Fixed Bed Reactors

Lecture notes in subject TKP4145
Reactor Technology
Spring 2011

Hugo A. Jakobsen[1]

Department of Chemical Engineering
Norwegian University of Science and Technology, NTNU

Contents

1 Introduction

1.1 What is a Fixed Bed Reactor?

The introduction of solid catalysts has led to a breakthrough of the chemical industry. Today many industrial processes are based on the use of solid catalysts, and the major part of these catalytic processes is carried out in fixed bed reactors.

So what is a fixed bed reactor?

- It is a reactor where a stationary solid catalyst is used to carry out reactions where the reactant is in a mobile fluid phase, most often a gas. The reaction takes place on the surface (interior or exterior) of the catalyst.

Some of the main fixed bed catalytic processes:

Basic Chemical Industry	Petrochemical Industry	Petroleum Refining
Primary steam reforming	Ethylene oxide	Catalytic reforming
Secondary steam reforming	Ethylene dichloride	Isomerization
Carbon monoxide conversion	Vinylacetate	Polymerization
Carbon monoxide methanation	Butadiene	(Hydro)desulfurization
Ammonia synthesis	Maleic anhydride	Hydrocracking
Sulfuric acid synthesis	Phthalic anhydride	
Methanol synthesis	Cyclohexane	
Oxo synthesis	Styrene	
	Hydrodealkylation	

The fixed bed reactors used today are mainly large-capacity units with typical size:
Catalyst volume: 3-100 m^3
Height: Up to 30 m
Diameter: Up to 5 m

Figure 1 shows a sketch of a steam reformer.

This kind of fixed bed reactors contain typically between 40 and 400 tubes with an internal diameter in the range 70-160 mm with tube thickness 10-20 mm. Burners are used to heat the reaction. The heated length is 6-12 m.

1.2 Where to find Fixed Bed Reactors in Norwegian Industry

The fixed bed reactor is so widely used that you can find one or more at almost any chemical plant in Norway.

- Norsk Hydro's ammonia plant at Herøya in Porsgrunn

- Statoil's methanol production plant at Tjeldbergodden

- Statoil's oil refinery at Mongstad

- Esso's oil refinery at Slagentangen

- Dyno's plant at Lillestrøm
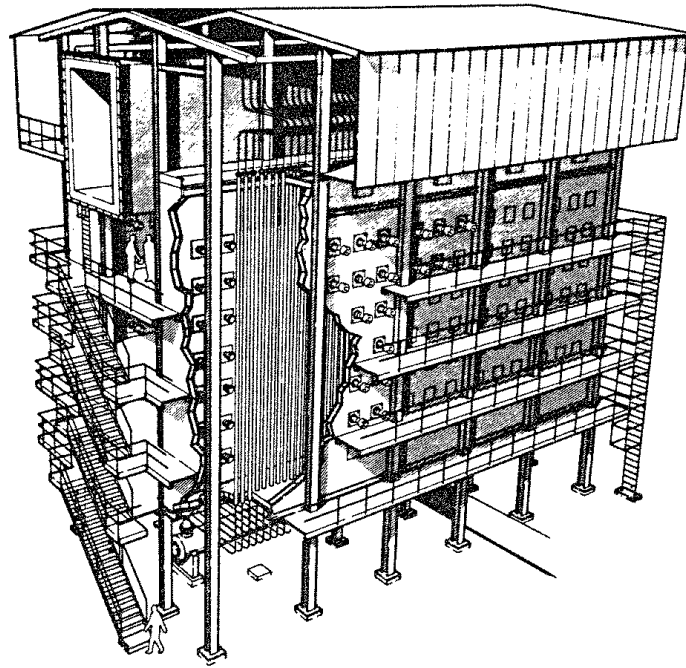
Figure 1: A steam reformer

These plants do not only include one fixed bed reactor. The ammonia process include nine different fixed bed reactors
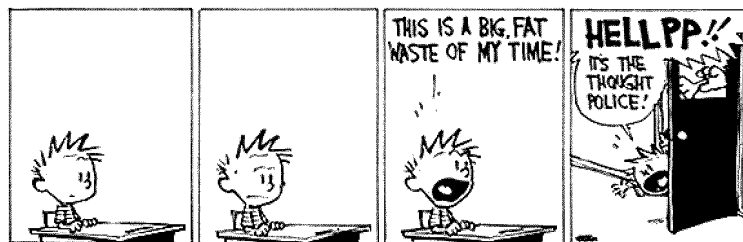
2 Selection of Fixed Bed Reactor Type

2.1 Limitations and Reactor Types

Main limitations:

a) Temperature control

b) Pressure drop for systems with low tolerance for pressure drop

c) Deactivation of the catalyst:

- The catalytic cracking of gasoil is carried out in fluidized bed reactors to enable continuous regeneration of the catalyst (i.e. this reactor will be described later in this course).
- Catalytic cracking deposits carbonaceous products on the catalyst, causing rapid deactivation of the catalyst.

There are many ways to construct a fixed bed reactor. Three common types are:

- single-bed
- multi-bed
- multi-tube
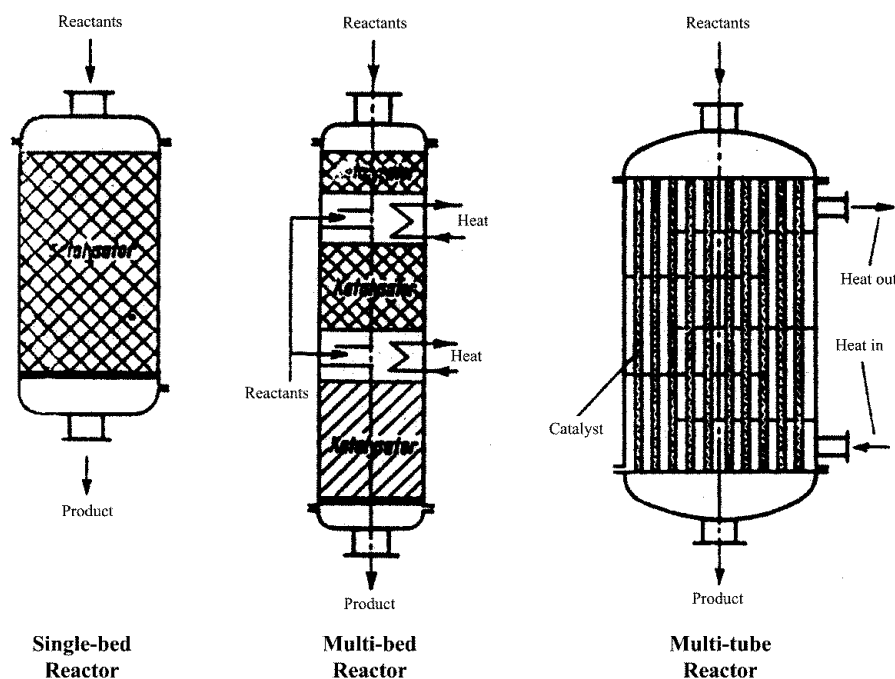
Figure 2: Different fixed bed reactors.

The single bed reactor is simply a vessel of relatively large diameter. This simple reactor is not always applicable. E.g. if the reaction is very endothermic, the

temperature drop may be such as to extinguish the reaction before the desired conversion is attained.

Strongly exothermic reactions lead to a temperature rise that may be prohibitive of several reasons:

- for its unfavorable influence on:
    - the equilibrium conversion
    - the selectivity
    - the catalyst stability

- it would lead to unsafe operation

For endothermic reactions the problem can be solved by dilute the reactant with a heat carrier. But more often the reactor is subdivided into several stages, with intermediate heat exchangers, the multi-bed reactor. In exothermic processes, like the synthesis of SO_3 and NH_3, the intermediate cooling may be achieved by mean of heat exchangers or by injection of cold feed.

A multi-bed reactor for synthesis of SO_3 is given in figure 3[2]
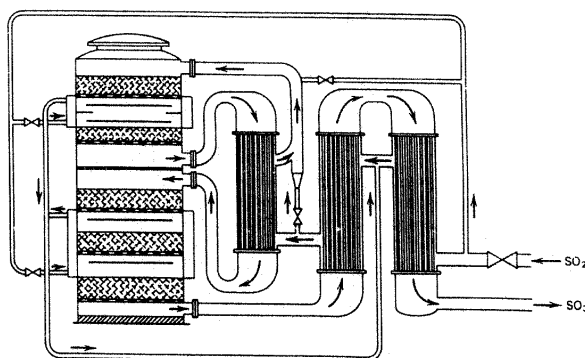
Figure 3: Multibed adiabatic reactor for SO_3 synthesis.

We can see from the figure that the heat exchangers are located outside of the reactor. This is generally the case for reactors used for this process.
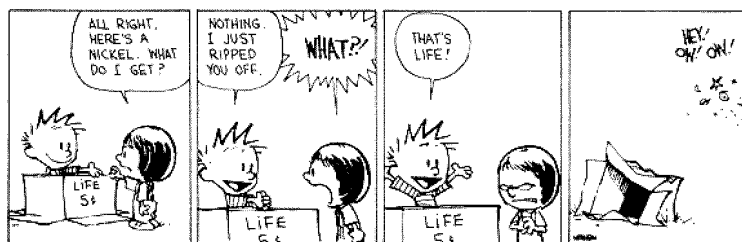
Figure 4[3] shows a multi-bed reactor for ammonia synthesis
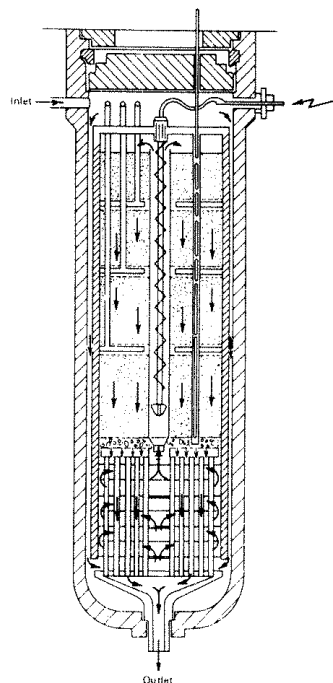
Figure 4: Multibed adiabatic reactor for NH_3 synthesis

With very exothermic reactions, such as air oxidation of aromatic hydrocarbons, the number of beds would have to be uneconomically large to limit the temperature increase per bed. This problem is solved by introducing the multitube reactor.

A multitube reactor used for the phthalic anhydride synthesis is shown in Figure 5[3]:
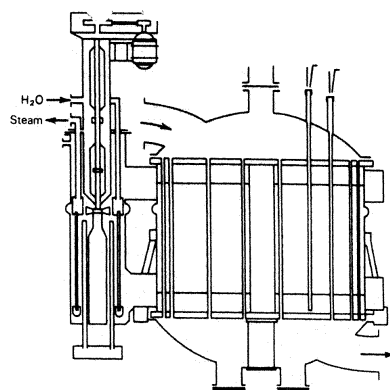
Figure 5: Multitubular reactor for phthalic anhydride synthesis

This kind of reactor may contain up to 10 000 tubes of 2.5 cm inside diameter. The diameter is limited to this small value to avoid excessive overtemperature

---

[3]Figure taken from: Froment, G. F. and Bischoff, K. B., Chemical Reactor Analysis and Design, 2nd ed, John Wiley & Sons, Inc. (1990)

on the axis.

In natural gas or naphtha reforming into hydrogen or synthesis gas, a different type of reactor must be applied. This is an endothermic reaction that usually is heated by burners.

Figure 6[4] shows a multitubular steam reformer
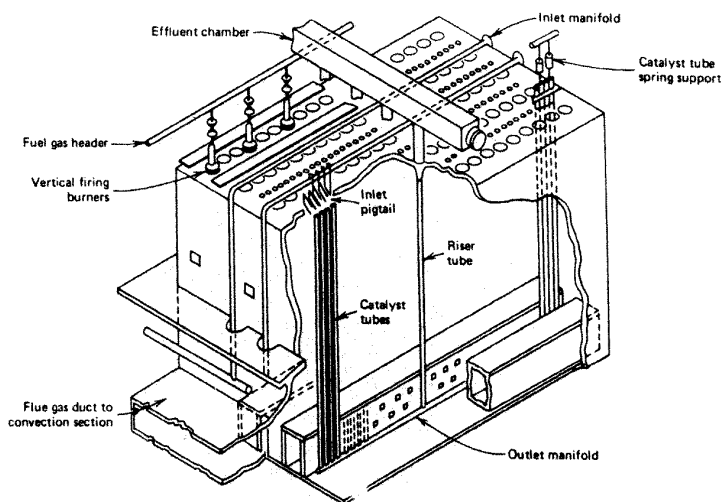
Figure 6: Multitubular steam reformer

This kind of reactor tubes, about 10 m long and 10 cm inner diameter, are suspended in two rows in a furnace that may contain as many as 300 tubes.
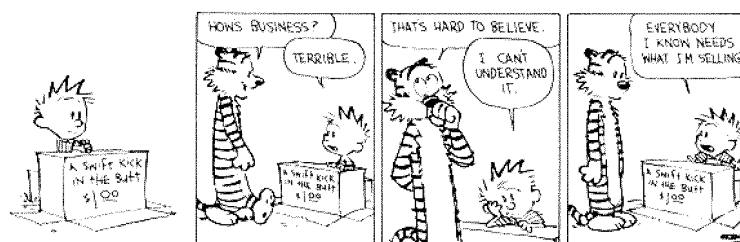
---

[4]Figure taken from: Froment, G. F. and Bischoff, K. B., Chemical Reactor Analysis and Design, 2nd ed, John Wiley & Sons, Inc. (1990)

2.2   Criteria for Selecting Reactor Type

The basis theory and mathematical analysis are discussed in appendix A.

The selection of fixed bed reactor type can be based on:

a) Temperature, guided by the "heat production potential" of the reaction[5]:

$$S = \frac{\Delta T_{ad}}{T_0} \frac{E_{\text{eff}}}{RT_0} \qquad (1)$$

and:

$$N = \frac{4U}{k_B d_t C_p M_m} \qquad (2)$$

The $\frac{N}{S}$-ratio and the value of S give an indication of whether the reactor is stabile or not by using figure 7[6].

S		Heat production potential
ΔT_{ad}	[K]	Adiabatic temperature rise
T_0	[K]	Feed temperature
E_{eff}	[J/mole]	Activation energy for the reaction (r_{eff}, see later)
R	[J/mol K]	Gas constant
U	[J/m^{2}sK]	Overall heat-transfer coefficient
k_B	[kmol/m^3(cat) s]	Rate constant
d_t	[m]	Tube diameter
C_p	[J/kg K]	Heat capacity for the reacting mixture per mole of reactant A
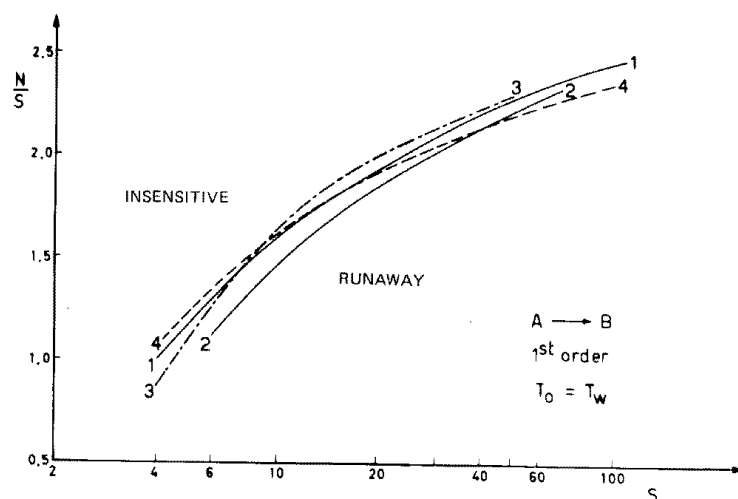
Figure 7: $\left(\frac{N}{S}\right)$ as a function of S. The figure is taken from Froment (1974).

Note:

The heat production potential consists of:

[5]Barkelew, C. H., Chem. Eng. Prog. Symp. Ser., Vol. 55, No. 25, pp. 37-46, (1959)
[6]Froment, G. F., Chemie-Ing.-Techn., Vol. 46, pp. 374-386, 1974.

i) The dimensionless adiabatic temperature rise (or temperature rise potential):

$$\frac{\Delta T_{ad}}{T_0} = \frac{T_{ad} - T_0}{T_0} = \frac{-\Delta H_r \cdot C_{A0}}{\rho_g C_p T_0} = \frac{-\Delta H_r \cdot p_{A0}}{M_m p_t C_p T_0} = \frac{-\Delta H_r \cdot y_{A0}}{M_m C_p T_0}$$

ii) The dimensionless activation energy (or the reaction rate temperature sensitivity):

$$\frac{E_{\text{eff}}}{RT_0}$$

ΔH_r	[kJ/mole]	Enthalpy calculated per mole reactant
C_{A0}	[mole/m^3]	Feed concentration of reactant A
ρ_g	[kg/m^3]	Density of the gas
M_m	[g/mole]	Mole mass of feed gas
p_{A0}	[Pa]	Partial pressure of reactant A
p_t	[Pa]	Total pressure
y_{A0}		Fraction of A in the feed gas

As a rule of thumb it can be it can be said that:

- for small values of S we usually apply an adiabatic single-bed reactor with simple design and operation.

- for intermediate values of S we usually apply an adiabatic multi-bed reactor with interstage heating or cooling.

- for high values of S we usually apply a polytrophic multi-tube reactor with cooling through the tube walls (polytrophic: the heat removed is less than in isothermal reactors, but the reactor is not adiabatic).

Unfortunately, to the authors knowledge the quantification of the S parameter determining the test criteria above are to a large extend based on experience and dependent on the chemical system involved[7]. No general guidelines quantifying the S values in the criteria above can be given.

b) The selection of fixed bed reactor type is also related to "pressure drop" over the reactor.

- The most common pressure drop equation for flow through packed beds is that of Ergun[8]

$$-\frac{dp_t}{dz} = f \cdot \rho_g \cdot \frac{u_s^2}{d_p} \tag{3}$$

---

[7]Hofmann, H., Hand written notes distributed at a lecture series (EEU-kurs) in Reactor modeling, institutt for kjemiteknikk, NTH, 1988

[8]Ergun, S., Chem. Eng. Prog., 48(2), 89 (1952)

$f = \frac{1-\epsilon}{\epsilon^3} \cdot (a + b \cdot \frac{1-\epsilon}{Re_p})$ Friction factor

$a = 1.75$

$b = 4.2 Re_p^{\frac{5}{6}}$

$Re_p = \frac{\rho_g u_s d_p}{\mu}$ The Reynold number gives the ration between inertia
                     forces and viscous forces.

ϵ Void fraction

u_s [m/s]   Superficial velocity (velocity based on total cross
                     section area, $u_s = \epsilon u$)

d_p [m]   Catalyst Particle diameter

μ [kg/ms]   Viscosity of gas phase

Note:

– In reactors with large pressure drop or low tolerance for pressure
  drop we often apply radial flow reactors.
– Normally, the pressure drop will be largest in multi-tube reactors.

3 Selection of Fixed Bed Reactor Models

In principle:

- A model should be tailored for its main purpose. It should be as simple as possible, but still include a sufficient representation of essential mechanisms involved.

The essential mechanisms involved in chemical reactors:
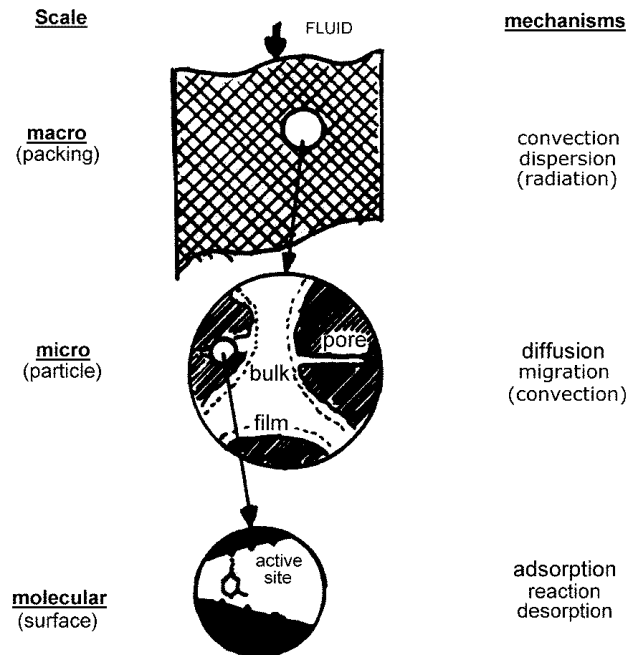
In real reactors, there will normally be gradients in all space directions for:

- Concentrations

- Temperature

- Pressure

- Velocity

The fundamental approach will be to formulate a sophisticated description for all the known mechanisms involved, but there are several problems related to that approach:

- Very different dynamics of the individual mechanisms

- To describe these dynamics we need to describe the interactions of the flow, chemical system properties and operating conditions

- The mathematical task may be very complex

Instead, it has become common practice to formulate simplified criteria for the selection of fixed bed reactor models with the goal to eliminate the mechanisms that is not essential for the reactor performance. Thus the required degree of sophistication depends on

- the reaction scheme.

- sensitivity to perturbations in operating conditions.

- degree of accuracy in kinetic and transport parameters.

- degree of macroscale (reactor) dependency on microscale mechanisms.
  $\Rightarrow$ Sophisticated models with interactions between phenomena on different scales.

3.1 Classification of Fixed Bed Reactor Models

The fixed bed reactor models are usually grouped in two broad categories:

- Pseudo homogeneous- and heterogeneous models

Pseudo homogeneous models do not account explicitly for the presence of catalyst, in contrast to heterogenous models, which lead to separate conservation equations for fluid phase and fluid inside catalyst pores. The distinction is based on an analysis of the difference in temperature and concentration from the gas (g) to the catalyst surface (s):

- Heterogeneous models are applied for systems with: $T_g \neq T_s$ or $C_g \neq C_s$

- Pseudo homogeneous models are applied for systems with: $T_g \approx T_s$ and $C_g \approx C_s$

The simplest heterogeneous/pseudo homogeneous is the model 1D plug flow model assuming ideal flow conditions.
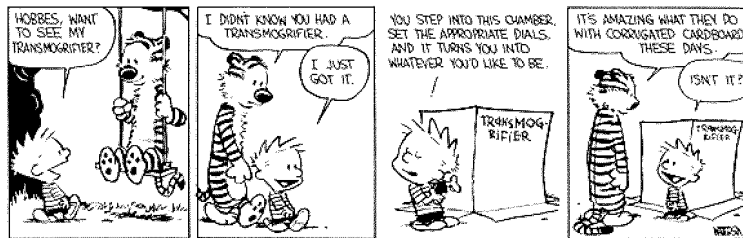
3.2   Model Selection Criteria

The derivation of the criteria used in this compendium is presented in appendix A.

The model selection criteria is based on the n-th order irreversible potential law. Pseudo homogeneous models are sufficient and can be used instead of heterogeneous models if both the interfacial concentration gradients and the interfacial temperature gradients are small.

3.2.1   Interfacial Gradients

The criteria presented here are taken from Mears (1971)[9]. A brief discussion of the theory is presented in appendix B.

Interfacial concentration gradients are negligible if:

$$\left| \frac{r_{\text{eff}} d_p}{2 C_{A0} k_s} \right| < \frac{0.15}{n} \tag{4}$$

Interfacial temperature gradients are negligible if:

$$\left| \frac{-\Delta H_r r_{\text{eff}} d_p}{2 T_0 h_s} \right| Ar < 0.15 \tag{5}$$

where:

r_{eff}	[mole/m^3]	Effective reaction rate per mass of catalyst
n		Reaction order
k_s	[m/s]	Interfacial mass transfer coefficient between fluid and catalyst
h_s	[W/m^{2}s]	Interfacial heat transfer coefficient between fluid and catalyst
$Ar = \frac{E_{\text{eff}}}{RT}$		

3.2.2   Intraparticle Gradients

The criterion presented here is taken from Mears (1971)[8].

The next step toward complexity is to take the gradients inside the catalyst into account.

Intraparticle mass and heat transfer limitation can be neglected if[10]:

$$Da_{II} |n - Ar \cdot P_t| < 1 \tag{6}$$

where:

---

[9]Mears D. E., Ind. Eng. Chem. Process Des. Develop., Vol 10, No. 4, (1971)
[10]For $n = 1 \pm 0.05$

$Da_{II} = \frac{r_{\text{eff}}d_p^2}{4D_{\text{eff}}C_s}$ Damköhler group II gives the ratio between chemical rate and molecular diffusion rate

$P_t = \frac{-\Delta H_r D_{\text{eff}}C_s}{\lambda_c T_s}$ Prater number. Expresses the maximum intraparticle temperature rise, $\frac{T_c - T_s}{T_s}$

D_{eff}	[m^2/s]	Effective diffusivity coefficient inside catalyst particle
C_s	[mole/m^3]	Concentration at the surface of the catalyst
λ_c	[J/msK]	Thermal conductivity of the catalyst
T_s	[K]	Temperature at the surface of the catalyst
T_c	[K]	Inner temperature of the catalyst

It has been experienced that if mass interphase gradients occur, then mass intraparticle gradients occur as well. And if temperature intraparticle gradients occur, then temperature interphase gradients occur. We have the following inequalities:

$$\text{Concentration: interphase } < \text{ intraparticle}$$
$$\text{Temperature: intraparticle } < \text{ interphase}$$

Thus both interfacial and intraparticle gradients in concentration and temperature have to be negligible to apply a pseudo homogeneous model.

3.2.3   Axial Dispersion

The criterion presented here is taken from Mears (1976)[11].

Mixing in the axial direction may be superimposed on the plug flow so as to account for non ideal flow conditions.

Axial dispersion is negligible at the inlet if:

$$\left| \frac{n \cdot Da_I}{Pe_{a,m}} - \frac{Ar \cdot Da_{III}}{Pe_{a,h}} \right| < 0.05 \tag{7}$$

where:

$Da_I = \frac{r_{\text{eff}}d_p}{u_s C_{A0}}$ The Damköhler group I gives the ratio between chemical reaction rate and bulk mass flow rate.

$Da_{III} = \frac{-\Delta H_r r_{\text{eff}}d_p}{\rho_g u_s T_w C_p}$ The Damköhler group III. The ratio between heat liberated and bulk transport of heat

$Pe_{a,m} = \frac{u_s d_p}{D_a}$ The Peclet number for mass. Ratio between bulk and conductive mass transfer.

$Pe_{a,h} = \frac{\rho_g u_s d_p C_p}{\lambda_a}$ The Peclet number for heat. Ratio between bulk and conductive heat transfer.

T_w	[K]	Temperature at the wall
λ_a	[J/msK]	Axial thermal dispersion coefficient
D_a	[m^2/s]	Axial dispersion coefficient

---

[11]Mears D. E., Ind. Eng. Chem. Fundam., Vol 15, No. 1, (1976)

- For design purposes, Pe_a, based on d_p, may be considered to lie between 1-2.

- λ_a and D_a implicitly contain the effect of the velocity profile

Correlations for the dispersion coefficients can be found in Section 8

Note that this test performed for the pseudo homogeneous model is still valid for the heterogeneous models.

3.2.4   Radial Dispersion

The criterion presented here is taken from Mears (1971)[12]. A brief discussion of the theory is presented in appendix B.

Mixing in the radial direction may be superimposed on either of the plug flow or axial dispersion models so as to account for non ideal flow conditions.

A one dimensional model can be applied if:

$$
\left| \frac{-\Delta H_r r_{\text{eff}}^* d_t^2}{\lambda_r T_w} \right| \cdot Ar < \frac{1.6}{1 + \frac{8}{Bi_w}}
\tag{8}
$$

where:

r_{eff}^*	[mole/m^{3}s]	Rate of reaction at the hot spot (i.e. maximum temperature can be obtained by solving the plug flow model or by rule of thumb: $T = T_0 + (20 - 30\%) \cdot \Delta T_{ab}$)
λ_r	[J/msK]	Radial thermal dispersion coefficient for the fluid
$Bi_w = \frac{\alpha_w d_t}{\lambda_{\text{eff,r}}}$		The thermal Biot number at the wall. Ratio between film- and bulk thermal resistance
α_w	[J/m^2 s K]	Heat transfer coefficient at the wall

- Note that often the axial dispersion is negligible while the radial dispersion is important!

- For practical purposes $Pe_r = \frac{\rho u_s d_p C_p}{\lambda_r}$ may be considered to lie between 8-10.

- The most likely radial gradient to occur is the temperature gradient.

- Note that the test performed for the pseudo homogeneous model is still valid for heterogeneous models.

---
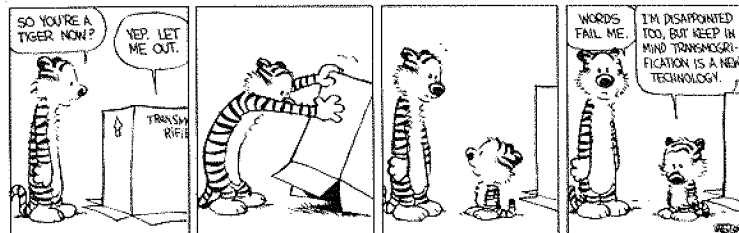
[12]Mears D. E., Ind. Eng. Chem. Process Des. Develop., Vol 10, No. 4, (1971)

3.2.5   Summary of the Tests

A summary of the tests is illustrated in Figure 8.

Figure 8: Summary of the tests

3.3   Example of Selecting a Reactor Model

3.3.1   Exercise

This is an example related to the production of phthalic anhydride (PSA) from o-xylole in a fixed bed reactor. It is a classical example of a fast oxidation reaction that can produce CO and CO_2 instead of the desired product if it's not under control.

We can here assume that only reaction 1 is taking place.

a) Which type of fixed bed reactor would be natural to choose for this process?

b) Which model should be chosen for the reactor?

c) Would it be reasonable to assume constant pressure in the reactor?

Kinetics

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

A - o-xylol
B - PSA
C - CO, CO_2 H_2O

$$A \xrightarrow{k_3} C$$

$$r_1 = k_1 \cdot P_A \cdot P_{O_2}$$
$$\ln k_1 = 19.837 - \frac{27000}{1.98 \cdot T}$$
$$k_1 \quad [=] \quad \text{kmol/kg kat·h·atm}^2$$

Since we have a large excess of oxygen, we can assume $P_{O_2} \approx P_{O_2,0}$ =constant, and we can consider the reaction to be pseudo first order.

Design data:

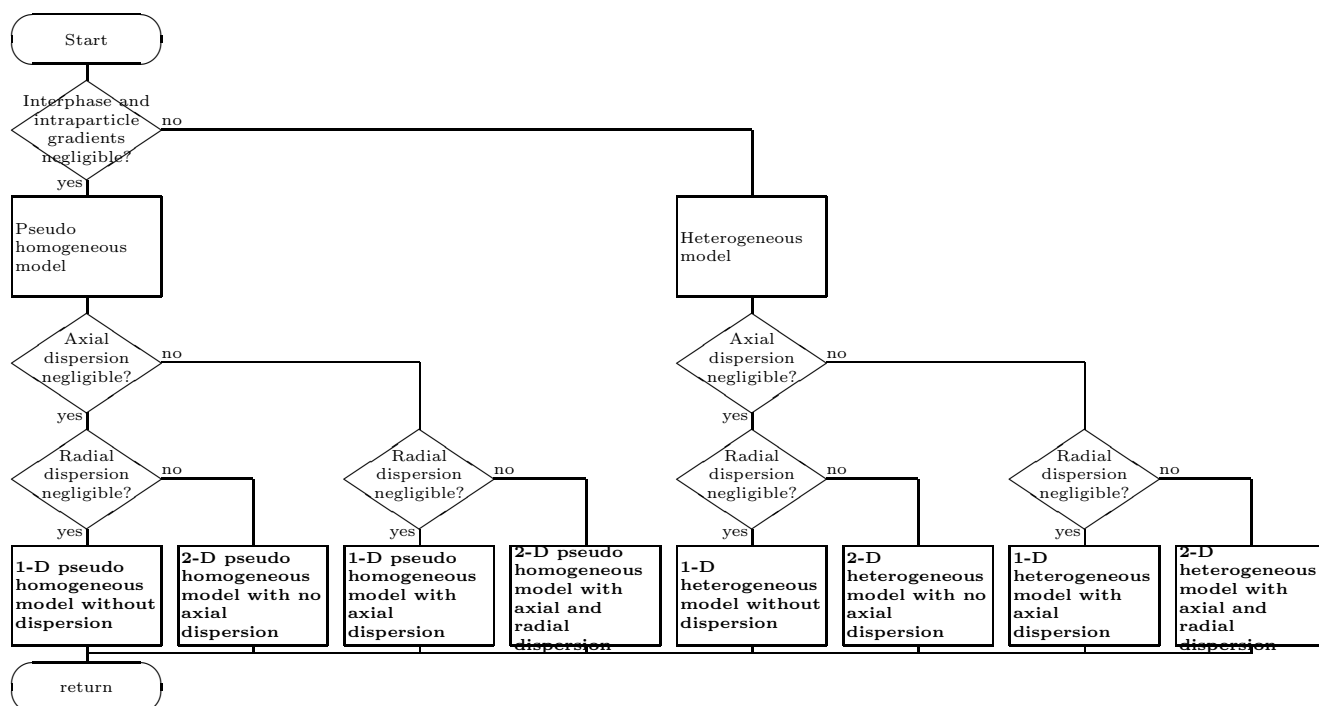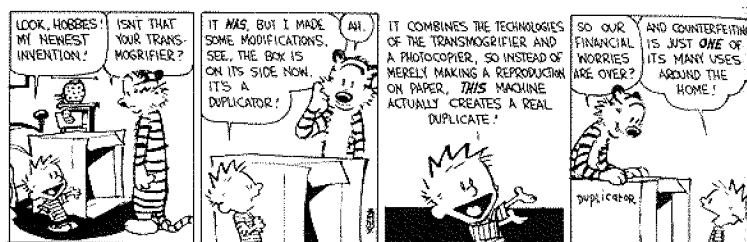|		
T	638 K	Feed temperature
d_t	0.025 m	Tube diameter
L	2.5 m	Tube length
ϵ	0.5 m$_g^3$/m$_r^3$	Void fraction in catalyst layer
d_p	0.003 m	Particle diameter catalyst
ρ_p	1300 kg(cat)/m$_r^3$	Bulk density catalyst
$X_{A,0}$	0.0093	Feed mole fractions
$X_{O_2 0}$	0.208	
P	1.25 atm	Pressure
$\overline{M_m}$	29.48 kg/kmol	Average mole mass
C_p	0.25 kcal/kgK	Average heat capacity
$-\Delta H_r$	307000 kcal/kmol	Reaction enthalpy
λ_r	0.61 kcal/mhK	Radial heat conductivity
λ_{fl}	1.2 ·10^{-5} kcal/msK	Thermal conductivity of the fluid
μ	$3.15 \cdot 10^{-5}$ kg/ms	Viscosity, gas
α_w	134 kcal/m^{2}hK	Heat transfer coefficient near the wall
G	4684 kg/m^{2}h	Flow velocity
D_M	10^{-5} m^2/s	Diffusivity in bulk gas
Pr	0.66	Prandtl's number

Correlations:

We are using some of the correlations given in Section 8. Actually, the correlations are specific for each reactor model, but we assume that we can apply the correlations for heterogeneous 1-D plug-flow model and pseudo homogeneous 1-D dispersion model:

$$\frac{1}{U} = \frac{1}{\alpha_w} + \frac{d_t}{8\lambda_r}$$

taken from Froment and Bischoff[13].

$$\epsilon Sh = 0.357 Re_p^{0.641} Sc^{0.33}$$

$$\epsilon Nu = 1.0(Re_p/\epsilon)^{0.563} Pr^{0.22}$$

$$\frac{1}{Pe_{a,m}} = \frac{0.3}{Re_p Sc} + \frac{0.5}{1 + \frac{3.8}{Re_p Sc}}$$

$$\frac{\lambda_a}{\lambda_{fl}} = 9 + 0.75 Re_p Pr$$

where

$$Sh = \frac{k_s d_t}{D_M}, \qquad Re_p = \frac{G d_p}{\mu}, \qquad Sc = \frac{\mu}{\rho D_M}, \qquad Nu = \frac{h_s d_t}{\lambda_{fl}}, \qquad Pe_{a,m} = \frac{\overline{u_0} d_p}{D_a}$$

---
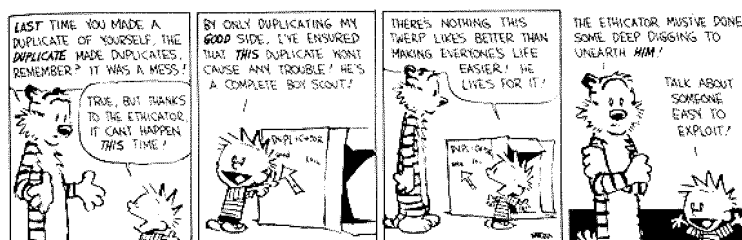
[13]Equation 11.7.4-1 in Froment, G. F. and Bischoff, K. B., Chemical Reactor Analysis and Design, 2nd ed, John Wiley & Sons, Inc. (1990)

3.3.2   Solution

a) Type of Reactor

The criteria is given by equation 1:

$$
\begin{aligned}
S &= \frac{\Delta T_{ad}}{T_0} \cdot \frac{E_{\text{eff}}}{RT_0} \\
&= \frac{-\Delta H_r \cdot X_{A0}}{\overline{M_m} C p T_0} \cdot \frac{E_{\text{eff}}}{RT_0} \\
&= \frac{0.0093 \cdot 307000}{0.25 \cdot 29.48 \cdot 638} \cdot \frac{27000}{1.98 \cdot 638} \\
&\approx 13
\end{aligned}
$$

To find the numerical value of the group N, equation 2, we have to use Barkelew's symbols and units. He expressed the rate as follows:

$$
r_A = k_B \cdot \frac{P_A}{P} \ [=] \ \frac{kmol}{m_p^3 \cdot s} \tag{9}
$$

while in this example we have a pseudo-first-order rate law:

$$
r_{A1} = k_1 P_A P_{O_2} = k_1' P_A \ [=] \ \frac{kmol}{kg(\text{kat}) \cdot h} \tag{10}
$$

This gives, after reformulating r_{A1} so that the reaction rates have the same units:

$$
\begin{aligned}
k_B \frac{P_A}{P} &= k_1' P_A \left[\frac{kmol}{kg(\text{kat}) \cdot h} \right] \cdot \rho_p \left[\frac{kg(\text{cat})}{m_r^3} \right] \cdot \frac{1}{1-\epsilon} \left[\frac{m_r^3}{m_p^3} \right] \cdot \frac{1}{3600} \left[\frac{h}{s} \right] \\
&\Downarrow \\
k_B &= \frac{k_1' \rho_p P}{3600(1-\epsilon)} \ [=] \ \frac{kmol}{m_p^3 \cdot s} \tag{11}
\end{aligned}
$$

Inserted into equation (1) and equation (2) yields:

$$
\frac{N}{S} = \frac{4U}{3600 \cdot M_m d_t C_p} \cdot \frac{3600(1-\epsilon)}{k_1' \rho_p P} \cdot \frac{1}{S} = \frac{4U(1-\epsilon)}{M_m d_t C_p k_1' \rho_p P} \cdot \frac{1}{S} \tag{12}
$$

The factor 3600 in the denominator comes from conversion of the units of k_B into $[\frac{kmol}{m_p^3 h}]$.

The overall heat-transfer coefficient calculated according to equation (9):

$$
\frac{1}{U} = \frac{1}{\alpha_w} + \frac{d_t}{8\lambda_r} = \frac{1}{134} + \frac{0.025}{8 \cdot 0.61} = 0.0126 \Longrightarrow U = 79.46 \left[\frac{kcal}{m^2 hK} \right] \tag{13}
$$

The rate konstant k_1' is:

$$
\begin{aligned}
ln\, k_1 &= 19.837 - \frac{27000}{1.98 \cdot T} \\
k_1 &= e^{\left(19.837 - \frac{27000}{1.98 \cdot 638}\right)} = 0.215 \left[\frac{kmol}{kg(\text{cat}) \cdot h \cdot atm^2}\right] \\
k_1' &= k_1 \cdot P_{O_2} = 0.215 \cdot 0.26 = 0.056 \left[\frac{kmol}{kg(\text{cat}) \cdot h \cdot atm}\right] \qquad (14)
\end{aligned}
$$

This gives:

$$
\frac{N}{S} = \frac{4 \cdot 79.46 \cdot (1 - 0.5)}{29.48 \cdot 0.025 \cdot 0.25 \cdot 0.056 \cdot 1300 \cdot 1.25} \cdot \frac{1}{13} = 0.73 \qquad (15)
$$

From figure 7 the critical value of $\left(\frac{N}{S}\right)$, $\left(\frac{N}{S}\right)_c$, is approximately 1.7 ($\beta$ is 0 for first order reactions (see Barkelew)), thus the reactor is unstable. This leads to the conclusion that more cooling is needed in the reactor. Hence, a multi-bed or a multi-tubular reactor has to be considered.

b) Type of Model

- **Pseudo homogeneous or heterogeneous model**

    Pseudo homogeneous model can be used if the interface gradients are small. They are negligible if the following demands are satisfied (equation 4 and equation 5):

$$
\begin{aligned}
\left|\frac{r_{\text{eff}} d_p}{2 C_{A0} k_s}\right| &< \frac{0.15}{n} \qquad &\text{(mass)} \\
\left|\frac{(-\Delta H_r) r_{\text{eff}} d_p}{2 T_0 h_s}\right| &< \frac{0.15 RT}{E_{\text{eff}}} \qquad &\text{(energy)}
\end{aligned}
$$

    Mass

    To find out whether the interfacial concentration gradients are negligible or not, we have to find the right parameter values:

    (Note that the dimension of k_1 gives $r_{\text{eff}}'[=]kmole/kg(\text{cat})h$)

$$
\begin{aligned}
r_{\text{eff}}' &= k_1 \cdot P_{A0} \cdot P_{O_2} \\
&= k_1 \cdot X_{A0} \cdot P_{\text{tot}} \cdot X_{O_2} \cdot P_{\text{tot}} \\
&= \exp\left(19.837 - \frac{27000}{1.98 \cdot 638}\right) \cdot (0.0093 \cdot 1.25) \cdot (0.208 \cdot 1.25) \\
&\approx 6.5 \cdot 10^{-4}\, kmol/kg(\text{cat})h
\end{aligned}
$$

$$r_{\text{eff}} = r'_{\text{eff}} \left[\frac{kmol}{kg(\text{cat})h} \right] \cdot \rho_p \left[\frac{kg(\text{cat})}{m_r^3} \right] \cdot \frac{1}{1-\epsilon} \left[\frac{m_r^3}{m_p^3} \right] \cdot \frac{h}{3600s}$$
$$\approx 4.7 \cdot 10^{-4} \, kmol/m_p^3 \cdot s$$

$$d_p = 3 \cdot 10^{-3} \, m$$

$$C_{A0} = \frac{p_{A0}}{RT}$$
$$= \frac{X_{A0} P_{tot}}{RT}$$
$$\approx 2.2 \cdot 10^{-4} \, kmol/m^3$$

k_s has to be calculated with a correlation:

$$\epsilon Sh = 0.357 Re_p^{0.641} Sc^{0.33}$$

The dimensionless groups in the correlation are calculated as:

$$Re_p \approx 124$$
$$\rho_g = \frac{p\overline{M_m}}{RT} \approx 0.7 kg/m^3$$
$$Sc \approx 4.5$$

Inserted in the correlation, this gives:

$$Sh \approx 26$$
$$\Downarrow$$
$$k_s \approx 1.0 \cdot 10^{-2} m/s$$

Then we can insert all the parameters in the first control expression (equation 4):

$$\left| \frac{4.7 \cdot 10^{-4} \cdot 3 \cdot 10^{-3}}{2 \cdot 2.2 \cdot 10^{-4} \cdot 1.0 \cdot 10^{-2}} \right| < \frac{0.15}{1}$$
$$\sim 0.32 \not< 0.15$$

The demand is not satisfied $\Rightarrow$ We can not neglect the interface concentration gradients. Use heterogeneous model.
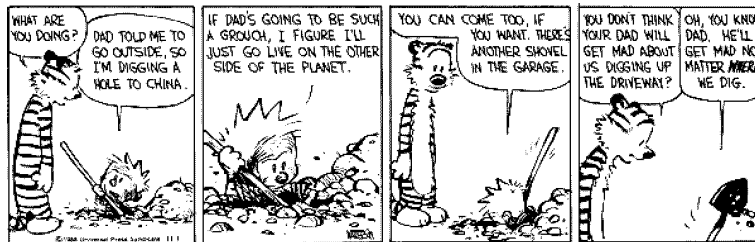
Energy

We can not make any conclusion yet. We have to find out if we can neglect the interfacial temperature gradients first. All the parameter values needed are availible, except from h_s which have to be calculated with a correlation:

$$\epsilon Nu = 1.0(Re_p/\epsilon)^{0.563} Pr^{0.22}$$

giving

$$Nu \approx 41$$

$$h_s \approx 1.9 \cdot 10^{-2} kcal/m^2 \, s \, K$$

Then we can insert all the parameters in the second control expression (eq. 5):

$$\left| \frac{307000 \cdot 4.7 \cdot 10^{-4} \cdot 3 \cdot 10^{-3}}{2 \cdot 638 \cdot 1.9 \cdot 10^{-2}} \right| < \frac{0.15 \cdot 1.98 \cdot 638}{27000}$$

$$1.8 \cdot 10^{-2} \not< 7.0 \cdot 10^{-3}$$

The demand is not satisfied $\Rightarrow$ We can not neglect the interfacial temperature gradients. Use a heterogeneous model.

Intraparticle Gradients

We have the following inequalities:

$$\text{Concentration: interphase} \ < \ \text{intraparticle}$$
$$\text{Temperature: intraparticle} \ < \ \text{interphase}$$

Our conclusion is that interphase gradients occur. Then we have to, according to the inequalities above, include mass intraparticle gradients. And when we have to include mass intraparticle gradients, we also have to include energy intraparticle gradients because of consistency.

- **Axial Dispersion**

  Now, we have to find out whether axial dispersion can be neglected or not. It is negligible if the following control expression is satisfied (Equation 7):

  $$\left| \frac{n \, Da_I}{Pe_a, m} - \frac{Ar \, Da_{III}}{Pe_a, h} \right| < 0.05$$

  where

  $$Da_I = \frac{r_{\text{eff}} d_p}{\overline{u_0} C_{A0}}$$

  $$Pe_{a,m} = \frac{\overline{u_0} d_p}{D_a}$$

  $$Ar = \frac{E_{\text{eff}}}{RT}$$

  $$Da_{III} = \frac{(-\Delta H_r) r_{\text{eff}} d_p}{\rho \overline{u_0} T_w C_p}$$

  $$Pe_{a,h} = \frac{\rho \overline{u_0} C_p d_p}{\lambda_a}$$

Other parameter values are:

$$\overline{u_0} = \frac{G}{\rho_g} \approx 1.8 m/s$$

$$Da_I = 3.4 \cdot 10^{-3}$$

$$Da_{III} = 2.1 \cdot 10^{-3}$$

Peclet's number for mass, $Pe_{a,m}$ can be found by the third correlation:

$$\frac{1}{Pe_{a,m}} = \frac{0.3}{Re_p Sc} + \frac{0.5}{1 + \frac{3.8}{Re_p Sc}}$$

$$\approx 2.0$$

To calculate Peclet's number for heat, $Pe_{a,h}$, we have to find λ_a first. It can be found by:

$$\lambda_a = \lambda_{fl}(9 + 0.75 Re_p Pr)$$

$$\approx 8.4 \cdot 10^{-4} \, kcal/m\,s\,K$$

Then we can calculate Pectlet's number:

$$Pe_a \approx 1.2$$

And finally, we can insert all the necessary parameters in the control expression (Equation 7):

$$\left| \frac{1 \cdot 3.4 \cdot 10^{-3}}{2.0} - \frac{\frac{27000}{1.98 \cdot 638} \cdot 2.1 \cdot 10^{-3}}{1.2} \right| < 0.05$$

$$0.036 < 0.05$$

The demand is satisfied $\Rightarrow$ We can ignore axial dispersion.

- **One/Two Dimensional Model**

  Finally, we have to calculate whether we can neglect radial dispersion or not. If we can, we can apply a one dimensional model, otherwise the radial dispersion terms have to be included and we have to apply a two dimensional model. The control expression is (Equation 8):

  $$\left| \frac{(-\Delta H_r) r^*_{\text{eff}} d_t^2}{\lambda_r T_w} \right| Ar < \frac{1.6}{1 + 8/Bi_w}$$

  where r^*_{eff} is the rate of reaction in the "hot-spot"[14] and

  $$Bi_w = \alpha_w d_t / \lambda_r$$

  $$= 5.5$$

---

[14]A usual assumption is to set it to 1.2 x reaction rate at the entrance.

When we insert the parameter values in the one dimensional model control expression (Equation 8) we get:

$$\left| \frac{307000 \cdot 1.2 \cdot 4.7 \cdot 10^{-4} \cdot 0.025^2}{0.61/3600 \cdot 638} \right| \frac{27000}{1.98 \cdot 638} < \frac{1.6}{1 + 8/5.5}$$

$$21 \not< 0.65$$

The demand is not satisfied$\Rightarrow$ Radial gradients have to be included in the model. Use a two dimensional model.

- **Summary of Model Selection**

  We have to choose a two dimensional, heterogeneous model with dispersion only in the radial direction and with calculation of intraparticle gradients.

c) Pressure Drop

To estimate the pressure drop in the reactor we have to apply the Ergun equation (Equation 3). If we assume that the parameter values are constant, we can insert the parameter values from the previous calculations:

$$-\frac{dp_t}{dz} = f \frac{\rho_g \overline{u_0}^2}{d_p} \tag{16}$$

where:

$$
\begin{aligned}
f &= \frac{1-\epsilon}{\epsilon^3} \left(1.75 + 4.2 Re_p^{\frac{5}{6}} \frac{1-\epsilon}{Re_p} \right) \\
&= 10.8
\end{aligned}
$$

We integrate the Ergun equation along the reactor:

$$
\begin{aligned}
\Delta p_t &= \int_0^L f \frac{\rho_g \overline{u_0}^2}{d_p} \, dz \\
&= f \frac{\rho_g \overline{u_0}^2}{d_p} L \\
&= 10.8 \frac{0.7 \cdot 1.8^2}{3 \cdot 10^{-3}} 2.5 \\
&= 2.1 \cdot 10^4 \, Pa
\end{aligned}
$$

The relative change in pressure is:

$$\frac{\Delta p_t}{P} = \frac{2.1 \cdot 10^4}{1.25 \cdot 10^5} = 17\%$$

It is reasonable to assume constant pressure in these approximations when the relative change is 17%. However, in simulations this magnitude of pressure drop is often unacceptable.
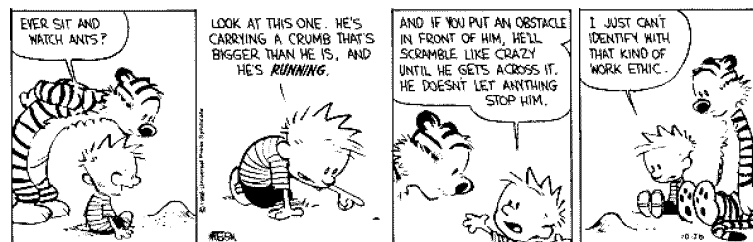
4   Runaway Criteria

Typical for strongly <u>exothermic</u> processes is that at a certain location in the reactor we will find a large maximum temperature, the "hot spot".

- An important problem associated with this is how to limit the hot spot in the reactor and how to avoid excessive sensitivity to variations in the variables.

The magnitude of this hot spot depends on:

- the heat of reaction

- the rate of reaction

- the heat transfer coefficient and heat transfer areas

Its location depends on the flow velocity.

In some processes with very strong <u>exothermic</u> reactions the "hot spot" temperature can raise beyond permissible limits. Such phenomenon is called runaway.

Main problem:

- Temperature control
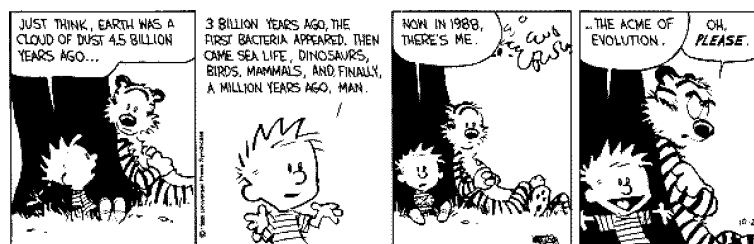
- Deactivation of catalyst

- Melting of reactor

- Explosion

The criteria for selection of fixed bed reactor type, discussed earlier, is in fact based on a criteria for avoiding runaway for a given process.

- The heat production potential, S.
  $S = f$(heat production potential, reaction rate sensitivity (how "nervous" the reaction is))

$\Rightarrow$ <u>Temperature control!!</u>

5 Reactor Model Equations

5.1 Fundamentals of Reactor Modeling

Deterministic models for fixed bed reactors are based on the conservation equations of mass, energy and momentum.

General balance equation (for a differential volume element dV):

$$\begin{bmatrix} \text{Rate of} \\ \text{accumulation} \end{bmatrix} = \begin{bmatrix} \text{Flux (in-out)} \\ \text{across volume boundary} \\ \text{by transport mechanism} \end{bmatrix} + \begin{bmatrix} \text{Rate of} \\ \text{consumption or} \\ \text{production by} \\ \text{sources} \end{bmatrix}$$

Transport mechanisms:

- Convection + dispersion (+ radiation)

Species mass balance:

$$\frac{\partial c_j}{\partial t} + \nabla \cdot (c_j \vec{u_s}) = \nabla \cdot (D_j \nabla c_j) + R_i \qquad (17)$$

$$(1) \qquad (2) \qquad (3) \qquad (4)$$

The respective terms arise from:

(1) Change of concentration with time
(2) Convective transport
(3) Molecular diffusion
(4) Reaction rate

Energy balance:

$$\sum_j \rho_j \cdot C_{pj} \frac{\partial T}{\partial t} + \sum_j \rho_j C_{pj} \vec{u_s} \cdot \nabla T = \nabla \cdot (\lambda \nabla T) + \sum_i (-\Delta H_{R_i}) R_i + Q \quad (18)$$

$$(1) \qquad\qquad (2) \qquad\qquad (3) \qquad\qquad (4) \qquad\quad (5)$$

The respective terms arise from:

(1) Change of heat content with time
(2) Advective transport
(3) Heat transport by conduction
(4) Heat effect of the chemical reactions
(5) Radiation heat flux

Momentum balance:

- Does often not depend on reaction

- Have to be solved simultaneously

- Can often be simplified to Ergun's equation for flow through porous media

In stationary models the rate of accumulation term can be ignored ($\frac{\partial}{\partial t} = 0$).

Mathematically a continuum model consists of a set of usually nonlinear ordinary or partial differential equations. Solutions have to be found numerically. Only simple cases can be solved analytically or graphically.

5.2 Equations for Pseudo Homogeneous Models

5.2.1 The Plug Flow Model

No dispersion is considered in this model.

The conservation equations for a dynamic system with a single reaction and carried out in a cylindrical tube:

$$\frac{\partial C_A}{\partial t} + \frac{\partial (u_s\, C_A)}{\partial z} = -r_A\, \rho_B \tag{19}$$

$$\rho_g\, C_p \frac{\partial T}{\partial t} + u_s\, \rho_g\, C_p \frac{dT}{dz} = (-\Delta H_r) r_A\, \rho_B \;-\; 4\frac{U}{d_t}(T - T_a) \tag{20}$$

$$-\frac{dp_t}{dz} = f\frac{\rho_g\, u_s^2}{dp} \tag{21}$$

Initial conditions:

The stationary model, $\frac{\partial}{\partial t} = 0$

for $z = 0$

$$C_A = C_{A1} \tag{22}$$
$$T = T_1 \tag{23}$$
$$p_t = p_{t1} \tag{24}$$

The dynamic model:

$t = 0$

$$\left.\begin{array}{l} C_A = C_{A0} \\ T = T_0 \\ p_t = p_{t0} \end{array}\right\} \qquad \text{specified/known for all z} \tag{25}$$

$t > 0$

$$\left.\begin{array}{l} C_A = C_{A1} \\ T = T_1 \\ p_t = p_{t1} \end{array}\right\} \qquad \text{for z=0} \tag{26}$$

r_A	[mole/kg cat s]	rate of consumption of component A
ρ_B	[kg/m^3]	Bulk density of catalyst per unit volume reactor
U	[W/m^{2}K]	Overall heat transfer coefficient
d_t	[m]	Tube diameter
T_a	[K]	Ambient temperature (outside tubes)

The numerical integration of this system of ordinary differential equations (ODE) can be performed using:

- Explicit Runge-Kutta methods (ode45 in Matlab)

- Implicit Runge-Kutta methods

- Implicit Multi-step backward differences for stiff equations (ode15s in Matlab)

- Implicit Backward differences formula (BDF) methods

Applications:

- Several aspects such as runaway, optimization and (transient) behavior due to catalyst deactivation can be analyzed using this model.

- In practice reactor design has been based on this model (convenient).

5.2.2   1D Model with Axial Dispersion

The balance of mass (component A) and energy can be written as:

$$-\frac{\partial C_A}{\partial t} + \varepsilon D_a \frac{\partial^2 C_A}{\partial z^2} - \frac{\partial (u_s\, C_A)}{\partial z} - r_A\,\rho_B = 0 \tag{27}$$

$$-\rho_g\, C_p \frac{\partial T}{\partial t} + \lambda_a \frac{\partial^2 T}{\partial z^2} - \rho_g\, u_s\, C_p \frac{\partial T}{\partial z} + (-\Delta H_r) r_A\,\rho_B - \frac{4U}{d_t}(T - T_a) = 0 \tag{28}$$

Boundary conditions (Danckwerts[15]. See also Section 5.6):

The stationary model $\frac{\partial}{\partial t} = 0$

$$\left. \begin{array}{l} u_s\,(C_{A1} - C_A) = -\varepsilon D_a \frac{dC_A}{dz} \\ \rho_g\, u_s\, C_p\,(T_1 - T) = -\lambda_a \frac{dT}{dz} \end{array} \right\} \qquad \text{for z} = 0 \tag{29}$$

$$\frac{dC_A}{dz} = \frac{dT}{dz} = 0 \qquad \text{for z} = \text{L} \tag{30}$$

The dynamic model can for example be solved by use of the following boundary and initial conditions (others can also be used):

$t = 0$

$$\left. \begin{array}{l} C_A = C_{A0} \\ T = T_0 \end{array} \right\} \qquad \text{specified/known for all z} \tag{31}$$

$t > 0$

$$\left. \begin{array}{l} u_s\,(C_{A1} - C_A) = -\varepsilon D_a \frac{dC_A}{dz} \\ \rho_g\, u_s\, C_p\,(T_1 - T) = -\lambda_a \frac{dT}{dz} \end{array} \right\} \qquad \text{for z} = 0 \tag{32}$$

$$\frac{dC_A}{dz} = \frac{dT}{dz} = 0 \qquad \text{for z} = \text{L} \tag{33}$$

[15]P.V. Danckwerts, Chem. Eng. Sci., 2, 1 (1953)

The numerical integration of this system of ODEs can be performed using:

- finite difference methods (finite volume methods)

- collocation

5.2.3   2D models

These are models including radial mixing

a) <u>with both axial and radial mixing</u>

$$-\frac{\partial C_A}{\partial t} + \varepsilon D_r \left(\frac{\partial^2 C_A}{\partial r^2} + \frac{1}{r}\frac{\partial C_A}{\partial r} \right) + \varepsilon D_a \frac{\partial^2 C_A}{\partial z^2} - \frac{\partial (u_s\, C_A)}{\partial z} - \rho_B\, r_A = 0$$
(34)

$$-\rho_g\, C_p \frac{\partial T}{\partial t} + \lambda_r \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} \right) + \lambda_a \frac{\partial^2 T}{\partial z^2} - \rho_g\, u_s\, C_p \frac{\partial T}{\partial z} + (-\Delta H_r) r_A\, \rho_B = 0$$
(35)

With boundary conditions:
The stationary model:

$$\left. \begin{aligned} u_s\,(C_{A1} - C_A) &= -\varepsilon D_a \frac{dC_A}{dz} \\ \rho_g\, u_s\, C_p\,(T_1 - T) &= -\lambda_a \frac{dT}{dz} \end{aligned} \right\} \qquad \text{at } z = 0 \qquad\qquad 0 \leq r \leq R_t \quad (36)$$

$$\frac{\partial C_A}{\partial z} = \frac{\partial T}{\partial z} = 0 \qquad \text{at } z = L \qquad\qquad 0 \leq r \leq R_t \quad (37)$$

$$\frac{\partial C_A}{\partial r} = 0 \qquad \text{at } r = 0 \text{ and } r = R_t \quad \text{all } z \qquad (38)$$

$$\frac{\partial T}{\partial r} = 0 \qquad \text{at } r = 0 \qquad\qquad \text{all } z \qquad (39)$$

$$\frac{\partial T}{\partial r} = -\frac{\alpha_w}{\lambda_r}(T_R - T_w) \qquad \text{at } r = R_t \qquad\qquad \text{all } z \qquad (40)$$

The dynamic model can for example be solved by use of the following boundary and initial conditions (others can also be used):

$t = 0$:

$$\left. \begin{aligned} C_A &= C_{A0} \\ T &= T_0 \end{aligned} \right\} \qquad \text{specified/known for all } z \text{ and } r \qquad (41)$$

$t > 0$:
Using the Equations 36-40.

D_r	$[m^2/s]$	Radial dispersion coefficient
R_t	[m]	Inside radius of tube
T_R	[K]	Temperature at radius R
T_w	[K]	Temperature at the wall

The numerical integration of this system of nonlinear 2nd order partial differential equations (PDE) can be performed using:

- finite difference methods (finite volume)
- collocation

Problem: No such algorithm in Matlab.

b) <u>without axial mixing</u>

$$-\frac{\partial C_A}{\partial t} + \varepsilon D_r \left(\frac{\partial^2 C_A}{\partial r^2} + \frac{1}{r}\frac{\partial C_A}{\partial r} \right) - \frac{\partial (C_A \, u_s)}{\partial z} - \rho_B \, r_A = 0 \qquad (42)$$

$$-\rho_g \, C_p \frac{\partial T}{\partial t} + \lambda_r \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} \right) - \rho_g \, u_s \, C_p \frac{\partial T}{\partial z} + (-\Delta H_r) r_A \, \rho_B = 0 \quad (43)$$

With boundary conditions:
The stationary model $\frac{\partial}{\partial t} = 0$

$$\left. \begin{array}{l} C_A = C_{A1} \\ T = T_1 \end{array} \right\} \qquad \text{at } z = 0 \qquad\qquad 0 \leq r \leq R_t \qquad (44)$$

$$\frac{\partial C_A}{\partial r} = 0 \qquad \text{at } r = 0 \text{ and } r = R_t \qquad \text{all } z \qquad (45)$$

$$\frac{\partial T}{\partial r} = 0 \qquad \text{at } r = 0 \qquad\qquad \text{all } z \qquad (46)$$

$$\frac{\partial T}{\partial r} = -\frac{\alpha_w}{\lambda_r}(T_R - T_w) \qquad \text{at } r = R_t \qquad\qquad \text{all } z \qquad (47)$$

The dynamic model:
$t = 0$

$$\left. \begin{array}{l} C_A = C_{A0} \\ T = T_0 \end{array} \right\} \qquad \text{specified/known for all } z \text{ and } r \qquad (48)$$

$t > 0$

Equations 44–47.

The numerical integration of this system of second order PDE can be performed by:

- finite difference methods (finite volume)
- collocation

Matlab: There are routines in matlab that can solve this system of equations.

- explicit discretization of the dispersion terms in radial direction using "dss020/dss042"
- explicit integration of the convective terms using "ode45"

or

- implicit integration of the dispersion terms (iterations) by use of "dss020/dss042" in combination with an equation solver like "fsolve" or "broyden".

  - implicit integration of convective terms using "ode15s"

dss020: 1D, 5-point biased upwind approximations for 1. order derivatives.

dss042: 1D, 3-point centered approximations for 2. order derivatives with Dirichlet and Neumann boundary conditions.

5.3   Equations for Heterogeneous Models

For very rapid reactions with an important heat effect, it may be necessary to distinguish between conditions in the fluid and on the catalyst surface or even inside the catalyst.

5.3.1   1D Model with Interfacial Gradients

This model is the plug flow model with no gradients inside the catalyst.

For fluid:

$$\frac{\partial C_A}{\partial t} + \frac{\partial (u_s\, C_A)}{\partial z} = -k_g\, a_v\, (C_A - C_{AS}^S) \tag{49}$$

$$\rho_g\, C_p\, \frac{\partial T}{\partial t} + u_s\, \rho_g\, C_p\, \frac{\partial T}{\partial z} = h_f\, a_v\, (T_S^S - T) - 4\frac{U}{d_t}(T - T_a) \tag{50}$$

For solid:

$$\frac{\partial C_A}{\partial t} = k_g\, a_v\, (C_A - C_{AS}^S) + \rho_B\, r_A \tag{51}$$

$$\rho_g\, C_p\, \frac{\partial T}{\partial t} = -h_f\, a_v\, (T_S^S - T) + (-\Delta H_r)\rho_B\, r_A \tag{52}$$

With initial conditions:

The stationary model ($\frac{\partial}{\partial t} = 0$):

$$\left.\begin{array}{l} C_A = C_{A1} \\ T = T_1 \end{array}\right\} \qquad \text{at } z = 0 \tag{53}$$

The dynamic model can for example be solved for the following boundary and initial conditions:

$t = 0$

$$\left.\begin{array}{l} C_A = C_{A0} \\ T = T_0 \end{array}\right\} \qquad \text{specified/known for all } z \tag{54}$$

$t > 0$

$$\left.\begin{array}{l} C_A = C_{A1} \\ T = T_1 \end{array}\right\} \qquad \text{for } z = 0 \tag{55}$$

k_g [m/s]   Mass transfer coefficient
a_v [m^2/m^3]   Catalyst surface area pr. volumetric unit of reactor
C_{AS} [mole/m^3]   Concentration of component A at catalyst surface
h_f [W/m^{2}K]   Heat transfer coefficient

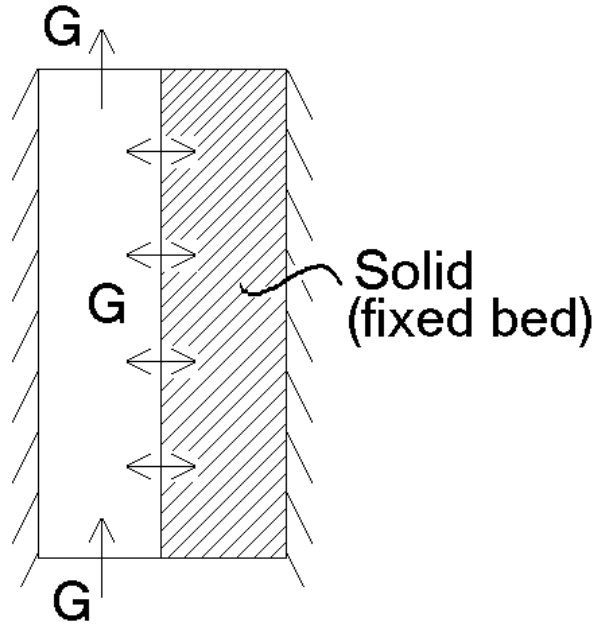Figure 9 shows a schematic representation of the heterogeneous model.

Figure 9: The reactor drawn schematically.

Note, the most likely interfacial gradient to occur is the temperature gradient.

5.3.2   1D Model with Interfacial and Intraparticle Gradients

This model is the plug flow model with gradients inside the catalyst.

- Used when the resistance to mass- and heat transfer inside the catalyst particle is important, the rate of reaction is not uniform throughout the particle.

For fluid:

$$\frac{\partial C_A}{\partial t} + \frac{\partial (u_s\, C_A)}{\partial z} = -k_g\, a_v\, (C_A - C_{AS}^S) \tag{56}$$

$$\rho_g\, C_p\, \frac{\partial T}{\partial t} + u_s\, \rho_g\, C_p\, \frac{\partial T}{\partial z} = h_f\, a_v\, (T_S^S - T) - 4\frac{U}{d_t}(T - T_a) \tag{57}$$

<u>For solid</u> (ξ = position on the radius of sphere):

$$\frac{\partial C_A}{\partial t} = \frac{D_{\text{eff}}}{\xi^2} \frac{\partial}{\partial \xi}\left(\xi^2 \frac{\partial C_{AS}}{\partial \xi}\right) + \rho_S\, r_A\left(C_{AS},T_S\right) \tag{58}$$

$$\rho_g\, C_p \frac{\partial T}{\partial t} = \frac{\lambda_c}{\xi^2}\frac{d}{d\xi}\left(\xi^2 \frac{dT_S}{d\xi}\right) + \rho_S\left(-\Delta H_r\right)r_A\left(C_{AS},T_S\right) \tag{59}$$

With initial and boundary conditions:

The stationary model $\frac{\partial}{\partial t} = 0$

$$\left.\begin{array}{c} C_A = C_{A1} \\ T = T_1 \end{array}\right\} \qquad\qquad \text{at } z = 0 \qquad \text{for fluid} \tag{60}$$

$$\frac{dC_{AS}}{d\xi} = \frac{dT_S}{d\xi} = 0 \qquad\qquad \text{at } \xi = 0 \tag{61}$$

$$k_g(C_{AS}^S - C_A) = -D_{\text{eff}}\frac{dC_{AS}}{d\xi} \qquad\qquad \text{at } \xi = \frac{d_p}{2} \tag{62}$$

$$h_f(T_S^S - T) = -\lambda_c\frac{dT_S}{d\xi} \qquad\qquad \text{at } \xi = \frac{d_p}{2} \tag{63}$$

The dynamic model:

$t = 0$:

$$\left.\begin{array}{c} C_A = C_{A0} \\ T = T_0 \end{array}\right\} \qquad\qquad \text{specified/known for all z, r and } \xi \tag{64}$$

$t > 0$:

Using Equations 60–63.

$$
\begin{array}{lll}
D_{\text{eff}} & [\text{m}^2/\text{s}] & \text{Effective diffusivity coefficient inside catalyst particle} \\
\xi & [\text{m}] & \text{Position on the radius of sphere} \\
\lambda_c & [\text{W/mK}] & \text{Effective conductivity inside catalyst particle}
\end{array}
$$

Note that a single particle is considered, not the solid as a whole, when intra-particle profiles are considered.

- The system of 2. order, nonlinear differential equations has to be integrated for <u>the solid phase</u> (B.V.P) in each node of the computational grid used in the integration of <u>the fluid field</u> equations (I.V.P).

The numerical integration of this system of equations can be performed by:

- finite difference methods

- collocation

Matlab: Solve the fluid phase as an initial value problem by "ode45" or "ode15s" and the particle equations as a boundary value problem at every step of the fluid integration. For the solid phase use implicit integration by "dss020/dss042" in combination with "broyden".

5.4   Thiele Modulus

$\Rightarrow$ Assume isothermal conditions within the particle, constant physical/chemical coefficients, thus analytical solution of the pellet mol balance possible for n-th order kinetics.

$$\frac{d^2 C_A}{dr_p^2} + \frac{2}{r_p}\frac{dC_A}{dr_p} - \frac{k_n}{D_e}C_A^n = 0 \tag{65}$$

BC:

$$\begin{aligned} C_A &= \text{finite} & \text{at } r_p = 0 \\ C_A &= C_{AS} & \text{at } r_p = R_p \end{aligned} \tag{66}$$

$\Rightarrow$ Writing the equation in dimensionless form where $\varphi = C_A/C_{AS}$ and $\lambda = r_p/R_p$ yields:

$$\frac{d^2\varphi}{d\lambda^2} + \frac{2}{\lambda}\frac{\varphi}{d\lambda} - \frac{k_n R_P^2 C_{AS}^{n-1}}{D_e}\varphi^n = 0 \tag{67}$$

BC:

$$\begin{aligned} \varphi &= \text{finite} & \text{at } \lambda = 0 \\ \varphi &= 1 & \text{at } \lambda = 1 \end{aligned} \tag{68}$$

Equation 67 can also be written as:

$$\frac{d^2\varphi}{d\lambda^2} + \frac{2}{\lambda}\frac{\varphi}{d\lambda} - \phi_n^2\varphi^n = 0 \tag{69}$$

where

$$\phi_n^2 = \frac{k_n R_P^2 C_{AS}^{n-1}}{D_e} = \frac{\text{a surface rx. rate}}{\text{a diffusion rate}} \tag{70}$$

It is a measure of the ratio of a surface reaction rate to a rate of diffusion through the catalyst pellet.

The Thiele modulus is then defined as:

$$\phi_n = \sqrt{\phi_n^2} = \sqrt{\frac{k_n R_P^2 C_{AS}^{n-1}}{D_e}} \tag{71}$$

When the Thiele modulus, ϕ_n, is large, diffusion usually limits the overall rate of reaction; when ϕ_n is small, thte surface reaction is usually rate-limiting.

5.5   Simplifications in Heterogeneous Models

- Even with strongly exothermic reactions the particle is found to be practically isothermal.

  - the main resistance inside the pellet is to mass transfer, and the main resistance in the film surrounding the particle is to heat transfer.

$\Rightarrow$ When gradients occur inside the catalyst particle, it is often used an effectiveness factor η (i.e. for first-order reaction and isothermal spherical particles)

$$\begin{aligned} \eta &= \frac{\text{rate of reaction with pore diffusion resistance}}{\text{rate of reaction with surface conditions}} \\ &= \frac{r_A(\text{observed})}{r_A\left(C_S^S\right)} \end{aligned} \tag{72}$$

η is a factor that multiplies the reaction rate at the particle surface conditions to yield the rate that is actually experienced when the conditions inside the particle is different.

- analytical solution of the particle equation only for first-order reactions.

$\Rightarrow$ The equations can then be reduced to:

For fluid:

$$\frac{\partial C_A}{\partial t} + u_s \frac{\partial C_A}{\partial z} = -k_g\, a_v\, (C_A - C_{AS}^S) \tag{73}$$

$$\rho_g\, C_p \frac{\partial T}{\partial t} + u_s\, \rho_g\, C_p \frac{\partial T}{\partial z} = h_f\, a_v\, (T_S^S - T) - 4\frac{U}{dt}(T - T_a) \tag{74}$$

For solid:

$$k_g\, a_v\, (C_A - C_{AS}^S) = \eta(C_S^S, T_S^S)\rho_B\, r_A\,(C_S^S, T_S^S) \tag{75}$$

$$h_f\, a_v\, (T_S^S - T) = \eta(C_S^S, T_S^S)\rho_B\,(-\Delta H_r)r_A\,(C_S^S, T_S^S) \tag{76}$$

With initial conditions:

The stationary model $\frac{\partial}{\partial t} = 0$

$$\left. \begin{aligned} u_s\,(C_{A1} - C_A) &= -\varepsilon D_a \frac{dC_A}{dz} \\ \rho_g\, u_s\, C_p\,(T_0 - T) &= -\lambda_a \frac{dT}{dz} \end{aligned} \right\} \quad \text{for } z = 0 \tag{77}$$

The dynamic model:

$t = 0$

$$\left. \begin{aligned} C_A &= C_{A0} \\ T &= T_0 \end{aligned} \right\} \quad \text{specified/known for all } z \text{ and } r \tag{78}$$

$t > 0$:

Using Equation 77.

5.6   Danckwerts Boundary Conditions

This section presents the Danckwerts boundary conditions[16]).
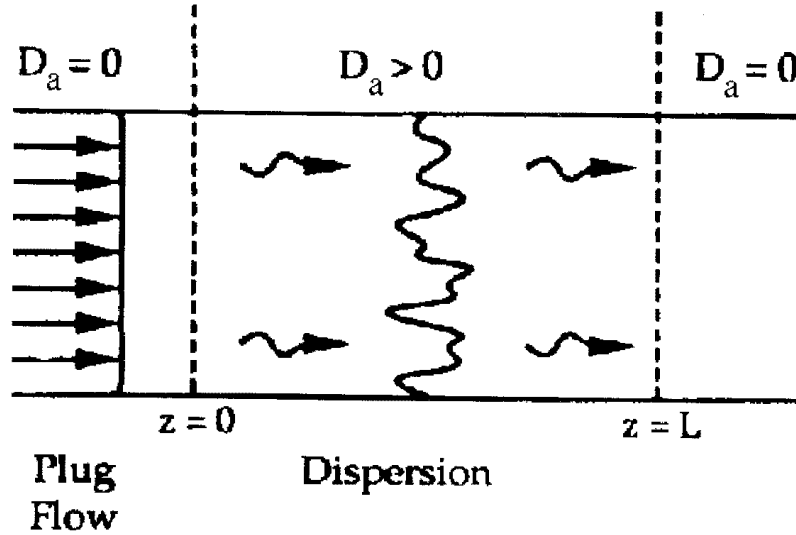
Closed vessel[17]

Figure 10: Closed vessel

- assume no dispersion or radial variation in concentration or temperature either upstream or downstream of the reaction section.

- $z = 0^- \Rightarrow$ plug flow

- $z = L^+ \Rightarrow$ plug flow

- In between $z = 0^+$ and $z = L^-$ dispersion and reaction

BC: Flux in $(z = 0^-) =$ Flux inside $(z = 0^+)$

$$\text{Inlet: } u_s\, A_t\, C_i\, (0^-, t) = -A_t\, D_a\, \left.\frac{dC_i}{dz}\right|_{z=0^+} + u_s\, A_t\, C_i\, (0^+, t) \qquad (79)$$

$$\text{Outlet: } C_i\, (L^-, t) = C_i\, (L^+, t) \qquad \text{or} \qquad \frac{dC_i}{dz} = 0 \qquad (80)$$

$\Rightarrow$ no gradient at outlet.

Similar for heat transfer (T).

A_t	[m^2]	Cross-section of tube
C_i	[mole/m^3]	Concentration of component i
D_a	[m^2/s]	Axial dispersion coefficient

---

[16]P.V. Danckwerts, Chem. Eng. Sci., 2, 1 (1953)

[17]Figure taken from H.Scott Fogler, "Elements of Chemical Reaction Engineering", 3rd edition

In general:

Boundary conditions of various types possible:

1) Dirichlet type of bc:

   - dependent variable is specified at z=0 and z=L

2) Neumann type of bc:

   - the derivative of the dependent variable is specified at z=0 and z=L

5.7   2D Cell Models

- An alternative to the dispersion model to account for nonideal flow.

- developed for mathematical convenience (simpler than dispersion models)

The cell models considers the bed to consist of a 2D network of perfectly mixed cells with 2 outlets to the subsequent row of cells.

- parameters like the cell size is chosen so as to match the results of the residence time distribution (RTD) experiments.

- perfectly mixed cells $\Rightarrow$ a set of algebraic equations must be solved.

$\Rightarrow$ They may seem closer to reality but are still far away from true hydrodynamical models.

$\Rightarrow$ Seldom applied!!!

6 Matlab Examples

6.1 One-Dimensional Pseudo Homogeneous Model

6.1.1 Problem

We want to find the partial pressure- and temperature profile in a fixed bed reactor, using the one-dimensional pseudo homogeneous model. This design example is suggested from hydrocarbon oxidation processes such as benzene oxidation into maleic anhydride. This is a strong exothermic process which is carried out in multi-tube reactors cooled by molten salt which is circulating around the tubes and exchanges heat to an internal or external boiler.

Given equations for the one-dimensional steady-state pseudo homogeneous model:

$$\frac{d(u_S\, C_A)}{dz} = -r_A\, \rho_B \tag{81}$$

$$u_S\, \rho_g\, C_p \frac{dT}{dz} = (-\Delta H)\rho_B\, r_A - 4\frac{U}{d_t}(T - T_a) \tag{82}$$

with initial conditions:

$$\left.\begin{array}{l} p_A = p_0 \\ T = T_0 = T_a \end{array}\right\} \text{at } z = 0 \tag{83}$$

The reaction will be assumed to be pseudo-first order, due to large excess of oxygen:

$$r_A = k\, p_B^0\, p_A \qquad [\frac{kmole}{kg\, cat\, h}] \tag{84}$$

$k\ [kmole/kg\, cat\, h\, Pa^2]$ is given by:

$$ln\, k = 19.837 - \frac{13636}{T} \tag{85}$$

Given values:

Tube length	$L = 3\ m$
Tube diameter	$d_t = 2.54\ cm$
Particle diameter	$d_p = 3\ mm$
Bulk density catalyst	$\rho_B = 1300\ kg/m^3$
Mean molar mass	$M_m = 29.48\ kg/kmole$
Superficial fluid velocity	$u_s = 1\ m/s$
Heat of reaction	$(-\Delta H_r) = 1\ 285\ 409\ kJ/kmole$
Specific heat	$C_p = 0.992\ kJ/kgK$
Total pressure	$p_t = 1.0\ bar$
Partial pressure of oxygen	$p_B^0 = 0.211\ bar$
Overall heat transfer coefficient	$U = 0.096\ kJ/m^2\ s$
Temperature outside tube	$T_a = 352^o C$

By assuming ideal gas ($C_A = \frac{p_A}{RT}$), equation 81 can be written as:

$$\frac{d}{dz}\left(\frac{u_S p_A}{RT}\right) = -r_A\, \rho_B \tag{86}$$

Applying the chain rule on equation 86 gives:

$$\frac{u_s}{RT}\frac{dp_A}{dz} + \frac{p_A}{RT}\frac{du_s}{dz} - \frac{u_s p_A}{RT^2}\frac{dT}{dz} = -r_A\,\rho_B \tag{87}$$

By assuming no change of u_s in the axial direction ($\frac{du_s}{dz} = 0$) and do some rearrangements, we get the partial pressure dependency of z:

$$\frac{dp_A}{dz} = \frac{p_A}{T}\frac{dT}{dz} - \frac{RT}{u_s}r_A\,\rho_B \tag{88}$$

Here, we need an expression for the axial temperature profile which we get by rearranging equation 82:

$$\frac{dT}{dz} = \frac{(-\Delta H_r)\rho_B\,r_a - 4\frac{U}{d_t}(T - T_a)}{u_S\,\rho_g\,C_p} \tag{89}$$

The gas density can be found by using the ideal gas law:

$$\rho_g = \frac{p_t\,M_m}{R\,T} \tag{90}$$

6.1.2   Matlab Solution

We have to make a simple program to simulate the partial pressure and the temperature profile. This program has to be written in an editor like M-file Editor of Matlab, Emacs or Notepad etc.

To avoid problems and a lot of confusion, a good habit when programming in Matlab, is to clear the memory for all variables from previous simulations before we start on a new one. Thus, the top line of the program should contain a clear-command.

So type:

```
clear all
```

Then we define the parameters that are going to be globally available. Type:

```
global supvel molmass ptot rhob pb0 Cp enthalpy U dt Tr R
```

The parameters have to be assigned values.
Type:

```
supvel   = 1.0;         %[m/s]
molmass  = 29.48;       %[kg/kmole]
ptot     = 1.0e5;       %[Pa]
rhob     = 1300;        %[kg/m^3]
pb0      = 0.211e5;     %[Pa]
Cp       = 0.992;       %[kJ/kg*K]
enthalpy = 1285409.0;   %[kJ/kmole]
```

```
U        = 0.096;     %[kJ/m^2*s]
dt       = 2.54e-2;   %[m]
Tr       = 625.0;     %[K]
R        = 8314.5;    %[J/kmole*K]
zstart   = 0;         %[m]
zend     = 3;         %[m]
pA0      = 0.015e5;   %[Pa]
T0       = 625;       %[K]
```

(Note: the %-sign means that Matlab shall ignore the rest of the line)

We want the program to integrate the partial pressure, p_A, and the temperature, T, with respect to the length, z. Since Matlab integrates numerically, we have to specify the integration interval over which Matlab should integrate. To do that, we make a z-span vector containing the end points in the integration interval (0 and 3). Matlab will then by itself chose appropriate intermediate values for the integration. However, if we want to evaluate the properties at specific z-points, we must make a z-span vector containing all the z-values to be used in the integration.

So type:

```
zspan=[zstart zend];
```

The initial values can be put into a vector called y_0.
Type:

```
y0=[pA0 T0];
```

Now, we are going to use an integration tool called ode15s. This tool requires an integration interval (z-span), initial values (y_0) together with the derivatives of the pressure and the temperature with respect to z. The output of ode15s is a vector of z and a matrix of y (note that y contains vectors of both partial pressure and temperature). The differential equations of the pressure and temperature are put into a script called yderiv.m.
Type:

```
[z,y]=ode15s('yderiv',zspan,y0);
```

Then we want to plot the result in two different plots: one $p - z$ plot and one $T - z$ plot. This is done by the subplot command. Subplot(m,n,nr) breaks the figure window into an m×n matrix of sub-windows and selects nr-th window for the current plot. Thus, when we are going to plot two plots, one standing below the other, we have to set m=2 and n=1. And if we want to plot the partial pressure profile in the upper window (nr=1), we have to type:

```
m=2;
n=1;
nr=1;
```

```
subplot(m,n,nr);
plot(z,y(:,1))
title('Partial pressure profile')
xlabel('z [m]')
ylabel('p [Pa]')
```

The plot command plots z-vector versus the first column in the y-matrix, that is the partial pressure. Then we can title the plot and label the x- and y-axis.

The temperature profile is plotted by typing:

```
nr=nr+1;
subplot(m,n,nr);
plot(z,y(:,2))
title('Temperature profile')
xlabel('z [m]')
ylabel('T [K]')
```

Here we want the temperature profile to be plotted in the lower window (nr=2). And the temperature is given by the second column in the y-matrix.

Now, we can save the file as *profile.m*.

As mentioned earlier the differential equations are put into a script called yderiv.m. To make this script we have to open a new file. The script has to contain a function where the input is z and y. The output is the derivative of y in a specific z-point, over which ode15s has to integrate.
Type:

```
function dydz=yderiv(z,y);
```

The parameters defined in the main program has to be made "visible" for this function. Type:

```
global supvel molmass ptot rhob pb0 Cp enthalpy U dt Tr R
```

Then, for simplicity, we can split the y-variable into pressure and temperature.
Type:

```
pA = y(1);
T  = y(2);
```

Now, we have to calculate the variables.
Type:

```
k=1.0e-10*exp(19.837-13636.0/T)/3600.0;
r=k*pb0*pA;
rhog=ptot*molmass/(R*T);
```

And finally we calculate the derivatives of y, and put them in the dydz-matrix again:
Type:

```
dTdz=1.0/(supvel*rhog*Cp)*(enthalpy*rhob*r-4.0*U/dt*(T-Tr));
dpdz=-1.0/supvel*(molmass*ptot*rhob/rhog*r)+pA/T*dTdz;
dydz=[dpdz;dTdz];
```

Now, we can save script as yderiv.m.

To run the program we just type the name of the script (without the extension ".m") in the Matlab window:
Type:

```
profile
```

6.1.3   Results from the Simulation
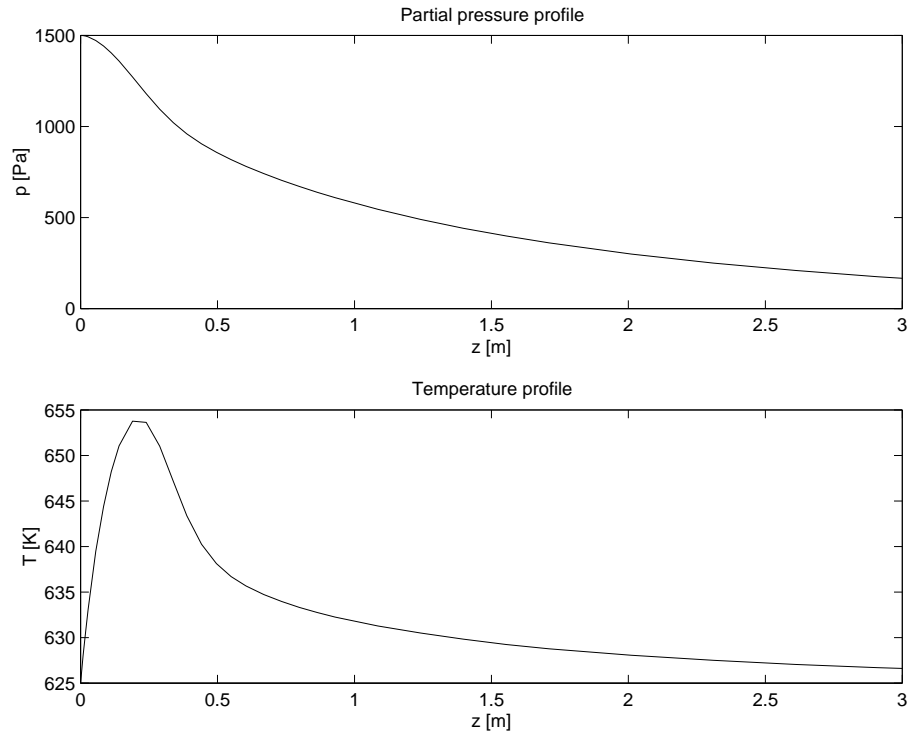
The program "profile" gives us these two profiles:

Figure 11: The result from the simulation "profile"

The figures reveal a "hot spot" in the bed. This is typical for strongly exothermic processes. The magnitude of this hot spot depends on:

- the heat of reaction

- the rate of reaction

- the heat transfer coefficient

- transfer areas

The location depends on the flow velocity.

The profile is also sensitive to the parameters from certain values onward. If p_{A0} increased from 0.0165 bar (figure 12) to 0.0166 bar (figure 13), this would raise the hot spot temperature beyond permissible limits. This phenomenon is called runaway.
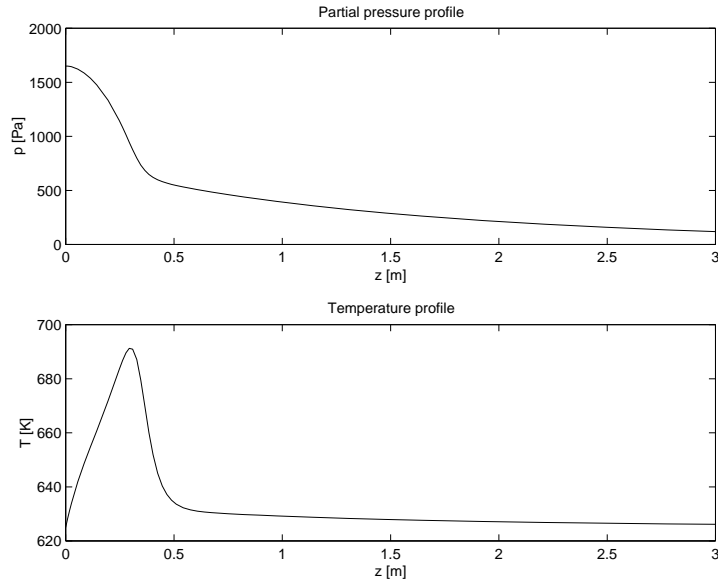

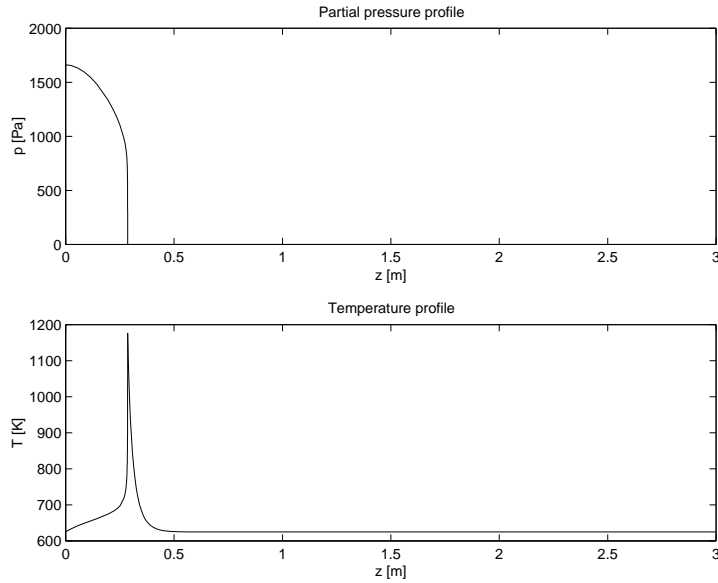Figure 12: Simulating with $p_{A0} = 0.0165$ bar

Figure 13: Simulating with $p_{A0} = 0.0166$ bar (runaway)

6.2   One-Dimensional Dynamic Pseudo Homogeneous Model

6.2.1   Problem

In this example we are going to use the same system as in the previous example, and introduce dynamic behavior.

Given equations for the one-dimensional pseudo-homogeneous model:

$$\frac{\partial C_A}{\partial t} + \frac{d(u_s\, C_A)}{dz} = -r_A\, \rho_B \tag{91}$$

$$\rho_g\, C_p \frac{\partial T}{\partial t} + u_S\, \rho_g\, C_p \frac{\partial T}{\partial z} = (-\Delta H_r)\rho_B\, r_A - 4\frac{U}{d_t}(T - T_a) \tag{92}$$

with initial conditions:

$$\left.\begin{array}{l} p_A = 0 \\ T = T_0 = T_a \end{array}\right\} \text{at } t = 0 \text{ for } 0 < z < L \tag{93}$$

$$\left.\begin{array}{l} p_A = p_0 \\ T = T_0 = T_a \end{array}\right\} \text{at } z = 0 \text{ for } t > 0 \tag{94}$$

The reaction kinetics and the other parameters are all the same as in the previous example.

We are going to do simulations when the initial partial pressure of component A is in the range of:

$$0.010\, bar \le p_A \le 0.018\, bar \tag{95}$$

Again, by assuming ideal gas, we get:

$$\frac{\partial}{\partial t}\left(\frac{p_A}{R\,T}\right) + \frac{\partial}{\partial z}\left(\frac{u_s p_A}{R\,T}\right) = -r_A\, \rho_B \tag{96}$$

Application of the chain rule results in:

$$\frac{1}{R\,T}\frac{\partial p_A}{\partial t} - \frac{p_A}{R\,T^2}\frac{\partial T}{\partial z} + \frac{u_s}{R\,T}\frac{\partial p_A}{\partial z} + \frac{p_A}{R\,T}\frac{\partial u_s}{\partial z} - \frac{u_s p_A}{R\,T^2}\frac{\partial T}{\partial z} = -r_A\, \rho_B \tag{97}$$

If u_s is not varying in the axial direction ($\frac{du_s}{dz} = 0$) and rearrangements, we get the partial pressure dependency of t:

$$\frac{\partial p_A}{\partial t} = \frac{p_A}{T}\frac{\partial T}{\partial t} - u_s\frac{\partial p_A}{\partial z} + u_s\frac{p_A}{T}\frac{\partial T}{\partial z} - r_A\, \rho_B\, R\,T \tag{98}$$

The energy equation (equation 92) can be rearranged as follows:

$$\frac{\partial T}{\partial t} = \frac{(-\Delta H_r)\rho_B\, r_a - 4\frac{U}{d_t}(T - T_a)}{\rho_g\, C_p} - u_s\frac{\partial T}{\partial z} \tag{99}$$

The gas density is evaluated as:

$$\rho_g = \frac{p_t\, M_m}{R\,T} \tag{100}$$

6.2.2   Matlab Solution

```
%Main program for the dynamic model

clear all

us   = 1.0;           %Superficial velocity [m/s]
Mm   = 29.48;         %Molemass [kg/kmole]
pt   = 1.0e5;         %Total pressure [Pa]
rhob= 1300;           %Catalyst density [kg/m^3]
pb0 = 0.211e5;        %Partial pressure of O2 [Pa]
Cp   = 0.992;         %Heat capacity [kJ/kgK]
H    = 1285409.0;     %Reaction enthalpy [kJ/kmole]
U    = 0.096;         %Heat transfer coefficient [kJ/m^2*s]
dt   = 2.54e-2;       %Tube diameter [m]
Tr   = 625.0;         %Temperature on the outside of the tube [K]
R    = 8314.5;        %Gas constant [J/kmole K]

z0   = 0;             %Lower integration boundary in z-direction
zend= 3;              %Upper integration boundary in z-direction
m    = 100;           %The number of discretization points in z-direction

t0   = 0;             %Lower time integration boundary
tend= 10;             %Upper time integration boundary
n    = 9;             %The number of integration points in t

pin = 0.015e5;        %Inlet partial pressure
Tin = 625;            %Inlet temperature

%Parameter vector which is known for the function (this is just an
%alternative for using global)
par = [us Mm pt rhob pb0 Cp H U dt Tr R m pin Tin];
%Index 1  2  3  4    5   6  7 8 9 10 11 12 13 14

%Initialization
p0   =zeros(1,m);     %Initial values for partial pressure and
p0(1)=pin;            %temperature for all discretization points
T0   =625*ones(1,m);

%Defining the z-interval (the length of the reactor) containing m points
z=[z0:(zend-z0)/(m-1):zend];

%Defining the t-interval containing n points
t=[t0:(tend-t0)/(n-1):tend];

%Vector containing both initial profiles for pressure and temperature
init=[p0 T0];

%The left boundary is an algebraic equation, and thus it should not
%be treated as a differential equation. To let ode15s distinguish
%between differential equations and algebraic equations, a so-called mass
%matrix, M, is introduced for solving M(t,y)*y' = f(t,y) problems. In this
%case M is the identity matrix.
M=eye(2*m,2*m);

%The left point in the vectors p0 and T0 are algebraic equations
```

```
M(1,1) = 0;
M(m+1,m+1) = 0;

%To save computation costs the matrix can be made sparse
M=sparse(M);

%Performs the integration
options = odeset('Mass',M,'Stats','on');

[t,x]=ode15s(@derivt,t,init,options,par,z);

%Splits x into one matrix for pressure p_out and one for temperature T_out
p_out=x(:,1:m);
T_out=x(:,(m+1):(m*2));

%Plotting the profiles using subplot
l=2;
n=1;
nr=1;

%The results contain all profiles for all timesteps. Hence, it is
%possible to define which instant to plot. This is done by specifying
%the row in the p_out and T_out matrix.

%Plots the partial pressure profile
nr=1;
subplot(l,n,nr);
%plot(z,p_out(1,:));
plot(z,p_out(2,:));
%plot(z,p_out(3,:));
%plot(z,p_out(9,:));
title('Partial pressure profile')
xlabel('z [m]')
ylabel('p [Pa]')

%Plots the temperature profile
nr=nr+1;
subplot(l,n,nr);
%plot(z,T_out(1,:));
plot(z,T_out(2,:));
%plot(z,T_out(3,:));
%plot(z,T_out(9,:));
title('Temperature profile')
xlabel('z [m]')
ylabel('T [K]')
```

The function deriv_t in the file deriv_t.m:

```
function derivt_alt=deriv(t,var,par,z)

%Set parameter values:
us  = par(1);
Mm  = par(2);
pt  = par(3);
rhob= par(4);
pb0 = par(5);
Cp  = par(6);
H   = par(7);
U   = par(8);
dt  = par(9);
Tr  = par(10);
R   = par(11);
m   = par(12);
pin = par(13);
Tin = par(14);

%Transposes the var-vector into a row vector
var=var';

%The var matrix must be divided into a pressure and a temperature matrix
p = var(1:m);
T = var((m+1):2*m);

%Discretizing the partial pressure and temperature to get dp/dz and dT/dz
dpdz=dss020(z(1),z(m),m,p,1);
dTdz=dss020(z(1),z(m),m,T,1);

%Takes out the inner points for the evaluations of dp/dt and dT/dt
p_i = p(2:m);
T_i = T(2:m);

%Calculates the values for rhog, k and r at every discretization point
rhog=(Mm*pt)./(R*T_i);
k=1.0e-10*exp(19.837-13636.0./T_i)/3600.0;
r=k.*p_i*pb0;

%Calculates the time derivatives of p and T at every discretization point
dTdt = 1.0./(rhog*Cp).*(H*rhob*r-(4.0*U/dt)*(T_i-Tr))-us*dTdz(2:m);
dpdt = p_i./T_i.*dTdt-us*dpdz(2:m)+us*p_i./T_i.*dTdz(2:m)-(Mm*pt*rhob./rhog.*r);

%A residual is introduced on the left boundary. This residual equals
%0 when convergency is achieved
resp = pin-p(1);
resT = Tin-T(1);

%Gathers the information which is going to be returned and transposes
%the total vector into a column vector
derivt_alt = [resp,dpdt,resT,dTdt]';
```

6.2.3 Results of the Simulation

The profiles obtained from the simulation are given in Figure 14, 15, 16 and 17

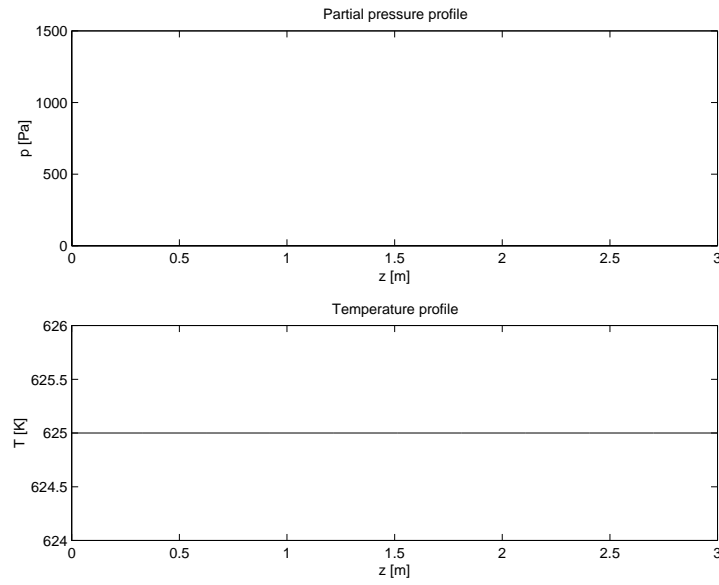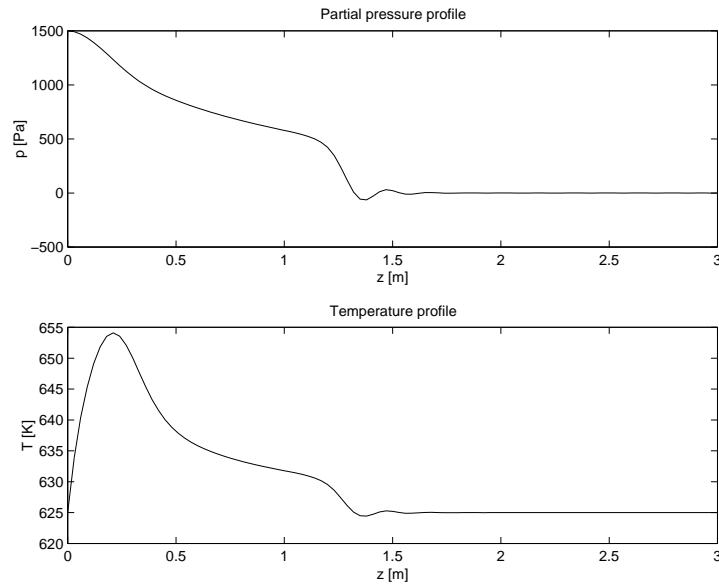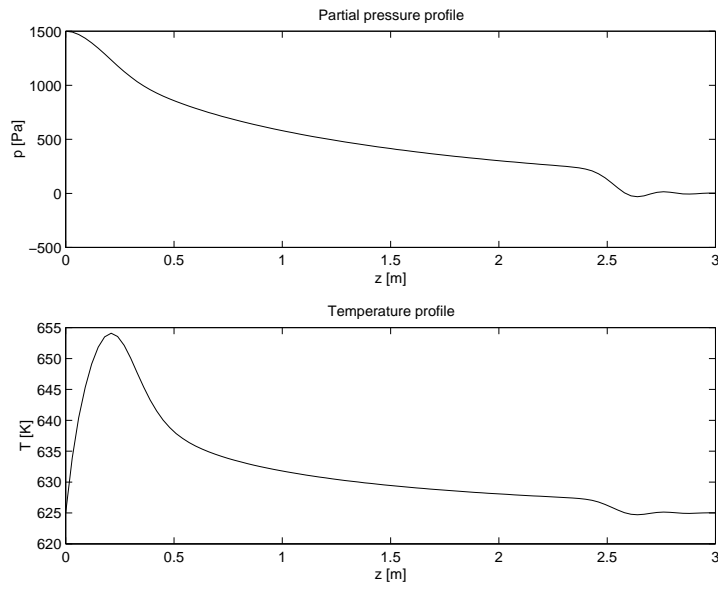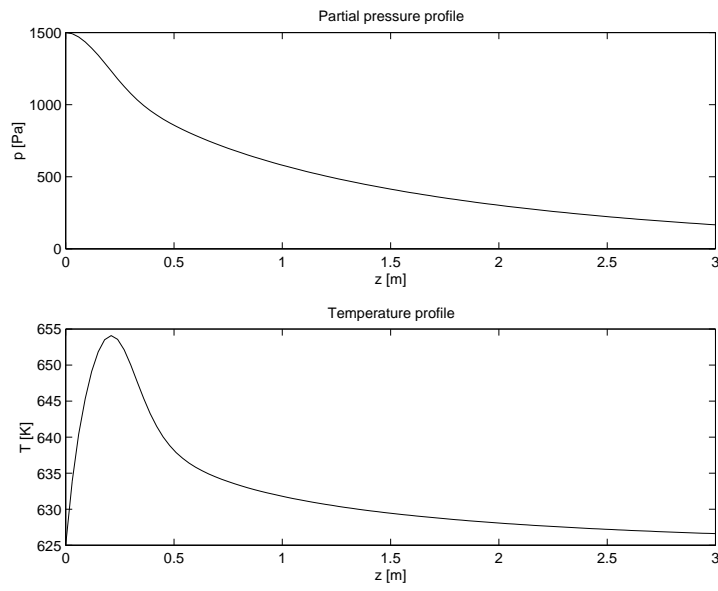
Figure 14: Profiles at t=0

Figure 15: Profiles at t=1.25 s

Figure 16: Profiles at t=2.5 s

Figure 17: Profiles at t=10 s

6.3   One-Dimensional Dynamic Heterogen Model

6.3.1   Problem

Analogues to heterogeneous catalytic processes in a fixed bed reactor can be found in biochemical processes. Here, one of the biggest problems may be to separate the product from the mixture containing non-reacted substrate and a cell culture or a solution of enzymes. A common way of solving this problem is to immobilize the enzymes or the cells by letting them grow on a porous material, or by deposition in a pellet-formed structure that can be fixed in the reactor. Generally, the substrate (reactant) will diffuse into the pellet, react, catalyzed by the enzyme, and the product will diffuse out again.

In this example we are going to model the process that takes place inside the pellets in the system where immunoglobulin G is adsorbed onto an adsorbent consisting of Protein A immobilized to agar-agar. The product stays in the gel and the process works as a separation system. The problems is described in Horstmann and Chase[18].

For diffusion within the adsorbing particle, the point concentration of solute is given by:

$$\epsilon \frac{\partial c_i}{\partial t} = \epsilon D \left(\frac{\partial^2 c_i}{\partial r^2} + \frac{2}{r} \frac{\partial c_i}{\partial r} \right) - (1 - \epsilon) \frac{\partial q_i}{\partial t} \tag{101}$$

The last term is the rate of adsorption (analogue to reaction rate). The units of c_i and q_i are kg/m^3.

If a second order rate of surface reaction is assumed, then the concentration of immunoglobulin G on the particle surface is:

$$\frac{\partial q_i}{\partial t} = k_1 c_i (q_m - q_i) - k_2 q_i \tag{102}$$

In a stirred tank reactor the bulk concentration, c [kg/m^3], of immunoglobulin G is given as:

$$\frac{dc}{dt} = - \left(\frac{3 v k_f}{RV} \right) (c - c_i(R)) \tag{103}$$

Initial conditions are:

$$c = c_0, \quad c_i = 0, \quad q_i = 0 \tag{104}$$

The boundary conditions are:

$$r = 0 \quad \frac{\partial c_i}{\partial r} = 0 \tag{105}$$

$$r = R \quad \frac{\partial c_i}{\partial r} = \frac{k_f}{D\epsilon} (c - c_i(R)) \tag{106}$$

Parameters needed for solving the system are:

---

[18]B.J. Horstmann and H.A. Chase, Modelling the Affinity Adsorption of Immunoglobulin G to Protein A Immobilised to Agarose Matrices, *Chem. Eng. Res. Dev.*, **67**, (243-254), 1989

| c_0	$=$	0.5 kg/m^3	Initial bulk concentration of immunoglobulin G
ϵ	$=$	0.96	Void fraction
D	$=$	$6 \cdot 10^{-12}$ m^2/s	Diffusion coefficient
k_1	$=$	0.001 m^3/kg·s	Forward rate constant of surface rx
K_d	$=$	0.019 kg/m^3	Dissociation constant
k_2	$=$	$K_d \cdot k_1$ 1/s	Reverse rate constant for surface rx
q_m	$=$	40 kg/m^3	Maximum concentration of immunoglobulin G on the particle surface
k_f	$=$	$44 \cdot 10^{-6}$ m/s	Liquid film mass transfer coefficient
R	$=$	$45 \cdot 10^{-6}$ m	Particle radius
V	$=$	$25 \cdot 10^{-6}$ m^3	Volume of liquid
v	$=$	$5.2 \cdot 10^{-6}$ m^3	Volume of adsorbent
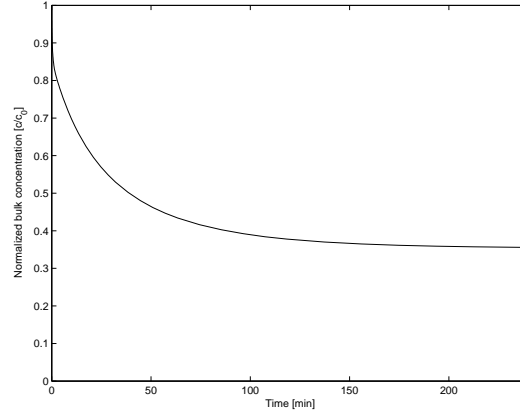
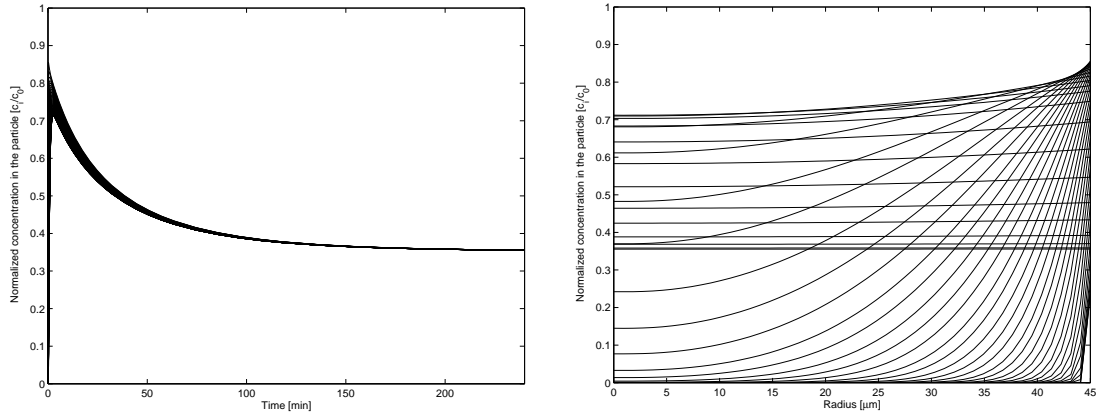Figure 18: Bulk concentration of immunoglobulin G as a function of time.

Figure 19: Normalized concentration of liquid and adsorbed immuniglobulin G in the particle as a function of time. There is one curve for each discretization point. These curves are so close to each other that they form a thick line.
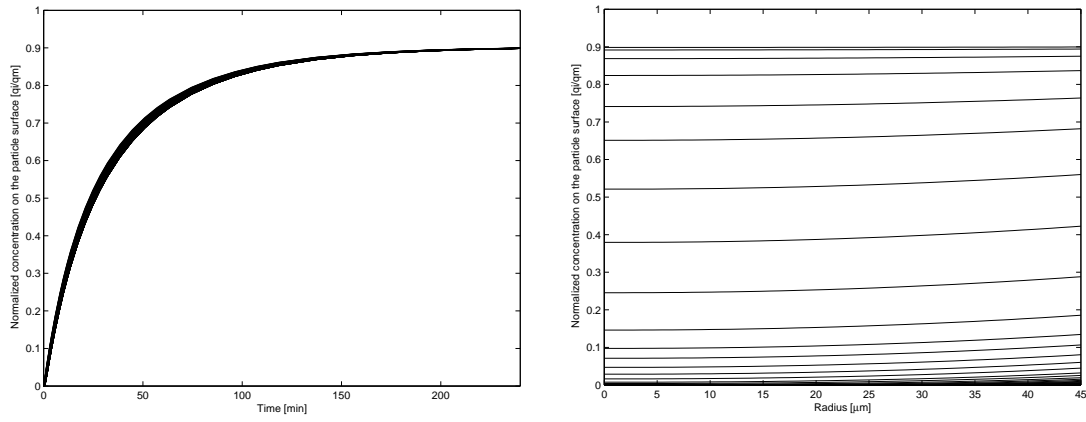
Figure 20: Normalized concentration of liquid and adsorbed immuniglobulin G in the particle as a function of radial position in the particle.
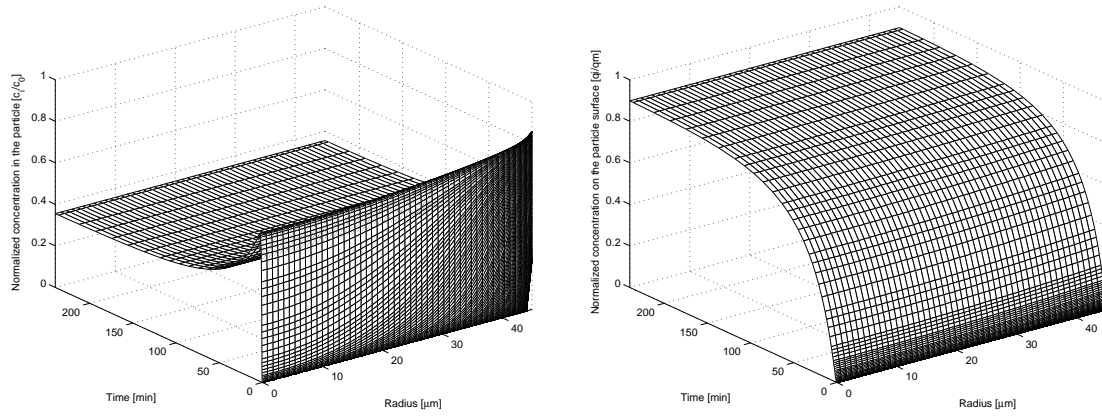

Figure 21: Normalized concentration of liquid and adsorbed immuniglobulin G in the particle as a function of both time and radial position in the particle.

gelmain.m

```
clear all
close all
epsilon = 0.96;  % Particle porosity
De = 6e-12;      % Effective diffusivity
kl = 0.0015;  % Forward rate constant for the surface reaction
Kd = 0.019;      % Dissotiation constant
qm = 40;      % Maximum concentration on the particle surface
kf = 4e-6;       % Liquid film mass transfer coefficient
Rp = 45e-6;      % Particle radius

r0 = 0;            % Lower integration limit in r-direction
rn = Rp;        % Upper integration limit in r-direction
ndisk = 50;       % Number of discretization points

V = 25e-6;      % Liquid volume
v = 5.2e-6;       % Volume of adsorbent

% Parameter vector which is sent into the function
rpar = [Rp epsilon qm Kd De r0 rn ndisk kf kl v V];
%index   1 2      3 4  5  6  7  8    9 10 11 12

% r-vector containing ndisk points
r = (r0:(rn-r0)/(ndisk-1):rn)';

% Initialization
ci0 = zeros(ndisk,1);
qi0 = zeros(ndisk,1);
c0 = 0.5;
init = [ci0; qi0; c0];

t0 = 0;
tf = 14400;
tspan = [t0 tf];

% The boundaries in the particle are algrbraic equations and shall
% therefore not be treated as differential equations. The way to
% let ode15s differ between the two kinds of equations is by
% introducing the mass matrix, M:
M=eye(2*ndisk+1,2*ndisk+1);

% First and last point (boundaries) in the vector ci0 are algebraic
% equations
M(1,1)=0.0;
M(ndisk,ndisk)=0.0;

%Gjor matrisen glissen for aa redusere beregningskostnadene
M=sparse(M);

options = odeset('Mass',M,'Stats','on');

% Solving the system of equations
[t,x] = ode15s(@gel,tspan,init,options,rpar,r);

% Plotting the results
```

```
ci = x(:,1:ndisk);
qi = x(:,ndisk+1:2*ndisk);
c = x(:,2*ndisk+1);

tplot = 3*[1:1:fix(length(t)/3)];

%C_exp = [1 0.8 0.74 0.65 0.55 0.44 0.39 0.36 0.33 0.31];
%t_exp = [0 5 10 20 40 80 120 160 200 240];

figure
%plot(t/60,c/c0,'k',t_exp,C_exp,'ko')
plot(t/60,c/c0,'k')
axis([0 240 0 1])
xlabel('Time [min]');
ylabel('Normalized bulk concentration [c/c_0]')

figure
plot(t/60,ci/c0,'k')
axis([0 240 0 1])
xlabel('Time [min]');
ylabel('Normalized concentration in the particle [c_i/c_0]');

figure
plot(r*1e6,ci(tplot,:)/c0,'k')
axis([0 45 0 1])
xlabel('Radius [{\mu}m]')
ylabel('Normalized concentration in the particle [c_i/c_0]');

figure
plot(t/60,qi/qm,'k')
axis([0 240 0 1])
xlabel('Time [min]');
ylabel('Normalized concentration on the particle surface [qi/qm]');

figure
plot(r*1e6,qi(tplot,:)/qm,'k')
axis([0 45 0 1])
xlabel('Radius [{\mu}m]')
ylabel('Normalized concentration on the particle surface [qi/qm]');

figure
mesh(r*1e6,t/60,ci/c0)
axis([0 45 0 240 0 1])
grid on
xlabel('Radius [{\mu}m]')
ylabel('Time [min]')
zlabel('Normalized concentration in the particle [c_i/c_0]');

figure
mesh(r*1e6,t/60,qi/qm)
axis([0 45 0 240 0 1])
grid on
xlabel('Radius [{\mu}m]')
ylabel('Time [min]')
zlabel('Normalized concentration on the particle surface [qi/qm]');
```

gel.m

```matlab
function deriv=gel(t,vari,rpar,r)

Rp=rpar(1);       % Particle radius
epsilon=rpar(2); % Particle porosity
qm=rpar(3);       % Maximum concentration on the particle surface
Kd=rpar(4);       % Dissotiation constant
Dh=rpar(5);       % Effective diffusivity
r0=rpar(6);       % Lower limit
rR=rpar(7);       % Upper limit
n =rpar(8);       % Number of discretization points
kf=rpar(9);       % Liquid film mass transfer coefficient
k1=rpar(10);      % Forward rate constant for the surface reaction
v =rpar(11);      % Volume of adsorbent
V =rpar(12);      % Liquid volume

ci = vari(1:n);
qi = vari(n+1:2*n);
c = vari(2*n+1);

% Discretation, finds the partial derivatives in r-direction

% Estimates the first derivatives of ci
dcidr = dss020(r0,rR,n,ci,-1)';

% Estimates the second derivatives of ci
dcidr2 = dss042(r0,rR,n,ci,dcidr,2,2)';

% Forming the equation system
dqidt = k1*ci.*(qm-qi) - k1*Kd*qi;
dcidt = Dh*(dcidr2(2:n-1) + (2./r(2:n-1)).*dcidr(2:n-1))...
- (((1-epsilon)/epsilon)*dqidt(2:n-1));
dcdt = -(3*v*kf/(Rp*V))*(c-ci(n));

% Boundary conditions
% Defining a residual which is going to zero when convergence is achieved
res1 = dcidr(1);
res2 = dcidr(n) - kf/(Dh*epsilon)*(c-ci(n));

% Merging all the vectors into one column vector
deriv = [res1; dcidt; res2; dqidt; dcdt];
```

7 Multiple Steady States in Fixed Bed Reactors

Steady state is obtained when the heat generated by the reaction equals the heat removed by cooling. By plotting curves of the heat generated and heat removed, the steady state is given by the intersection of the curves. When more than one intersection occur, there is more than one set of conditions that satisfy both the energy balance and mass balance, consequently there will be multiple steady states at which the reactor may operate.

Pseudohomogeneous models[19]

Multiple steady states can occur in adiabatic reactor systems when there is an opportunity for feedback of heat along the reaction path, which may take several forms:

- Heat may be exchanged between feed and product streams in the reactor to obtain maximum heat recovery (autothermal operation). Note, in the catalytic bed itself, the reaction is carried out adiabatically.

- Heat may be conducted against the direction of flow along the reactor wall and catalyst bed and transferred diffusively through the reacting mixture.

In any case, an increase in product temperature means an increased feed temperature and thus new steady states are possible at the same flow rates. For modeling purposes this means that the feed temperature cannot be fixed and specified independently of the product temperature. This feedback of heat may make the autothermal reactors unstable, unlike a non-autothermal reactor which is unconditionally stable.

For further reading, see e.g. Dougherty and Thygeson (1993)[20] and Paderna et al. (1997)[21].

Heterogeneous models

Multiple steady states can also be caused by intraparticle gradients, but it is possible only for extremely exothermic reactions[22].

When only interfacial gradients are present, we consider a single reaction and a catalyst particle with uniform temperature T_S and partial pressure P_{AS} of the key component. The bulk fluid surrounding it is at a temperature T and the parial pressure P_A. The heat generated in the reaction is given by[23]:

$$Q_R = (-\Delta H)k_1 P_{AS} \tag{107}$$

While the heat removed, that is heat transferred to the bulk fluid is given by:

$$Q_T = h_f(T_S - T) \tag{108}$$

At steady state, equalities exist between heat generated and heat removed, and between the chemical rate and mass transfer:

[19]Rase, H. F., Chemical Reactor Design for Process Plants, p. 415, John Wiley & Sons, Inc. (1977)

[20]Dougherty, R. C. and Thygeson, J. R., Chem. Eng. Comm., Vol. 126, pp. 155-177, 1993.

[21]Pederna, M., Borio, D. O., and Porras, J. A., AlChE J., Vol. 43, No. 1, pp. 127-134, 1997

[22]Froment, G. F. and Bischoff, K. B., Chemical Reactor Analysis and Design, 2nd ed., p. 480, John Wiley & Sons, (1990)

[23]Carberry, J. J. and Varma, A., Chemical Reaction and Reactor Engineering, pp. 407-409, Marcel Dekker, Inc. (1987)

$$k_1 P_{AS} \quad = \quad k_g a_v (P_A - P_{AS})$$

$$\Downarrow$$

$$P_{AS} \quad = \quad P_A \frac{k_g a_v}{k_g a_v + k_1} \qquad (109)$$

Hence, when the rate equation is expressed on the Arrhenius form ($K_1 = Ae^{\frac{-E}{RT_S}}$):

$$Q_R \quad = \quad (-\Delta H) P_A \frac{k_g a_v A e^{\frac{-E}{RT_S}}}{k_g a_v + A e^{\frac{-E}{RT_S}}} \qquad (110)$$

$$Q_T \quad = \quad h_f (T_S - T) \qquad (111)$$
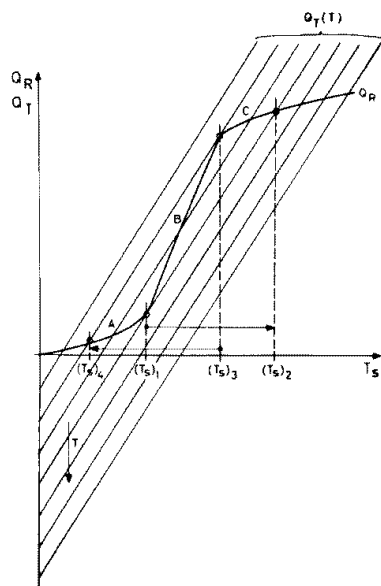
Q_R and Q_T are plotted in figure 22[24]:

Figure 22: Heat production and heat transfer rates for various gas and catalyst temperatures.

Suppose that the system operates in a point of branch A. As soon as the gas temperature is increased above a value leading to the solid temperature $(T_S)_1$, the latter will jump to a value $(T_S)_2$. Upon heating, the points described in the range $(T_S)_1$, $(T_S)_2$ do not correspond a steady state for T_S. If the particle is initially at $(T_S)_2$ and its temperature is slightly lowered below $(T_S)_3$, the temperature will drop to $(T_S)_4$ and the reaction will practically extinguish.

The occurence of multiple steady states in industrial tubular reactions[25]

Each possibility for multiple steady states has been subjected to rather extensive analytical studies. However, it is fear to say that the range of variables over which

[24]Figure taken from Carberry, J. J. and Varma, A., Chemical Reaction and Reactor Engineering, p.409, Marcel Dekker, Inc. (1987)

[25]Rase, H. F., Chemical Reactor Design for Process Plants, p. 417, John Wiley & Sons, Inc. (1977)

multiple steady states can occur are either extremely narrow and/or beyond the range of practical operation.

Most industrial reactors are of such length that axial diffusion is negligible, and the possibility for multiple steady states from this source is remote. Certain higly exothermic reactions that are conducted adiabatically could exhibit multiple steady states even with modest amounts of axial diffusion, but such reactions are not normally handeled in totally adiabatic systems.

The operating range for multiple steady states due to interfacial gradients is quite narrow. Even when the phenomenon exists, it is probably occuring only locally, so that the overall effect on the reactor is negligible.

The range of variables in which multiple steady states occur when it is caused by intraparticle gradients are also quite narrow. In fact, an elaborate numerical analysis of this phenomenon has shown that such multiple steady states will occur only at values of the Lewis number ($\frac{\Lambda_c}{\rho C_p D_{\text{eff}}}$) which can not exist in practice.
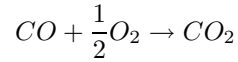
However, the situation may be different in the future applying fixed bed technology to micro scale reactors like care engines.
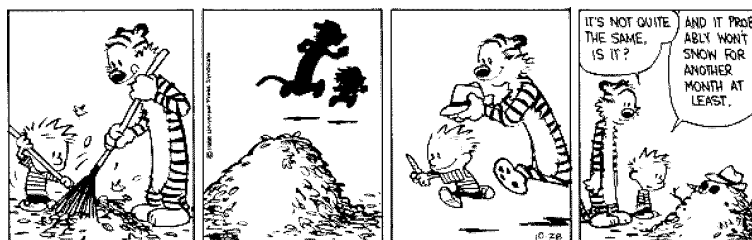
7.1 Example

7.1.1 Problem

The gas from a combustion engine contains 3.4 vol% CO which is going to be oxidized in a combustion chamber. The reaction is:

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

We have a large excess of oxygen and can assume that the reaction is a pseudo 1.order reaction. The reaction rate can be expressed by the following equation:

$$-r_{CO} = 5.56 \cdot 10^{13} \exp(\frac{-25000}{T})C_{CO} \qquad [kmol/m^3 s]$$

The combustion chamber can be modelled as a CSTR.

Data:

V	= 0.1 m^3	Reactor volume
$-\Delta H_r$	= 10000 kJ/mol	Reaction enthalpy
C_p	= 33.33 kJ/kmolK	Total heat capacity
F_{tot0}	= 0.001 kmol/s	Incoming molar gas velocity
P_{tot}	= 101325 Pa	Total pressure

a) Calculate the conversion in the reactor when the temperature is constant T=800K.

b) Calculate the conversion under adiabatic circumstances when the entering temperature of the gas is T_0=710K.

c) When the reactor in b) is steady-state, we notice that the temperature gradually decreases to 650K. How will this influence the conversion?

d) What is the conversion under adiabatic circumstances when the gas has a constant entering temperature T_0=650K from the start?

e) At which temperature is it possible that the reactor jumps from low conversion to high conversion by gradually increasing the entering temperature?
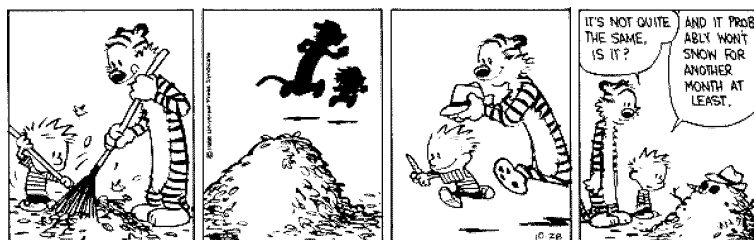
7.1.2   Solution

a) The mass balance is given by equation 17:

$$\frac{\partial c_j}{\partial t} + \nabla \cdot (c_j \vec{u}_s) = \nabla \cdot (D_j \nabla c_j) + R_j \tag{112}$$

$$\text{(1)} \qquad \text{(2)} \qquad \text{(3)} \qquad \text{(4)}$$

When we have a steady-state operation of a CSTR and look at only one component, we can ignore the first term. When defining $R_i = r_A$ the mass balance becomes:

$$\nabla \cdot (c_A \vec{u}_s) = \nabla \cdot (D_A \nabla c_A) + r_A \tag{113}$$

Now we multiply with dV on both sides and integrate.

$$\int_V \nabla \cdot (c_A \vec{u}_s) dV = \int_V \nabla \cdot (D_A \nabla c_A) dA + \int_V r_A dV \tag{114}$$

Since we are integrating over the whole system from inlet to outlet, the dispersion term will vanish. Assuming constant $\vec{u}_s$, we can rewrite the term on the RHS by using Gauss' theorem:

$$\int_V \vec{u}_s \cdot \nabla c_A dV = \vec{u}_s \cdot \int_V \nabla c_A dV = \vec{u}_s \cdot \int_A c_A \vec{n} da = u_s \left[(c_A A_t) - (c_A A_t)_0 \right]$$

where A_{t0} and A_t are the cross section areas of the inlet and outlet of the reactor. Setting $u_s c_A A_t = F_A$ we get the design equation for a CSTR as we know from Scott Fogler:

$$F_{A0} - F_A = -r_A V \qquad \text{where} \qquad F_A = F_{A0}(1 - x_A) \tag{115}$$

Rearranging this gives:

$$
\begin{aligned}
x_A &= \frac{-r_A V}{F_{A0}} & \text{where} \quad -r_A &= kC_A \\
&= \frac{kc_A V}{F_{A0}} & \text{where} \quad c_A &= c_{A0}(1 - x_A) \\
&= \frac{kc_{A0}(1 - x_A)V}{F_{A0}} & \text{where} \quad c_{A0} &= \frac{p_{A0}}{RT} \\
&= \frac{kp_{A0}V(1 - x_A)}{RTF_{A0}} & & \\
&= \frac{kp_{A0}V}{F_{A0}RT + kp_{A0}V} & & \text{(116)} \\
&= \frac{5.56 \cdot 10^{13} e^{\frac{-25000}{800}} \cdot 0.034 \cdot 101325 \cdot 0.1}{0.034 \cdot 0.001 \cdot 10^3 \cdot 8.314 \cdot 800 + 5.56 \cdot 10^{13} e^{\frac{-25000}{800}} \cdot 0.034 \cdot 101325 \cdot 0.1} & & \\
&\approx 0.694 & &
\end{aligned}
$$

b) Now we have to use the energy equation.

$$\sum_j \rho_j C_{pj} \frac{\partial T}{\partial t} + \sum_j \rho_j C_{pj} \vec{u}_s \cdot \nabla T = \nabla \cdot (\lambda \nabla T) + \sum_i (-\Delta H_{R_i}) R_i + Q \qquad (117)$$

$$(1) \qquad\qquad (2) \qquad\qquad (3) \qquad\qquad (4) \qquad (5)$$

Again, when we consider a steady-state operation of a CSTR (no internal gradients in temperature and concentration) in which cooling and a first-order reaction is taking place, we can ignore the first term, and Q is given by:

$$Q = Ua\,(T_a - T) \qquad (118)$$

Where:

U	[W/m² K]	Heat resistance coefficient
a	[m²/m³]	Area of cooling element per reactor volume
T_a	[K]	Temperature of the cooling fluid (ambient temperature)
T_0	[K]	Feed temperature

If we consider only one component, the energy balance becomes:

$$\rho C_p \vec{u}_s \cdot \nabla T = \nabla \cdot (\lambda \nabla T) - r_A(-\Delta H_r) + Ua\,(T_a - T) \qquad (119)$$

Now we multiply with dV on both sides and integrate over the volume V:

$$\int_V \rho C_p \vec{u}_s \cdot \nabla T dV = \int_V \nabla \cdot (\lambda \nabla T) dV - \int_V r_A(-\Delta H_r) dV + \int_V Ua\,(T_a - T)\,dV \qquad (120)$$

The volume integral of the conductive term will now equal zero. If $\vec{u}_s$, C_p and ρ are constant, we can rewrite the term on the LHS by using Gauss' theorem:

$$\int_V \rho C_p \vec{u}_s \cdot \nabla T dV = \rho C_p \vec{u}_s \cdot \int_V \nabla T dV = \rho C_p \vec{u}_s \cdot \int_A T \vec{n} da = \rho C_p u_s (TA_t - T_0 A_{t0})$$

Thus:

$$\rho C_p u_s \left[(TA_t) - (TA_t)_0 \right] = -r_A V(-\Delta H_r) + UaV\,(T_a - T) \qquad (121)$$

If the cross section area is constant $(A_{t0} = A_t)$ and the total area in contact with the heat exchanger is given by $A_h = aV$, this gives:

$$u_s \rho C_p A_t\,(T - T_0) = -r_A V(-\Delta H_r) + U A_h\,(T_a - T) \qquad (122)$$

If $C_p[=]$kJ/moleK, then we have to divide the density, ρ by the mol mass, M_m. Equation 122 then becomes:

$$\frac{u_s \rho C_p A_t\,(T - T_0)}{M_m} = -r_A V(-\Delta H_r) + U A_h\,(T - T_a) \qquad (123)$$

Rearranging and setting $\frac{u_s \rho A_t}{M_m} = F_{A0}$ and finally dividing by F_{A0} gives the equation we know from Scott Fogler (p. 491):

$$\frac{(-r_A V)\,(-\Delta H_r)}{F_{A0}} = C_p\,(T - T_0) + \frac{U A_h}{F_{A0}}\,(T - T_a) \qquad (124)$$

The left-hand side of equation 124 is referred to as the heat-generated term:

$$G(T) = \frac{(-r_A V)\,(-\Delta H_r)}{F_{A0}} \qquad (125)$$

while right-hand side of equation 124 is referred to as the heat-removed term:

$$R(T) = C_p \left(T - T_0 \right) + \frac{UA_h}{F_{A0}} \left(T - T_a \right) \tag{126}$$

By using equation 125 we have:

$$
\begin{aligned}
G(T) &= \frac{-r_A V(-\Delta H_r)}{F_{A0}} \qquad \text{where} \qquad -r_A V = F_{A0} x_A \\
&= \Delta H_r x_A \qquad \text{where} \qquad x_A = \frac{k p_A V}{F_{A0} R T + k p_A V} \qquad \text{from equation 116} \\
&= \frac{\Delta H_r k p_{A0} V}{F_{A0} R T + k p_{A0} V} \qquad \text{where} \qquad k = 5.56 \cdot 10^{13} \cdot e^{-\frac{25000}{T}} \\
&= \frac{\Delta H_r \cdot 5.56 \cdot 10^{13} \cdot e^{-\frac{25000}{T}} p_{A0} V}{F_{A0} R T + 5.56 \cdot 10^{13} \cdot e^{-\frac{25000}{T}} p_{A0} V} \tag{127}
\end{aligned}
$$

And if the reactor is adiabatic, equation 126 gives:

$$R(T) = C_p(T - T_0) \tag{128}$$

G(T) and R(T) are plotted in Figure 23.

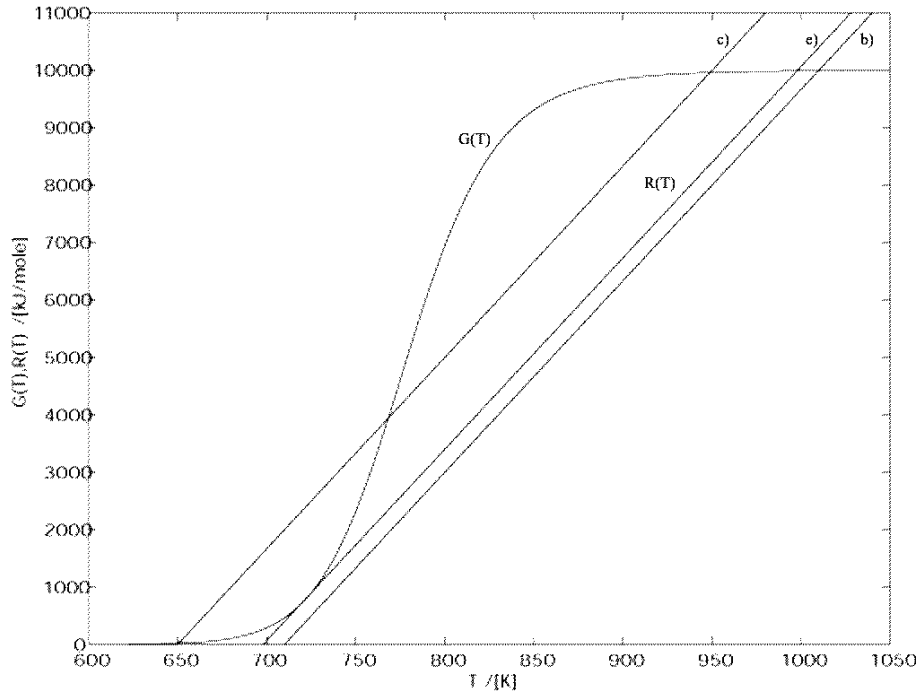
Figure 23: G(T) and R(T) plotted with T_0=710K (b), T_0=650K (c) and T_0=698K (e)

From the plot we can see that G(T) and R(T) at the intersection point is approximately 10000 kJ/kmole. The conversion is given by:

$$
\begin{aligned}
x_A &= \frac{G(T)}{\Delta H_r} \tag{129} \\
&\approx \frac{10000}{10000} = 1.0
\end{aligned}
$$

c) By decreasing the entering temperature to 650K we can see from the plot that we still have approximately the same conversion as in b).

d) Now the conversion will be very low. G(T) and R(T) at the intersection point is now approximately 150 kJ/kmole. And the conversion is:

$$
\begin{aligned}
x_A &= \frac{G(T)}{\Delta H_r} \\
&\approx \frac{100}{10000} = 0.01
\end{aligned}
\tag{130}
$$

e) When we gradually increase the entering temperature, the R(T) curve will shift to the right. And we find the ignition point when the entering temperature is approximately 698K. Further increase in the entering temperature will make a jump in the conversion.
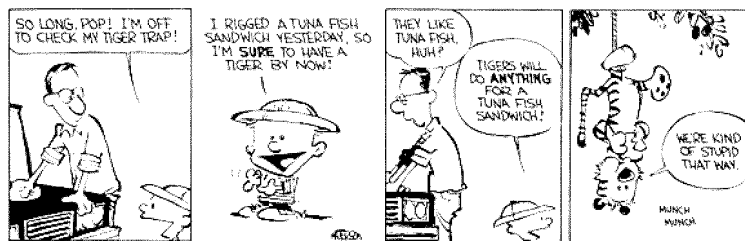
8 Correlations

When we are calculating the dimensionless groups, we often are in lack of parameters. By using different correlations which are specific for the reactor models, we can estimate the necessary parameters.

Pseudo homogeneous One-dimensional dispersion Model

λ_a can be found by

$$\frac{\lambda_a}{\lambda_{\text{fl}}} = 8....10 + 0.75 Re_p Pr \tag{131}$$

D_a can be found by:

$$\frac{D_a}{u_s d_p} = \frac{0.3}{Re_p Sc} + \frac{0.5}{1 + \frac{3.8}{Re_p Sc}} \tag{132}$$

Pseudo homogeneous Two-dimensional Dispersion Model

D_r can be found by:

$$\frac{\epsilon D_r}{u_s d_p} \left(1 + 19.4 \left(\frac{d_p}{d_t} \right)^2 \right) = \frac{0.09}{1 + \frac{10}{Re_p Sc}} + \frac{0.4}{(Re_p Sc)^2} \tag{133}$$

D_a can be found by:

$$\frac{\epsilon D_a}{u_s d_p} = \frac{0.5}{1 + \frac{3.8}{Re_p Sc} + \frac{0.3}{Re_p Sc}} \tag{134}$$

Heterogeneous One-dimensional Plug-flow Model

k_s can be found by:

$$\epsilon Sh = 0.357 Re_p^{0.641} Sc^{0.33} \tag{135}$$

h_s can be found by:

$$\epsilon Nu = \left(\frac{Re_p}{\epsilon} \right)^{0.563} Pr^{0.33} \tag{136}$$

Approximate Values of Effective Transport Parameters

Effective thermal conductivities:

$$k_{er} = \text{1-10} \quad [\text{J/msK}] \quad \text{Effective radial thermal conductivity}$$

$$\frac{\lambda_a}{\lambda_{\text{fl}}} = \text{1-300} \quad \frac{\text{Effective axial thermal conductivity}}{\text{Thermal conductivity of the fluid}}$$

$$\frac{\lambda_r}{\lambda_{\text{fl}}} = \text{1-12} \quad \frac{\text{Effective radial thermal conductivity}}{\text{Thermal conductivity of the fluid}}$$

Heat transfer coefficients:

$$h_s = \text{15-75} \quad [J/m^2sK] \quad \text{Heat transfer coefficient for the one-dimensional model}$$

$$\alpha_w = \text{100-250} \quad [J/m^2sK] \quad \text{Wall coefficient for the two-dimensional model}$$

Effective diffusivities:

$$Pe_a = \text{0.1-5} \quad \text{Axial fluid-mechanical Peclet number}$$

A Qualitative discussion of reactor stability

The energy balance for a steady-state plug flow reactor can be given by:

$$u_s \rho_g C_p \frac{dT}{dz} = (-\Delta H_r) r_A - \frac{4U}{d_t}(T_a - T) \tag{137}$$

where $r_A = k c_A g(x)$. The term $g(x)$ is included to allow for reactions other than first order.

The equation 137 can be transformed to a dimensionless form by making the following substitutions:

$$c_A = c_{A0}(1 - x_A) \tag{138}$$

$$z = \frac{u_{s0}\zeta}{\epsilon A' e^{\gamma T_a}} \text{ where } \gamma = \frac{E}{RT_a^2} \tag{139}$$

$$T = T_a - \frac{\tau}{\gamma} \tag{140}$$

This gives:

$$\frac{u_s \rho_g C_p \epsilon A' e^{\gamma T_a}}{\gamma u_{s0}} \frac{d\tau}{d\zeta} = (-\Delta H_r) k c_{A0}(1 - x_A) g(x) - \frac{4U}{d_t} \frac{\tau}{\gamma} \tag{141}$$

Multiplying all terms in equation 141 with $\frac{\gamma}{\rho_{g0} C_p}$ gives:

$$\frac{u_s \rho_g \epsilon A' e^{\gamma T_a}}{u_{s0} \rho_{g0}} \frac{d\tau}{d\zeta} = \frac{(-\Delta H_r) c_{A0} \gamma}{\rho_{g0} C_p} k(1 - x_A) g(x) - \frac{4U}{d_t \rho_{g0} C_p} \tau \tag{142}$$

Using Barkelew's exponential rate expression instead of the usual Arrhenius form to simplify the analysis:

$$k = A' e^{\gamma T} = A' e^{\tau + \gamma T_a} = A' e^{\gamma T_a} e^{\tau} \tag{143}$$

Introduces $S = \frac{(-\Delta H_r) c_{A0} \gamma}{\rho_{g0} C_p}$, $N = \frac{4U}{d_t \rho_{g0} C_p \epsilon A' e^{\gamma T_a}}$ and divides all the terms with $A' e^{\gamma T_a}$. Including constant mass velocity og the gass ($G = \rho_g u_s$) this gives:

$$\frac{d\tau}{d\zeta} = S(1 - x_A) g(x) e^{\tau} - N\tau \tag{144}$$

The mass balance for a steady-state plug flow reactor can be given by:

$$\frac{d(u_s c_A)}{dz} = -r_A \tag{145}$$

Assuming constant velocity in equation 145:

$$u_s \frac{dc_A}{dz} = -k c_A g(x) \tag{146}$$

Using the dimensionless groups above gives:

$$-\frac{u_s \epsilon A' e^{\gamma T_a} c_{A0}}{u_{s0}} \frac{dx_A}{d\zeta} = -k c_{A0}(1 - x_A) g(x) \tag{147}$$

Substitutes the expression for k (equation 143) and divides all the terms with $A' e^{\gamma T_a}$:

$$\frac{dx_A}{d\zeta} = (1 - x_A) g(x) e^{\tau} \tag{148}$$

A better form for puposes of computation is obtained by dividing equation 144 with equation 148:

$$\frac{d\tau}{dx_A} = S - \frac{N \tau e^{-\tau}}{(1 - x_A) g(x)} \tag{149}$$

For computation purposes equation 148 is sometimes expressed as:

$$\frac{d\zeta}{dx_A} = \frac{e^{-\tau}}{(1 - x_A) g(x)} \tag{150}$$

τ attains a maximum value at the *hot spot* of the reactor. The relation between conversion and temperature at the hot spot is obtained by setting $\frac{d\tau}{dx_A} = 0$ in equation 149.

$$(1 - x_m) g(x_m) = \frac{N}{S} \tau_m e^{-\tau_m} \tag{151}$$

The subscript m is used to indicate that the relation is valid only at the point of maximum temperature.

B   On the Criteria for Model Selection Describing Non-Isothermal Packed-Bed Catalytic Reactors.

Mathematical models of chemical reactors may be useful for predicting the conversion and temperature profiles in packed bed reactors. While very general models can be written down, these model formulations are usually not used either because of the computational complexity or because it is difficult or impossible to estimate the parameters in the model. Several criteria have thus been formulated over the years intended as guidlines obtaining simplified models that still contain the important physical mechanisms involved.

B.1   Axial Dispersion

The Role of axial dispersion in fixed bed reactors has been analyzed by Young and Finlayson (1993)[26], Mears (1976)[27] and Mears (1971)[28]. An inlet rate criterion is derived for detecting significant effects of axial heat and mass transfer in non-isothermal reactors with uniform wall temperature. The criterion is based on perturbation theory comparing the plug flow and axial dispersion model solutions approximated by Taylor series. The mole balance for a steady-state reactor can be given in terms of an axial dispersion model:

$$D_a \frac{d^2 C}{dz^2} - v_z \frac{dC}{dz} - \rho_B r = 0 \tag{152}$$

with boundary conditions:

$$D_a \frac{dC}{dz}|_{z=0^+} = -v_z(C|_{z=0^+} - C|_{z=0^-}) \tag{153}$$

and

$$\frac{dC}{dz}|_{z=L^-} = 0 \tag{154}$$

or by a corresponding plug flow model:

$$v_z \frac{dC}{dz} = -\rho_B r \tag{155}$$

with initial conditions:

$$C|_{z=0} = C_0 \tag{156}$$

Both sets of model equations are made dimensionless by introducing the following variables: $z^* = z/L$, $X = (C_0 - C)/C_0$. In addtion, the kinetic model is linearized as $\rho_B R = \rho_B R_0(1 - X)$. The model equations in dimensionless form are then given by:

$$\frac{1}{Pe_{m,z}} \frac{d^2 X}{dz^{*2}} - \frac{dX}{dz^*} - \beta R_0(1 - X) = 0 \tag{157}$$

with boundary conditions:

---

[26]Young, L. C. and Finlayson, Ind. Eng. Chem. Fundam., Vol. 12, No. 4, pp. 412-422, 1973

[27]Mears, D. E., Ind. Eng. Chem., Fundam., Vol. 15, No. 1, pp. 20-23, 1976

[28]Mears, D. E., Chem. Eng. Sci., Vol. 26, pp. 1361-1366, 1971

$$\frac{1}{Pe_{m,z}}\frac{d^2 X}{dz^{*,2}}|_0 = X \tag{158}$$

and

$$\frac{dX}{dz}|_{z^*=1^-} = 0 \tag{159}$$

The corresponding plug flow model yields:

$$\frac{dX}{dz^*} = -\beta R_0(1 - X) \tag{160}$$

with initial conditions:

$$X|_{z=0} = 0 \tag{161}$$

The plug flow problem can be solved analytically:

$$X_p = 1 - exp(-\beta R_0 z^*) \tag{162}$$

For small deviations from plug flow and for first order reactions, the solution of the dispersion model can be expressed as:

$$X_d \approx 1 - \frac{1}{1 + \gamma \beta R_0} \approx 1 - [1 - \gamma \beta R_0] \tag{163}$$

where $\gamma = \frac{\beta R_0}{Pe_{m,z}\frac{d_p}{L}}$.

The deviation at the inlet (i.e., for $z^* \to 0$) is then

$$X_d - X_p \approx 1 - [1 - \gamma \beta R_0] - (1 - exp(-\beta R_0 z^*) \approx \gamma \beta R_0 \tag{164}$$

The deviation is thus proportional to $\gamma \beta R_0$. In physical variables we have the necessary condition that axial dispersion in unimportant:

$$\gamma \beta R_0 = \frac{\rho_B R_0 d_p}{v_z C_0 Pe_{m,z}} \ll 1 \tag{165}$$

A similar analysis for temperature give rise to the following criterion:

$$\frac{(-\Delta H)\rho_B R_0 d_p}{(T_0 - T_w)\rho v_z C_P Pe_{h,z}} \ll 1 \tag{166}$$

In which the axial Peclet numbers for mass ($Pe_{m,z}$) and heat ($Pe_{h,z}$) are based on particle diameter.

Unfortunately, these criteria do not apply to the most frequently encountered case in which $T_0 = T_w$ or to endothermic reactions. Also the relative importance of concentration and temperature deviations depends greatly on the reaction order and temperature response of the reaction, which are not taken into account by the above criteria. An alternative criteria has been derived by the perturbation approach for the case in which $T = T_w$, assuming a n-order power law rate expression of the Arrhenius type:

$$R = Aexp(-E/RT)(1 - X)^n \tag{167}$$

Linearising this equation with a Taylor series about the plug flow value and truncating after the first term in X and T yields:

$$R = R_p[1 - n(X - X_p) + Ar\frac{(T - T_p)}{T_w}]$$ (168)

Substituting the dimensional form of the expressions for the deviations $(X - X_p)$ and $(T - T_p)$ at the inlet gives:

$$R = R_p[1 - \frac{nDA_I}{Pe_{m,z}} + \frac{ArDa_{III}}{Pe_{h,z}}]$$ (169)

If dispersion effects are to affect the reaction rate by less than $\pm 5\%$, the necessary condition is:

$$|\frac{nDA_I}{Pe_{m,z}} - \frac{ArDa_{III}}{Pe_{h,z}}| < 0.05$$ (170)

B.2   Intraparticle Transport

Mears (1971)[29] derived a criterion for the absence of significant diffusion effects within a catalyst particle. It was assumed that Ficks first law governs diffusion in the porous media, that the effective diffusivity, D_e, remains independent of the nature of the reaction, and that the intrinsic catalytic activity is distributed uniformly throughout. The starting point for the mathematical analysis is a simplified model expressing a balance between mass diffusion and chemical reaction in the particle:

$$D_e(\frac{d^2C}{dr^2} + \frac{1}{r}\frac{dC}{dr}) = R$$ (171)

Introducing the dimensionless variables $X = C/C_s$ and $r^* = r/r_p$, gives

$$(\frac{d^2X}{dr^{*,2}} + \frac{1}{r^*}\frac{dX}{dr^*}) = \frac{Rr_p^2}{D_eC_s}$$ (172)

To ensure that the effectiveness factor, $\eta \geq 0.95$ in an isothermal spherical particle with a first order reaction, the criterion requires:

$$\frac{Rr_p^2}{D_eC_s} < 1$$ (173)

By use of perturbation analysis and the simple power law kinetics, $R_s = kC_s^n$, an extended criterion yields:

$$\frac{Rr_p^2}{D_eC_s} < \frac{1}{|n|}$$ (174)

A similar perturbation approach has also been used to derive a criterion for the lack of importance of temperature gradients in catalyst particles. The reaction is assumed to follow an Arrhenius temperature dependence. For quasi-isothermal behavior, the observed R must not differ from the rate that would prevail at constant temperature by more than an acceptable amount, say 5%. The result is:

---

[29]Mears, D. E., Ind. Eng. Chem. Process Des. Develop., Vol. 10, No. 4, pp. 541-547, 1971

$$\frac{|\Delta H| R r_p^2}{T_s \lambda} < \frac{T_s R}{E} \tag{175}$$

Finally, a modified criteria involving perturbations in both temperature and concentrations have been derived. The criterion given below ensures $\eta > 0.95$ provided that:

$$Da_{II} |n - ArPt| < 1 \tag{176}$$

B.3   Interfase Transport

A criterion for detecting the onset of a heat transport limitation in the film has been derived by Mears (1971)[30] with the perturbation approach. It was assumed that the rate of reaction depends on temperature in the Arrhenius fashion:

$$R = A exp(-E/R_g T) f(c) \tag{177}$$

where $f(c)$ is a function of concentration. Then the rate at any temperature T close to T_0, the temperature of the adjacent bulk fluid, is given by a Taylor expansion about T_0 with terms higher than the first neglected:

$$R = A exp(-E/R_g T) f(c) \approx R_0 [1 + \frac{T - T_0}{T_0} \frac{E}{R_g T}] \tag{178}$$

where R_0 is the rate which would prevail if the particle temperature were at T_0.

An energy balance for a spherical catalyst particle gives:

$$(-\Delta H) R \frac{4\pi}{3} (r_p)^3 = h(T - T_p) 4\pi (r_p)^2 \tag{179}$$

where h is the heat transfer coefficient from fluid to catalyst particle. Heat conduction to adjacent touching particles is assumed negligible. Combining the two relations gives:

$$\frac{R}{R_0} = 1 + \frac{(-\Delta H) R r_p E}{3h T_0^2 R_g} \tag{180}$$

In order for the rate R not to deviate from R_0 by more than an acceptable amount, say 5%, the second term on the right must be less than 0.05. The resulting dimensionless criterion:

$$\frac{(-\Delta H) R r_p E}{3h T_0^2 R_g} < 0.05 \tag{181}$$

or

$$\frac{(-\Delta H) R r_p}{h T_0} < 0.15 \frac{R_g T_0}{E} \tag{182}$$

This criterion is valid whether diffusion limitations exist in the particle or not.

For isothermal cases with first order kinetics it has been shown that the effect of bulk mass transport across the film is expressed by:

---
[30]Mears, D. E., Journal of Catalysis, Vol. 20, pp. 127-131, 1971

$$\rho_B R = \rho_B \eta k C_s = k_c a (C - C_s) \tag{183}$$

The film resistance can be assumed negligible relative to surface reaction kinetics provided that:

$$\frac{(C - C_s)}{\rho_B C_s} = \frac{\eta k}{k_c a} < 0.1 \tag{184}$$

in which k_c is the gas-particle mass transfer coefficient, and a is the external surface-to-volume ratio of the particle. This expression was later generalized to other reaction orders by the perturbation approach, allowing a 5% deviation as before. The criterion can be expressed as:

$$\frac{R r_p}{C_b k_c} < \frac{0.15}{n} \tag{185}$$

B.4   Radial Dispersion

Mears (1971)[31] derived an approximate criterion determining the existance of radial interparticle heat transport limitations.

At the *hot spot*, the transport equation can be simplified to:

$$k_e \left(\frac{d^2 T}{dr^2} + \frac{1}{r} \frac{dT}{dr} \right) = R(-\Delta H) \tag{186}$$

It was assumed that intraphase and interphase transport limitations are negligible at the onset of the interparticle limitation.

An analytical solution was given for the radial temperature profiles:

$$\theta - \theta_{\max} = -2 ln(Bu^2 + 1) \tag{187}$$

where $\theta = E(T - T_w)/(R_g T_w^2)$, $u = r/R_t$, $B = \delta/8 exp|\theta_{\max}|$ and $\delta = (-\Delta H) R_w R_t^2 E/(k_e T_w^2 R_g)$.

First, we apply the following boundary conditions at the wall: $u = 1$ for $\theta = 0$.

The result is:

$$\delta = 8[exp(-0.5|\theta_{\max}|) - exp(-|\theta_{\max}|)] \tag{188}$$

For small δ and B values, the natural log term in the analytical solution can be expanded so that the equation reduces to a parabola:

$$\theta - \theta_{\max} = -2Bu^2 \tag{189}$$

Adopting the given boundary condition and expanding the exponential, an expression for $\theta_{\max}$ was obtained:

$$\theta_{\max} = \frac{\delta/4}{1 - \delta/4} \approx \delta/4 \tag{190}$$

---

[31] Mears, D. E., Journal of Catalysis, Vol. 20, pp. 127-131, 1971

In small laboratory reactors, the heat transfer resistance at the wall cannot be neglected. A more appropriate boundary condition may then be:

$$k_e \frac{dT}{dr}\Big|_{r=R_t} = h_w(T - T_w)\big|_{r=R_t} \tag{191}$$

in which h_w is the heat transfer coefficient at the wall.

In dimensionless terms the boundary condition is given by:

$$\frac{d\theta}{du}\Big|_{u=1} = \frac{h_w R_t}{k_e}\theta_{u=1} = \frac{(Biot)_w}{2}\frac{R_t}{r_p}\theta_{u=1} \tag{192}$$

where the *Biot* number at the wall, $(Biot)_w = \frac{h_w r_p}{k_e}$, expresses the ratio of thermal transport at the reactor wall to that in the core of the bed.

Using the alternative boundary condition, one obtains the following approximate solution:

$$\theta_{\max} \approx \frac{\delta}{4}[1 + \frac{4k_e}{R_t h_w}] \approx \frac{\delta}{4}[1 + \frac{8}{(Biot)_w}\frac{r_p}{R_t}] \tag{193}$$

which reduces to $\delta/4$ when the wall heat transfer resistance is small (i.e., $r_p/R_t \ll 1$).

The effect of the radial temperature gradient on the reaction rate can now be determined. As for the interfase transport criterion we start with:

$$R = R_0[1 + \frac{T - T_0}{T_0}\frac{E}{R_g T_0}] \tag{194}$$

Introducing the dimensionless temperature variable, the solution obtained using the first boundary condition, and integrating across the reactor cross-section:

$$\pi(1)^2 \overline{R} = R_w \int_o^1 (1 + \theta_{\max} - 2Bu^2)2\pi u\,du \tag{195}$$

The result is:
$$\frac{\overline{R}}{R_w} = (1 + \theta_{\max} - B) \tag{196}$$

where $\overline{R}$ is the averaged reaction rate at the cross-section at the axial position of the hot spot. For quasi-isothermal behavior across the bed, $\overline{R}$ must not deviate from R_w by more than an acceptable 5%. Hence,

$$|\theta_{\max} - B| < 0.05 \tag{197}$$

That is, when the heat transfer resistance at the wall is negligible (i.e., $R_t/r_p > 100$), the criterion yields:
$$\frac{(-\Delta H)\overline{R}R_t^2}{k_e T_w} < 0.4\frac{R_g T_w}{E} \tag{198}$$

When the heat transfer resistance at the wall is significant, we apply the solution obtained using the second boundary condition, and the extended interparticle criterion becomes:
$$\frac{(-\Delta H)\overline{R}R_t^2}{k_e T_w} < \frac{0.4\frac{R_g T_w}{E}}{[1 + 8\frac{r_p}{R_t(Biot)_w}]} \tag{199}$$