.6\text{-}3$$

η is a function of the Thiele modulus ϕ’‘, for the axial profile of fractional conversion, f_A, and amount of catalyst, W, respectively:

$$\frac{\mathrm{d}f_\mathrm{A}}{\mathrm{d}x} - \frac{\pi r^2 \rho_B \eta(-r_\mathrm{A})_{int}}{F_{\mathrm{A}o}} = 0 \qquad 21.6\text{-}4$$

and

$$W = F_{\mathrm{A}o} \int \frac{\mathrm{d}f_\mathrm{A}}{\eta(-r_\mathrm{A})_{int}} \qquad 21.6\text{-}5$$

The simplest case to utilize η is that of an isothermal situation with no axial gradient in T. In this case, a constant, average value of η may describe the situation reasonably well, and equation 21.6-5 becomes

$$W = \frac{F_{Ao}}{\eta}\int \frac{\mathrm{d}f_A}{(-r_A)_{int}} \qquad (\eta \text{ constant}) \qquad 21.6\text{-}6$$

To calculate W from equation 21.6-5, ϕ'' and η must be calculated at a series of axial positions or steps, since each depends on T and C_A; $(-r_A)_{obs}$ is then calculated from η and $(-r_A)_{int}$ at each step.

For adiabatic operation, an algorithm for this purpose (analogous to that in Example 21-5) is as follows:

1) Choose a value of f_A.
2) Calculate T from an integrated form of 21.6-2, such as 21.5-9.
3) Calculate $(-r_A)$int at f_A and T from a given rate law.
4) Calculate ϕ'', e.g., from equation 8.5-20b; if necessary, use ρ_p to convert k_A (mass basis) to k_A (volume basis).
5) Calculate η from ϕ'' (Section 8.5).
6) Calculate $(-r_A)$ & from equation 21.6-3.
7) Repeat steps (1) to (6) for values of f_A between $f_{A,in}$ and $f_{A,out}$.
8) Evaluate the integral in equation 21.6-5
9) Calculate W from equation 21.6-5.

Problems

21-1 (a) What is the mean residence time (t) of gas flowing through a fixed bed of particles, if the bed voidage is 0.38, the depth of the bed is 1.5 m, and the superficial linear velocity of the gas is 0.2 m s^{-1}?

(b) What is the bulk density of a bed of catalyst, if the bed voidage is 0.4 and the particle density is 1750 kg m^{-3} (particle)?

(c) What is the mass (kg) of catalyst contained in a l00-m^3 bed, if the catalyst particles are made up of a solid with an intrinsic density of 2500 kg m^{-3}, the bed voidage is 0.4, and the particle voidage is 0.3?

21-6 Consider a fixed-bed catalytic reactor (FBCR), with axial flow, for the dehydrogenation of ethyl benzene (A) to styrene (S) (monomer). From the information given below, calculate the temperature (T/K) in the first-stage bed of the reactor,

(a) at the outlet of the bed (i.e., at Lt); and

(b) L = 0.38 L1.

Assume steady-state, adiabatic operation, and use the pseudo homogeneous, one-dimensional plug-flow model.

Data:

Feed: $T_o = 925$ K; $P_o = 2.4$ bar; $F_{Ao} = 85$ mol s^{-1}; F_{H_2O}(inert) = 1020 mol s^{-1}
Fractional conversion at outlet: $f_{A1} = 0.45$
Rate law: $(-r_A) = k_A(p_A \quad p_S p_{H_2}/K_p)$
k_A/mol (kg cat)$^{-1}$ s^{-1} bar^{-1} = $3.46 \times 10^3 \exp(-10,980/T)$
K_p/bar = $8.2 \times 10^6 \exp(-15,200/T)$
(T in K for k_A and K_p)
$\Delta H_{RA} = 126,000$ J mol^{-1}; $c_P = 2.4$ J g^{-1} K^{-1}
$W_1 = 25,400$ kg (of catalyst)

21-7 Consider a two-stage fixed-bed catalytic reactor (FBCR), with axial flow, for the dehydrogenation of ethyl benzene (A) to styrene (S) (monomer). From the data given below, for adiabatic operation, calculate the amount of catalyst required in the first stage, W_1/kg.

Feed: T_o = 925 K; P_o = 2.4 bar;

F_{Ao} = 100 mol s^{-1}‘; F_{H2O}(inert) = 1200 mol s^{-1}

Fractional conversion at outlet: f_{A1} = 0.4; use the model and other data as in problem 21-6.

21-10 For the SO_2 converter in a l000-tonne day^{-1} H_2SO_4 plant (100% H2SO4 basis), calculate the following:

(a) The amount (kg) of catalyst (V_2O_5) required for the first stage of a four-stage adiabatic reactor, if the feed temperature (T,) is 430 ^oC, and the (first-stage) outlet fractional conversion of SO_2(f_{SO2}) is 0.687; the feed composition is 9.5 mol % SO_2, 11.5% 02, and 79 % N2.

(b) The depth (L/m) and diameter (D/m) of the first stage.

Data:

Use the Eklund rate law (equation 21.3-14), with data for k_{SO2} from problem 8-19 (B particles); assume K_P/MPa$^{-1/2}$ = 7.97 X 10^{-5} exp(l2,100/T), with T in K;

For bed of catalyst: r_B = 500 kg m^{-3}; ε_B = 0.40;

For gas: μ_f = 4 X 10^{-5} kg m^{-1} s^{-1}; cp = 0.94 J g^{-1} K^{-1}; f_{SO2} is 0.98 over four stages; P_0 = 101 kPa; ΔH_R = - 100 kJ (mol SO_2; Allowable ($-\Delta P$) for first stage is 2.5 kPa.

18-19

Fluidized-Bed and Other Moving-Particle Reactors for Fluid-Solid Reactions

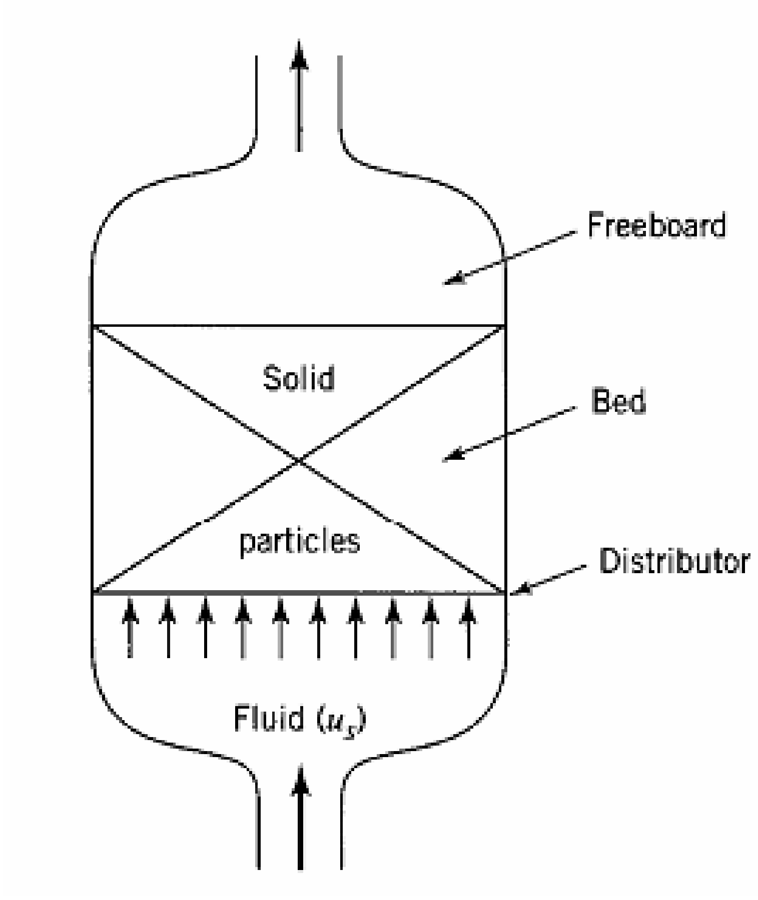
Introductions

- Reactors for fluid-solid reactions in which the solid particles are in motion (relative to the wall of the vessel) in an arbitrary pattern brought about by upward flow of the fluid
- We focus mainly on the fluidized-bed reactor as an important type of moving-particle reactor
- The first commercial use of a fluidized-bed reactor, in the 1920s was for the gasification of coal to supply CO and H, for the production of synthetic chemicals
- Since the catalyst is rapidly deactivated by coking, it was desired to replace intermittent operation of fixed-bed reactors with continuous operation for both the cracking process and the regeneration process

MOVING-PARTICLE REACTORS

- Some Types
  - Fluidized-Bed and Related Types
    - Consider a bed of solid particles initially fixed in a vessel, and the upward flow through the bed of a fluid introduced at many points below the bed, as indicated schematically in Figure 23.1.
    - The rate of flow of fluid is characterized by the superficial linear velocity u_s, that is, the velocity calculated as though the vessel were empty.

Figure 23.1 Schematic representation of (incipient) particle movement brought about by upward flow of a fluid, leading to fluidization



- These range from a fixed-bed reactor to a fluidized-bed reactor without significant carryover of solid particles, to a fast-fluidized-bed reactor with significant carryover of particles, and ultimately a pneumatic-transport or transport-riser reactor in which solid particles are completely entrained in the rising fluid.

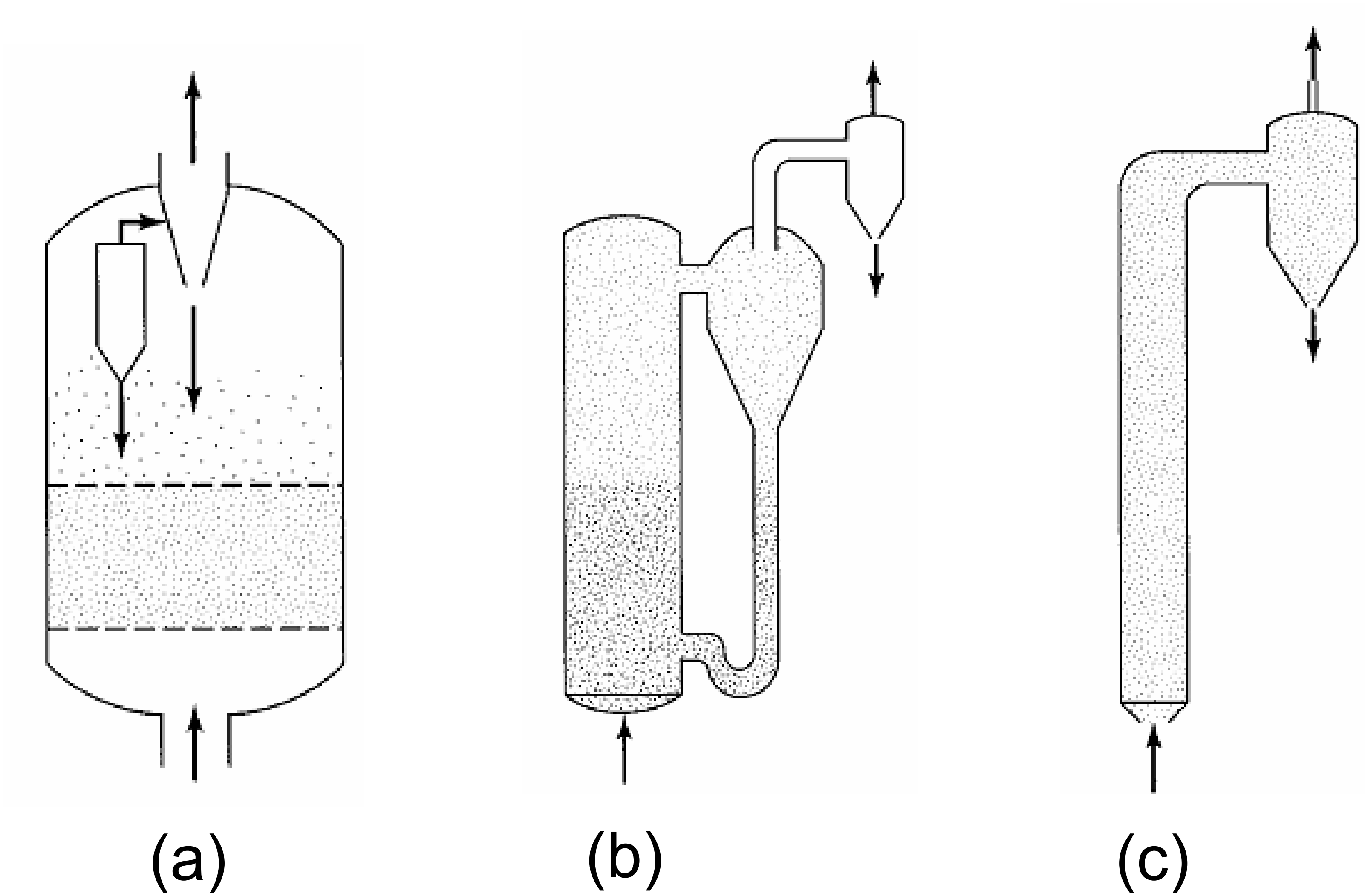


Figure 23.2 Some features of (a) a fluidized-bed reactor; (b) a fast-fluidized-bed reactor; and (c) a pneumatic-transport reactor

Fast-fluidized-bed reactor

- Figure 23.2(b) shows a fast-fluidized-bed reactor, together with external equipment, such as cyclones, for separation of fluid and solid particles carried out of the reactor, and subsequent recirculation to the reactor.
- In a fast-fluidized bed, the fluidization velocity is very high, resulting in significant entrainment of solid particles
- Continuous addition of fresh solid particles may be required for some operations (e.g., coal gasification)
- Applications of fast-fluidized beds are in fluidized-bed combustion and Fischer-Tropsch synthesis of hydrocarbons from CO and H_2

Figure 23.2(c) shows a pneumatic-transport reactor

- In this type, fluid velocities are considerably greater than the terminal velocities of the particles, so that virtually all of the particles are entrained.
- The vessel may be extremely tall, with no solid recirculation (e.g., coal combustion), or it may provide for solid recirculation with external cyclones.
- The process stream is extremely dilute in solid particles because of the high volume of gas passing through the “bed.” Fluid-catalyzed cracking of gasoil is an important example of pneumatic transport with external recirculation (and regeneration) of catalyst pellets.
- A major design issue is the configuration of the recirculation system, which must carry out heat transfer, catalyst regeneration, solid recovery, and recirculation.

Spouted Bed

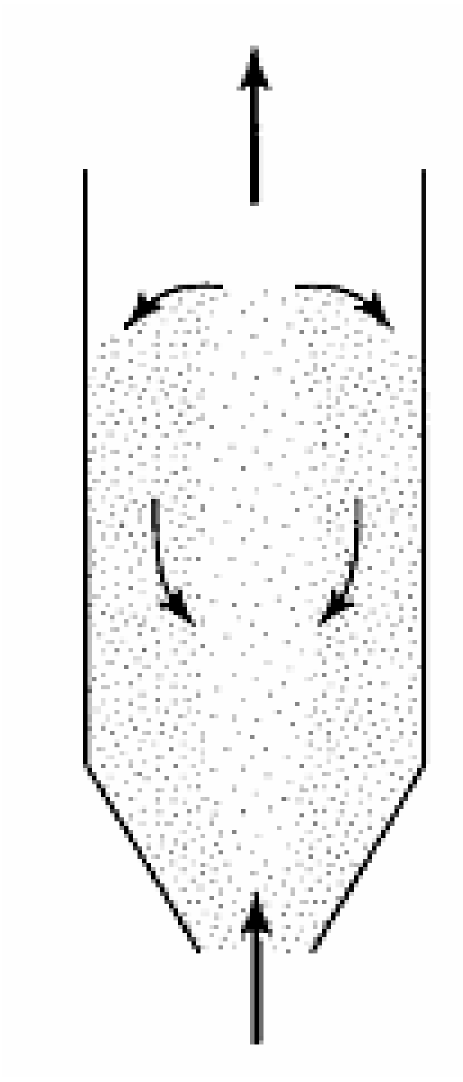


Fig. 23.3

- If the fluid enters the vessel at one central point, as indicated in Figure 23.3, rather than at many points spaced across a circular distributor, as in Figure 23.1, the action is different as u_s, increases: a spouted bed results rather than a fluidized bed.
- A spouted bed is characterized by a high-velocity spout of gas moving up the center of the bed, carrying particles to the top.
- This action induces particle circulation, with particle motion toward the wall and downward around the spout and toward the center.
- The particles in a spouted bed are relatively large and uniformly sized.

Examples of Reactions

- Catalytic cracking of gas oil: an impetus for the development of fluidized-bed reactors over 50 years ago was the desire to make the catalytic cracking of gas oil (to gasoline) a continuous process, in spite of the rapid deactivation of the catalyst particles by coke and tarry deposits.
- Originally, both the catalytic-cracking reactor (“cracker”) it self and the catalyst regenerator were fluidized-bed reactors, with solid particles moving continuously between the two in an overall continuous process, but more recently the cracker is made a pneumatic-transport reactor

Production of acrylonitrile by ammoxidation of propylene (SOHIO process):

$$2NH_3 + 3O_2 + 2C_3H_6 \rightarrow 2C_3H_3N + 6H_2O$$

- The fluidized-bed process for this reaction has several advantages over a fixed-bed process.
- First, the process is highly exothermic, and the selectivity to C_3H_3N is temperature dependent.
- The improved temperature control of the fluidized-bed operation enhances the selectivity to acrylonitrile, and substantially extends the life of the catalyst, which readily sinters at temperatures in excess of 800 K.
- Furthermore, since both the reactants and products are flammable in air, the use of a fluidized bed enables the moving particles to act to quench flames, preventing combustion and ensuring safe operation.

Oxidation of napthalene to produce phthalic anhydride:

$$C_{10}H_{10} + 0_2 \rightarrow C_8H_4O_3 \rightarrow CO_2 + H_2$$

- The reaction may proceed directly to phthalic anhydride, or it may proceed via naphthaquinone as an intermediate.
- Phthalic anhydride may also undergo subsequent conversion to CO_2 and H_2O. Thus, the selectivity to phthalic anhydride is a crucial aspect of the design.
- Proper control of temperature is required to limit napthaquinone production and avoid the runaway (and possibly explosive) reaction which leads to the production of CO2 and H2O.
- A fluidized-bed is thus preferred over a fixed-bed process.

Production of synthetic gasoline by the Fischer-Tropsch process:

$$nCO + 2nH_2 \rightarrow (CH_2)_n + nH_2O$$

- This is another example of a highly exothermic process which requires strict temperature control to ensure appropriate selectivity to gasoline, while limiting the production of lighter hydrocarbons.
- Again, the enhanced temperature control provided by a fluidized-bed system greatly improves the feasibility of this process.

Noncatalytic roasting of ores such as zinc and copper concentrates:

$$2ZnS + 30_2 \rightarrow 2ZnO + 2SO_2$$

- The fluidized-bed process replaced rotary kilns and hearths; its primary advantages are its higher capacity and its lower air requirement, which leads to a product gas richer in SO_2 for use in a sulfuric acid plant.

Noncatalytic complete or partial combustion of coal or coke in fluidized-bed combustors:

$$C + O_2 \rightarrow CO_2$$

$$C + \frac{1}{2}O_2 \rightarrow CO$$

- These reactions may serve as a means of regeneration of coked catalysts.
- Both reactions are exothermic, and the improved temperature control provided by a fluidized bed is critical for regeneration of catalysts prone to sintering.
- This process (usually with addition of steam) can also be used to generate gas mixtures from partial oxidation of coal for synthetic gasoline production

Advantages and Disadvantages

- Advantages
  - *Mode of operation*: operation can be made continuous with respect to both the processing fluid and the solid; this allows, for example, for the continuous regeneration of a deactivating catalyst.
  - *Thermal*: there is near-uniformity of T throughout the bed, which allows for better control of T and avoidance of hot spots in highly exothermic reactions; the uniformity of T is due to such things as the high degree of turbulence (resulting in relatively high heat transfer coefficients), and the large interfacial area between fluid and small particles.
  - *Chemical performance*: the use of relatively small particles (e.g., 0.1 to 0.3 mm) can result in lower pore-diffusion resistance in solid particles and an effectiveness factor (η) much closer to 1; by itself, this, in turn, results in a smaller catalyst holdup.

- Disadvantages:
  - *Mechanical*: abrasion causes erosion of pipes and internal parts (e.g., heat transfer surface); attrition of particles leads to greater entrainment and elutriation, requiring equipment (cyclones) for recovery; these mechanical features lead to higher operating and maintenance costs, as well as greater complexity.
  - *Fluid-mechanical*: There is a larger ($-\Delta P$), requiring greater energy consumption; the complex flow and contacting patterns are difficult to treat rationally, and create difficulties of scale-up from small-diameter, shallow beds to large-diameter, deep beds.
  - *Chemical performance*: in fluidized-beds, there is a "bypassing effect" which leads to inefficient contacting; fluid in large bubbles tends to avoid contact with solid particles; this leads to a larger catalyst holdup and/or lower conversion, which may even be lower than that predicted on the basis of BMF, which in turn is lower than that based on PF, the turbulence and resulting back-mixing may result in adverse effects on selectivity.

Design Considerations

- For moving-particle reactors, in addition to the usual reactor process design considerations, there are special features that need to be taken into account.
- Many of these features, particularly those that relate to fluid-particle interactions, can only be described empirically.
- Typical design requirements include calculations of catalyst or reactant solid holdup for a given fractional conversion and production rate, the bed depth, the vessel diameter and height, and heat transfer requirements.
- The reactor model may also need to account for conversion in regions of the vessel above (“freeboard” region) and below (“distributor” region) the bed, if there is a significant fraction of the solid in these regions, and/or the reaction is very rapid.
- The overall design must consider special features related to the superficial velocity, and the flow characteristics of the solid and fluid phases within the vessel.
- A reactor model which incorporates all of these features together with a kinetics model can be rather complicated.

FLUID-PARTICLE INTERACTIONS

- This section is a continuation of Section 21.3.2 dealing with pressure drop ($-\Delta P$) for flow through a fixed bed of solid particles. Here, we make further use of the Ergun equation for estimating the minimum superficial fluidization velocity, u_{mf}.
- In addition, by analogous treatment for free fall of a single particle, we develop a means for estimating terminal velocity, u_t, as a quantity related to elutriation and entrainment.

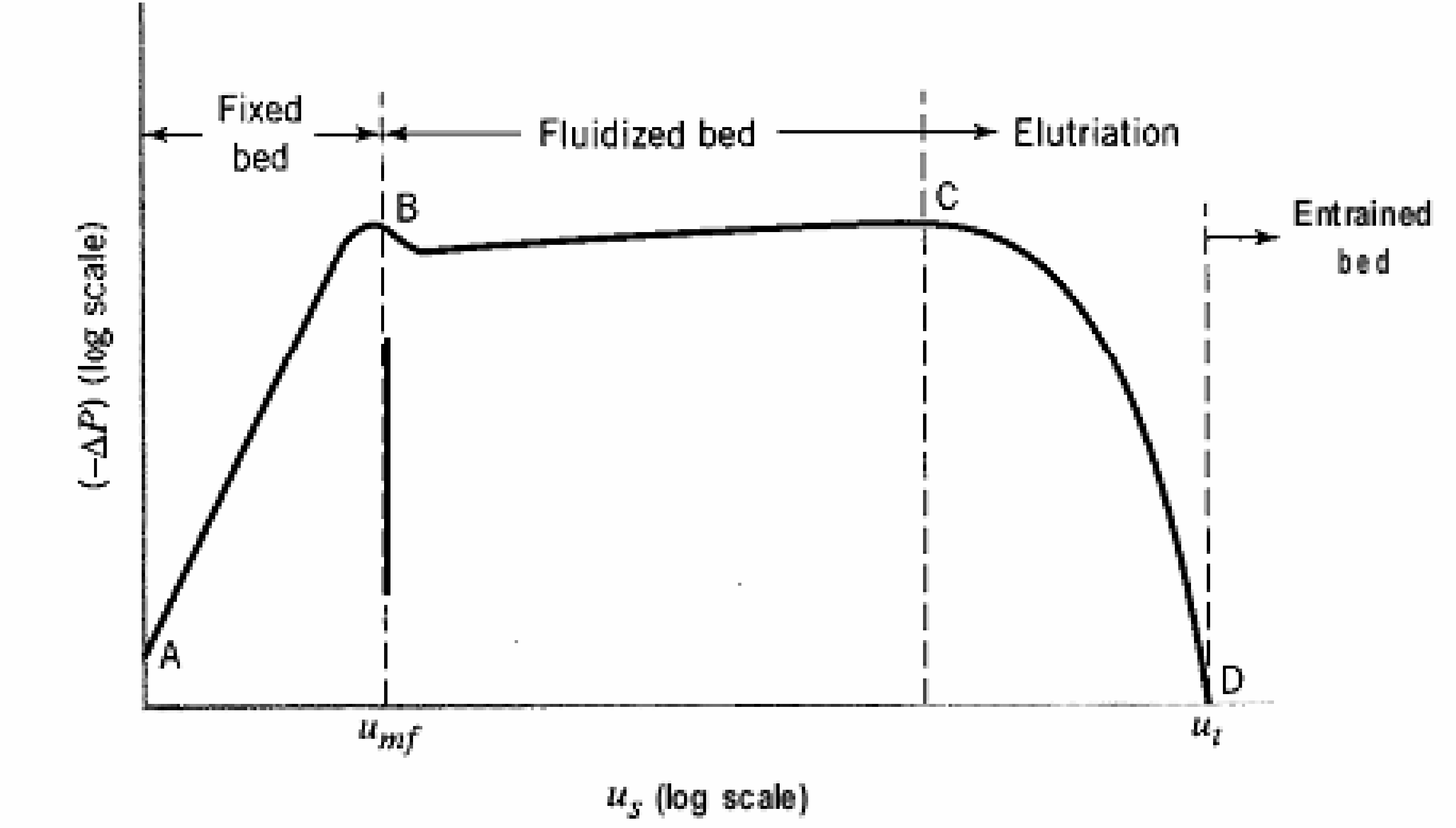


Figure 23.4 Dependence of pressure drop $(-\Delta P)$ on fluid velocity (u_t) for upward flow of fluid through bed of particles illustrating different conditions of the bed (schematic)

Minimum Fluidization Velocity (u_{mf})

- The minimum fluidization velocity (u_{mf}) can be estimated by means of the Ergun equation (Chapter 21) for pressure drop, (- ΔP), for flow of fluid through a bed of particles (Bin, 1986).
- In this case, the flow is upward through the bed. At incipient fluidization, the bed is on the point of “lifting.”
- This condition is characterized by the equality of the frictional force, corresponding to (-ΔP), acting upward, and the gravity force on the bed, acting downward:

$$
\begin{aligned}
(-\Delta P)_{mf} A_c &= gW = g\rho_{B,app} V \\
&= g(\rho_p - \rho_f)(1 - \epsilon_{mf}) L_{mf} A_c
\end{aligned}
$$

From which,

$$
(-\Delta P)_{mf} = g(\rho_p - \rho_f)(1 - \epsilon_{mf}) L_{mf} \qquad 23.2\text{-}1
$$

- where subscript *mf* refers to the bed at minimum-fluidization conditions.
- In equation 23.2-1 $\rho_{B,app}$ is the apparent density of the bed, which is $(\rho_p - \rho_f)$ on allowing for the buoyancy of the fluid

Rewriting the definition of the friction factor *f* from equation 21.3-5, and the Ergun correlation for *f* given by equation 21.3-7, both at *mf*, we obtain

$$f = \frac{d_p'(-\Delta P)_{mf}}{L_{mf} u_{mf}^2 \rho_f} \qquad 23.2\text{-}2$$

and

$$f = \frac{1-\epsilon_{mf}}{\epsilon_{mf}^3}\left(1.75 + 150\,\frac{1-\epsilon_{mf}}{\mathrm{Re}_{mf}'}\right) \qquad 23.2\text{-}3$$

where

$$\mathrm{Re}_{mf}' = d_p' u_{mf} \rho_f / \mu_f \qquad 23.2\text{-}4$$

and d'_p is the effective particle diameter given by equation 21.3-6.

Eliminating $(\Delta P)_{mf}$, f, and Re'_{mf} by means of equation 23.1 to -4, we obtain a quadratic equation for u_{mf} in terms of parameters for the fluid, solid, and bed:

$$u_{mf}^2 + \frac{150(1-\epsilon_{mf})\mu_f}{1.75\rho_f d'_p} u_{mf} - \frac{g(\rho_p - \rho_f)\epsilon_{mf}^3 d'_p}{1.75\rho_f} = 0 \qquad 23.2\text{-}5$$

Example 23-1

Obtain the special forms of equation 23.2-5 for (a) relatively small particles, and (b) relatively large particles.

Solution

(a) For relatively small particles, Re is relatively small, and, in equation 23.2-3, we assume that

$$1.75 \ll 150(1-\epsilon_{mf})/Re'_{mf}$$

This is equivalent to ignoring the first term (***u_{mf}***) in equation 23.2-5, which then may be written as:

$$u_{mf} \simeq \frac{g(\rho_p - \rho_f)(d'_p)^2}{K\mu_f} \quad (\mathrm{Re}'_{mf} \text{ small}) \qquad 23.2\text{-}6$$

where

$$K = 150(1 - \epsilon_{mf})/\epsilon_{mf}^3 \qquad 23.2\text{-}7$$

This is a commonly used form, with K = 1650, which corresponds to ε_{mf} = 0.383.

(b) For relatively large particles, Re is relatively large, and, in equation 23.2-3, we assume that

$$1.75 \gg 150(1 - \varepsilon_{mf})/\mathrm{Re}'_{mf}$$

This is equivalent to ignoring the second (linear) term in equation 23.2-5, which then becomes

$$u_{mf} = \left[\frac{g(\rho_p - \rho_f)\epsilon_{mf}^3 d'_p}{1.75\rho_f}\right]^{1/2} \quad (\mathrm{Re}'_{mf} \text{ large}) \qquad 23.2\text{-}8$$

Example 23-2

Calculate u_{mf} for particles of ZnS fluidized by air at 1200 K and 200 kPa. Assume $d'_p = 4 \times 10^{-4}$ m, $\varepsilon_{mf} = 0.5$, $\rho_P = 3500$ kg m^{-3}, and $\mu_f = 4.6 \times 10^{-5}$ N s m^{-2}; g = 9.81 m s^{-2}

Solution

At the (T,P) conditions given, the density of air (ρ_f), assumed to be an ideal gas (z = 1) with M_{av} = 28.8, is

$$\rho_f = \frac{m}{V} = \frac{PM_{av}}{RT} = \frac{200(1000)28.8}{8.314(1200)1000} = 0.577 \text{ kg m}^{-3}$$

Since the particles are relatively small, we compare the results obtained from equations 23.2-5 and -6. With given values of parameters inserted, the former becomes

$$u_{mf}^2 + 8.542u_{mf} - 1.700 = 0$$

from which u_{mf} = 0.195 m s^{-1} (the units of each term should be confirmed for consistency). From equation 23.2-6,

$$u_{mf} = \frac{9.81(3500)4^2(10^{-4})^2(1-0.5)^3}{150(1-0.5)4.6(10^{-5})} = 0.199 \, \mathrm{m\,s^{-1}}$$

which is within 2% of the more accurate value above.

Elutriation and Terminal Velocity (U_t)

- At sufficiently high velocity of fluid upward through a bed of particles, the particles become entrained and do not settle; that is, the particles are carried up with the fluid.
- Elutriation is the selective removal of particles by entrainment, on the basis of size.
- The elutriation velocity (of the fluid) is the velocity at which particles of a given size are entrained and carried overhead.
- The minimum elutriation velocity for particles of a given size is the velocity at incipient entrainment, and is assumed to be equal to the terminal velocity (u_t) or free-falling velocity of a particle in the fluid.

This is calculated, in a manner analogous to that used for u_{mf}, by equating the frictional drag force F_d (upward) on the particle with the gravity force on the particle (downward):

$$\begin{aligned} F_d &= g(\rho_p - \rho_f)V_p \\ &= \pi g(\rho_p - \rho_f)d_p^3/6 \end{aligned} \qquad 23.2\text{-}9$$

for a spherical particle of diameter $\boldsymbol{d_p}$.
The dimensionless drag coefficient $\boldsymbol{C_d}$, analogous to the friction factor, is defined by

$$\begin{aligned} C_d &= 2F_d/A_{proj}\rho_f u^2 \\ &= 8F_d/\pi d_p^2 \rho_f u^2 \end{aligned} \qquad 23.2\text{-}10$$

for a spherical particle at terminal velocity, where A_{Proj} is the projected area of the particle in the direction of motion ($\pi d_p^2/4$ for a sphere). C_d depends on Re and shape of the particle. Correlations have been given by Haider and Levenspiel (1989). For small spherical particles at low Re (< 0.1), these reduce to the result for the Stokes' regime:

$$C_d = 24/\mathrm{Re} \qquad 23.2\text{-}11$$

where, at u_t

$$\mathrm{Re} \equiv \mathrm{Re}_t = d_p u_t \rho_f / \mu_f \qquad 23.2\text{-}12$$

To obtain an expression for u_t, we eliminate F_d, C_d, and Re_t from equations 23.2-9 to -12:

$$u_t = g(\rho_p - \rho_f)d_p^2/18\mu_f \qquad 23.2\text{-}13$$

(spherical particles, small Re_t)

Comparison of u_{mf} and u_t

- ➢To obtain proper fluidization, the actual fluid velocity, u_{fl}, must be considerably greater than the minimum fluidization velocity, u_{mf}.
- ➢ However, to avoid excessive entrainment, u_{fl} should be less than the terminal velocity, u_t.
- ➢Thus, the ratio u_t/u_{mf} is a guide toselection of the value of u_{fl}.

Since relatively small particles are used in a fluidized bed, corresponding to relatively small Re, we use equations 23.2-6 and -13 for comparison of spherical particles ($d_p' = d_p$). The result is

$$\frac{u_t}{u_{mf}} = \frac{150(1 - \epsilon_{mf})}{18\epsilon_{mf}^3} \qquad 23.2\text{-}14$$

(small, spherical particles)

This ratio is very sensitive to the value of ε_{mf}, ranging from 15 at $\varepsilon_{mf} = 0.60$ to 92 at $\varepsilon_{mf} = 0.383$. In practice, values of u_{fl} (actual velocity) are 30 to 50 times the value of u_{mf}.

HYDRODYNAMIC MODELS OF FLUIDIZATION

- A hydrodynamic model of fluidization attempts to account for several essential features of fluidization:
- mixing and distribution of solids and fluid in a so-called “emulsion region,
- ”the formation and motion of bubbles through the bed (the “bubble region”), the nature of the bubbles (including their size) and how they affect particle motion/ distribution, and
- the exchange of material between the bubbles (with little solid content) and the predominantly solid emulsion.

Models fall into one of three classes (Yates, 1983, pp. 74-78):

(1) two-region models, which take into account a bubble region and an emulsion region, with very little variation in properties within each region;

(2) bubble models, which are based upon a mean bubble size; all system properties are functions of this bubble size;

(3) bubble-growth models, which also endeavor to account for bubble coalescence and bubble splitting.

- The first two classes of models are simplest, but may require substantial experimental information to predict rates of exchange between the bubble and emulsion regions.
- Class (1) models are too simplistic to be of practical use,
- while class (3) models tend to be relatively complicated.
- Yates (1983, Chapter 2) gives an excellent discussion of the various types of models and their assumptions.

- Overall, the hydrodynamic behavior of a fluidized bed depends upon the nature of the particles used, and the ease of fluidization.
- Spherical solid particles that are not “sticky” fluidize easily; “sticky” particles, conversely, do not fluidize well,
- Since they tend to agglomerate, leading to uneven distribution of solid through the bed, and nonuniform circulation of solid and fluid.
- A more detailed description of types of particles and their effect upon fluidization is provided by Geldart (1973,197s) and by Grace (1986).

The fluid may be a liquid or a gas

- If the fluid is a liquid, the bed tends to expand uniformly with increasing fluidization velocity u_{fl}, and bubbles are generally not formed; this is called particulate fluidization.
- If the fluid is a gas, bubbles are usually formed at the inlet distributor; these bubbles travel upward through the bed, and may drag solid particles along with them as a “wake”; bubbles may coalesce and/or split,
- depending upon local conditions; in this “bubbling fluidization,” the fluidized bed may resemble a boiling liquid, as bubbles burst upon reaching the upper “surface” of the bed.

Two-Region Model (Class (1))

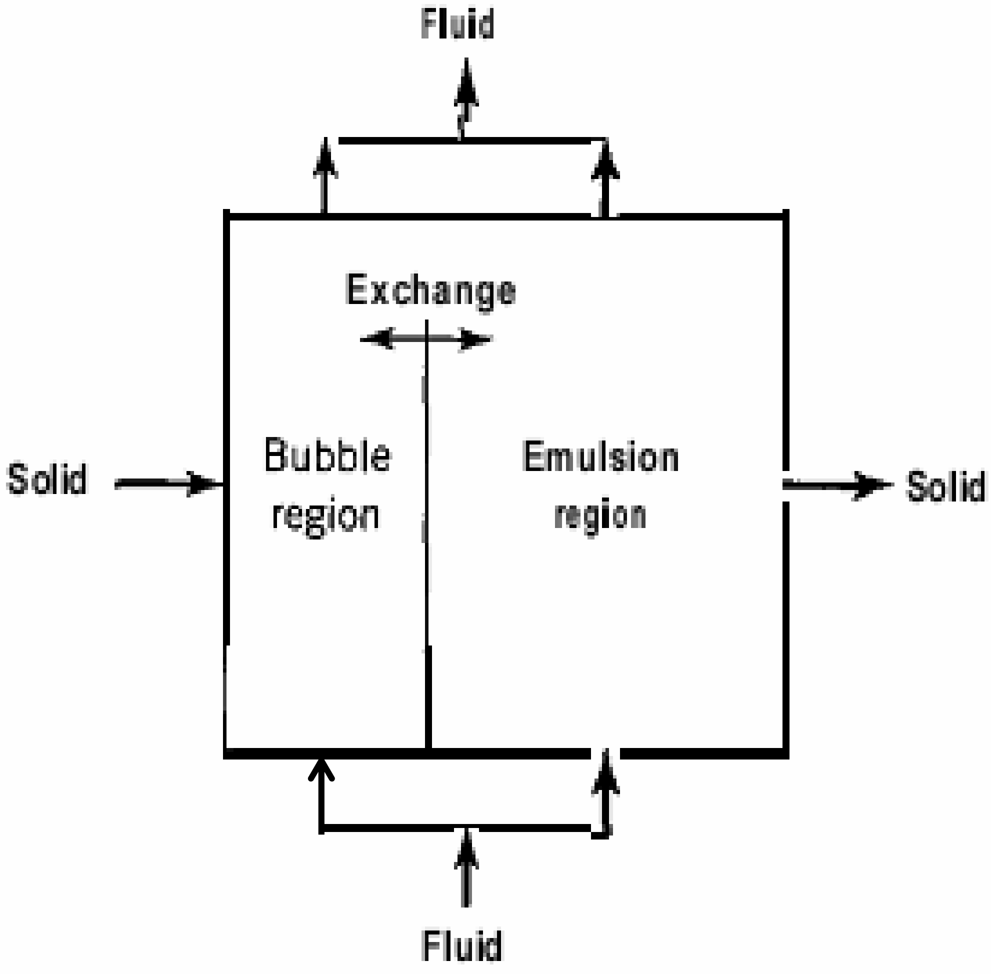


Figure 23.5 Schematic representation of two- region model for fluidized bed

- The discussion above suggests a hydrodynamic flow model based on two distinct regions in the fluidized bed:
- a “bubble” region made up mostly of gas, but also containing solid particles, and a fluid + solid (“emulsion”) region, resembling the bed at mf conditions.
- This is illustrated schematically in Figure 23.5; the two regions are actually interspersed.

- In Figure 23.5, the fluid entering is depicted as being split between the two regions;
- most fluid flows through in the bubble region, and there is provision for exchange (“mass transfer”) between the two regions characterized by an exchange coefficient K_{be}.
- The solid entering (in a continuous-flow situation) is also depicted as split between the two regions, but most solid is in the emulsion region.

- This model can have as many as six parameters for its characterization: K_{be}, Pe_b, Pe_e, and ratios of volumes of regions, of solid in the regions, and of fluid in the regions.
- The number can be reduced by assumptions such as PF (Plug Flow) for the bubble region ($Pe_b \rightarrow \infty$), all solid in the emulsion, and all fluid entering in the bubble region.
- Even with the reduction to three parameters, the model remains essentially empirical, and doesn’t take more detailed knowledge of fluidized-bed behavior into account

Kunii-Levenspiel (KL) Bubbling-Bed Model (Class (2))

The assumptions are as follows (Levenspiel, 1972, pp. 310-311):

(1) Bubbles are all the same size, and are distributed evenly throughout the bed, rising through it.

(2) Gas within a bubble essentially remains in the bubble, but recirculates internally, and penetrates slightly into the emulsion to form a transitional cloud region around the bubble; all parameters involved are functions of the size of bubble (Davidson and Harrison, 1963).

(3) Each bubble drags a wake of solid particles up with it (Rowe and Partridge, 1965). This forms an additional region, and the movement creates recirculation of particles in the bed: upward behind the bubbles and downward elsewhere in the emulsion region.

(4) The emulsion is at mf conditions.

For small, sand-like particles that are easily fluidized, an expression is given for bubble diameter, d_b as a function of bed height x by Werther (Kunii and Levenspiel, 1991, p. 146):

$$d_b/\text{cm} = 0.853[1 + 0.272(u_{fl} - u_{mf})]^{1/3}(1 + 0.0684x)^{1.21} \tag{23.3-1}$$

where u_{fl} and u_{mf} are in cm s^{-1} and x is in cm

The rise velocity of bubbles is another important parameter in fluidized-bed models, but it can be related to bubble size (and bed diameter, D). For a single bubble, the rise velocity, u_{br} relative to emulsion solids is (Kunii and Levenspiel, 1991, p. 116):

$$u_{br} = 0.711(gd_b)^{1/2} \quad [\text{small bubbles, } (d_b/D) < 0.125] \qquad (23.3\text{-}2)$$

$$u_{br} = [0.711(gd_b)^{1/2}]1.2e^{-1.49d_b/D} \quad [0.125 < (d_b/D) < 0.6] \qquad (23.3\text{-}3)$$

(For $(d_b/D) > 0.6$, the bed is not a bubbling bed; slugging occurs.)

- Another measure of bubble velocity is the absolute rise velocity of bubbles in the bed, u_b;
- this can be taken in the first instance as the sum of u_{br} and the apparent rise velocity of the bed ahead of the bubbles, $u_{fl} - u_{mf}$:

$$u_b = u_{br} + u_{fl} - u_{mf} \qquad (23.3\text{-}4)$$

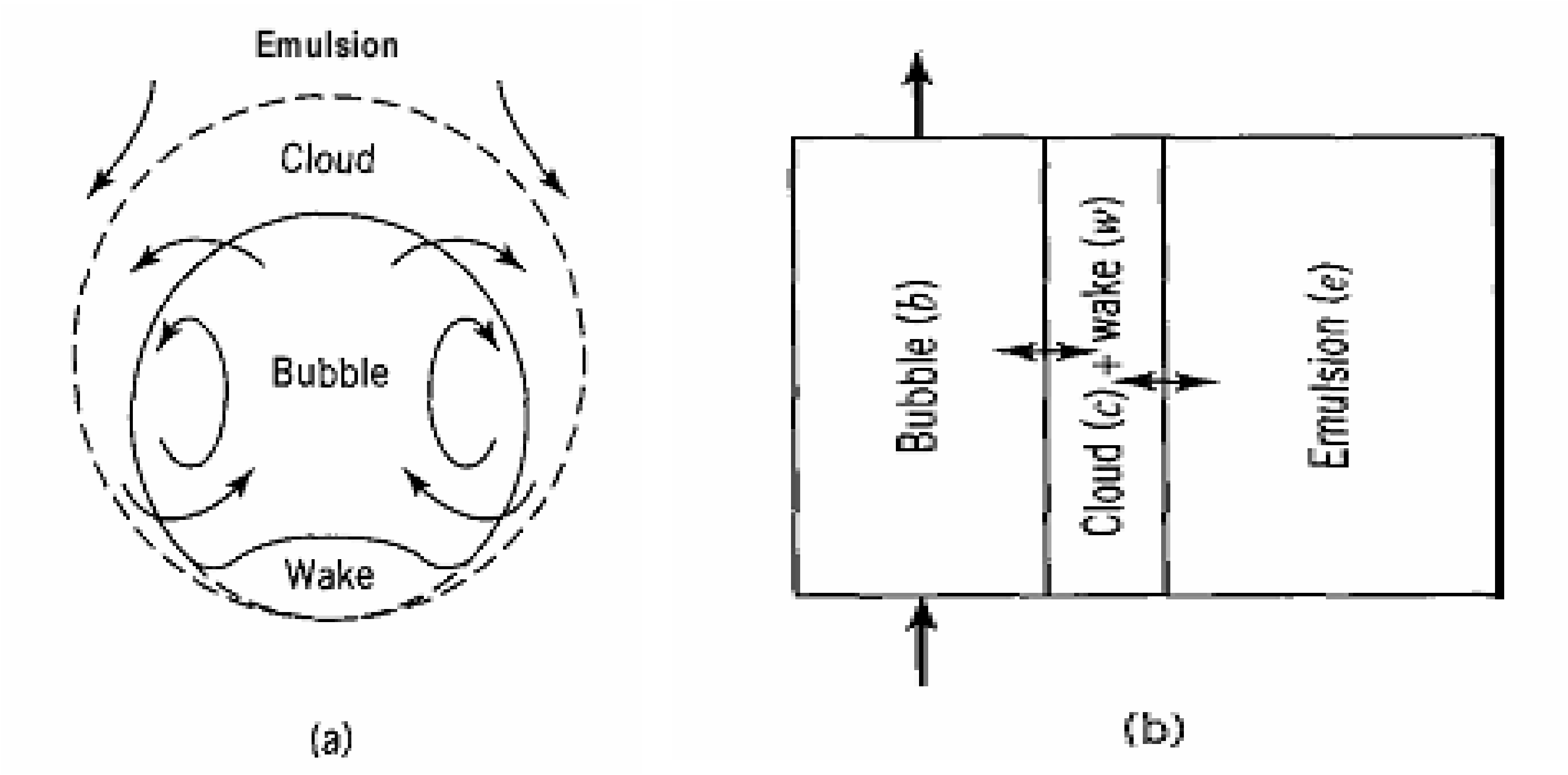


Figure 23.6 Bubbling-bed model representation of (a) a single bubble and (b) regions of a fluidized bed (schematic)

- The volume fraction of bubbles, f_b, m^3 bubbles (m^3 bed)$^{-1,}$ can be assessed from the point of view of either voidage or velocity.
- In terms of voidage, if we assume the void fraction in the bubbles is 1 and the remainder of the bed is at mf conditions with voidage ε_{mf},
- the volume-average voidage in the fluidized bed is

$$\epsilon_{fl} = f_b(1) + (1 - f_b)\epsilon_{mf}$$

from which

$$f_b \simeq \frac{\epsilon_{fl} - \epsilon_{mf}}{1 - \epsilon_{mf}} \qquad (23.3\text{-}5)$$

In terms of velocity, if we assume, for a vigorously bubbling bed with $u_{fl} >> u_{mf}$, that gas flows through the bed only in the bubble region ($q \approx q_b$, or $u_{fl}A_c \approx f_b u_b A_c$, where A_c is the cross-sectional area of the bed),

$$f_b \simeq u_{fl}/u_b \tag{23.3-6}$$

Equation 23.3-6 may need to be modified to take into account the relative magnitude of u_b (Kunii and Levenspiel, 1991, pp. 156-157):

(1) For slowly rising bubbles, $u_b < u_{mf}/\varepsilon_{mf}$,

$$f_b = (u_{fl} - u_{mf})/(u_b + 2u_{mf}) \tag{23.3-6a}$$

(2) For the intermediate case, $u_{mf}/\epsilon_{mf} < u_b < 5u_{mf}/\epsilon_{mf}$,

$$f_b = (u_{fl} - u_{mf})/(u_b + u_{mf}); \text{ for } u_b \simeq u_{mf}/\epsilon_{mf} \qquad (23.3\text{-}6b)$$

$$f_b = (u_{fl} - u_{mf})/u_b; \text{ for } u_b \simeq 5u_{mf}/\epsilon_{mf} \qquad (23.3\text{-}6c)$$

(3) For fast bubbles, $u_b > 5u_{mf}/\epsilon_{mf}$,

$$f_b = (u_{fl} - u_{mf})/(u_b - u_{mf}) \qquad (23.3\text{-}6d)$$

The ratio of cloud volume to bubble volume is given by Kunii and Levenspiel (1991, p. 157), and from this we obtain the volume fraction in the cloud region

$$f_c = \frac{3u_{mf}}{\varepsilon_{mf} u_{br} - u_{mf}} f_b \qquad (23.3\text{-}7)$$

The ratio of wake volume to bubble volume is difficult to assess, and is given by Kunii and Levenspiel (1991, p. 124)

$$f_w \simeq \alpha f_b \quad (\alpha = 0.2 \text{ to } 0.6) \tag{23.3-8}$$

The bed fraction in the emulsion, f_e is obtained by difference, since

$$f_b + f_c + f_w + f_e = 1 \tag{23.3-9}$$

For the distribution of solid particles in the various regions, we define the following ratios:

γ_b = (m^3 solid in bubbles)(m^3 bubbles)$^{-1}$

γ_{cw} = (m^3 solid in cloud + wake)(m^3 bubbles)$^{-1}$

γ_e = (m^3 solid in emulsion)(m^3 bubbles)$^{-1}$

The sum of these can be related to ε_{rnf} and f_b:

$$\gamma_b + \gamma_{cw} + \gamma_e \equiv \frac{\text{m}^3 \text{ total solid}}{\text{m}^3 \text{ bubbles}}$$

$$\equiv \left(\frac{\text{m}^3 \text{ total solid}}{\text{m}^3 \text{ bed at } mf}\right)\left(\frac{\text{m}^3(c + w + e)}{\text{m}^3\ fl \text{ bed}}\right)\left(\frac{\text{m}^3\ fl \text{ bed}}{\text{m}^3 \text{ bubbles}}\right)$$

$$= (1 - \epsilon_{mf})(f_c + f_w + f_e)/f_b$$

$$= (1 - \epsilon_{mf})(1 - f_b)/f_b \qquad (23.3\text{-}10)$$

To obtain equation 23.3-10, it is assumed that the volume of (cloud + wakes + emulsion) in the fluidized bed is equal to the volume of the bed at mf conditions. The first of these quantities, γ_b, is relatively small, but its value is uncertain. From a range of experimental data (γ_b = 0.01 to 0.001) it is usually taken as:

$$\gamma_b = 0.005 \qquad (23.3\text{-}11)$$

The second quantity, γ_{cw}, can also be related to ε_{mf} and bed-fraction quantities:

$$\gamma_{cw} = \frac{\text{m}^3\text{ solid in }(\text{c} + w)}{\text{m}^3\text{ bubbles}} \equiv \frac{\text{m}^3\text{ solid in c}}{\text{m}^3\text{ bubbles}} + \frac{\text{m}^3\text{ solid in }w}{\text{m}^3\text{ bubbles}}$$

$$\equiv \left(\frac{\text{m}^3\text{ total solid}}{\text{m}^3\text{ bed at }mf}\right)\left(\frac{\text{m}^3\text{ bed in }c}{\text{m}^3\ fl\text{ bed}}\right)\left(\frac{\text{m}^3\ fl\text{ bed}}{\text{m}^3\text{ bubbles}}\right)$$

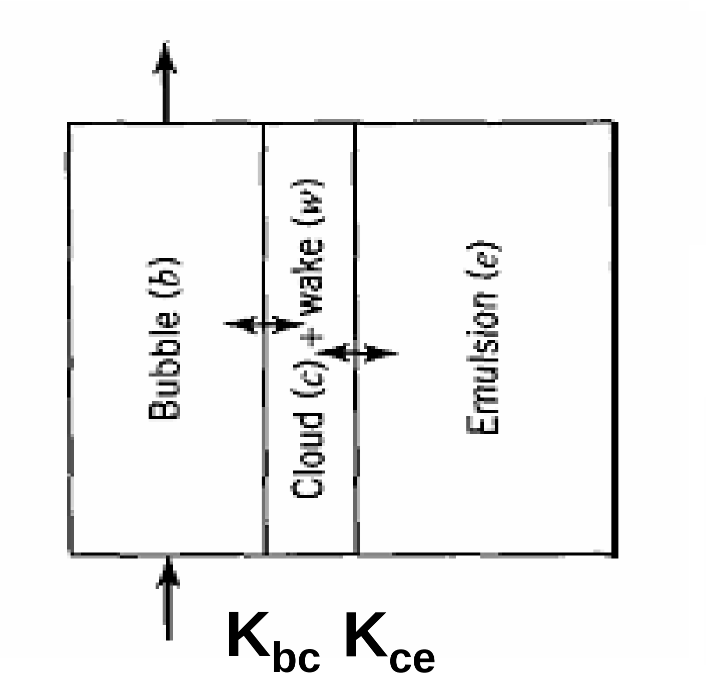
$$+ \left(\frac{\text{m}^3\text{ total solid}}{\text{m}^3\text{ bed at }mf}\right)\left(\frac{\text{m}^3\text{ bed in }w}{\text{m}^3\ fl\text{ bed}}\right)\left(\frac{\text{m}^3\ fl\text{ bed}}{\text{m}^3\text{ bubbles}}\right)$$

$$= (1 - \epsilon_{mf})(f_c + f_w)/f_b \qquad (23.3\text{-}12)$$

The third quantity, γ_e, is obtained by difference from equations 23.3-10 to -12.

Finally, we extend the hydrodynamic model to include exchange of gas between pairs of regions, analogous to mass transfer. Figure 23.6(b)

Those coefficients (K_{bc} and K_{ce}) are calculated by the following semi-empirical relations



$$K_{bc}/\mathrm{s}^{-1} = 4.5\left(\frac{u_{mf}}{d_b}\right) + 5.85\left(\frac{D_m^{1/2} g^{1/4}}{d_b^{5/4}}\right)$$

(23.3-13)

$$K_{ce}/\mathrm{s}^{-1} = 6.77\left(\frac{D_m \epsilon_{mf} u_{br}}{d_b^3}\right)^{1/2}$$ (23.3-14)

FLUIDIZED-BED REACTOR MODELS

- A fluidized-bed reactor consists of three main sections (Figure 23.1):
  1) the fluidizing gas entry or distributor section at the bottom, essentially a perforated metal plate that allows entry of the gas through a number of holes;
  2) the fluidized-bed itself, which, unless the operation is adiabatic, includes heat transfer surface to control T;
  3) the freeboard section above the bed, essentially empty space to allow disengagement of entrained solid particles from the rising exit gas stream; this section may be provided internally (at the top) or externally with cyclones to aid in the gas-solid separation.

- A model of a fluidized-bed reactor combines a hydrodynamic model of bubble and emulsion flow and interphase mass transfer with a kinetics model. As discussed in Section 23.3, various hydrodynamic models exist; their suitability as reactor models depends upon the actual flow and mixing conditions within the bed.
  - If the reaction is very slow, or the residence time through the bed is very short, then the choice of the hydrodynamic model is not important.
  - However, for very fast reactions, or if the contact time is very long, the details of the interphase mass transfer, the location of the solid, and the nature of mixing and flow within each region become important.

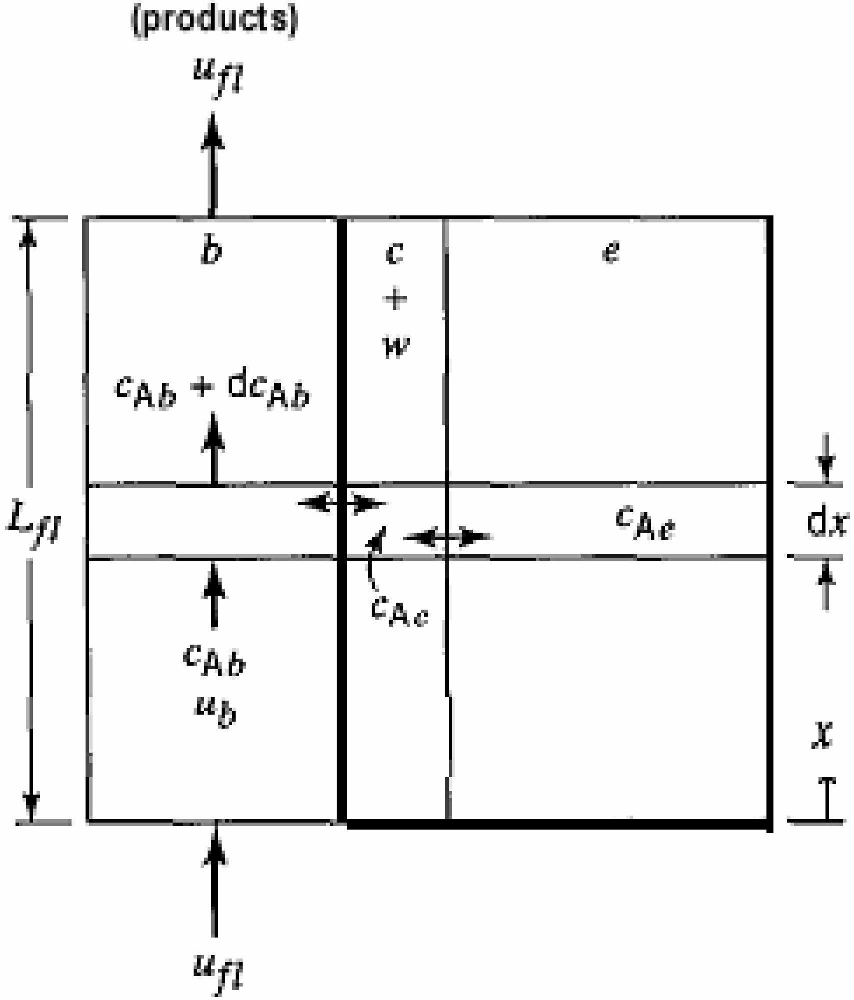
In the following sections, we discuss reactor models for fine, intermediate, and large particles, based upon the Kunii-Levenspiel (KL) bubbling-bed model, restricting our-selves primarily to first-order kinetics.

KL Model for Fine Particles

The following assumptions are made in addition to those in Section 23.3.2:

1. The reaction is A(g) + . . . → products, catalyzed by solid particles that are fluidized by a gas stream containing A and, perhaps, other reactants and inert species.
2. The reactor operates isothermally at constant density and at steady-state.

Figure 23.7 Schematic representation of control volume for material balance for bubbling-bed reactor model



A + … → product

3. The fluidizing (reactant) gas is in convective flow through the bed only via the bubble-gas region (with associated clouds and wakes); that is, there is no convective flow of gas through the emulsion region.
4. The bubble region is in PF (upward through the bed).
5. Gas exchange occurs (i) between bubbles and clouds, characterized by exchange coefficient K_{bc} (equation 23.3-13) and (ii) between clouds and emulsion, characterized by K_{ce} (equation 23.3-14).

The continuity or material-balance equations for A stem from the flow/kinetics scheme shown in Figure 23.8, which corresponds to the representation in Figure 23.7.

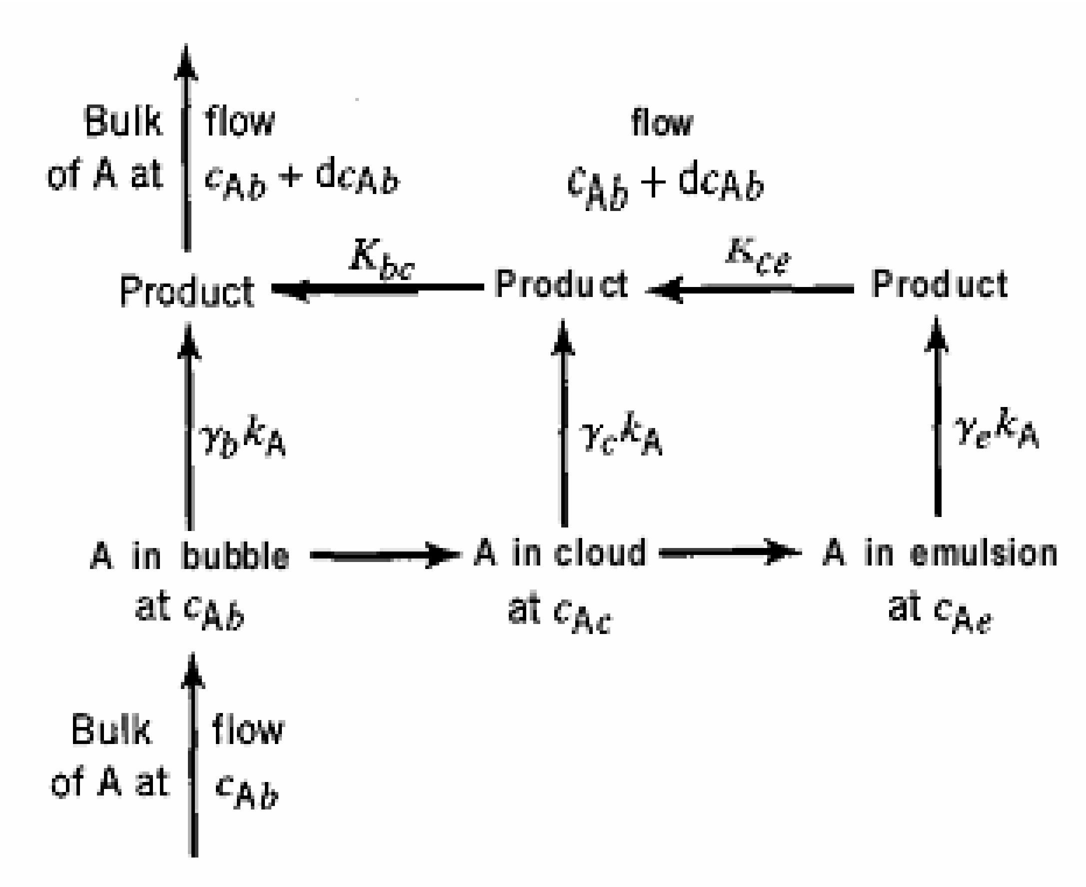


Figure 23.8 Flow/kinetics scheme for bubbling-bed reactor model for reaction A(g) + … → product(s)

The continuity equations for the three main regions lead eventually to the performance equation for the reactor model.

Continuity equation for the bubble region:

$$-u_b \frac{dC_{Ab}}{dx} = -\frac{dC_{Ab}}{dt} = \gamma_b k_A C_{Ab} + K_{bc}\left(C_{Ab} - C_{Ac}\right) \qquad (23.4\text{-}1)$$

which states that the rate of disappearance of A from the bubble region is equal to the rate of reaction in the bubble region + the rate of transfer to the cloud region; note that γ_b serves as a weighting factor for the intrinsic rate constant k_A.

Continuity equation for the cloud + wake region:

$$K_{bc}(c_{\mathrm{A}b} - c_{\mathrm{A}c}) = \gamma_{cw} k_{\mathrm{A}} c_{\mathrm{A}c} + K_{ce}(c_{\mathrm{A}c} - c_{\mathrm{A}e}) \qquad (23.4\text{-}2)$$

Continuity equation for the emulsion region:

$$K_{ce}(c_{\mathrm{A}c} - c_{\mathrm{A}e}) = \gamma_e k_{\mathrm{A}} c_{\mathrm{A}e} \qquad (23.4\text{-}3)$$

Eliminating C_{Ac} and C_{Ae} from equations 23.4-1 to -3, and dropping the subscript b from C_{Ab}, We obtain

$$-\frac{dC_A}{dt} = k_{overall} C_A \qquad (23.4\text{-}4)$$

Where,

$$k_{overall} = \gamma_b k_A + \cfrac{1}{\cfrac{1}{K_{bc}} + \cfrac{1}{\gamma_{cw} k_A + \cfrac{1}{\cfrac{1}{K_{ce}} + \cfrac{1}{\gamma_e k_A}}}} \qquad (23.4\text{-}5)$$

Integrating equation 23.4-4 from the bed inlet $(c_A = c_{Ao}, t = x = 0)$ to the bed Outlet $(c_A = c_A, t = L_{fl}/u_b)$,

we have

$$1 - f_A = c_A/c_{Ao} = \exp(-k_{overall} L_{fl}/u_b) \qquad (23.4\text{-}6)$$

The fluidized-bed depth, L_{fl}, is calculated from the fixed-bed packed depth, L_{pa}, as follows. Since, from a balance for bed solid,

$$(1 - \epsilon_{fl})L_{fl} = (1 - \epsilon_{pa})L_{pa} \qquad (23.4\text{-}7)$$

and, from equation 23.3-5,

$$1 - \epsilon_{fl} = (1 - \epsilon_{mf})(1 - f_b) \qquad (23.4\text{-}7a)$$

we have, on elimination of $1- \varepsilon_{fl}$ from 23.4-7,

$$L_{fl} = \frac{(1 - \epsilon_{pa})L_{pa}}{(1 - \epsilon_{mf})(1 - f_b)} \qquad (23.4\text{-}7b)$$

Equation 23.4-6 is one form of the performance equation for the bubbling-bed reactor model. It can be transformed to determine the amount of solid (e.g., catalyst) holdup to achieve a specified f_A or C_A:

$$W_{cat} = \frac{\rho_p q(1-\epsilon_{mf})u_{br}}{k_{overall}u_{fl}} \ln\left(\frac{c_{Ao}}{c_A}\right) \qquad (23.4\text{-}8)$$

Example 23.3

(a) Estimate the amount of catalyst (Wcat/kg) required for a fluidized-bed reactor, according to the Kunii-Levenspiel bubbling-bed model, for the production of 60,000 Mg year^{-1} of acrylonitrile by the ammoxidation of propylene with air.

Data and assumptions:

- The heat transfer configuration within the bed (for the exothermic reaction) and other internal features are ignored.
- Only C3H3N is formed (with water).
- The feed contains C3H6 and NH3 in the stoichiometric ratio and 20% excess air (79 mole% N2, 21% 02); there is no water in the feed.
- Conversion based on C3H6 (A) is 70%.
- T=400°C; P=2 bar.
- The annual stream service factor (fraction of time in operation) is 0.94.
- db = 0.1 m; dp = 0.05 mm; ρp = 2500 kg m^3; μf = 1.44 kg h^{-1} m^{-1}.

- umf = 0.002 m s^{-1}; α = 0.6; D_m = 0.14 m^2 h^{-1} at 4OO°C; εpa = 0.5.
- ε_{mf}= 0.6; k_A = 1.0 s^{-1}; u_{fl} = 720 m h^{-1}; γb = 0.004.

(b) Calculate the vessel diameter and the bed depth (fluidized) in m.

(c) For comparison, calculate W_{cat}, for the two cases (assume constant density for both):

(i) The reactor is a PFR.

(ii) The reactor is a CSTR.

Solution

(a) To calculate W_{cat}, we use equation 23.4-8 in conjunction with 23.4-5 and -6 For this purpose, we also need to calculate other quantities, as indicated below. The reaction is

$$C_3H_6(A) + NH_3 + \frac{3}{2}O_2 \rightarrow C_3H_3N(B) + 3H_2O$$

$$F_{A0} = \left(60{,}000(1000)\frac{\text{kg B}}{\text{yr}}\right)\left(\frac{1}{53}\,\frac{\text{kmol B}}{\text{kg B}}\right)\left(1\,\frac{\text{kmol A(reacted)}}{\text{kmol B(formed)}}\right)\left(\frac{1}{0.70}\,\frac{\text{kmol A(in feed)}}{\text{kmol A(reacted)}}\right)$$

$$\times \frac{1}{365(24)3600(0.94)}\,\frac{\text{yr}}{\text{s}} = 0{,}0546 \text{ kmol s}^{-1}$$

$$F_{t0} = 10.57(0.0546) = 0.577 \text{ kmol s}^{-1}$$

Catatan: tiap 1 mol A terdapat F_{t0} = 10.57 kmol/s

The total volumetric feed rate is

$$q_o = \frac{F_{Ao}RT}{P} = \frac{0.577(1000)8.314(673)}{2(105)} \simeq 16\;1\ \mathrm{m^3\,s^{-1}}$$

To calculate $k_{overall}$ in equation 23.4-5, we require K_{bc}, K_{ce}, γ_{cw}, and γ_e; these, in turn, require calculations of u_{br}, u_b, f_b, and (f_c+f_w), as follows (with each equation indicated):

$$u_{br} = 0.711(gd_b)^{1/2} = 0.711[9.81(0.1)]^{1/2} = 0.704\ \mathrm{m\,s^{-1}} \qquad (23.3\text{-}2)$$

$$u_b = u_{f1} - u_{mf} + u_{br} = (720/3600) - 0.002 + 0.704 = 0.902\ \mathrm{m\,s^{-1}} \qquad (23.3\text{-}4)$$

$$\begin{aligned} K_{bc} &= 4.5(u_{mf}/d_b) + 5.85(D_m^{1/2}g^{1/4}/d_b^{5/4}) \\ &= 4.5(0.002/0.1) + 5.85[(0.14/3600)^{1/2}(9.81)^{1/4}(0.1)^{5/4}] = 1.24\ \mathrm{s^{-1}} \end{aligned} \qquad (23.3\text{-}13)$$

$$K_{ce} = 6.77(\epsilon_{mf}\, D_m u_{br}/d_b^3)^{1/2} = 6.77[0.6(0.14/3600)0.704/(0.1)^3]^{1/2} = 0.868\ \mathrm{s^{-1}}$$

(23.3-14)

$$f_b = u_{fl}/u_b = 0.2/0.902 = 0.222 \qquad (23.3\text{-}6)$$

$$f_c = \frac{3u_{mf}f_b}{\epsilon_{mf}\,u_{br} - u_{mf}} = \frac{3(0.002)0.222}{(0.60)(0.704) - 0.002} = 0.0032 \qquad (23.3\text{-}7)$$

$$f_w = \alpha f_b = (0.60)(0.222) = 0.133 \qquad (23.3\text{-}8)$$

$$f_e = 1 - 0.222 - 0.0032 - 0.133 = 0.642 \qquad (23.3\text{-}9)$$

$$\gamma_{cw} = (1 - \epsilon_{mf})(f_c + f_w)/f_b = (1 - 0.60)(0.0032 + 0.133)/0.222 = 0.245 \qquad (23.3\text{-}12)$$

$$Ye = \frac{(1 - \epsilon_{mf})(1 - f_b)}{fb} - \gamma_b - \gamma_{cw} \qquad (23.3\text{-}14)$$

$$= \frac{(1 - 0.60)(1 \quad 0.222)}{0.222} - 0.004 - 0.245 = 1.153$$

$$k_{\text{overall}} = \gamma_b k_A + \cfrac{1}{\cfrac{1}{K_{bc}} + \cfrac{1}{\gamma_{cw} k_A + \cfrac{1}{\cfrac{1}{K_{ce}} + \cfrac{1}{\gamma_e k_A}}}} \qquad (23.4\text{-}5)$$

$$= (0.004)(1.0) + \cfrac{1}{\cfrac{1}{1.24} + \cfrac{1}{(0.245)(1.0) + \cfrac{1}{\cfrac{1}{0.868} + \cfrac{1}{(1.153)(1.0)}}}} = 0.467\ \text{s}^{-1}$$

The bed depth, L_{fl} can now be determined using 23.4-6:

$$L_{fl} = \frac{-[\ln(1 - f_A)]u_b}{k_{overall}} = \frac{-[\ln(1 - 0.70)](0.902\ \text{m s}^{-1})}{0.467\ \text{s}^{-1}} \simeq 2\ 33\ \text{m}$$

The catalyst requirement can be determined from 23.4-8:

$$W_{cat} = \frac{2500(16.1)(1-0.60)0.704[-\ln(1-0.70)]}{0.467(720/3600)} = \mathbf{1.46} \times 10^5 \text{ kg}$$

(b) From $q = u_{fl}A_c = u_{fl}\pi D^2/4$,

$$D = (4q/\pi u_{fl})^{1/2} = [4(16.1)/\pi(720/3600)]^{1/2} = 10.1 \text{ m}$$

From (a), $L_{fl} = 2.33$ m

(c) (i) For a PFR,

$$W_{cat} = \rho_p V_{cat} = (\rho_p q/k_A)\int_0^{f_A} \mathrm{d}f_A/(1-f_A)$$

$$= [2500(16.1)/1.0][-\ln(1-0.70)] = 0.48 \times 10^5 \text{ kg}$$

(ii) For a CSTR,

$$W_{cat} = \rho_p V_{cat} = (\rho_p q / k_A)[f_A/(1 - f_A)]$$

$$= [2500(16.1)/1.0][0.70/(1 - 0.70)] = 0.94 \ x\ 10^5 \text{ kg}$$

The amount of catalyst required in (a) is even greater than that required for a CSTR, which may be accounted for by the “by passing effect” (Section 23.1.3).

KL Model: Special Cases of First-Order Reaction

- For an extremely fast reaction, with kA relatively large, very little A reaches the emulsion and 23.4-5 reduces to:

$$k_{overall} = \gamma_b k_A + K_{bc} \qquad (23.4\text{-}9)$$

If the reaction is intrinsically slow, with $k_A << K_{ce}$ and K_{bc}, equation 23.4-5 reduces to:

$$k_{overall} = (\gamma_b + \gamma_e + \gamma_{cw})k_A \qquad (23.4\text{-}10)$$

In both cases, f_A is then determined using equation 23.4-6.

KL Model: Extension to First-Order Complex Reactions

- We illustrate the development of the model equations for a network of two parallel reactions, A → B, and A → C, with k_1 and k_2 representing the rate constants for the first and second reactions, respectively.
- Continuity equation for A in the bubble region:

$$u_b \frac{\mathrm{d}c_{\mathrm{A}b}}{\mathrm{d}x} = -\gamma_b(k_1 + k_2)c_{\mathrm{A}b} - K_{bc\mathrm{A}}(c_{\mathrm{A}b} - c_{\mathrm{A}c}) \tag{23.4-11}$$

Continuity equation for A in the cloud + wake region:

$$K_{bc\mathrm{A}}(c_{\mathrm{A}b} - c_{\mathrm{A}c}) = \gamma_{cw}(k_1 + k_2)c_{\mathrm{A}c} + K_{ce\mathrm{A}}(c_{\mathrm{A}c} - c_{\mathrm{A}e}) \qquad (23.4\text{-}12)$$

Continuity equation for A in the emulsion region:

$$K_{ce\mathrm{A}}(c_{\mathrm{A}c} - c_{\mathrm{A}e}) = \gamma_e(k_1 + k_2)c_{\mathrm{A}e} \qquad (23.4\text{-}13)$$

Continuity equation for B in the bubble region:

$$u_b \frac{\mathrm{d}c_{\mathrm{B}b}}{\mathrm{dx}} - \gamma_b k_1 c_{\mathrm{A}b} + K_{bc\mathrm{B}}(c_{\mathrm{B}b} - c_{\mathrm{B}c}) \qquad (23.4\text{-}14)$$

Continuity equation for B in the cloud + wake region:

$$K_{bc\mathrm{B}}(c_{\mathrm{B}b} - c_{\mathrm{B}c}) = -\gamma_{cw}k_1 c_{\mathrm{A}c} + K_{ce\mathrm{B}}(c_{\mathrm{B}c} - c_{\mathrm{B}e}) \qquad (23.4\text{-}15)$$

Continuity equation for B in the emulsion region:

$$K_{ce\mathrm{B}}(c_{\mathrm{B}c} - c_{\mathrm{B}e}) = -\gamma_e k_1 c_{\mathrm{A}e} \qquad (23.4\text{-}16)$$

Note that the continuity equations for product B reflect the fact that B, formed in the cloud + wake and emulsion regions, transfers to the bubble region. This is in contrast to reactant A, which transfers from the bubble region to the other regions.

Example 23.4

Phthalic anhydride is produced in the following process:

$$\text{naphthalene (A)} \xrightarrow{k1} \text{phthalic anhydride (B)} \xrightarrow{k2} CO_2 + H_2O$$

The reaction occurs in a fluidized-bed reactor, with sufficient heat exchange to ensure isothermal operation. The bed (before fluidization) is 5 m deep (L_{pa}), with a voidage (ε_{pa}) of 0.52. The reaction rate constants for the two steps are $k_1 = 1.5$ m^3 gas (m^3 cat)$^{-1}$ s^{-1} and $k_2 = 0.010$ m^3 gas (m^3 cat)$^{-1}$ s^{-1}. Additional data are:

$u_{mf} = 0.005 \text{ m s}^{-1}$ $\quad d_b = 0.05 \text{ m}$ $\quad D_A = 8.1 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$

$\epsilon_{mf} = 0.57$ $\quad u_b = 1.5 \text{ m s}^{-1}$ $\quad D_B = 8.4 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$

$u_{fl} = 0.45 \text{ m s}^{-1}$ $\quad \gamma_b = 0.005$ $\quad f_w / f_b = 0.6$

Determine the overall fractional conversion of naphthalene, and the selectivity to phthalic anhydride.

Solution:

20-21

Reactors for Fluid-Fluid Reactions

Di dalam bab ini, kita mempertimbangkan aspek perancangan proses dari reaktor-reaktor untuk reaksi-reaksi yang multiphase di mana masing-masing tahap adalah suatu fluida. Ini termasuk reaksi-reaksi gas-cair dan cair-cair.

TYPES OF REACTORS

- The types of reactors used for fluid-fluid reactions may be divided into two main types:
  - (1) tower or column reactors, and
  - (2) tank reactors.

Tower or Column Reactors

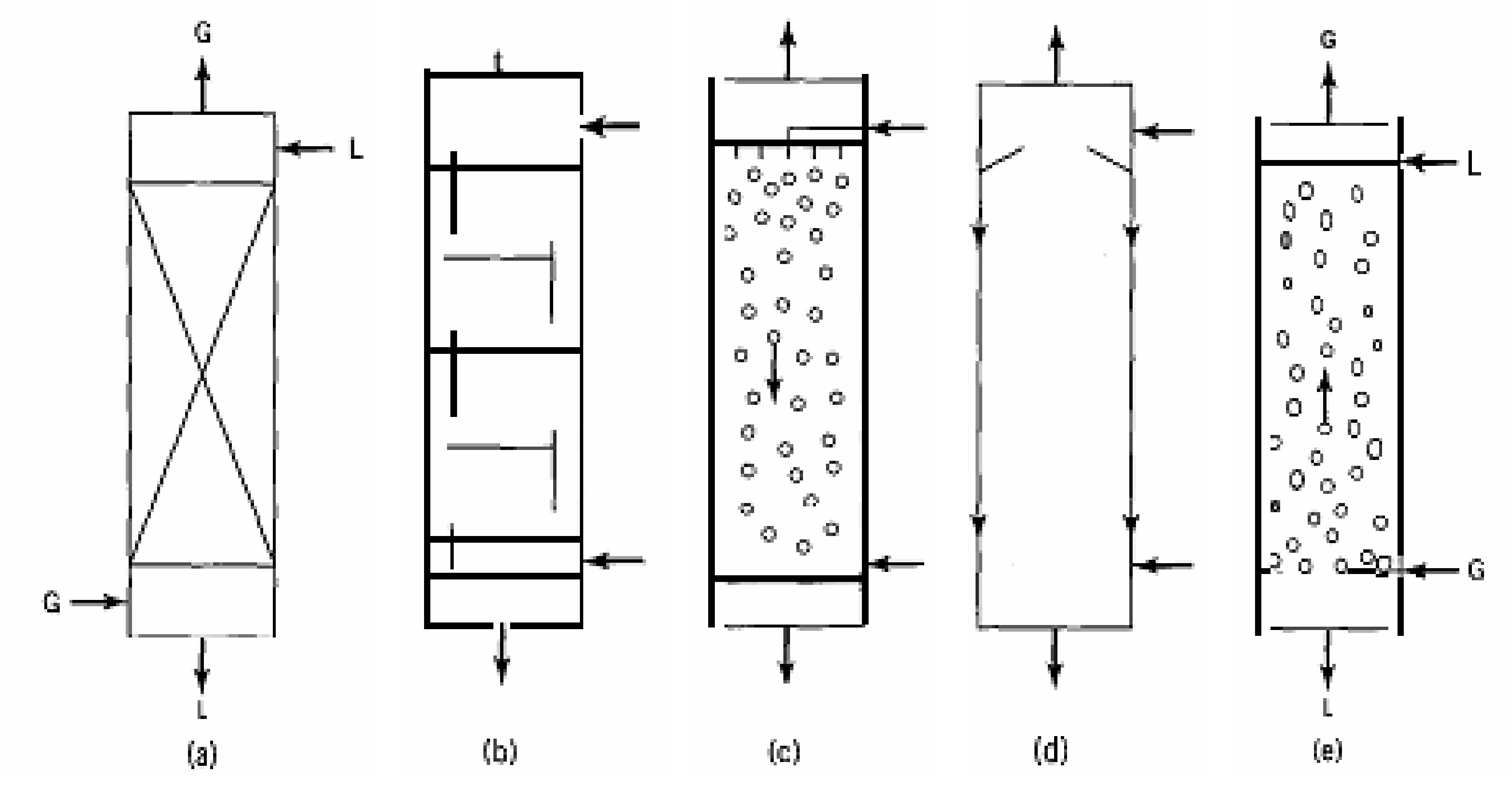
- Tower or column reactors, without mechanical agitation, are used primarily for gas-liquid reactions.
- If used for a liquid-liquid reaction, the arrangement involves vertically stacked compartments, each of which is mechanically agitated.
- In either case, the flow is countercurrent, with the less dense fluid entering at the bottom, and the more dense fluid at the top.
- In the case of a gas-liquid reaction without mechanical agitation, both interphase contact and separation occur under the influence of gravity.
- In a liquid-liquid reaction, mechanical agitation greatly enhances the contact of the two phases.
- We consider here primarily the case of gas-liquid reactions.

(1) Packed tower

- A packed tower (Figure 24.1(a)) contains solid shapes such as ceramic rings or saddles to ensure appropriate flow and mixing of the fluids.
- The flow is usually countercurrent, with the less dense fluid entering at the bottom of the tower. Both phases are considered to be continuous and ideally in PF.
- Gas-liquid interfacial area is enhanced by contact of gas rising through the void space between particles of packing with a liquid film flowing down over the packing surface

Types of tower or column reactors for gas-liquid reactions:

(a) packed tower; (b) plate tower; (c) spray tower; (d) falling-film tower; (e) bubble column



(2) Plate tower.

- A plate tower (Figure 24.1(b)) contains, for example, bubble-cap or sieve plates at intervals along its height.
- The flow of gas and liquid is counter-current, and liquid may be assumed to be distributed uniformly radially on each plate.
- On each plate or tray, gas is dispersed within the continuous liquid phase.
- The gas-liquid interfacial area is relatively large, and the gas-liquid contact time is typically greater than that in a packed tower.

(4) Falling-Film column

- A falling-film column (Figure 24.1(d)) is also an “empty” vessel, with liquid, introduced at the top, flowing down the wall as a film to contact an upward-flowing gas stream.
- Ideal flow for each phase is PF.
- Since neither liquid nor gas is dispersed, the interfacial area developed is relatively small, and gas-liquid contact is relatively inefficient.
- This type is used primarily in the experimental determination of mass transfer characteristics, since the interfacial area is well defined.

(5) Bubble column

- A bubble column (Figure 24.1(e)) is also an “empty” vessel with gas bubbles, developed in a sparger (see below) rising through a downward-flowing liquid stream.
- The gas phase is dispersed, and the liquid phase is continuous; the assumed ideal flow pattern is PF for the gas and BMF for the liquid.
- Performance as a reactor may be affected by the relative difficulty of controlling axial and radial mixing.
- As in the case of a packed tower, it may also be used for catalytic systems, with solid catalyst particles suspended in the liquid phase.

Tank Reactors

- Tank reactors usually employ mechanical agitation to bring about more intimate contact of the phases, with one phase being dispersed in the other as the continuous phase.
- The gas phase may be introduced through a “sparger” located at the bottom of the tank; this is a circular ring of closed-end pipe provided with a number of holes along its length allowing multiple entry points for the gas.
- Tank reactors are well suited for a reaction requiring a large liquid holdup or a long liquid-phase residence time
- Tank reactors equipped with agitators (stirrers, impellers, turbines, etc.) are used extensively for gas-liquid reactions

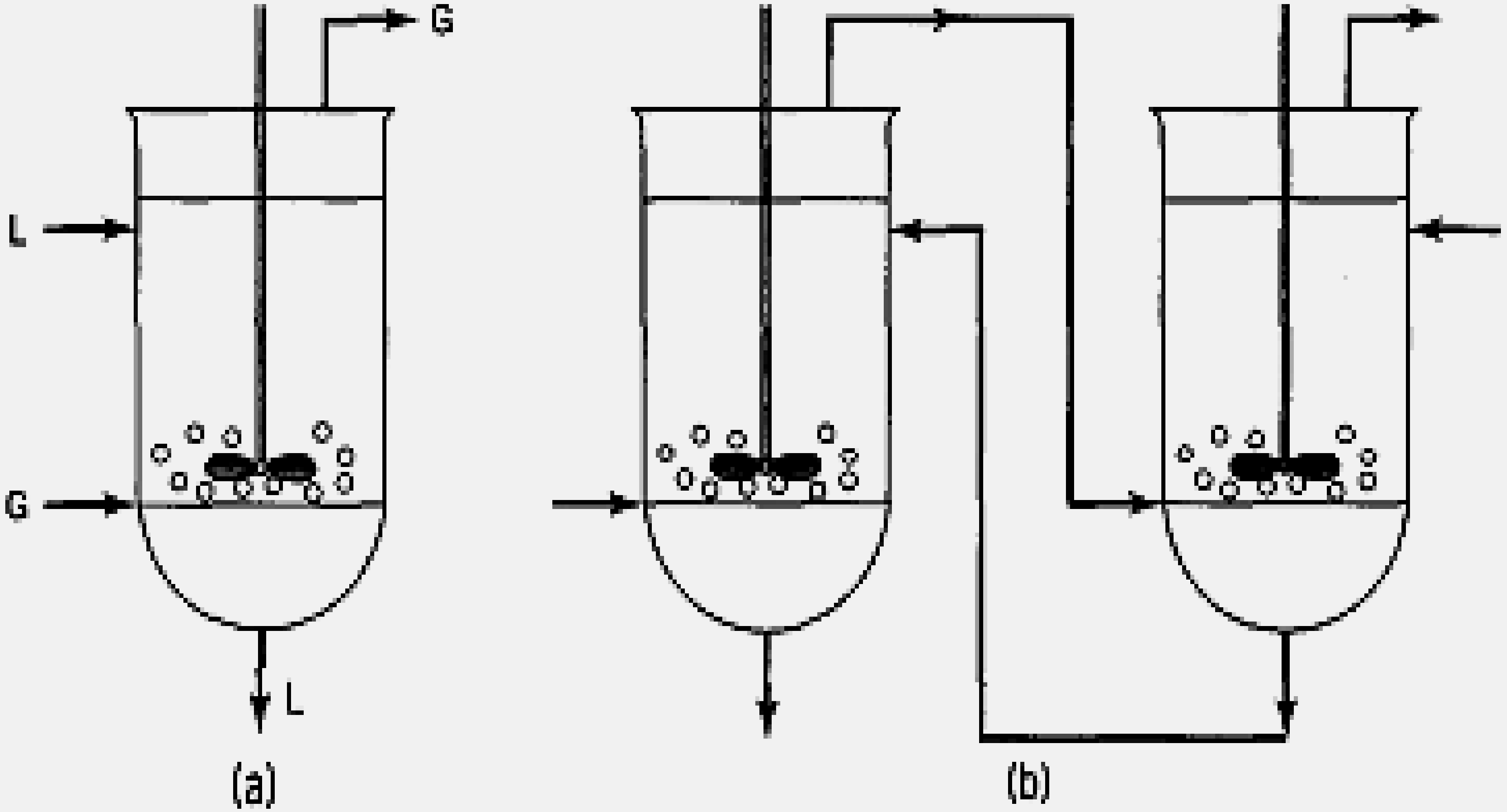


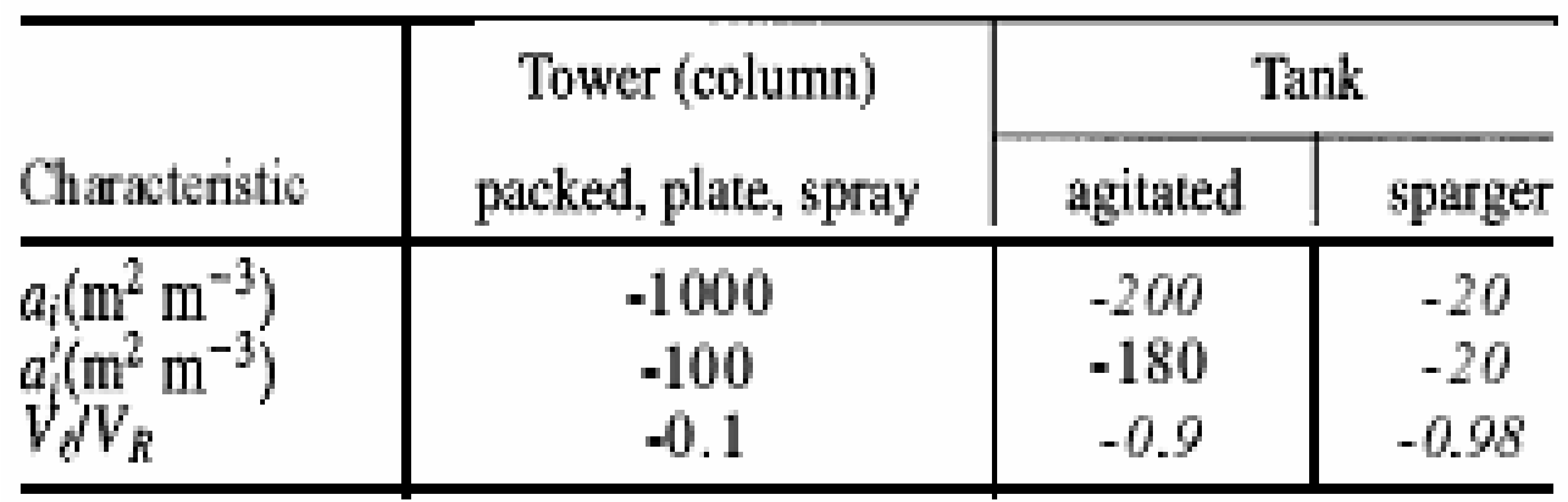
Figure 24.2 Agitated tank reactors for gas-liquid reactions: (a) single-stage; (b) two-(or multi-) stage

CHOICE OF TOWER OR TANK REACTOR

- The choice between a tower-type and a tank-type reactor for a fluid-fluid reaction is determined in part by the kinetics of the reaction. As described by the two-film model for gas-liquid reactions

Typical values of gas-liquid interfacial area (a_i and a_i') for various types of vessels

- The two extremes for a nonvolatile liquid-phase reactant, are virtually instantaneous reaction in the liquid-film,



Characteristic	Tower (column)	Tank	
	packed, plate, spray	agitated	sparger
$a_i(\mathrm{m}^2\ \mathrm{m}^{-3})$	-1000	-200	-20
$a_i'(\mathrm{m}^2\ \mathrm{m}^{-3})$	-100	-180	-20
V_ℓ/V_R	-0.1	-0.9	-0.98

a_i interfacial area based on unit volume of liquid phase, m^2/m^3 (liquid) a_i' interfacial area based on unit volume of vessel (occupied by fluids), m^2/m^3 (vessel)

- ai interfacial area based on unit volume of liquid phase, $m^2\ m_P^{-3}$ (liquid)
- Ai' interfacial area based on unit volume of vessel (occupied by fluids), $m^2\ m^{-3}$ (vessel)
- The two quantities a_i and are related by

$$a_i' = (V_\ell/V_R)a_i = (1 - \epsilon_g)a_i$$

TOWER REACTORS

- Packed-Tower Reactors
  - We consider the problem of determining the height, h, of a tower (i.e., of the packing in the tower) and its diameter, D, for a reaction of the model type:

$$\mathrm{A(g)} + b\mathrm{B}(\ell) \rightarrow \text{products}$$

  - in which A transfers from the gas phase to react with nonvolatile B in the liquid phase.
  - The height h is determined by means of appropriate material balances or forms of the
  - continuity equation.

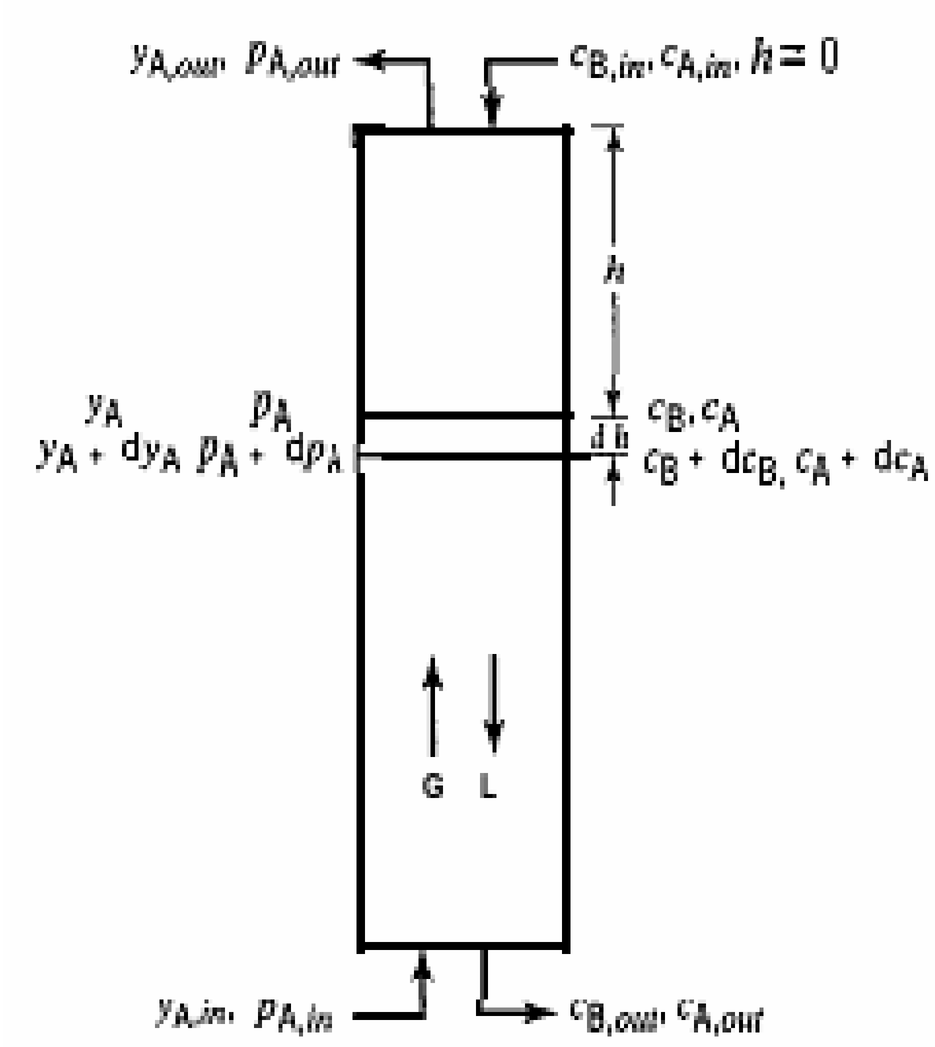


Figure 24.3 Flow diagram and notation for packed-tower reactor for reaction $A(g) + bB(\ell) \rightarrow$ products

For simplification, we make the following assumptions:

(1) The gas and liquid flow rates are constant throughout the column;

(2) Each phase is in PF.

(3) T is constant.

(4) P is constant.

(5) The operation is at steady state.

(6) The two-film model is applicable

In Figure 24.3, the other symbols are interpreted as follows:

G = total molar mass flow rate of gas, mol mm^2 s^{-1}

L = total liquid volumetric flow rate, m^3 m^2 s^{-1} (both G and L are related to unit cross-sectional area A, of the unpacked column)

c_A = liquid-phase concentration of A, mol m^{-3}

c_n = liquid-phase concentration of B, mol m^{-3}

y_A = mole fraction of A in gas

p_A = partial pressure of A in gas = y_AP

Note that h is measured from the top of the column.

Continuity equation for A in the gas phase (PF):

$$\begin{pmatrix}\textit{rate of input}\\ \textit{of A}\\ \textit{by bulk flow}\end{pmatrix} = \begin{pmatrix}\textit{rate of output}\\ \textit{of A}\\ \textit{by bulk flow}\end{pmatrix} + \begin{pmatrix}\textit{rate of transfer}\\ \textit{of A}\\ \textit{to liquid film}\end{pmatrix}$$

The second term on the right is the flux of A at the gas-liquid interface, NA(z = 0).
Thus, the continuity equation may be written as

$$(y_A + dy_A)GA_c = y_A GA_c + N_A(z = 0)a_i' A_c dh \qquad (24.4\text{-}1)$$

which becomes, with $y_A = p_A/P$, $\frac{G\,dp_A}{P\,dh} = N_A(z = 0)a_i'$ (24.4-2)

Continuity equation for A in the bulk Liquid phase (PF):

- For A in the bulk liquid, with reference to the control volume in Figure 24.3, in which the input of A is at the bottom,

$$\begin{pmatrix}\textit{rate of input}\\ \textit{of A}\\ \textit{by bulk flow}\end{pmatrix}+\begin{pmatrix}\textit{rate of transfer}\\ \textit{of A}\\ \textit{from L film}\end{pmatrix}=\begin{pmatrix}\textit{rate of output}\\ \textit{of A}\\ \textit{by bulk flow}\end{pmatrix}+\begin{pmatrix}\textit{rate of reaction}\\ \textit{of A}\\ \textit{in bulk liquid}\end{pmatrix}$$

The second term on the left is the flux of A at the fictitious liquid film-bulk liquid interface, NA (z = 1). That is,

$$(c_A + \mathrm{d}c_A)LA_c + N_A(z=1)a_i'A_c\mathrm{d}h = c_ALA_c + (-r_A)_{int}(a_i'/a_i)A_c\mathrm{d}h \qquad (24.4\text{-}3)$$

where $(-r_A)_{int}$, in mol m^{-3} (liquid) s^{-1}, is the intrinsic rate of reaction of A in the liquid phase, as given by a rate law for a homogeneous reaction. Equation 24.4-3 becomes

$$L\frac{dc_A}{dh} = (-r_A)_{int}(a_i'/a_i) - N_A(z = 1)a_i' \qquad (24.4\text{-}4)$$

Continuity equation for B in the bulk liquid phase (PF): With reference to the control volume in Figure 24.3, in which the input of B is at the top,

$$\begin{pmatrix} \textit{rate of input} \\ \textit{of B} \\ \textit{by bulk flow} \end{pmatrix} = \begin{pmatrix} \textit{rate of output} \\ \textit{of B} \\ \textit{by bulk flow} \end{pmatrix} + \begin{pmatrix} \textit{rate of reaction} \\ \textit{of B} \\ \textit{in bulk liquid} \end{pmatrix} + \begin{pmatrix} \textit{rate of transfer} \\ \textit{of B} \\ \textit{to liquid film} \end{pmatrix}$$

That is, since the rate of diffusion of B in the liquid film is $N_B = -bN_A$, for counter-diffusion,

$$c_B L A_c = (c_B + \mathrm{d}c_B) L A_c + b(-r_A)_{int}(a_i'/a_i) A_c \mathrm{d}h - bN_A(z = 1) a_i' A_c \mathrm{d}h \qquad (24.4\text{-}5)$$

or

$$-L\frac{\mathrm{d}c_B}{\mathrm{d}h} = b[(-r_A)_{int}(a_i'/a_i) - N_A(z = 1)a_i'] = bL\frac{\mathrm{d}c_A}{\mathrm{d}h}$$

That is,

$$-\frac{\mathrm{d}c_B}{\mathrm{d}h} = b\frac{\mathrm{d}c_A}{\mathrm{d}h} \qquad (24.4\text{-}6)$$

Overall material balance around column:

- For A: rate of moles entering in gas + rate of moles entering in liquid = rate of moles leaving in gas + rate of moles leaving in liquid + rate of moles lost by reaction:

$$A_c \frac{G}{P} p_{A,in} + A_c L c_{A,in} = A_c \frac{G}{P} p_{A,out} + A_c L c_{A,out} + A_r \text{“}r_A\text{”}$$

which can be written

$$\text{“}r_A\text{”} = \frac{G}{P}(p_{A,in} - p_{A,out}) + L(c_{A,in} - c_{A,out}) \qquad (24.4\text{-}7)$$

where “r_A” is the total rate of consumption of A (in liquid film and bulk liquid) over the entire column.

Similarly, for B:

$$\text{“}r_B\text{”} = L(c_{B,in} - c_{B,out}) = b\text{“}r_A\text{”} \qquad (24.4\text{-}8)$$

- Combining 24.4-7 and -8, we obtain

$$\frac{G}{P}(p_{A,in} - p_{A,out}) = \frac{L}{b}(c_{B,in} - c_{B,out}) + L(c_{A,out} - c_{A,in}) \qquad (24.4\text{-}9)$$

around the top,

$$\frac{G}{P}(p_A - p_{A,out}) = \frac{L}{b}(c_{B,in} - c_B) + L(c_A - c_{A,in}) \qquad (24.4\text{-}9a)$$

around the top,

$$\frac{G}{P}(p_{A,in} - p_A) = \frac{L}{b}(c_B - c_{B,out}) + L(c_{A,out} - c_A) \qquad (24.4\text{-}9b)$$

Determination of the tower diameter D depends on what is specified for the system. Thus, the cross-sectional area is

$$A_c = \frac{\pi D^2}{4} = \frac{q_g}{u_{sg}} = \frac{F_{tg}}{G} = \frac{q_\ell}{L} \tag{24.4-10}$$

where q_g, u_{sg}, and F_{tg} are the volumetric flow rate, superficial linear velocity, and molar flow rate of gas, respectively, and q_l is the volumetric flow rate of liquid. The gas flow rate quantities are further interrelated by an equation of state. Thus, for an ideal gas,

$$q_g = F_{tg}RT/P \tag{24.4-11}$$

Example 24.1

If, for the situation depicted in Figure 24.3, the partial pressure of A in the gas phase is to be reduced from $P_{A,in}$ to $P_{A,out}$ at a specified gas flow rate G and total pressure P, what is the minimum liquid flow rate, L_{min}, in terms of G, P, and the partial pressures/ concentrations of A and B? Assume that there is no A in the liquid feed.

SOLUTION

The criterion for $L \rightarrow L_{min}$ is that $C_{B,out} \rightarrow 0$. That is, there is just enough input of B to react with A to lower its partial pressure to $p_{A,out}$ and to allow for an outlet liquid-phase concentration of $C_{A,\ out}$. From equation 24.4-9, with $C_{B,out} = C_{A,in} = 0$ and $L = L_{min}$,

$$L_{min} = \frac{bG(p_{A,in} \quad p_{A,out})}{P(c_{B,in} + bc_{A,out})} \qquad (24.4\text{-}12)$$

For reaction in the liquid film only, $C_{A,out} = 0$, and equation 24.4-12 reduces to

$$L_{\min} = \frac{bG\left(P_{A,in} - P_{A,out}\right)}{P\left(C_{B,in}\right)} \qquad (24.4\text{-}13)$$

Then,

$$L = \alpha L_{min} \; (\alpha > 1) \qquad (24.4\text{-}14)$$

To establish α (i.e., L), it is necessary to take flooding and wetting of packing into account (see Zenz, 1972).

Bubble-Column Reactors

- In a bubble-column reactor for a gas-liquid reaction, Figure 24.1(e), gas enters the bottom of the vessel, is dispersed as bubbles, and flows upward, countercurrent to the flow of liquid.
- We assume the gas bubbles are in PF and the liquid is in BMF, although non-ideal flow models (Chapter 19) may be used as required.
- The fluids are not mechanically agitated.
- The design of the reactor for a specified performance requires, among other things, determination of the height and diameter.

Continuity Equations for Bubble-Column Reactors

Continuity equation for A in the gas phase (PF):

$$\frac{G\,\mathrm{d}p_{\mathrm{A}}}{P\,\mathrm{dh}} = N_{\mathrm{A}}(z = 0)a_i' \qquad (24.4\text{-}2)$$

Continuity equation for A in the bulk liquid phase (BMF):

$$c_{\mathrm{A},in}q_{\ell} + a_i'\int_0^V N_{\mathrm{A}}(z = 1)\mathrm{d}V = c_{\mathrm{A},out}q_{\ell} + (1 - \epsilon_g)(-r_{\mathrm{A}})_{int}V \qquad (24.4\text{-}15)$$

- The integral on the left side of equation 24.4-15 is required, since, although c_A(= $c_{A,out}$) is constant throughout the bulk liquid from top to bottom (BMF for liquid), P_A decreases continuously from bottom to top.
- These quantities are both included in N_A(z = 1) (see Example 24-2, below).

Overall material balance around column:

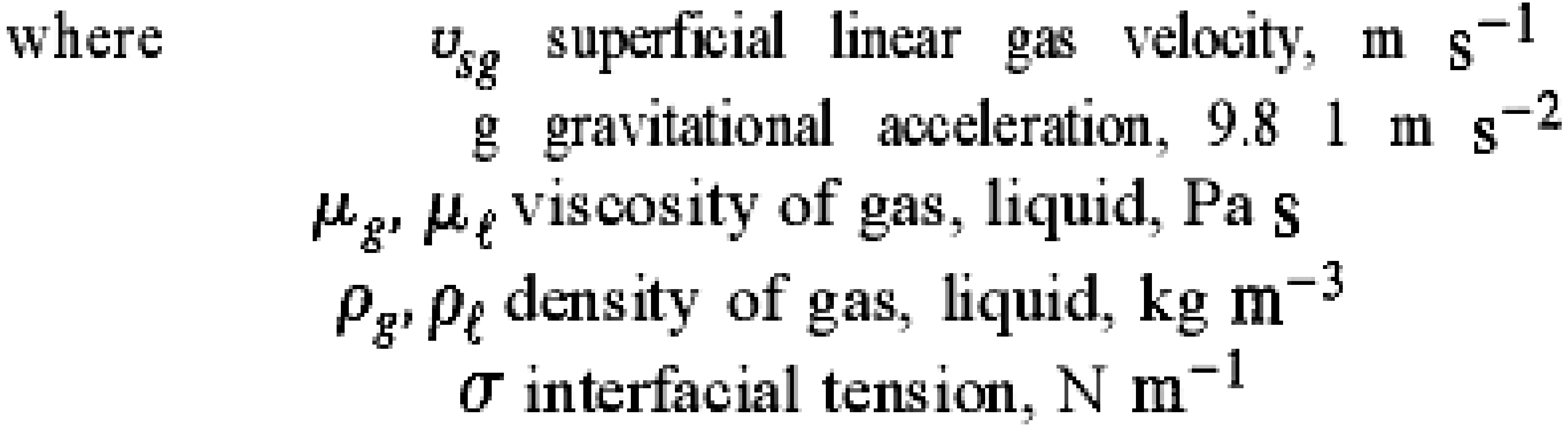
$$\frac{G}{P}\left(p_{A,in} - p_{A,out}\right) = \frac{L}{b}\left(c_{B,in} - c_{B,out}\right) + L\left(c_{A,out} - c_{A,in}\right) \qquad (24.4\text{-}9)$$

Correlations for Design Parameters for Bubble-Column Reactors

Gas holdup, ε_g:

For a nonelectrolyte liquid phase, the correlation of Hikita et al. (1980) is

$$\epsilon_g = 0.672\left(\frac{u_{sg}\mu_\ell}{\sigma}\right)^{0.578}\left(\frac{\mu_\ell^4 g}{\rho_\ell \sigma^3}\right)^{-0.131}\left(\frac{\rho_g}{\rho_\ell}\right)^{0.062}\left(\frac{\mu_g}{\mu_\ell}\right)^{0.107} \qquad (24.4\text{-}16)$$



where u_{sg} superficial linear gas velocity, $m\ s^{-1}$

g gravitational acceleration, $9.81\ m\ s^{-2}$

μ_g, μ_ℓ viscosity of gas, liquid, Pa s

ρ_g, ρ_ℓ density of gas, liquid, $kg\ m^{-3}$

σ interfacial tension, $N\ m^{-1}$

Mass transfer coeficient, k_{Al}

The liquid-film mass transfer coefficient may be given as a correlation for k_{Al} (k_i in general for species i, or often denoted simply by k_L.), or for $k_{Al}a_i'$, the product of the mass transfer coefficient and the interfacial area based on vessel volume (often denoted simply as k_La).

For k_{Al}, the correlation of Calderbank and Moo-Young (1961) for small bubbles is

$$k_{\mathrm{A}\ell} = 0.0031\left[\frac{(\rho_\ell - \rho_g)\mu_\ell g}{\rho_\ell^2}\right]^{1/3}\left(\frac{\mu_\ell}{\rho_\ell D_{\mathrm{A}}}\right)^{-1/3} \qquad (24.4\text{-}17)$$

where D_A= molecular diffusivity of A in the liquid phase, $m^2\ s^{-1}$ and k_{Al} is in $m\ s^{-1}$,

For $k_{Al}a_i'$, the correlation of Hikita et al. (1981) is

$$k_{\mathrm{A}\ell}a_i' = 14.9\left(\frac{g}{u_{sg}}\right)\left(\frac{u_{sg}\mu_\ell}{\sigma}\right)^{1.76}\left(\frac{\mu_\ell^4 g}{\rho_\ell \sigma^3}\right)^{-0.248}\left(\frac{\mu_g}{\mu_\ell}\right)^{0.243}\left(\frac{\mu_\ell}{\rho_\ell D_{\mathrm{A}}}\right)^{-0.604} \qquad (24.4\text{-}18)$$

With units given above, $k_{Al}a_i$’ is in s^{-1} as derived from the factor g/u_{sg} since the other factors are dimensionless.

Interfacial area, a_i’:

An expression for a_i’ given by Froment and Bischoff (1990, p. 637) may be written

$$a_i' = 2u_{sg}(\rho_\ell^3 g/\sigma^3)^{1/4} \qquad (24.4\text{-}19)$$

With units given above, ai’ is in m^{-1} (i.e., m^2 interfacial area (m^3 reactor)$^{-1}$).

Mass transfer coefficient, k_{Ag}:

- Shah et al. (1982) made no recommendation for the determination of k_{Ag}; in particular, no correlation for k_{Ag} in a bubble column had been reported up to that time.
- If the gas phase is pure reactant A, there is no gas-phase resistance, but it may be significant for a highly soluble reactant undergoing fast reaction.

TANK REACTORS

- Continuity Equations for Tank Reactors
  - – Continuity equation for A in the gas phase (BMF):
    - Since the gas phase is in BMF, the continuity equation corresponding to 24.4-1, and
    - based on the entire vessel of volume

$V = A_c h = (\pi D^2/4)h$, is

$$y_{A,in} G A_c = y_{A,out} G A_c + N_A(z=0) a_i' A_c h \qquad 24.5\text{-}1$$

Or, with $y_A = p_A/P$,

$$\frac{G}{P}(p_{\mathrm{A},in} \quad p_{\mathrm{A},out}) = N_{\mathrm{A}}(z = 0)a_i'h \qquad (24.5\text{-}2)$$

Continuity equation for A in the bulk liquid phase (BMF): Since the liquid phase is in BMF, the continuity equation for A in the bulk liquid phase is similar to equation 24.4-15,

$$(p_{\mathrm{A}} = p_{\mathrm{A},out}, \text{ and } c_{\mathrm{A}} = c_{\mathrm{A},out})$$

Thus, we have

$$c_{\mathrm{A},in}q_\ell + a_i'N_{\mathrm{A}}(z = 1)V = c_{\mathrm{A},out}q_\ell + (1 - \epsilon_g)(-r_{\mathrm{A}})_{int}V \qquad (24.5\text{-}3)$$

Overall material balance around tank: is again given by equation 24.4-9:

$$\frac{G}{P}(p_{\mathrm{A},in} - p_{\mathrm{A},out}) = \frac{L}{b}(c_{\mathrm{B},in} - c_{\mathrm{B},out}) + L(c_{\mathrm{A},out} \quad c_{\mathrm{A},in}) \qquad (24.4\text{-}9)$$

Correlations for Design Parameters for Tank Reactors

Power input, P_I:

Michell and Miller (1962) proposed the following correlation for P_I (in kW):

$$P_I = 0.34 n_{b,imp}^{1/2} (P_{Io} \dot{n}_{imp} d_{imp}^3 / q_g)^m \tag{24.5-4}$$

P_{Io}	power input without gas flow, kW
$n_{b,imp}$	number of impeller blades
$\dot{n}_{imp}$	rate of rotation of impeller, Hz
d_{imp}	diameter of impeller, m
m	0.45 for normal coalescing fluids
	0.33 for ionic solutions which suppress coalescence

In equation 24.5-4, q_g is in $m^3\ s^{-1}$.

Interfacial area, a_i':

The correlation of Calderbank (1958) for a_i' is

$$a_i' = 22.8\left(\frac{P_I}{V_\ell}\right)^{0.4}\left(\frac{u_{sg}}{u_{br}}\right)^{0.5}\left(\frac{\rho_\ell}{\sigma^3}\right)^{0.2} \qquad (24.5\text{-}5)$$

where u_{br} is the rise velocity of a bubble through a quiescent liquid (equation 23.3-2).

Mass transfer coefficient, $k_{A\ell}\ a_i'$:

The correlations of Meister et al. (1979) for kAl a_i' for one and two impellers per stage, respectively, are:

$$k_{A\ell} a_i' = 0.0291 (P_I/V_\ell)^{0.801} u_{sg}^{0.248} \qquad \text{(1 impeller)} \qquad (24.5\text{-}6)$$

$$k_{A\ell} a_i' = 0.0193 (P_I/V_\ell)^{0.707} u_{sg}^{0.305} \qquad \text{(2 impellers)} \qquad (24.5\text{-}7)$$

With P_I in kW, V_ℓ in m^3, and u_{sg} in mm s^{-1}, $k_{A\ell} a_i'$ has units of s^{-1}

Chandrasekharan and Calderbank (1981) proposed the following correlation, which shows a much stronger inverse dependence on vessel diameter:

$$k_{A\ell} a_i' = 0.0248 (P_I/V_\ell)^{0.55} q_g^{0.55} D^{-4.5} \qquad (24.5\text{-}8)$$

It was shown to be accurate to within 7.5% over a range of vessel diameters.

Gas holdup, ϵ_g:

The correlations of Hassan and Robinson (1977) for gas holdup, $\varepsilon_{\mathbf{g}}$, for both non-electrolyte and electrolyte liquid phases are:

$$\epsilon_g = 0.11(q_g \dot{n}_{imp}^2/\sigma)^{0.57} \quad \text{(nonelectrolyte)} \qquad (24.5\text{-}9)$$

$$\epsilon_g = 0.21(q_g \dot{n}_{imp}^2/\sigma)^{0.44} \quad \text{(electrolyte)} \qquad (24.5\text{-}10)$$

These two correlations were based on laboratory-scale and pilot-plant-scale reactors (D < 1 m), and do not take into account vessel and impeller geometry.