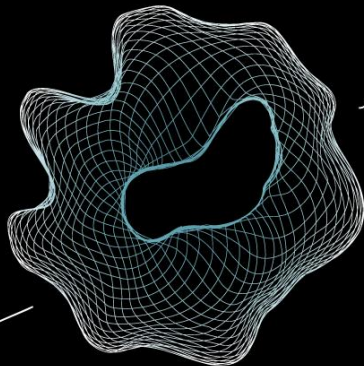


# Multiphase Reactor Technology

## Fixed Bed Reactors (introduction)

Sascha Kersten

Fausto Gallucci



# Content

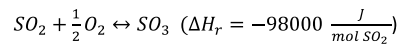
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- Discussing the archetype multiphase reactors
  - Descriptive
  - Pros and cons
  - Modelling
- Selection and design of a reactor for a certain reaction system

# An example of an exam (takes the whole day)

## Oxidation of SO<sub>2</sub>

The catalytic (V<sub>2</sub>O<sub>5</sub>) oxidation of SO<sub>2</sub> to SO<sub>3</sub> is an important step in a Sulfuric Acid production plant.



$$K_p = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2} \sqrt{P_{\text{O}_2}}}$$

with:

$$\ln(K_p) = \frac{11830}{T} - 11.4$$

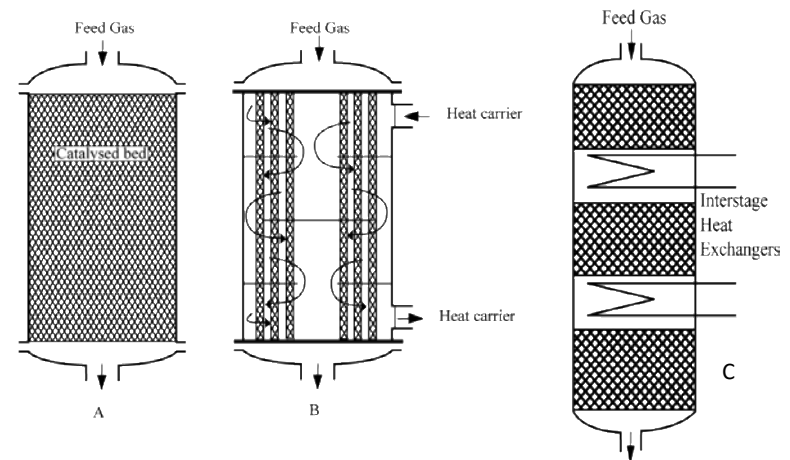
In the equations above, T is in K and P in bar. In your further calculations you may assume  $\Delta H_r$  to be constant. The conversion of the reaction is limited by thermodynamic equilibrium.

The reactor that needs to be designed is for a plant that produces **0.5 million ton H<sub>2</sub>SO<sub>4</sub> per year** ( 1 year = 8000 hours). The SO<sub>2</sub> conversion needs to be higher than **96%** in order to meet the emission requirements. The composition of the feed stream is **8 vol% SO<sub>2</sub>, 11 vol% O<sub>2</sub>, 0 vol% SO<sub>3</sub>**, rest is N<sub>2</sub>. The inlet temperature is: **420 °C**. Inlet pressure is **1.2 bar** and the maximal allowable pressure drop is **0.2 bar**. The maximal superficial velocity in the reactor is 5 m/s. **The reactor is a fixed bed.**

**Question A:** Select a suitable fixed bed configuration. You may choose from: A1) single adiabatic bed, A2) single externally cooled bed, B) cooled multi-tubular reactor and C) multi adiabatic beds with interstage cooling. Schematics are given below. Motivate your choice! Use (simple) calculations to support your reasoning. Do not only advocate your selection, also show the disadvantages / impossibilities of the others. **(35 pts)**

Molten salt at **410 °C** (you can assume a constant temperature) is available for cooling the multi-tubular reactor (B) and the single bed(A2). With interstage cooling the temperature is reduced to **430 °C** after each stage.

Data and equations that you might use to support your reasoning for question A can be found on the pages below.



# An example of an exam (takes the whole day)

**Question B:** Design (size) the reactor of your choice. You may assume that the conversions of the other reactors in the plants are 100%. (65 pts)

You may use a 1D model.

The molar concentration can be calculated with the ideal gas law and may be assumed constant (use for the calculation the inlet P and T). For the density of the gas ( $\text{kg/m}^3$ ) you make the value for  $\text{N}_2$  (28 g/mol). You may further assume that the velocity does not change in the reactor. In the model you can also assume the pressure to be constant. The pressure drop can be calculated based on the inlet conditions.

Provide:

- 1) The diameter and length of the bed (A), the diameter and length of the tubes and the number of tubes required (B), the diameter and length of the beds (C)
- 2) Axial profiles of the concentrations (mole fractions) and temperature in the bed(s)/tubes.
- 3) The particle size of the catalyst.
- 4) The pressure drop. (you don't have to solve the pressure drop equation as ODE, instead it can be evaluated at inlet conditions).

As **catalyst** you may select particles with a characteristic length ( $d_p$ ) of 3mm, 7 mm, 1 cm or 2 cm.

In case you selected the multi-tubular system, tubes with a diameter of 5, 10 and 15 cm are available. (you may neglect the wall thickness).

$$-r_{SO_2} = \frac{K_1 P_{O_2} P_{SO_2} \left( 1 - \frac{P_{SO_3}}{\sqrt{P_{O_2} P_{SO_2} K_p}} \right)}{(1 + K_2 P_{SO_2} + K_3 P_{SO_3})^2} \left( \frac{\text{mol}}{\text{kg}_{\text{catalyst}} \cdot \text{s}} \right)$$

p is in bar,  $K_{1-3}$  are defined below with T in K. There are no heat / mass transfer limitations at the level of the catalyst particles.

$$K_1 = 0.013 e^{\left( 12.16 - \frac{45500}{RT} \right)} \left( \frac{\text{mol}}{\text{kg}_{\text{catalyst}} \cdot \text{bar}^2 \cdot \text{s}} \right)$$

$$K_2 = e^{\left( -9.953 + \frac{71650}{RT} \right)} (\text{bar}^{-1})$$

$$K_3 = e^{\left( -71.745 + \frac{437300}{RT} \right)} (\text{bar}^{-1})$$

To calculate the pressure drop the equation below is given:

$$\frac{\Delta p}{\Delta x} = 150 \frac{(1 - \varepsilon)^2}{\varepsilon^3} \frac{\mu_g}{d_p^2} u + 1.75 \frac{(1 - \varepsilon)}{\varepsilon^3} \frac{\rho_g}{d_p} u^2$$

In this equation, u is the superficial velocity and  $\rho_g$  the density of the gas.

To calculate the overall heat transfer from tube (bed) to coolant the following relation can be used.

$$Nu = \frac{U d_t}{\lambda_g} = 3.5 Re_p^{0.7} e^{\left( \frac{-4.6 d_p}{d_t} \right)}$$

$$Re_p = \frac{\rho_g d_p u}{\mu_g}$$

$d_t$  is the diameter of the bed and U is the overall heat transfer coefficient ( $\text{W/m}^2/\text{K}$ ).



# Study material

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- Lecture slides / notes
- “Chemical reactor analysis and design”, Froment and Bischoff Publisher: John Wiley & Sons (1990) → on blackboard is the 1979 edition available
- “Fluidization engineering”, Daizo Kunii and Octave Levenspiel Publisher: Butterworth Heineman series in chemical engineering(1991)
- “Ullmann's Encyclopedia of Industrial Chemistry



# Contents Fixed bed reactors

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## ➤ Introduction

- Industrial applications of fixed bed reactors

## ➤ Design considerations and operation modes

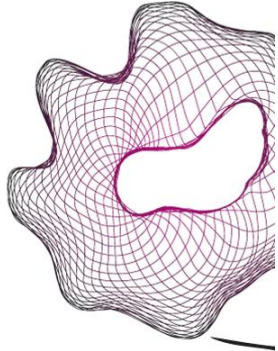
- Adiabatic versus non adiabatic operation mode
- Equilibrium reactions
- Autothermal operation
- Pressure drop limitations
- Catalyst Materials



# Contents Fixed bed reactors

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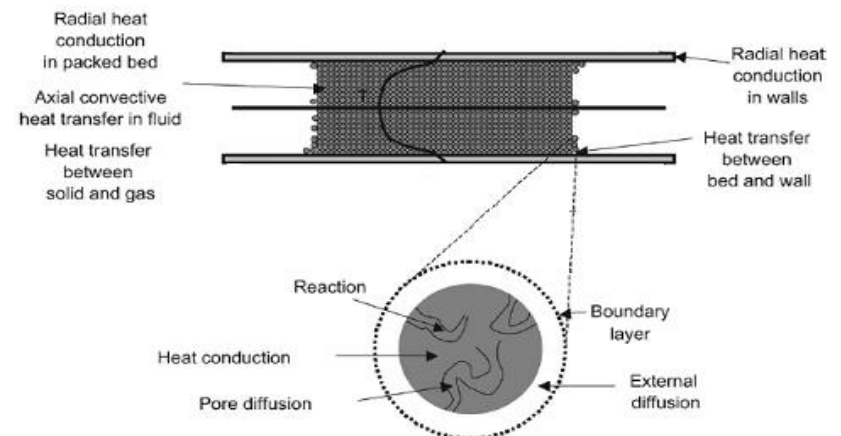
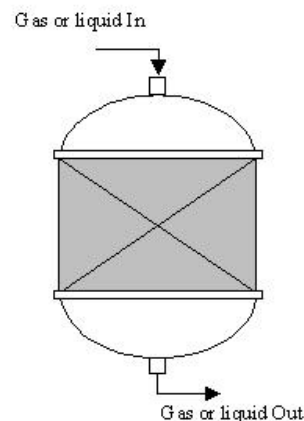
- **Transport phenomena in fixed bed reactors**
  - Description of prevailing phenomena
  - Frictional pressure drop and flow field
  - Mass and heat transport at macro scale
- **Design models for fixed bed reactors**
  - **Homogeneous one-dimensional model**
  - Homogeneous two-dimensional model (extra)
  - **Heterogeneous one-dimensional model**
  - Heterogeneous two-dimensional model (extra)



# What is a Fixed bed reactor

In a Fixed-bed reactor the catalyst (generally pellets) is held in place and does not move with respect to a fixed reference frame

To design a fixed bed reactor, material and energy balances are required for both the **fluid phase** (which occupies the interstitial region between catalyst particles), and the **catalyst particles** (in which the reactions occur)



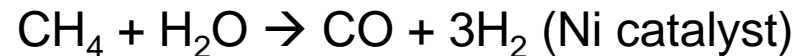


## Type of reactions

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Solid-catalyzed gas phase reactions

Only for very slow (preferably years) catalyst deactivation.



Gas solid reactions

Moving bed operation for reacting solid



Non steady state operation for e.g.



# Fixed bed reactor characteristics

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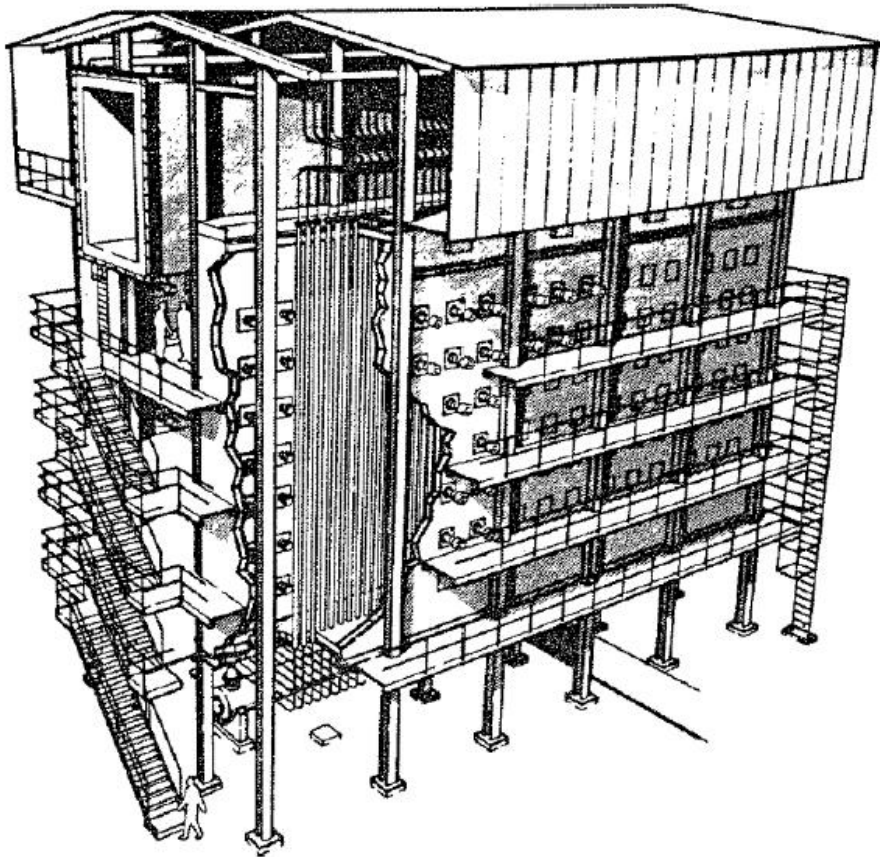
Particles	Must be fairly <b>large</b> and uniform for acceptable pressure drop. With poor temperature control these may <b>sinter</b> and <b>clog</b> in the reactor
Pressure drop	When using <b>larger particle sizes</b> pressure drop is not a serious problem
Heat exchange / transport	<b>Slow heat transfer (relatively) in the bed.</b> <b>Heat management</b> is often the limiting factor in <b>scale-up</b>
Temperature distribution in the bed	Where much heat is involved <b>large temperature gradients</b> can occur
Conversion	With plug flow of gas and proper temperature control (which is difficult) close to 100% of the theoretical conversion possible



# Industrial applications of fixed bed catalytic reactors

- ✓ Dehydrogenation of lower alkanes to corresponding alkenes
- ✓ Dehydrogenation of lower alcohols to corresponding aldehydes
- ✓ Partial oxidation reactions (o-xylene to phthalic anhydrides)
- ✓ Hydrogenation reactions
- ✓ Steam reforming of methane (synthesis gas production)
- ✓ Ammonia Synthesis
- ✓ Ammoxidation of Propane (Acrylonitrile)
- ✓ Oxychlorination of ethylene (vinyl chloride)
- ✓ Alkylation of aromatic compounds (ethylbenzene)
- ✓ Ammonia oxidation in nitric acid synthesis

# Industrial applications of fixed bed catalytic reactors



Multi-tubular reactor  
Hundred to thousands of tubes

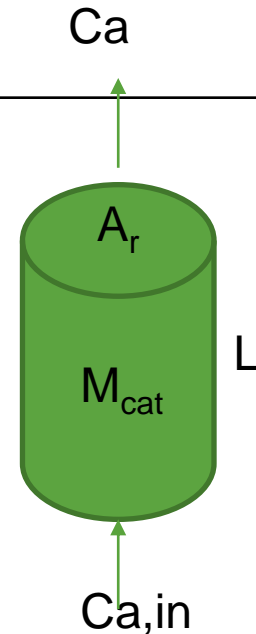
Table 11.6. Reactor Tube Data

	Syngas process
Inner tube diameter (m)	0.102
Outer tube diameter (m)	0.132
Tube length (m)	8
Temperature outside the wall (K)	1100
Heat coefficient for the metal (J/msK)	52

The Topsoe reformer design with tube and burner arrangement

# The simplest model of a fixed bed

- Isothermal
- First order catalytic reaction ( $A \rightarrow P$ )
  - $-R_a = kC_a$  (mol/kg<sub>catalyst</sub>/s)
- No gradients in catalyst particle
  - Superficial velocity,  $U_o = \phi_v/A_r$
  - Voidage,  $\varepsilon = \text{m}^3 \text{ fluid} / \text{m}^3 \text{ reactor}$
  - Density catalyst,  $\rho_c$  (kg / m<sup>3</sup> catalyst),  $\rho_{cr}$  (kg / m<sup>3</sup> reactor)
    - $\rho_{cr} = \rho_c(1-\varepsilon)$



$$C_a = C_{a,in} e^{\frac{-k\rho_c(1-\varepsilon)A_r L}{\phi_v}} = C_{a,in} e^{\frac{-kM_{cat}}{\phi_v}}$$

- Derive this yourself



## Selecting the operating temperature

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- Decomposition temperature of **reactants and products**. (safety)
- **Reactions rates** → **conversion and selectivity**.
- Effect of temperature and pressure on **equilibrium** in the case of reversible reactions.
- Properties of **materials** of construction.
- Cost of maintaining the operating temperature



# Non isothermal operations

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Non-Isothermal Reactor operation may be due to:

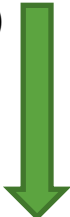
- High rates of reaction in combination with highly exo/endothermic reactions and poor heat transfer rates
- *Temperature may be varied deliberately to achieve optimum rate of reaction/selectivity or for material problems*

Non-Isothermal operation – Two cases:

- Adiabatic operation
- Non-adiabatic operation

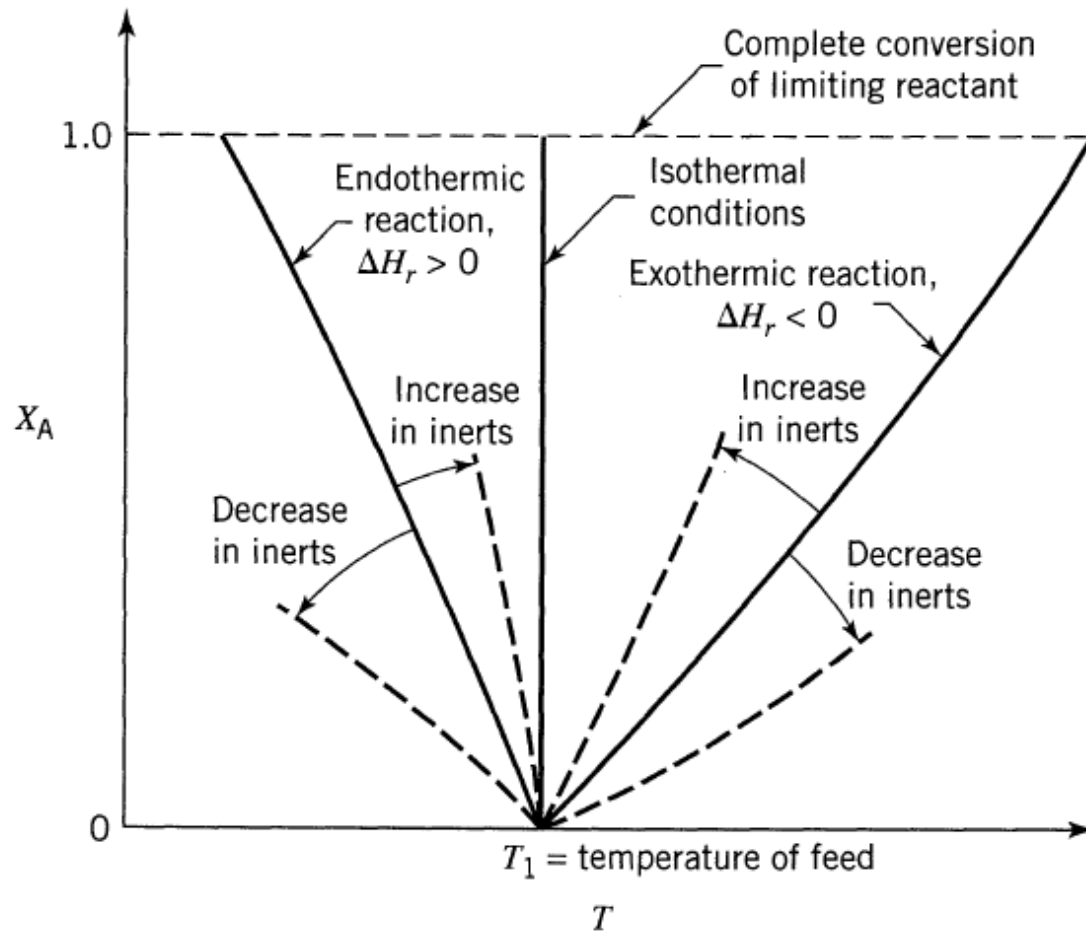
# Adiabatic versus non-adiabatic operation mode

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- Adiabatic operation
    - Due to the **simplicity of construction and operation** first possibility to be considered.
    - For large  $\Delta H_r$  a (single) adiabatic bed is not possible ( $\Delta T$  over catalyst bed has to be limited)
- 
- Non-adiabatic operation
    - Staging with intermediate heating for endothermic reactions
    - Cold reactant injection for mildly exothermic reactions
    - Multi-tubular type for strong exothermic reactions (small diameter tubes → high heat transfer rates)



## Energy balance (equation) for adiabatic operation



# Energy balance for non-adiabatic operation Ethylene oxide example

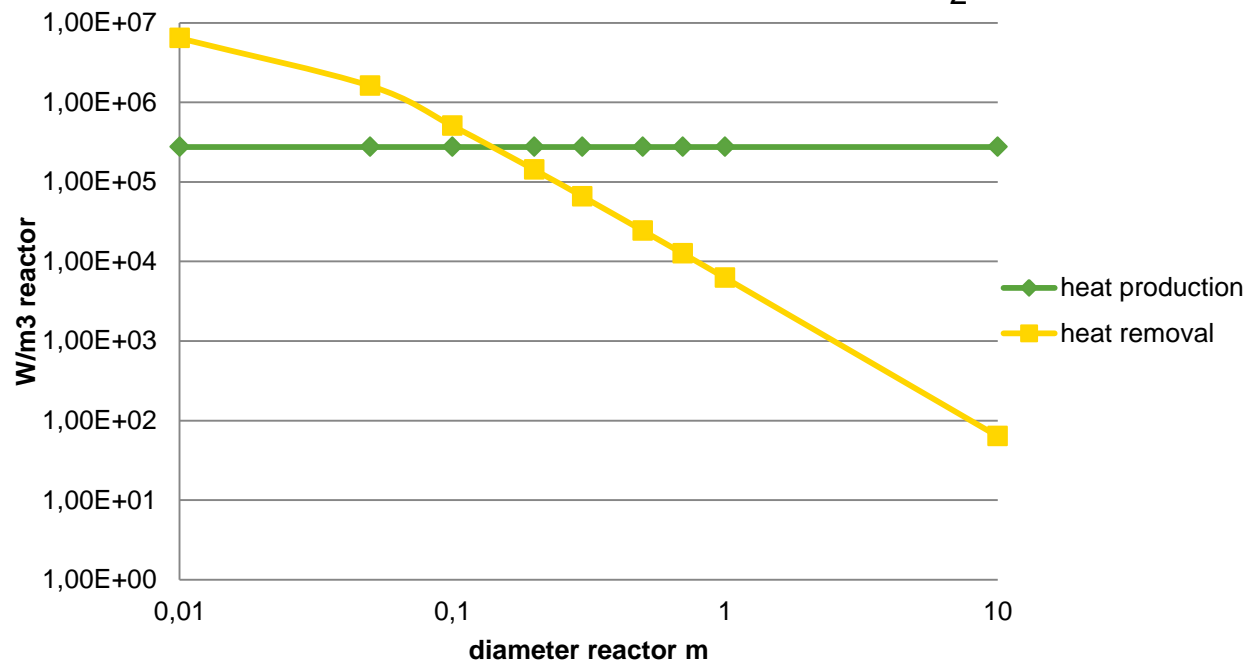
$R_p$  in mol/kg cat/s  
Production rate of P

$$Heat_{production} = R_p(T^f) * \rho_{cr} * (-\Delta H_r)$$

$$Heat_{removal} = \frac{4}{d_t} \alpha [T^f - T^c]$$

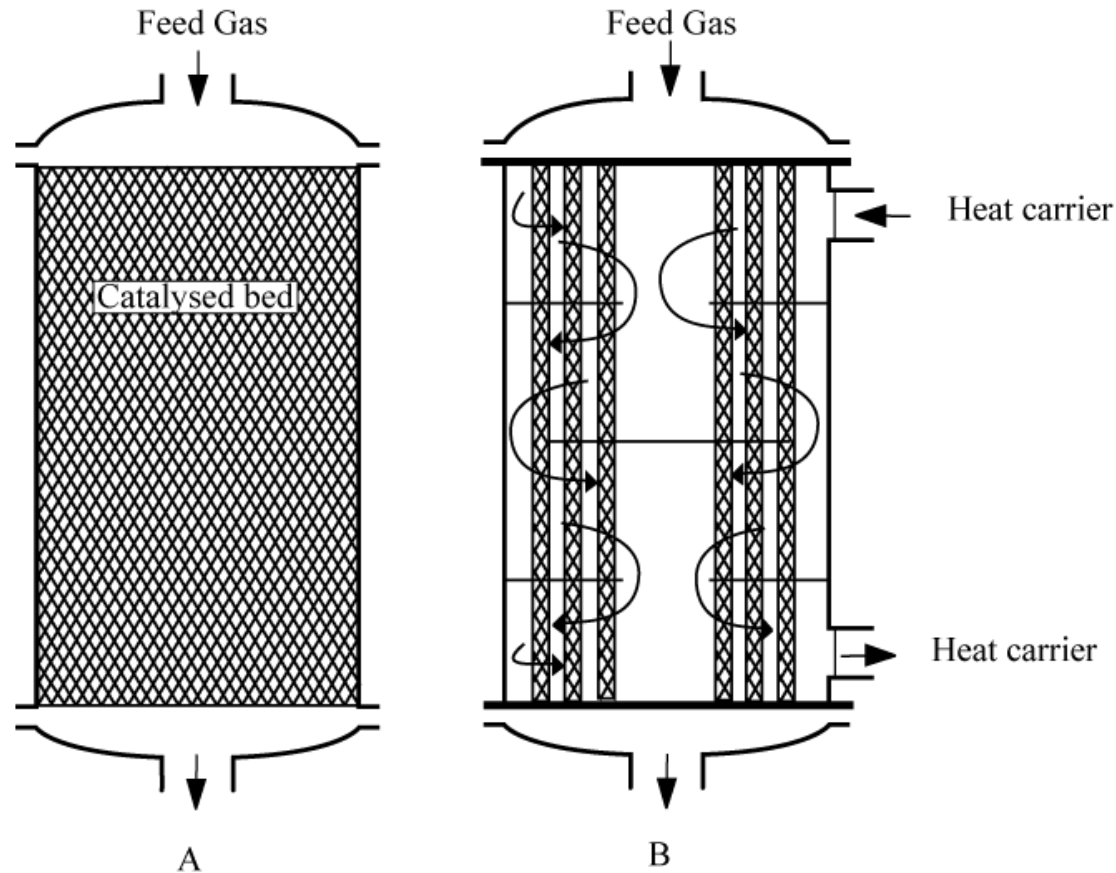
$$\frac{\alpha d_t}{\lambda_g} = 3,5 \left( \frac{d_p \rho_f u}{\mu} \right)^{0,7} e^{-4,6 \frac{d_p}{d_t}}$$

$T^f = 275 \text{ } ^\circ\text{C}$ ,  $T^c = 225$ , 10 bar, 7%  $\text{O}_2$



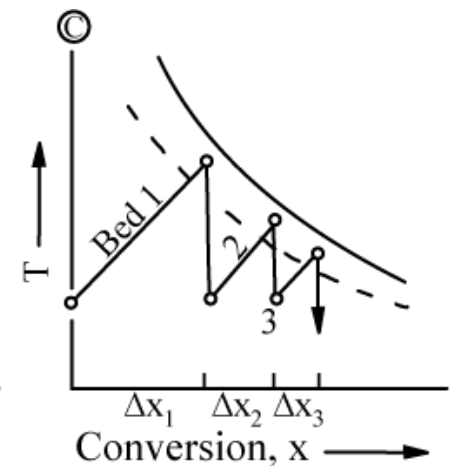
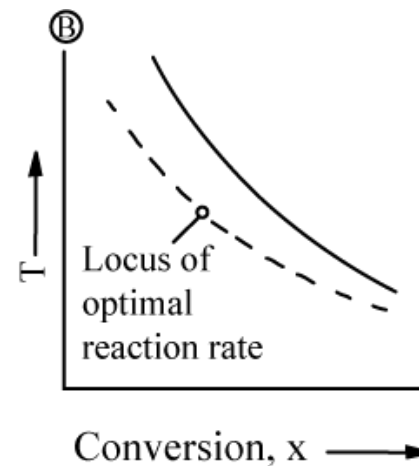
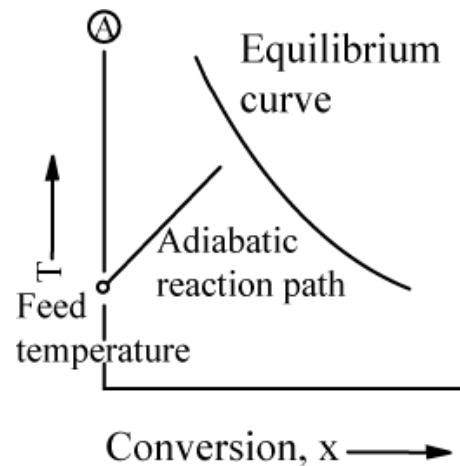
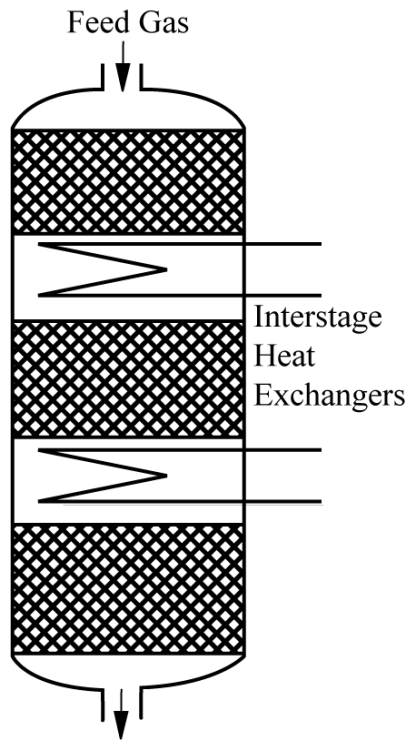
## Adiabatic versus non-adiabatic operation mode

- Single adiabatic bed (A)
  - Used for reactions with a small heat effect
- Multitubular reactor (B)
  - Used for reactions with a large heat effect



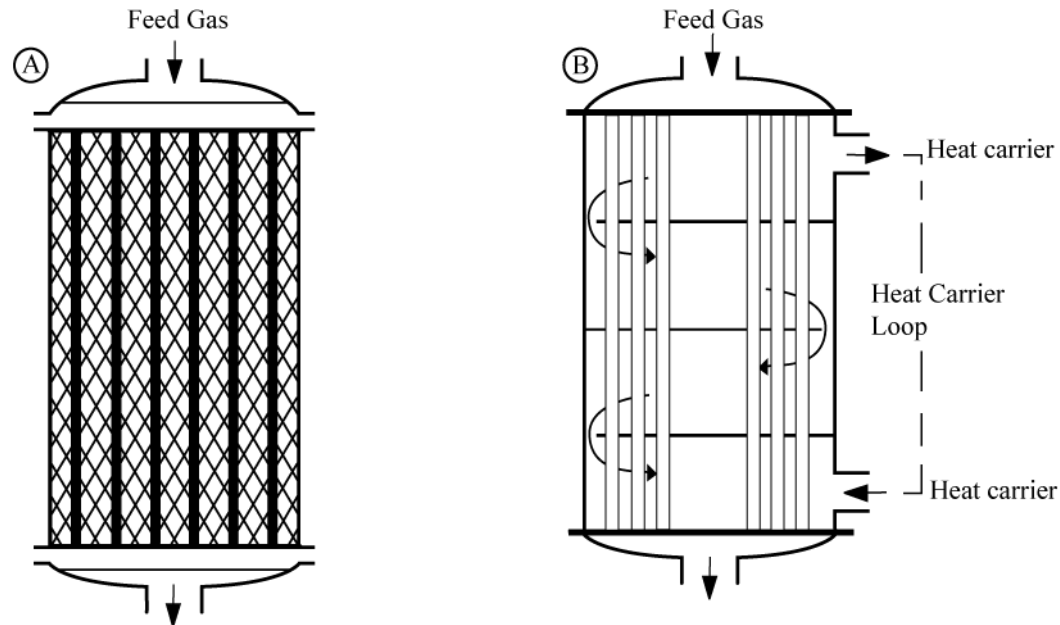
## Exothermic equilibrium reactions

- Multibed adiabatic reactor with intermediate cooling + corresponding temperature versus conversion profile (“sawtooth” profile)



## Multi-tubular fixed bed

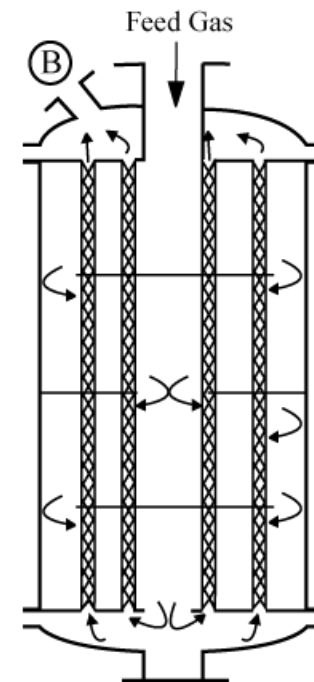
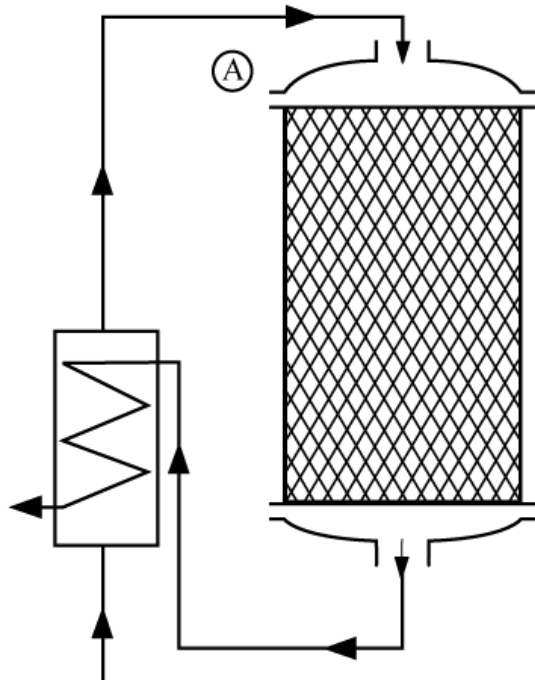
- Cooling tubes inside catalyst bed (A)
- Multitubular bed with exterior cooling agent (B)



Note: for highly exothermic reactions like partial oxidations the multitubular reactor concept is preferred (intrinsically safer)

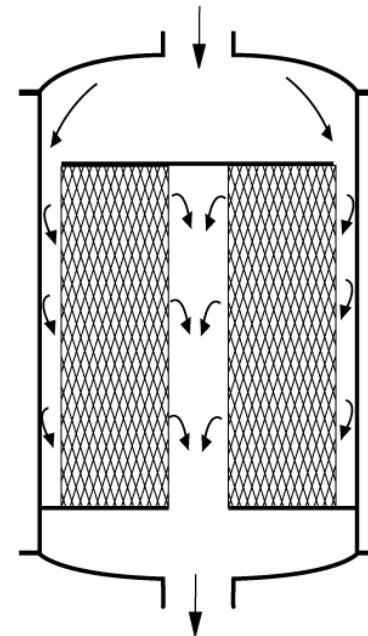
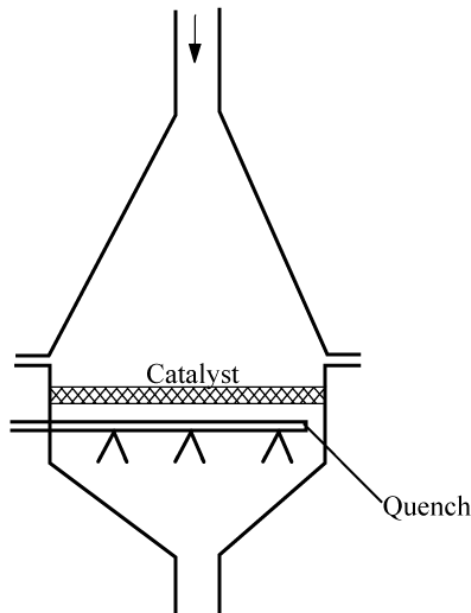
## Autothermal operation

- For mildly exothermic reactions autothermal reactor operation is possible: the **heat of reaction** is used to **heat the reactant mixture** to the desired reaction temperature: external and internal heat exchange



# Limiting the pressure drop

Limitation of pressure drop  $\Delta p$  due to necessity of recycling unconverted reactants (compression important cost item) low depth of catalyst bed but leads (for a given volumetric flow rate  $\Phi_v$  and catalyst volume  $V_s$ ) to fixed bed reactors with excessive diameters. This has led to the use of disk reactors and radial flow reactors

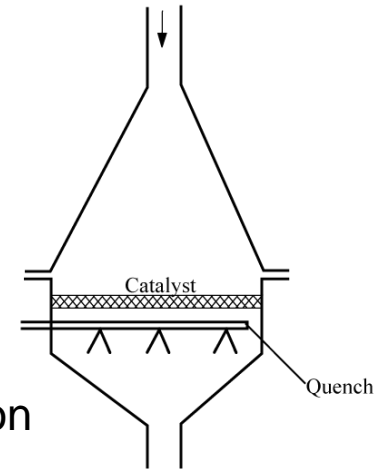


## Disk (pancake) reactors

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### ➤ Characteristics of disk reactors

- ✓ Adiabatic operation
- ✓ Thin catalyst “layer” consisting of wires
- ✓ Very low pressure drop
- ✓ Extremely short contact time
- ✓ Immediate quenching of product mixture to avoid back-conversion



### ➤ Typical applications

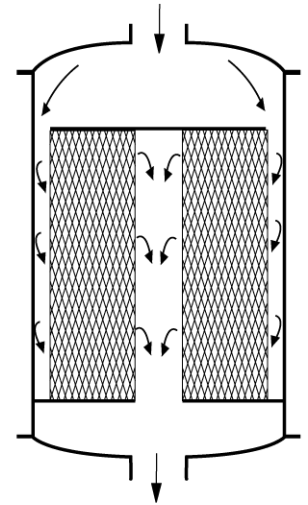
- ✓ Ammonia oxidation in nitric acid production
- ✓ Oxidative dehydrogenation of methanol in formaldehyde production



## Radial flow

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- Characteristics of radial flow reactors
  - ✓ Adiabatic operation
  - ✓ Catalyst contained between two permeable cylindrical screens
  - ✓ Low pressure drop
  - ✓ Catalyst volume (reactor capacity) can be increased with  $L$  (axial dimension) without alternating contact time  $\tau$  in the catalyst bed
  - ✓ Alternative for disk reactor if a large amount of catalyst is needed
  - ✓ Sealing of upper portion of the bed is critical
  
- Typical applications: gas purification processes (removal of traces of impurities from huge gas streams low  $\Delta p$  is necessity)



## pressure drop limitations

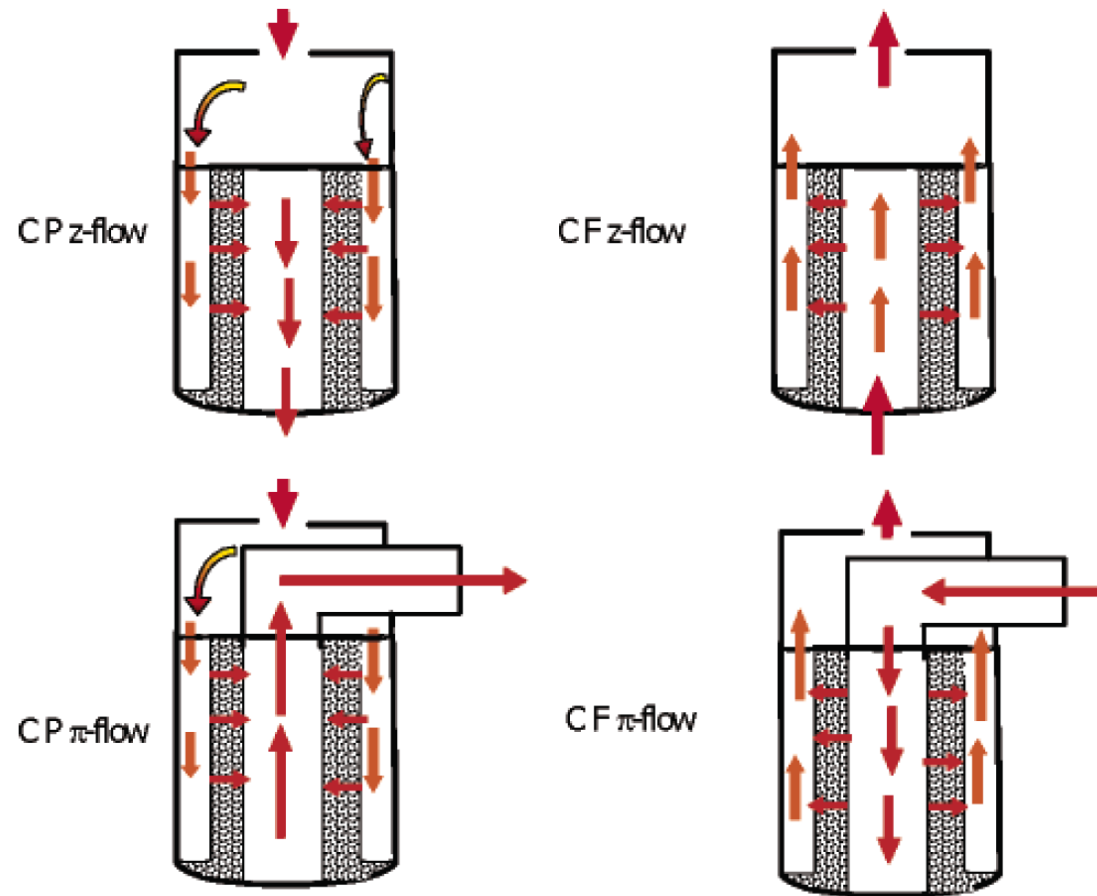
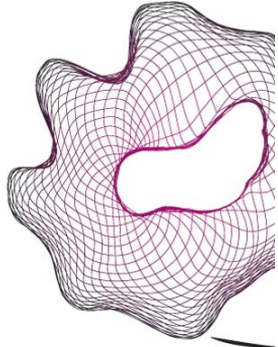


Figure 1. Four possible flow configurations for a radial flow reactor.



## Catalyst materials (for details see catalysis courses)

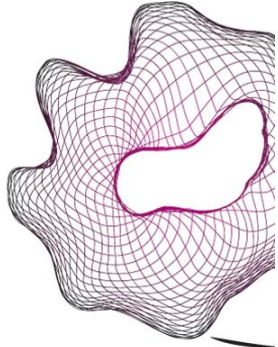
- Requirements for catalyst material
  - ✓ Uniform reaction conditions inside catalyst particles (internal concentration and temperature gradients as small as possible)
  - ✓ Uniform flow distribution to achieve good contacting
  - ✓ High external transport rates of mass and heat
  - ✓ Low frictional pressure drop
  - ✓ High catalyst concentration
  - ✓ Mechanical strength
  - ✓ Low deactivation rate
  
- note: some of the requirements for the catalyst material can not be satisfied simultaneously and some kind of compromise has to be accepted in practice



## Catalyst materials

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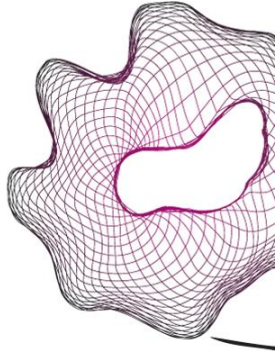
- Catalyst geometries can roughly be divided in two important classes: **random packings** and **monolith structures**
- Some important properties of random packings such as spheres and solid hollow cylinders
  - ✓ Turbulent flow conditions: small external mass transfer resistance
  - ✓ High catalyst conductivity: small internal heat transfer resistance
  - ✓ External mass and heat transport rates vary locally to large extent
  - ✓ Careful filling procedure required for tubes of multitubular reactor to minimize nonuniform feed stream distribution over the tubes
  - ✓ Relatively cheap



## Random packings

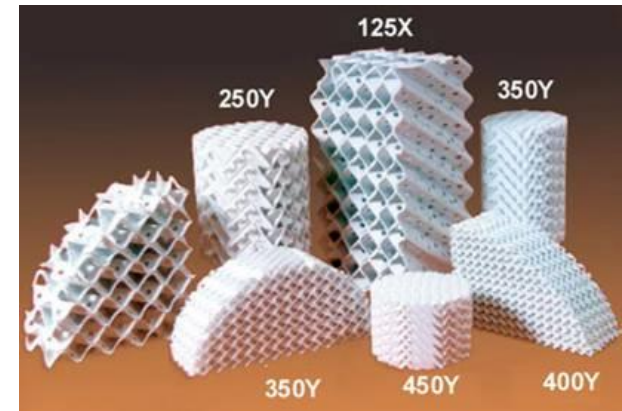
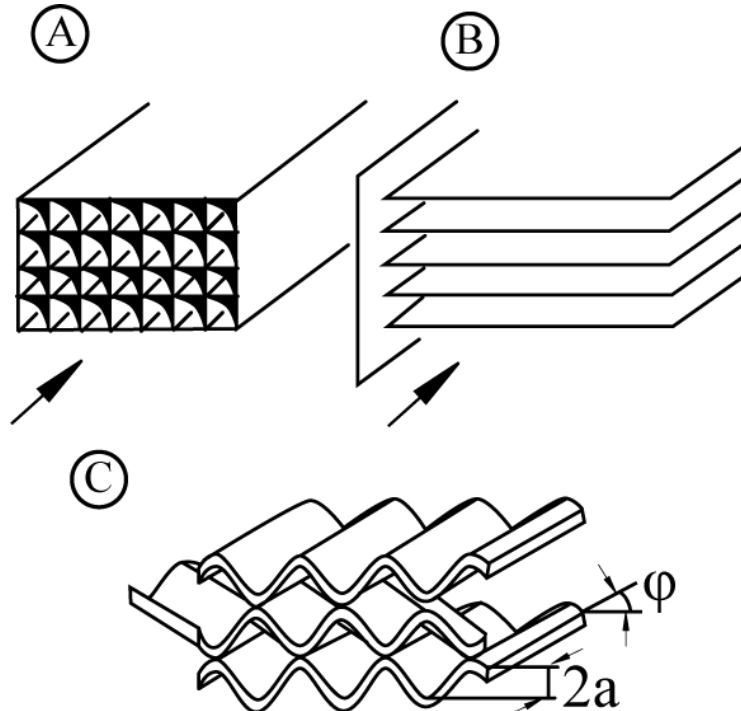


ALUMINA CATALYST CARRIERS / BASES & TOWER PACKINGS



## Monolith structures

Square channel monolith (A), Parallel plate monolith (B) and Corrugated plate monolith (C)



## Monoliths

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- Some important properties of monolith structures which typically consist of narrow parallel channels (excepted corrugated plate monolith)
  - ✓ More uniform mass and heat transfer due to geometry (no wakes as encountered with spheres and cylinders)
  - ✓ Due to small hydraulic diameter  $d_h$  laminar flow conditions prevail with typically external mass transfer limitation
  - ✓ Sherwood (Sh) and Nusselt (Nu) numbers for external mass and heat transfer depend on channel geometry
  - ✓ Due to small hydraulic diameter of monolith structures the external mass and heat transfer coefficients are constant (fully developed mass and heat transfer regimes)
  - ✓ Fouling is an important issue