Let's put it all together...

Kinetics of heterogeneously catalyzed reactions:

- surface-specific reaction rate \( r'' \) (often also: weight-specific rate \( r' \))
- comprises three steps: adsorption, desorption and reaction
- often \( r_{ads}, r_{des} \gg r_r \) \( \rightarrow \) LH-kinetics
- all catalysts are subject to “aging” = deactivation over time
- need to consider mass transfer limitations (external & internal)

Despite all these differences to homogeneous kinetics, we can still apply our previously derived design equations towards the design of catalytic reactors, but:

- we have to account for the reduced “empty volume” of the reactor (\( \varepsilon \))
- we have to use the “right” reaction rate \( r: \quad r = r'' \frac{A_{cat}}{V_R} \eta a_s a_p a_c \)

So, what do catalytic reactors look like?
Catalytic Reactors: PBR

The most simple (and hence also very commonly used) catalytic reactor is the packed bed reactor (PBR).

It is essentially a PFR and hence can be designed with the PFR design equations. However, since a significant part of the reactor is now filled with solid catalyst, we have to adjust the reactor volume for that fact.

Total reactor volume: \( V_R = \)

We define the fraction of the reactor volume that is not filled with catalyst (i.e. the “empty part”) as

\[
\text{void fraction } \epsilon = \]

The flow velocity in a PBR is often given as \( u_0 \), which is the (hypothetical) velocity of the fluid in the reactor tube, if the reactor was empty.

Heterogeneous Catalysis not only changes the reaction kinetics, it also affects the fluid flow in the reactor!
Design of Catalytic Reactors: Re"}

We saw before, that the reaction rate for a heterogeneously catalysed reaction is a surface-specific rate rather than a volume specific rate. How can we handle that in our reactor design equation?

For a catalyst bed with volume $V_{\text{cat}}$ consisting of pellets with density of $\rho_{\text{cat}}$ (as usual in weight/volume) and a specific surface area of $S_g$ (in area per weight of catalyst, i.e. in $[\text{m}^2/\text{g}]$).

$$S_g \times \rho_{\text{cat}} = \frac{\text{catalyst surface area}}{\text{catalyst volume}}$$

$$S_g \times \rho_{\text{cat}} \frac{V_{\text{cat}}}{V_R} = S_g \times \rho_{\text{cat}} (1 - \varepsilon)$$
Weight-Specific Rate: $r'$

Since the surface area of a pellet is much harder to determine than its weight, it is common in industry to give catalytic reaction rates per catalyst weight, $r'$. Hence the pseudo-homogeneous reaction rate must now be calculated from:

In this case, we can size a PBR from the PFR design equation simply by replacing the reactor volume with the catalyst weight and $r$ with $r'$, for example:

\[
\text{PFR:} \quad \text{PBR:}
\]

where $W$ denotes the weight (mass) of the catalyst.

This equation will yield (after integration) the catalyst mass necessary to obtain a desired conversion. How do you convert this into a reactor volume?

What else should you be aware of??
How about the Energy Balance?

PFR/BR energy balance (steady state):

volume-specific

weight-specific

How about the CSTR?
Catalytic Reactors II: Fluidized Bed

If the flow velocity of the fluid in a (partially filled) PBR is sufficiently increased, the fluid starts to entrain the solid catalyst. This is called 'fluidization' of the catalyst bed and the resulting reactor is called 'fluidized bed reactor'.

Fluidization of the catalyst bed is a quite effective way of achieving a good mixing in a fixed-bed reactor. We get a CSTR-like behavior in a fluidized bed!

Like in the PBR-vs-PFR example before, the reactor volume is now different from the empty CSTR and has to be accounted for in the design equation:

\[ \text{where now:} \]

(Like so often in reaction engineering, the CSTR equation yields a decent approximation of the 'true' reactor behaviour of a fluidised bed. A precise and detailed design is considerably more complex, and one of the reasons of the 'scale-up' problems that plague fluidized beds!)
Solids Fluidization...

Change of fluidization with gas flow rate \((u_{mf} = \text{minimal fluidization velocity})\)

- **onset of fluidization**
- **bubble formation**
- **bubbles \(\rightarrow\) slugs**
- **entrainment and separation of solids**
- **circulating bed**

Increasing velocity of fluid flow
More Catalytic Reactors: 3-Phase

The above mentioned reactors are 2-phase reactors (typically solid catalyst with gaseous or liquid reactants). Many reactions involve 3 phases, with typically the catalyst being solid, one of the reactants in the liquid phase and one being gaseous.

(slurry reactor)

’trickle bed’ reactor

(A detailed description of 3-Phase reactors is very complex and beyond the scope of this class)
One More Problem: Pressure Drop

Before proceeding to 'design' a catalytic reactor, however, we have to have a brief look at one more complication: the pressure drop in catalytic reactors.

Flow through a pipe always leads to pressure drop (it is in fact the pressure differential which induces the flow through the reactor!). For gaseous flow in sufficiently wide reactor tubes, this pressure drop is often negligible. However, for packed beds, this pressure drop can become severe!

Liquids are incompressible, hence (reasonable) pressure increases do not change density, hence do not affect concentrations: the reaction rates remain unchanged.

Gas density (and hence concentrations) changes with pressure, and hence the reaction rate can be significantly affected by pressure changes!

Generally, the pressure drop can be calculated from a momentum balance for the fluid flow in the reactor. However, in practice, empirical equations are almost always used to calculate pressure drop in PBRs.
The Ergun Equation

For packed bed reactors, a largely empirical equation is most often used to calculate the pressure drop: the ‘Ergun Equation’:

\[ P = \frac{150 \mu G^2 \varepsilon}{D_p^2 \rho} + \frac{1.75 \mu G \varepsilon}{D_p \rho} + \frac{9 \mu G \varepsilon}{D_p^2 \rho} \]

with:
- \( P \) - pressure
- \( z \) - axial coordinate (‘length’)
- \( \varepsilon \) - void fraction = (void volume)/(total bed volume)
- \( D_p \) - catalyst particle diameter
- \( \mu \) - gas viscosity
- \( G = \rho u \) = superficial mass velocity (= (mass flow)/(reactor cross section))
- \( \rho \) - gas density

Use SI units!
Ergun Equation, Cont’d

Of all the parameters on the right hand side, only the (fluid) density varies with P. How?

Hence, the Ergun equation becomes:
The Ergun Equation, Cont’d

Usually, the ‘Ergun Equation’ is re-written in a simplified form (‘simplified only with regard to writing; it is still the complete equation!’):

\[ \text{density of catalyst} = (1-\varepsilon) \cdot \text{area of reactor} \cdot \text{density} \]

where we have lumped all parameters from the Ergun equation into \( \beta_0 \):

For PBR, we often write the design equations in terms of catalyst weight rather than reactor length:

\[ \text{catalyst weight} = \text{catalyst volume} \cdot \text{density} = (1-\varepsilon) \cdot \text{area of reactor} \cdot \text{z} \cdot \text{density} \]

\[ \frac{dW}{dz} = (1-\varepsilon) \cdot \text{area of reactor} \cdot \text{density} \]

Hence, we get:

\[ (\text{alternate form}) \]
Designing Catalytic Reactors: PBR

Energy Balance:

Mass Balance(s):

Pressure Drop: (momentum balance)

Ergun Parameter:

Variable Density:

‘little helper equations’
The BIG Example

Ethylene oxide (EO) is a major commodity chemical, with a production of about 3 million tons/a in the US (1997). (At 1997 price levels for ethylene oxide this corresponds to a market value of about $4 billion!) Major uses for EO are antifreeze (30%), polyester (30%), and surfactants and solvents (~ 10% each).

Your consulting company MeMyself&Others Inc. has taken on a new assignment to design a fixed-bed reactor for EO production via the catalytic reaction of ethylene with oxygen \( \left( C_2H_4 + 0.5 \text{ O}_2 \rightarrow \text{EO} \right) \), using a secret (but silver-based) catalyst.

The reactor is operated isothermally at 260°C, and ethylene is fed at a rate of 200 mol/h at an inlet pressure of 10 atm. A stoichiometric amount of oxygen is added through an air feed. The reactor is a multitubular reactor with 1000 parallel tubes, each with an inner diameter of 1.5" (38.1 mm). The tubes are filled with catalyst particles (diameter = 0.25" (6.35 mm), particle density \( \rho_{cat} = 120 \text{ lb/ft}^3 = 1922 \text{ kg/m}^3 \)), resulting in a bed void fraction of \( \varepsilon = 0.45 \).

The kinetics have been determined as: \(-r'_{C_2H_4} = k' P_{C_2H_4}^{1/3} P_{O_2}^{2/3} \) [mol/(lb cat · h)] with a rate coefficient at 260°C of \( k' = 4 \text{ mol/(atm lb · cat h)} \).

How much catalyst is needed to achieve 60% ethylene conversion?

(For simplicity, assume that the properties of the reaction mixtures are at this temperature always identical to those of air.)