Notes for X-REA3
Modelling and Simulation of Non-ideal Reactors
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Publication date:
2010

Document version
Peer reviewed version

Citation for published version (APA):

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NOTES for X-REA3
Modelling and Simulation of Non-ideal Reactors

1st Edition

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2010
1. Dispersion models for Fixed Bed Reactors

In both fixed bed and turbular reactors the ideal assumption is, that the gas or liquid flow is plug flow. Though this assumption in an early design phase is quite accurate in real life severe deviations from this ideal might be encountered. These deviations can to some extent be predicted based on the reactor geometry, fluid properties and for fixed beds, solid catalyst properties. The simplest predictive models that include these factors are the so called dispersion models which will be derived below.

1.1 The Pseudohomogeneous Molar Balance for Turbular Fixed Beds

The basic assumption in the pseudohomogeneous model for turbular reactors is, that the fixed bed behaves as a continuum. The model thus does not directly take into account that the reactor consists of both porous catalyst pellets and the gas or liquid between the individual pellets. Instead these factors are incorporated in the model parameters. Based on this assumption a relatively simple 2-dimensional transport model can be setup for turbular reactors.

In order to set up the pseudohomogeneous model for a turbular fixed bed reactor a molar balance is first set up over a small shell from $z$ to $z+\Delta z$ and $r$ to $r+\Delta r$ inside the reactor as shown in figure 1.1.

![Figure 1.1. Shell for setting up molar and heat balances over a fixed bed reactor.](image)

The steady state molar balance is

\[
\begin{align*}
\text{In} & + \quad \text{Generated} \quad = \\
& \\
& \\
& \\
& \\
& \\
\end{align*}
\]

\[
\begin{align*}
& u_{\text{fx}} \cdot A_z \cdot C_{A} \cdot \Delta t + N_{A_A} \cdot A_z \cdot \Delta t + N_{A_r} \cdot A_t \cdot \Delta t + \rho_p \cdot (1 - \varepsilon_{\text{fx}}) \cdot \eta_g \cdot r_A \cdot A_z \cdot \Delta z \cdot \Delta t = \\
& \\
& \\
& \\
& \\
& \\
\end{align*}
\]

\[
\begin{align*}
& \\
& \\
& \\
& \\
& \\
\end{align*}
\]

\[\text{(1.1)}\]
Where $A_r$ is the radial cross sectional area at radius $r$ (see figure (1.1)) [m$^2$]
$A_z$ is the axial cross sectional area at length $z$ (see figure (1.1)) [m$^2$]

$C_A$ is the molar concentration of component A $\left[ \frac{\text{mol}}{\text{m}^3} \right]$

$N_{Ar}$ is the radial dispersive flux of component A $\left[ \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right]$

$N_{Az}$ is the axial dispersive flux of component A $\left[ \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right]$

$r$ is the radial position (see figure (1.1)) [m]

$r_A$ is the kinetic rate of formation of component A $\left[ \frac{\text{mol}}{\text{kg \text{cat} \cdot \text{s}}} \right]$

$u_{\text{fix}}$ is the velocity in the fixed bed $\left[ \frac{\text{m}}{\text{s}} \right]$

$z$ is the axial position (see figure (1.1)) [m]

$\Delta r$ is the small control radial width interval over which the molar balance is setup (see figure (1.1)) [m]

$\Delta t$ is the small control time interval over which the molar balance is setup [s]

$\Delta z$ is the small control axial length interval over which the molar balance is setup (see figure (1.1)) [m]

$\varepsilon_{\text{fix}}$ is the porosity of the fixed bed, typically around 0.4 to 0.5.

$\eta_G$ is the efficiency factor for the catalyst pellet, including internal and external mass transfer limitations

$\rho_p$ is the density of the catalyst pellet $\left[ \frac{\text{kg}}{\text{m}^3} \right]$

The cross sectional area in the axial direction $A_z$ and the radial area in the radial direction $A_r$ are equal to:

$$A_z = \pi \cdot (r + \Delta r)^2 - \pi \cdot r^2 - 2 \cdot \pi \cdot r \cdot \Delta r \cdot r \tag{1.2}$$

$$A_r |_{r} = 2 \cdot \pi \cdot \Delta z \cdot r |_{r}$$

This inserted in equation (1.1), the molar balance, yields:

$$2 \cdot \pi \cdot r \cdot \Delta t \cdot (u_{\text{fix}} \cdot C_A |_{z=\Delta z} - u_{\text{fix}} \cdot C_A |_{z}) \cdot (N_{Ar} |_{r=\Delta r} - N_{Ar} |_{r}) \tag{1.3}$$

$$\Delta z$$

$$\Delta t$$

In order to be useful, formula (1.3) has to be restated in partial differential form. This is done as follows:

$$\frac{u_{\text{fix}} \cdot C_A |_{z=\Delta z} - u_{\text{fix}} \cdot C_A |_{z}}{\Delta z} + \frac{N_{Az} |_{z=\Delta z} - N_{Az} |_{z}}{\Delta z} + \frac{1}{r} \cdot \frac{N_{Ar} |_{r=\Delta r} - N_{Ar} |_{r}}{\Delta r} + \rho_p \cdot (1 - \varepsilon_{\text{fix}}) \cdot \eta_G \cdot (-r_A) = 0 \tag{1.4}$$

Taking the limit as $\Delta z$ and $\Delta r$ approach zero leads to:

$$\frac{\partial (u_{\text{fix}} \cdot C_A)}{\partial z} + \frac{\partial N_{Az}}{\partial z} + \frac{1}{r} \cdot \frac{\partial (r \cdot N_{Ar})}{\partial r} + \rho_p \cdot (1 - \varepsilon_{\text{fix}}) \cdot \eta_G \cdot (-r_A) = 0 \tag{1.5}$$
Equation (1.5) as it stands has three dependent variables, the concentration, $C_A$, the axial flux $N_{Az}$ and the radial flux $N_{Ar}$. This can be reduced to only one dependent variable, the concentration, by assuming that the fluxes can be described by a Fick’s First Law like equation:

$$N_{Az} = -D_{rfix} \cdot \frac{dC_A}{dz}$$

$$N_{Ar} = -D_{rfix} \cdot \frac{dC_A}{dr}$$

Where $D_{rfix}$ is the radial dispersion coefficient $\left[\frac{m^2}{s}\right]$

$D_{rfix}$ is the axial dispersion coefficient $\left[\frac{m^2}{s}\right]$

Inserting equations (1.6) into the molar balance (1.4) yields:

$$\frac{\partial (u_{fix} \cdot C_A)}{\partial z} + \frac{\partial \left(-D_{rfix} \cdot \frac{dC_A}{dz}\right)}{\partial z} + \frac{1}{r} \cdot \frac{\partial \left(-r \cdot D_{rfix} \cdot \frac{dC_A}{dr}\right)}{\partial r} + \rho_p \cdot (1 - \epsilon_{fix}) \cdot \eta_A \cdot (-r_A) = 0$$

which can be reshaped into the final equation for the molar balance for the pseudohomogeneous fixed bed reactor:

$$\frac{\partial (u_{fix} \cdot C_A)}{\partial z} - \frac{\partial}{\partial z \cdot \frac{d^2 C_A}{dz^2}} - D_{rfix} \cdot \frac{\partial^2 C_A}{\partial r} - D_{rfix} \cdot \frac{\partial C_A}{\partial r} + \rho_p \cdot (1 - \epsilon_{fix}) \cdot \eta_A \cdot (-r_A) = 0$$

with the boundary conditions:

$$\begin{align*}
\text{at:} & \quad z = 0: \quad u_{fix} \cdot (C_{A0} - C_A) = -\epsilon_{fix} \cdot D_{rfix} \cdot \frac{\partial C_A}{\partial z} \\
\text{at:} & \quad z = L_{fix}: \quad \frac{\partial C_A}{\partial z} = 0 \\
\text{at:} & \quad r = 0: \quad \frac{\partial C_A}{\partial r} = 0 \\
\text{at:} & \quad r = R_{fix}: \quad \frac{\partial C_A}{\partial r} = 0
\end{align*}$$

Where $C_{A0}$ is the molar concentration of component A in the feed to the reactor $\left[\text{mol m}^{-3}\right]$

$L_{fix}$ is the length of the reactor [m]

$R_{fix}$ is the internal radius of the reactor tube [m]
1.2 The Pseudohomogeneous Heat Balance for Turbular Fixed Beds

A heat balance can be set up in similar fashion:

Heat Balance:

\[
\begin{align*}
\text{In} & + \text{Generated} = \\
& u_{\text{fx}} \cdot A_z \cdot C_{\text{tot}} \cdot H_{\text{tot}} |_{t} \cdot \Delta t + J_z \cdot A_z |_{t} \cdot \Delta t + J_r \cdot A_A |_{t} \cdot \Delta t + \rho_p \cdot (1 - \epsilon_{\text{fx}}) \cdot \eta_G \cdot (-r_A) \cdot (-\Delta H_{r_A}) \cdot A_z \cdot \Delta z \cdot \Delta t = \\
& \text{Out} + \text{Accumulated} \\
& u_{\text{fx}} \cdot A_z \cdot C_{\text{tot}} \cdot H_{\text{tot}} |_{t+\Delta t} + J_z \cdot A_z |_{t+\Delta z} \cdot \Delta t + J_r \cdot A_A |_{t+\Delta r} \cdot \Delta t + 0 \\
\end{align*}
\]

(1.10)

Where

- \( C_{\text{tot}} \) is the total molar concentration of the fluid \( \left[ \frac{\text{mol}}{\text{m}^3} \right] \)
- \( H_{\text{tot}} \) is the molar enthalpy of the fluid mixture \( \left[ \frac{\text{J}}{\text{mol}} \right] \)
- \( J_z \) is the the radial heat flux \( \left[ \frac{\text{J}}{\text{m}^2 \cdot \text{s}} \right] \)
- \( J_r \) is the the axial heat flux \( \left[ \frac{\text{J}}{\text{m}^2 \cdot \text{s}} \right] \)
- \( \Delta H_{r_A} \) is the molar enthalpy of reaction based on component A \( \left[ \frac{\text{J}}{\text{mole of A}} \right] \)

Inserting the equations (1.6) for the cross sectional areas into equation (1.10) leads to:

\[
\begin{align*}
2 \cdot \pi \cdot r \cdot \Delta r \cdot \left( (u_{\text{fx}} \cdot C_{\text{tot}} \cdot H_{\text{tot}} |_{t+\Delta z} - u_{\text{fx}} \cdot C_{\text{tot}} \cdot H_{\text{tot}} |_{t} \cdot J_z |_{t+\Delta z} - J_z |_{t} \cdot \Delta z + 2 \cdot \pi \cdot r \cdot \Delta z \cdot (J_r |_{t+\Delta r} - J_r |_{t}) \right) \\
+ \rho_p \cdot (1 - \epsilon_{\text{fx}}) \cdot \eta_G \cdot (-r_A) \cdot \Delta H_{r_A} \cdot 2 \cdot \pi \cdot r \cdot \Delta r \cdot \Delta z = 0 \\
\end{align*}
\]

(1.11)

which is then restated as:

\[
\begin{align*}
\frac{u_{\text{fx}} \cdot C_{\text{tot}} \cdot H_{\text{tot}} |_{t+\Delta z} - u_{\text{fx}} \cdot C_{\text{tot}} \cdot H_{\text{tot}} |_{t}}{\Delta z} + J_z |_{t+\Delta z} - J_z |_{t} \cdot \frac{1}{\Delta z} + \frac{J_r |_{t+\Delta r} - J_r |_{t}}{\Delta r} \cdot \frac{1}{r} + \rho_p \cdot (1 - \epsilon_{\text{fx}}) \cdot \eta_G \cdot (-r_A) \cdot \Delta H_{r_A} \\
= 0 \\
\end{align*}
\]

(1.12)
Letting $\Delta z$ and $\Delta r$ approach zero yields:

$$
\frac{\partial (u_{\text{fix}} \cdot C_{\text{tot}} \cdot H_{\text{tot}})}{\partial z} + \frac{\partial J_z}{\partial z} + \frac{1}{r} \cdot \frac{\partial (r \cdot J_r)}{\partial r} + \rho_p \cdot (1 - \epsilon_{\text{fix}}) \cdot \eta_d \cdot (-r_s) \cdot \Delta H_{r_s} = 0
$$

(1.13)

In order to achieve further simplifications the enthalpy based on total mass, $H_{m_{\text{tot}}}$, is used instead of based on total number of moles:

$$
A_z \cdot u_{\text{fix}} \cdot C_{\text{tot}} \cdot H_{\text{tot}} \left[ \frac{m^2 \cdot m \cdot \text{mol} \cdot \text{kJ}}{s \cdot m^3 \cdot \text{mol}} \right] = A_z \cdot u_{\text{fix}} \cdot \rho_{\text{fluid}} \cdot H_{m_{\text{tot}}} \left[ \frac{m^2 \cdot m \cdot \text{kg} \cdot \text{kJ}}{s \cdot m^3 \cdot \text{kg}} \right] = \dot{m} \cdot H_{m_{\text{tot}}}
$$

(1.14)

Where $H_{m_{\text{tot}}}$ is the specific enthalpy of the fluid mixture $[\text{J/kg}]$

$\dot{m}$ is the mass flow of the fluid $[\text{kg/s}]

\rho_{\text{fluid}}$ is the density of the fluid $[\text{kg/m}^3]$

As steady-state has been assumed the mass flow $\dot{m}$ is independent of position $z$ in the reactor and one gets:

$$
\frac{\partial (u_{\text{fix}} \cdot C_{\text{tot}} \cdot H_{\text{tot}})}{\partial z} = \frac{1}{A_z} \cdot \frac{\partial (\dot{m} \cdot H_{m_{\text{tot}}})}{\partial z} = \frac{1}{A_z} \cdot \dot{m} \cdot \frac{\partial H_{m_{\text{tot}}}}{\partial z} = u_{\text{fix}} \cdot \rho_{\text{fluid}} \cdot \frac{\partial H_{m_{\text{tot}}}}{\partial z}
$$

(1.15)

Finally using the chain rule of differentiation:

$$
\frac{\partial H_{m_{\text{tot}}}}{\partial z} = \frac{\partial (H_{m_{\text{tot}}})}{\partial T} \cdot \frac{\partial T}{\partial z} = C_{p_{\text{fluid}}} \cdot \frac{\partial T}{\partial z}
$$

(1.16)

Where $C_{p_{\text{fluid}}}$ is the specific heat capacity of the fluid mixture $[\text{J/kg} \cdot \text{K}]$

$T$ is the temperature $[\text{K}]$

leads to:

$$
\dot{m} \cdot \rho_{\text{fluid}} \cdot C_{p_{\text{fluid}}} \cdot \frac{\partial T}{\partial z} + \frac{\partial J_z}{\partial z} + \frac{1}{r} \cdot \frac{\partial (r \cdot J_r)}{\partial r} + \rho_p \cdot (1 - \epsilon_{\text{fix}}) \cdot \eta_d \cdot (-r_s) \cdot \Delta H_{r_s} = 0
$$

(1.17)
In analogy to Fourier’s law an axial and a radial thermal conductivity is introduced:

$$J_{zfix} = -\lambda_z \frac{dT}{dz}$$

$$J_r = -\lambda_{rfix} \frac{dT}{dr}$$

(1.18)

where $\lambda_{rfix}$ is the radial thermal conductivity $\left[ \frac{W}{m \cdot s \cdot K} \right]$

$\lambda_{zfix}$ is the axial thermal conductivity $\left[ \frac{W}{m \cdot s \cdot K} \right]$

Inserting these equations in the heat balance generates:

$$u_{fix} \cdot \rho_{fluid} \cdot C_{pmn} \frac{\partial T}{\partial z} + \frac{1}{r} \left( -r \cdot \lambda_{rfix} \frac{dT}{dr} \right) + \rho_p \cdot (1 - \epsilon_{fix}) \cdot \eta_0 \cdot (-r \lambda) \cdot \Delta H_{\lambda} = 0$$

(1.19)

which can be reformulated to give the final heat balance equation for the pseudohomogeneous fixed bed reactor:

$$u_{fix} \cdot \rho_{fluid} \cdot C_{pmn} \frac{\partial T}{\partial z} - \lambda_{zfix} \frac{\partial^2 T}{\partial z^2} - \lambda_{rfix} \frac{\partial^2 T}{\partial r^2} - \lambda_{rfix} \frac{1}{r} \frac{\partial T}{\partial r} + \rho_p \cdot (1 - \epsilon_{fix}) \cdot \eta_0 \cdot (-r \lambda) \cdot \Delta H_{\lambda} = 0$$

(1.20)

with the boundary conditions:

@: $z = 0$: $u_{fix} \cdot C_{tot} \cdot C_{fluid} \cdot (T_0 - T) = -\lambda_{zfix} \frac{\partial T}{\partial z}$

$$z = L_{fix}: \frac{\partial T}{\partial z} = 0$$

$r = 0$: $\frac{\partial T}{\partial r} = 0$

$$z = R_r: \quad T = T_w$$

(1.21)

Where $C_{fluid}$ is molar heat capacity of the fluid feed mixture $\left[ \frac{J}{kg \cdot K} \right]$

$T_0$ is the feed temperature [K]

$T_w$ is the reactor wall temperature [K]
1.3 The Pressure Drop in Turbular Fixed Beds
Finally the pressure drop inside the reactor can be estimated using the Ergun equation [1]:

\[
\frac{dp}{dz} = - \frac{u_{\text{fix}}}{\Phi_s \cdot d_p} \cdot \frac{1 - \epsilon_{\text{fix}}}{\epsilon_{\text{fix}}} \left( \frac{150 \cdot (1 - \epsilon_{\text{fix}}) \cdot \mu_{\text{fluid}}}{\Phi_s \cdot d_p} + 1.75 \cdot \rho_{\text{fluid}} \cdot u_{\text{fix}} \right)
\]  

(1.22)

Where \( d_p \) is the characteristic length of the catalyst pellet \([\text{m}]\),
\( P \) is the pressure \([\text{Pa}]\),
\( u_{\text{fix}} \) is the velocity in the fixed bed \([\text{m/s}]\),
\( \Phi_s \) is the sphericity of the catalyst pellet,
\( \mu_{\text{fluid}} \) is the viscosity of the fluid mixture \([\text{kg/m/s}]\),

with the boundary condition:

\[@:z = 0: P = P_0\]  

(1.23)

Where \( P_0 \) is the pressure at the entrance to the reactor \([\text{Pa}]\).

1.4 Dispersion coefficients in Fixed Bed Reactors
The dispersion coefficient in fixed bed reactors is a complex function of fluid flow conditions, fluid transport properties and solid particle size and shape. Even so a set of semi-empirical correlations exist that describe the available experimental data well. These equations are given below.

1.4.1 Gunn’s Correlation for Axial Dispersion in Fixed Beds
Gunn has in a series of papers [2,3] derived and described the following equation describing the axial dispersion in fixed beds:

\[
\frac{D_{\text{fix}}}{u_{\text{fix}} \cdot d_p} \cdot \frac{\epsilon_{\text{fix}}}{\epsilon_{\text{fix}}} \cdot (1 - \varphi(Re))^2 \\
+ \varphi(Re) \cdot \left( \frac{Re \cdot Sc}{\epsilon_{\text{fix}} \cdot \Gamma} \right)^2 \cdot (1 - \varphi(Re))^3 \cdot \left( \exp \left( \frac{-\epsilon_{\text{fix}} \cdot \Gamma}{\varphi(Re) \cdot (1 - \varphi(Re)) \cdot Re \cdot Sc} \right) - 1 \right) + \frac{\epsilon_{\text{fix}}}{\tau_{\text{fix}} \cdot Re \cdot Sc}
\]

(1.24)

where \( \varphi(Re) \) the likelihood that a molecule diffuses into the fixed bed is found from the formulas given in table 1.1.
\( Re_p \) is the particulate Reynolds number defined in equation (1.25)
\( Sc \) is the Schmidt number defined in equation (1.26)
the \( \Gamma \)-function is defined by equation (1.27)
\( \tau_{\text{fix}} \) is the axial tortuosity factor for the fixed bed as given in table 1.1.
The pellet Reynolds number in the fixed bed is given by

\[ Re_p = \frac{u \cdot \rho_{\text{fluid}} \cdot d_p}{\mu_{\text{fluid}}} \]  

(1.25)

Where \( u \) is the superficial velocity in the reactor, for equation (1.24) \( u_{\text{sf}} \) \[ \text{m} / \text{s} \].

The Schmidt number is defined as

\[ Sc = \frac{\mu_{\text{fluid}}}{\rho_{\text{fluid}} \cdot D_{ij}} \]  

(1.26)

where \( D_{ij} \) is the diffusivity of component \( i \) in \( j \) \[ \text{m}^2 / \text{s} \].

and the \( \Gamma \)-funktion is given as

\[ \Gamma = \frac{4 \cdot (1 - \varepsilon_{\text{fix}}) \cdot \alpha_i^2}{\varepsilon_{\text{fix}}} \]  

(1.27)

where \( \alpha_i \) is the first root in the Bessel function \( J_0(x) \) which is approximatedly 2.405.

### 1.4.2 Gun’s Correlation for Radial Dispersion in Fixed Beds

The radial dispersion can according to Gunn [3] be calculated as

\[ \frac{D_{\text{rfix}}}{u_{\text{rfix}} \cdot d_p} = \frac{\varepsilon_{\text{fix}}}{\text{Pe}_{\text{fluid}}} + \frac{\varepsilon_{\text{fluid}}^2}{\tau_r \cdot Re_p \cdot Sc} \]  

(1.28)

where \( \text{Pe}_{\text{fluid}} \) is the fluid Peclét number as stated in table 1.1.

\( \tau_{\text{rfix}} \) is the radial tortuosity factor for the fixed bed as given in table 1.1.
Table 1.1 Formulas for use in connection with estimation of axial and radial dispersion coefficients.

<table>
<thead>
<tr>
<th>Pellet shape</th>
<th>Axial Dispersion</th>
<th>Radial Dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Phi(Re_p)$</td>
<td>$\tau_{fix}$</td>
</tr>
<tr>
<td>Sphere</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$0.17 + 0.33 \cdot \exp\left(-\frac{24}{Re_p}\right)$</td>
<td>1.4</td>
</tr>
<tr>
<td>Cylinder</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$0.17 + 0.29 \cdot \exp\left(-\frac{24}{Re_p}\right)$</td>
<td>1.93</td>
</tr>
<tr>
<td>Tube</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$0.17 + 0.20 \cdot \exp\left(-\frac{24}{Re_p}\right)$</td>
<td>1.8</td>
</tr>
</tbody>
</table>

1.5. Heat Conduction in Fixed Bed Reactors

The heat conduction in fixed bed reactors is a complex function of fluid flow conditions, fluid transport properties and solid particle properties. Even so a set of semi-empirical correlations exist that describe the available experimental data. These equations are given below.

1.5.1 Wakao’s Correlation for Axial Heat Conduction in Fixed Beds

Wakao et al have in a series of papers [4] derived and described the following semi-empirical equation describing the axial heat conduction in fixed beds

$$\lambda_{e_{fix}} = \lambda_{e_{ax}}^0 + 0.5\cdot d_p \cdot \varepsilon_{fix} \cdot u_{efix} \cdot C_{pm_{fluid}} \cdot \rho_{fluid}$$ (1.29)

where $\lambda_{e_{ax}}^0$ is the effective axial heat conductance of the fixed bed at zero flow $[\frac{W}{\text{m} \cdot \text{K} \cdot \text{s}}]$.
According to Wakao et al [3] the heat of conductance for the fixed bed with zero flow can be estimated as

\[ \lambda^0_{\text{ex}} = \lambda^0_{\text{ex, conductance}} + \lambda^0_{\text{ex, radiation}} \]  \hspace{1cm} (1.30)

where \( \lambda^0_{\text{ex, conductance}} \) is the effective axial pure heat conductance of the fixed bed at zero flow \( \left[ \frac{J}{m \cdot K \cdot s} \right] \)

\( \lambda^0_{\text{ex, radiation}} \) is the axial heat transport by radiation in the fixed bed at zero flow \( \left[ \frac{J}{m \cdot K \cdot s} \right] \)

The pure heat conductance term can be estimated from

\[ \lambda^0_{\text{ex, conductance}} = \lambda_{\text{fluid}} \left( \frac{\lambda_p}{\lambda_{\text{fluid}}} \right)^{n_{\text{fix}}} \]  \hspace{1cm} (1.31)

where \( \lambda_{\text{fluid}} \) is the heat conductance of the fluid \( \left[ \frac{J}{m \cdot K \cdot s} \right] \)

\( \lambda_p \) is the heat conductance of pellet \( \left[ \frac{J}{m \cdot K \cdot s} \right] \)

and the exponent \( n_{\text{fix}} \) is found from

\[ n_{\text{fix}} = 0.280 - 0.329 \cdot \ln(c_{\text{fix}}) - 0.025 \cdot \ln \left( \frac{\lambda_p}{\lambda_{\text{fluid}}} \right) \]  \hspace{1cm} (1.32)

The heat transported by radiation can according to Wakao et al [4] be described by

\[ \lambda^0_{\text{ex, radiation}} = 0.707 \cdot \lambda_{\text{fluid}} \cdot \text{Nu}_{\text{radiation}}^{0.76} \cdot \left( \frac{\lambda_p}{\lambda_{\text{fluid}}} \right)^{1.11} \]  \hspace{1cm} (1.33)

For \( 20 < \frac{\lambda_p}{\lambda_{\text{fluid}}} < 1000 \) and \( \text{Nu}_{\text{radiation}} < 0.3 \)

where \( \text{Nu}_{\text{radiation}} \) is the radiation Nusselt number as given by equation (1.34).

The radiation Nusselt number can be calculated from

\[ \text{Nu}_{\text{radiation}} = \frac{h_{\text{rad, radiation}} \cdot d_p}{\lambda_{\text{fluid}}} \]  \hspace{1cm} (1.34)

where \( h_{\text{rad, radiation}} \) is the axial heat radiation transfer coefficient given by equation (1.35) \( \left[ \frac{W}{m^2 \cdot K} \right] \)
The axial heat radiation transfer coefficient is calculated from

\[
h_{\text{ax, radiation}} = \frac{0.2268}{2} \left( \frac{T}{100} \right)^3 - 0.264 \varepsilon_{\text{emi}}
\]  
(1.35)

where \( \varepsilon_{\text{emi}} \) is the emissivity of the catalyst pellet, 0 for black, 0.5 for gray and 1 for white bodies.

### 1.5.2 Correlation for Radial Heat Conductance in Fixed Beds

The radial dispersion can according to Froment and Bischoff [5] be calculated as

\[
\lambda_{\text{rfix}} = \lambda_{\text{er}}^0 + \frac{0.14 \cdot \lambda_{\text{fluid}}}{1 + 46 \cdot \left( \frac{d_p}{d_{\text{fix}}} \right)^2 \cdot \text{Re}_p \cdot \text{Pr}_{\text{fluid}}}
\]  
(1.36)

where \( d_{\text{fix}} \) is the diameter of the internal reactor diameter [m]

\( \text{Pr}_{\text{fluid}} \) is the Prandtl number defined by equation (1.37)

\( \lambda_{\text{er}}^0 \) is the effective radial conductance of the fixed bed at zero flow [\( \frac{J}{m \cdot K \cdot s} \)]

The Prandtl number is defined as

\[
\text{Pr}_{\text{fluid}} = \frac{C_{\text{pm, fluid}} \cdot \mu_{\text{fluid}}}{\lambda_{\text{fluid}}}
\]  
(1.37)

The effective radial conductance of the fixed bed at zero flow can according to Zehner and Schlünder in [5] be estimated from

\[
\lambda_{\text{er}}^0 = \lambda_{\text{fluid}} \cdot \left( 1 - \sqrt{1 - \varepsilon_{\text{fix}}} \right) \cdot \left( 1 + \frac{\varepsilon_{\text{fix}}}{\lambda_{\text{fluid}}} \cdot h_{\text{r, radiation}} \cdot d_p \right) + \left( \frac{2 \cdot \sqrt{1 - \varepsilon_{\text{fix}}}}{1 + \left( \frac{h_{\text{r, radiation}} \cdot d_p}{\lambda_{\text{fluid}}} - B \right) \cdot \frac{\lambda_{\text{fluid}}}{\lambda_p}} \right) \cdot \Theta
\]  
(1.38)

where \( B \) is defined by equation (1.39)

\( h_{\text{r, radiation}} \) is the radial heat radiation transfer coefficient given by equation (1.41) [\( \frac{W}{m^2 \cdot K} \)]

\( \Theta \) is defined by equation (1.40)
The value of $B$ is found from

$$B = b \cdot \left( \frac{1 - \epsilon_{\text{fix}}}{\epsilon_{\text{fix}}} \right)^{10/9} \quad (1.39)$$

where $b$ is a shape factor as given in table 1.2.

The value of $\Theta$ is found from

$$\Theta = \left( 1 + \left( \frac{h_{r,\text{radiation}} \cdot d_p}{\lambda_{\text{fluid}}} - 1 \right) \cdot \frac{\lambda_{\text{fluid}}}{\lambda_p} \right) \cdot B \cdot \ln \left( \frac{1 + \frac{h_{r,\text{radiation}} \cdot d_p}{\lambda_{\text{fluid}}}}{\frac{\lambda_{\text{fluid}}}{\lambda_p} \cdot B} \right)$$

$$- \frac{B - 1}{1 + \left( \frac{h_{r,\text{radiation}} \cdot d_p}{\lambda_{\text{fluid}}} - B \right) \cdot \frac{\lambda_{\text{fluid}}}{\lambda_p}} + \frac{B + 1}{2 \cdot B} \left( \frac{h_{r,\text{radiation}} \cdot d_p}{\lambda_{\text{fluid}}} - B \right) \quad (1.40)$$

The radial heat radiation transfer coefficient $h_{r,\text{radiation}}$ can be estimated from

$$h_{r,\text{radiation}} = 0.227 \cdot \frac{\epsilon_{\text{emi}}}{2 - \epsilon_{\text{emi}}} \left( \frac{T}{100} \right)^3 \quad (1.41)$$
Table 1.2  Values of $b$ for use in connection with estimation of radial heat of conductance.

<table>
<thead>
<tr>
<th>Pellet shape</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>1.25</td>
</tr>
<tr>
<td>Cylinder</td>
<td>2.5</td>
</tr>
<tr>
<td>Tube</td>
<td>2.5</td>
</tr>
</tbody>
</table>
2. Models for Fluid Bed Reactors

For very exothermic reactions like partial oxidation of hydrocarbons, heat control is not only essential for economical success, it is literally essential for the survival of the production plant and the employees. This was realized after several cases of runaway reactions leading to explosions during phthalic anhydride production in fixed bed reactors. Though reactant conversion and heat generation and removal is fairly predictable in fixed reactors the heat removal rate might not be sufficient for safe production.

Another draw back of fixed bed reactors are the pressure drop generated by the flow through the bed. As catalysts becomes more active industrial catalyst pellets have to decrease in size in order to benefit from the increased kinetic reaction rate. Decreasing the pellet size leads to a higher efficiency factor but also a higher pressure drop in the fixed bed reactor. Thus even though the fixed bed reactor because of it’s relative ease of maintenance, normally high conversion to volume ratio and simple rugged construction in most cases is the preferred choice for bulk chemical productions, it has it’s limitations.

One type of reactor that overcomes some of these limitations is the fluid bed reactor. In fluid bed reactors the catalyst pellets are suspended in the fluid stream, gas or liquid, leading to a better heat removal, safer operation mode and a limited pressure drop. The trade of is a more complex reactor design and often much larger reactor volume.

2.1 Fluidization of pellets

If pellets are placed on a perforated plate in a tall tube they will be at rest, see figure 2.1. The pressure the pellets and fluid exert on the plate can be calculated directly as

\[
\Delta P_0 = L_0 \cdot g \cdot \rho_{\text{flb}} = L_0 \cdot g \cdot (\varepsilon_{\text{flb}} \cdot \rho_{\text{fluid}} + (1 - \varepsilon_{\text{flb}}) \cdot \rho_p)
\] (2.1)

where
- \( g \) is the gravitational constant 9.84 [m/s\(^2\)]
- \( L_0 \) is the height of the bed at rest [m]
- \( \Delta P_0 \) is pressure on the perforated plate [Pa]
- \( \varepsilon_{\text{flb}} \) is the fluid bed porosity at rest
- \( \rho_{\text{flb}} \) is the fluid bed density [kg/m\(^3\)]

The buoyant force of the fluid displaced by the pellets though are given by equation (2.2)

\[
\Delta P = L \cdot g \cdot (1 - \varepsilon_{\text{flb}}) \cdot (\rho_p - \rho_{\text{fluid}})
\] (2.2)

If the fluid flow is slowly increased the pressure drop across the pellet bed will increase up to a point where the pressure drop caused by the fluid flow will equal the relative pressure exerted by the pellet bed. At this flow, the minimum fluidization flow, all pellet particles will become suspended in the moving fluid. This increases the bed porosity so that the pressure drop becomes nearly constant. Further increase of the fluid velocity will expand the bed leading to a higher bed porosity, but not an appreciably increase in pressure drop. At some point the pellets will be dragged out of the tube with the fluid. This happens when the fluid velocity increases beyond the individual pellets terminal gravitational velocity. Predicting the actual behavior of fluid and particles in a fluid bed in general is difficult, but for catalyst pellets which normally have a narrow size and density distribution it is possible to at least give some approximative guidelines as to what to expect.
The pressure drop in the reactor prior to fluidization is adequately described by the Ergun equation:

\[
\frac{dP}{dz} = -\frac{u}{\Phi_s \cdot d_p} \left( 1 - \varepsilon_{fb,0} \right) \left( \frac{150 (1 - \varepsilon_{fb,0}) \cdot \mu_{fluid}}{\Phi_s \cdot d_p} + 1.75 \cdot \rho_{fluid} \cdot u_{fb} \right) \tag{1.22}
\]

Where \( u_{fb} \) is the superficial fluid velocity in the fluid bed \( \left[ \frac{m}{s} \right] \)

If the fluid viscosity, superficial fluid velocity, fluid density and bed porosity is considered constant the Ergun equation integrates to

\[
\Delta P = -\frac{u_{fb}}{\Phi_s \cdot d_p} \left( 1 - \varepsilon_{fb,0} \right) \left( \frac{150 (1 - \varepsilon_{fb,0}) \cdot \mu_{fluid}}{\Phi_s \cdot d_p} + 1.75 \cdot \rho_{fluid} \cdot u_{fb} \right) \cdot L_0 \tag{2.3}
\]

If equation (2.3) and (2.2) are set equal, the velocity at minimum fluidization is found:

\[
L \cdot g \cdot (1 - \varepsilon_{fb,min}) \cdot (\rho_p - \rho_{fluid}) = u_{fb,min} \cdot \frac{1 - \varepsilon_{fb,min}}{\Phi_s \cdot d_p} \left( \frac{150 (1 - \varepsilon_{fb,min}) \cdot \mu_{fluid}}{\Phi_s \cdot d_p} + 1.75 \cdot \rho_{fluid} \cdot u_{fb,min} \right) \cdot L_0 \tag{2.3}
\]

where \( \varepsilon_{fb,min} \) is the bed porosity at minimum fluidization.

\( u_{fb,min} \) is the superficial minimum fluidization velocity \( \left[ \frac{m}{s} \right] \)

Equation (2.3) in it’s dimensionless form

\[
Ar = \frac{150 (1 - \varepsilon_{fb,min}) \cdot Re_p}{\Phi_s^2 \cdot \varepsilon_{fb,min}^3} + \frac{1.75 \cdot Re_p^2}{\Phi_s \cdot \varepsilon_{fb,min}^3} \tag{2.4}
\]

where \( Ar \) is the Archimedes number defined in equation (2.5)

\( Re_p \) is the Reynolds number defined in equation with the superficial velocity \( u_{fb,min} \) (1.25)

is often called the Kunii-Levenspiel equation after two of the most influential professors within the 20th century fluidized bed reactor engineering. It’s importance lies in the fact, that if the Archimedes number

\[
Ar = \frac{g \cdot (\rho_p - \rho_{fluid}) \cdot d_p^3 \cdot \rho_{fluid}}{\mu_{fluid}^2} \tag{2.5}
\]

and the minimum porosity is known, the Kunii-Levenspiel equation predicts the minimum fluidization velocity fairly accurate for catalyst pellets. In general the porosity at minimum fluidization is not known but for fairly spherical pellets, which most catalyst pellets used for fluidization are, the porosity at minimum fluidization is between 0.4 and 0.45.
The minimum fluidization velocity $u_{\text{min}}$ gives the lower velocity boundary for fluidization. The upper velocity boundary, beyond which the reactor changes from a fluidized bed to a flow through reactor, where both fluid and catalyst pellets leave the reactor, can be found as the terminal fall velocity of the catalyst pellet.

The terminal fall velocity $u_{\text{term}}$ is found from

$$u_{\text{term}} = \sqrt{\frac{4 \cdot g \cdot (\rho_{\text{pellet}} - \rho_{\text{fluid}}) \cdot d_p \cdot \Phi_p}{3 \cdot C_D \cdot \rho_{\text{fluid}}}}$$

(2.6)

where $u_{\text{term}}$ is the terminal fall velocity or maximum fluidization velocity \[
m \quad \frac{m}{s}
\]

$C_D$ is the Cunningham factor given by equation (2.7):

$$C_D = \frac{24}{Re_p} + 3.3643 \cdot Re_p^{-0.3471} + \frac{0.4607 \cdot Re_p}{Re_p + 2682.5}$$

(2.7)

When equation (2.6) and (2.7) are combined in dimensionless form the maximum fluidization Reynolds number can be described as

$$18 \cdot Re_{p,\text{term}} + 2.5232 \cdot Re_{p,\text{term}}^{1.6529} + \frac{0.3455 \cdot Re_{p,\text{term}}^3}{Re_{p,\text{term}} + 2682.5} = \Phi_p \cdot Ar$$

(2.8)

Where $Re_{p,\text{term}}$ is the Reynolds number for the pellet terminal fall velocity as stated in equation (2.9)

The maximum fluidization velocity is then found from

$$Re_{p,\text{term}} = \frac{u_{\text{term}} \cdot d_p \cdot \rho_{\text{fluid}}}{\mu_{\text{fluid}}}$$

(2.9)

While this gives the flow limits for true fluidization, the actual mixing of catalyst pellets and fluid within these boundaries are a more complex matter.
2.2 Classification of fluidization

Fluidized systems behave very differently depending on the fluid and particle properties. For particles of a fairly homogeneous density and particle size as used for heterogeneously catalyzed reactions the fluid and particle flow patterns generally fall into one of nine patterns. These nine basic patterns are shown in figure 2.1.

![Fluidization regimes](image)

Figure 2.1 Fluidization regimes after [5]. (a) Fixed bed. (b) Minimum fluidization. (c) Homogeneous bubble free fluidization (particulate fluidization). (d) Bubbling fluidization. (e) Axial slugging fluidization. (f) Flat slugging fluidization. (g) Turbulent fluidization. (h) Lean fluidization with pneumatic transport of solids. (i) Spouting fluidization [6].

The fixed bed state (a) can be accomplished for all fluid-solid systems as long as the fluid flow is below the minimum fluidization velocity. As the fluid flow reaches the minimum fluidization velocity the homogeneous minimal fluidization situation is reached (b). For liquid-solid systems if the flow is increased beyond the minimal fluidization the particle fluid bed expands homogeneously with a nearly even solid distribution, a particulate phase. The solids though move freely in the up moving liquid creating a situation where the liquid phase moves nearly as plug flow while the solid phase is back mixing. For gas-solid systems the homogeneous fluidized phase can also be attained with small fine particles fluidized in dense gases at high pressure, normally though the homogeneous fluidized system of the minimal fluidized bed breaks down into less well ordered systems immediately as the velocity is increased beyond the minimal fluidization velocity. Typically gas bubbles nearly free of solid particles are formed and appear as if they travel through a sea of a stagnant dense particulate gas-solid phase. This of cause is not correct as both solids and gas in the dense particulate phase moves under appreciable back mixing. Depending on the properties of the solids and gas, and size of the fluidized bed, the bubbling fluidization will either develop into a homogeneous
bubbling phase (d) or into larger gas slugs (e) and (f). Slugging appears when the gas bubbles formed at the bottom of the column coalesce to form larger bubbles of dimensions close to the fluidized bed diameter. Axial slugs develop with fine particles. The fine particles appear to rain down the side of the fluidized bed as the gas slugs move upward through the bed. For coarse particles flat slugs appear. The gas slugs seems to form and disintegrate as they move upwards the column moving in a piston like fashion. The coarse solids rains down in the wake from the slugs. Slugging mainly appears in high narrow columns. If the velocity is increased beyond the terminal fall velocity of fine particles entrainment occurs and the fine particles are carried out of the bed in what is termed turbulent fluidization (g). If the velocity is increased further lean pneumatic transportation (h) will occur. Pneumatic transportation can in principle be attained for all fluid solid systems. For coarse particles central channeling might occur leading to sprouted fluidization (i). In this case a fast moving central gas stream transports parts of the solids upwards where these seems to sprout out like a fountain. The particles then moves downwards in a dense phase along the bed’s sides. If bubbles occur in the dense phase a sprouting bubbling bed is formed. [6].

As seen the gas-solid fluidization is more complex than liquid-solid fluidization. In order to predict the fluidization behavior for a given gas-solid system Geldart developed a classification system based on the relative density between pellet and gas, and particle diameter, as shown in figure 2.2.

Figure 2.2 Geldart classification system for gas-solid fluidization [6].

**Geldart A:**
Particles with low mean diameter and/or low particle density (\( < \sim 1.4 \text{ [g/cm}^3\text{]} \)) particles. These particles fluidize easily. When fluidization occur these particles first form a particulate fluidized bed which expands smoothly. Beyond a certain minimum fluidization velocity \( u_{mf} \) controlled bubbling occurs. The bobbling fluidized state is characterized by:
- Gas bubbles rise more rapidly than the rest of the gas, which percolates through the emulsion phase.
- These gas bubbles appear to split and coalesce frequently as they rise through the bed. There is a minimum bubble size, usually less than 10 cm even in large beds.
- Gross circulation of solids occurs even when only few bubbles are present. This circulation is especially pronounced in large beds.
- When bubbles grow to the vessel diameter, they turn into axial slugs.
These properties are typical for fluid catalytic cracking catalysts. The A’ zone being the ideal situation sought for.

**Geldart B:**
Sandlike particles. Holds for most particles between 40 \( \mu \text{m} \) and 500 \( \mu \text{m} \) in diameter with a density between 1.4 and 4 [g/cm\(^3\)]. These particles fluidize well with vigorously bubbling as soon as the minimum fluidization velocity is
exceeded. The bubbling fluidization state is characterized by:
- Small bubbles form at the gas distributor and grow and coalesce as they rise through the bed.
- Bubble size increases roughly linearly with distance above the distributor and excess gas velocity \( u - u_{\text{min}} \).
- Bubble size is roughly independent of particle size.
- Vigorous bubbling increases the solid circulation in the bed.
Most non-catalytic gas-solid reactions are run in this regime as particle mean size and distribution is determined by upstream processing of the solids.

**Geldart C:**
Cohesive or very fine powders. Fluidization is extremely difficult for these powders as the solid cohesive forces are greater than those resulting from the action of gas. Face powder, flour and starch belongs to this group.
In small-diameter fluidized beds the particles tends to rise as plugs of solids and in large diameter beds channels form from the distributor plates to the bed surface with no fluidization of solids.

**Geldart D:**
Large and/or dense particles. Deep beds formed from these particles are difficult to fluidize. They behave erratically, giving large exploding bubbles, severe channeling or sprouting behavior if the gas distribution is very uneven. Drying of grains and peas, coffee beans, gasifying coals and some roosting ores belongs to this group of particles which is why these operations are typically carried out in shallow fluidized beds.
The bubbling fluidization state is characterized by:
- Bubbles coalesce rapidly and grow to large size.
- Bubbles rise more slowly than the rest of the perculating gas through the emulsion.
- The dense phase has a low voidage
- When the bubble size approach the bed diameter, flat slugs are observed.
- Contrary to Geldart B particles, Geldart D particles sprout easily.

As reaction engineering is mostly concerned with catalytic reactions where catalyst pellet size and distribution can be carefully controlled and tailored to purpose, only particulate liquid-solid fluidization and bubbling gas-solid fluidization will be considered further in these notes.

### 2.3 Particulate Liquid-Solid Fluidization
Sizing of liquid-solid fluidized reactors depends not only on the conversion expected of the reactor, but also on the inherent properties of the fluid bed operation. Fluid bed height \( L \) and fluid bed diameter \( d \) cannot be chosen independently of the superficial liquid velocity, as these factors influence each other irrespectively of the chemical conversion in the reactor.
In the following sections the basic equations needed to size liquid fluidized beds will be stated.

#### 2.3.1 Basic Correlations for Particulate Liquid-Solid Fluid Bed Properties
The relation between fluid bed height, diameter, porosity and total amount catalyst particles is simple, as seen from figure 2.3:

\[
m_{\text{flb,cat}} = (1 - \varepsilon_{\text{flb}}) \cdot \frac{\pi}{4} \cdot d_{\text{flb}}^2 \cdot L_{\text{flb}} \cdot \rho_p
\]  

(2.10)

Where
- \( d_{\text{flb}} \) is the bed diameter [m]
- \( L_{\text{flb}} \) is the bed height [m]
- \( m_{\text{flb,cat}} \) is the total amount of catalyst in the bed [kg]
As the porosity of the fixed bed is normally known and nearly identical to the porosity at minimum fluidization the height of the bed at minimum fluidization can be found as

\[
L_{\text{fb},\text{min}} = \frac{m_{\text{fb},\text{cat}}}{(1 - \varepsilon_{\text{fb},\text{min}}) \cdot \frac{\pi}{4} \cdot d_{\text{fb}}^2 \cdot \rho_p}
\]  
(2.11)

Where \( L_{\text{fb},\text{min}} \) is the height of the bed at minimum fluidization [m]

The increase in bed height with bed porosity as the superficial liquid velocity is increased above the minimum fluidization velocity, is often stated relative to the minimum fluidization height:

\[
\frac{m_{\text{fb}}}{L_{\text{fb},\text{min}}} = \frac{(1 - \varepsilon_{\text{fb},\text{min}}) \cdot \frac{\pi}{4} \cdot d_{\text{fb}}^2 \cdot L_{\text{fb},\text{min}} \cdot \rho_p}{(1 - \varepsilon_{\text{fb}}) \cdot \frac{\pi}{4} \cdot d_{\text{fb}}^2 \cdot L_{\text{fb}} \cdot \rho_p}
\]  
(2.12)
If the bed porosity is known, the height of the bed is therefore automatically given. Equally if the total volumetric feed flow to the reactor, \( v_0 \), is known, the bed diameter can be determined from the superficial liquid velocity through the bed:

\[
v_{\text{fb}} = u_{\text{sflb}} \cdot \frac{\pi}{4} \cdot d_1^2
\]

\[
d_{\text{fb}} = \sqrt{\frac{4 \cdot v_{\text{fb}}}{\pi \cdot u_{\text{sflb}}}}
\]

Where \( u_{\text{sflb}} \) is the superficial fluidization velocity \( \left[ \frac{m}{s} \right] \)

\( v_{\text{fb}} \) is the volumetric feed flow \( \left[ \frac{m^3}{s} \right] \)

What is needed further is a connection between the porosity in the fluidized bed and the chosen superficial liquid velocity. One such equation that seems to have been universally accepted is the Lewis-Gilliland-Baur (LGB) correlation [7]:

\[
\frac{u_{\text{fb}}}{u_{\text{erm}}} = \epsilon_{\text{fb}}^n
\]

Where \( n_{\text{fb}} \) is an exponent to be found from experiments.

The LGB-correlation seems in general to describe experimental data for liquid-solid fluidization well. It does though require a value for the exponent \( n \) in order to have predictive qualities.

Many different correlations for \( n \) has been put forward but the one that seems to cover most of the experimental evidence to a reasonable extent is the Richardson-Zaki correlation [7]:

\[
n_{\text{fb}} = \begin{cases} 
4.35 + 17.5 \cdot \frac{d_2}{d_1} \cdot \text{Re}_p^{0.03} & 0.2 \leq \text{Re}_p < 1 \\
4.45 + 18 \cdot \frac{d_2}{d_1} \cdot \text{Re}_p^{0.1} & 1 \leq \text{Re}_p \leq 200 \\
4.45 \cdot \text{Re}_p^{0.1} & 200 \leq \text{Re}_p \leq 500 \\
2.39 & \text{Re}_p > 500
\end{cases}
\]
2.3.2 Mass Balances for a Particulate Liquid-Solid Fluid Bed

Even though there seems to be general agreement about how a particulate liquid-solid fluidized bed behaves on the macroscopic scale, the microscopic mixing properties are still open to debate. The general view seems to be, that the liquid phase behaves nearly as plug flow with some backmixing while the solid particles mix more vigorously, some actually assuming total mixing (batch like) behavior. These views can be difficult to reconcile. The reason for this discrepancy might lay in the fact that solid particle motion is inhibited in dense fluidized beds leading to hindered backmixing, while in lean fluidized beds the particles move more freely. In any case the choice of mixing pattern for the particles in the bed must for the time being be done a little arbitrary and models for both situations will therefore be presented here.

2.3.2.1 Liquid Phase Mass Balances for a Particulate Liquid-Solid Fluid

If the general view, that the liquid phase behaves as a plug flow with some backmixing, is followed, the mass balance for the liquid phase can be described with a dispersion model. Furthermore it might be assumed that no chemical reaction occur in the liquid phase, only inside the catalyst pellets does the reactants get into contact with the catalyst producing the product. Should a chemical reaction occur in the liquid phase, the model can easily be expanded also to include this situation.

Based on these assumptions the mass balance for the liquid phase can be setup as follows.

![Figure 2.4 Shell for setting up a molar balance for the liquid phase in a particulate liquid-solid fluidized bed.](image-url)
The steady state molar balance is

\[
\begin{align*}
\text{In} & \quad + \quad \text{Generated} \quad = \quad \text{Out} \quad + \quad \text{accumulated}
\end{align*}
\]

\[
\begin{align*}
& u_{fb} \cdot A_z \cdot C_A | z \cdot \Delta t + N_{Az} \cdot A_z | z \cdot \Delta t + N_{Ar} \cdot A_r | r \cdot \Delta t + \\
& u_{fb} \cdot A_z \cdot C_A | z + \Delta z \cdot \Delta t + N_{Az} \cdot A_z | z + \Delta z \cdot \Delta t + N_{Ar} \cdot A_r | r + \Delta r \cdot \Delta t + k_z \cdot a_{cat} \cdot A_z \cdot \Delta z \cdot (C_A - C_{As}) \cdot \Delta t + 0
\end{align*}
\]

(2.14)

Where
- \( a_{cat} \) is the outer catalyst surface area per volume of fluidized bed \( \left[ \frac{m^2}{m^3} \right] \)
- \( C_{As} \) is the molar concentration of component A at the catalyst pellets outer surface \( \left[ \frac{mol}{m^3} \right] \)
- \( k_z \) is the mass transfer coefficient for component A across the film layer around the catalyst pellet \( \left[ \frac{m}{s} \right] \)
- \( r \) is the radial position (see figure (2.4)) \([m]\)
- \( u_{fb} \) is the fluid velocity in the fluid bed \( \left[ \frac{m}{s} \right] \)
- \( z \) is the axial position (see figure (2.4)) \([m]\)
- \( \Delta t \) is the small control time interval over which the molar balance is setup \([s]\)
- \( \Delta r \) is the small control radial width interval over which the molar balance is setup \([m]\)
- \( \Delta z \) is the small control axial length interval over which the molar balance is setup \([m]\)

The cross sectional area in the axial direction \( A_z \) and the radial area in the radial direction \( A_r \) are equal to:

\[
A_z = \pi \cdot (r + \Delta r)^2 - \pi \cdot r^2 - 2 \cdot \pi \cdot \Delta r \cdot r
\]

(1.2)

This inserted in equation (2.14), the molar balance, yields:

\[
2 \cdot \pi \cdot r \cdot \Delta r \cdot \left( (u_{fb} \cdot C_A | z + \Delta z - u_{fb} \cdot C_A | z) + (N_{Az} \cdot A_z | z + \Delta z - N_{Az} \cdot A_z | z) \right) + 2 \cdot \pi \cdot \Delta z \cdot (N_{Ar} \cdot A_r | r + \Delta r - N_{Ar} \cdot A_r | r) + k_z \cdot a_{cat} \cdot 2 \cdot \pi \cdot r \cdot \Delta r \cdot \Delta z \cdot (C_A - C_{As}) = 0
\]

(2.15)

In order to be useful, formula (2.15) has to be restated in partial differential form. This is done as follows:

\[
\frac{u_{fb} \cdot C_A | z + \Delta z - u_{fb} \cdot C_A | z}{\Delta Z} + \frac{N_{Az} \cdot A_z | z + \Delta z - N_{Az} \cdot A_z | z}{\Delta Z} + \frac{1}{r} \cdot \frac{N_{Ar} \cdot A_r | r + \Delta r - N_{Ar} \cdot A_r | r}{\Delta r} + k_z \cdot a_{cat} \cdot (C_A - C_{As}) = 0
\]

(2.16)

Taking the limit as \( \Delta z \) and \( \Delta r \) approach zero leads to:

\[
\frac{\partial (u_{fb} \cdot C_A)}{\partial z} + \frac{\partial N_{Az}}{\partial z} + \frac{1}{r} \cdot \frac{\partial (r \cdot N_{Ar})}{\partial r} + k_z \cdot a_{cat} \cdot (C_A - C_{As}) = 0
\]

(2.17)
Equation (2.17) as it stands has three dependent variables, the concentration, $C_A$, the axial flux $N_A$, and the radial flux $N_r$. This can be reduced to only one dependent variable, the concentration, by assuming that the fluxes can be described by a Fick’s First Law like equation:

\[ N_A = -D_{efb} \frac{dC_A}{dz} \]
\[ N_r = -D_{efb} \frac{dC_A}{dr} \]  

(1.6)

Where $D_{efb}$ is the liquid radial dispersion coefficient \([\frac{m^2}{s}]\)

$D_{efb}$ is the liquid axial dispersion coefficient \([\frac{m^2}{s}]\)

Inserting equations (1.6) into the molar balance (2.17) yields:

\[
\frac{\partial(u_{fb} \cdot C_A)}{\partial z} + \frac{\partial}{\partial z} \left( -D_{efb} \frac{dC_A}{dz} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( -r \cdot D_{efb} \frac{dC_A}{dr} \right) + k_i \cdot a_{cat} \left( C_A - C_A^* \right) = 0
\]  

(2.18)

which can be reshaped into the final equation for the liquid phase molar balance for a particulate liquid-solid fluidized bed:

\[
\frac{\partial(u_{fb} \cdot C_A)}{\partial z} - D_{efb} \frac{\partial^2 C_A}{\partial z^2} - D_{efb} \frac{\partial^2 C_A}{\partial r^2} - D_{efb} \frac{r}{r} \frac{\partial C_A}{\partial r} + k_i \cdot a_{cat} \left( C_A - C_A^* \right) = 0
\]  

(2.19)

with the boundary conditions:

\[ \begin{align*}
@: & \quad z = 0: & D_{efb} \frac{\partial C_A}{\partial z} &= u_{fb} \cdot (\epsilon_{fb} \cdot C_A - C_{A0}) \\
& & \frac{\partial C_A}{\partial z} &= 0 \\
\end{align*} \]  

(2.20)

\[ \begin{align*}
@: & \quad z = L_{fb}: & \frac{\partial C_A}{\partial z} &= 0 \\
& & \frac{\partial C_A}{\partial r} &= 0 \\
\end{align*} \]

\[ \begin{align*}
@: & \quad r = 0: & \frac{\partial C_A}{\partial r} &= 0 \\
& & \frac{\partial C_A}{\partial r} &= 0 \\
\end{align*} \]

Where $R_{efb}$ is the internal radius of the fluid bed tube [m]

$\epsilon_{fb}$ is the fluid bed porosity
2.3.2.2 Solid Phase Dispersion Mass Balance for a Particulate Fluid Bed

If it is assumed that the solid phase can be described as a mainly stagnant phase with some backmixing, the mass balance for the solid phase can be described with a dispersion model. During steady state operation there will be no convective transport of the pellets, only random mixing by diffusion. Furthermore, it might be assumed that diffusion inside the catalyst pellet is important. This leads to the following mass balance for the components trapped inside the catalyst pellets:

\[
\begin{align*}
\text{In} & + \text{Generated} = \\
N_{A_x}^\delta \cdot A_x \cdot \Delta t + N_{A_y}^\delta \cdot A_y \cdot \Delta t + \eta_{\text{int}} \cdot r_{\text{kin}}(C_{A_y}) \cdot (1 - \epsilon_{\text{fb}}) \cdot \rho_p \cdot A_z \cdot \Delta z \cdot \Delta t \\
\text{Out} & + \text{accumulated} \\
N_{A_x}^\delta \cdot A_x \cdot \Delta t + N_{A_y}^\delta \cdot A_y \cdot \Delta t & + 0
\end{align*}
\] (2.21)

Where \( N_{A_x}^\delta \) is the radial dispersive flux of component A with the pellet \[\text{mol} \, \text{m}^2 \cdot \text{s}^{-1}\] \( N_{A_x}^\delta \) is the axial dispersive flux of component A with the pellet \[\text{mol} \, \text{m}^2 \cdot \text{s}^{-1}\] \( \eta_{\text{int}} \) is the internal efficiency factor for the catalyst pellet, excluding external mass transfer limitations

When the cross-sectional area in the axial direction \( A_z \) and the radial area in the radial direction \( A_r \) as given by equation (1.2), is inserted in equation (2.21), the molar balance, yields:

\[
2 \cdot \pi \cdot r \cdot \Delta r \left[ N_{A_x}^\delta \cdot A_x \cdot \Delta z - N_{A_x}^\delta \cdot A_x \right] \\
+ 2 \cdot \pi \cdot r \cdot \Delta z \left[ N_{A_x}^\delta \cdot A_\rho \cdot A_r \cdot \Delta \rho - N_{A_x}^\delta \cdot A_\rho \right] + \eta_{\text{int}} \left( - r_{\text{kin}}(C_{A_y}) \right) \cdot (1 - \epsilon_{\text{fb}}) \cdot \rho_p \cdot 2 \cdot \pi \cdot r \cdot \Delta r \cdot \Delta z = 0
\] (2.22)

In order to be useful, formula (2.22) has to be restated in partial differential form. This is done as follows:

\[
\frac{N_{A_x}^\delta \cdot A_x \cdot \Delta z - N_{A_x}^\delta \cdot A_x}{\Delta z} + \frac{1}{r} \left[ \frac{N_{A_x}^\delta \cdot A_\rho \cdot A_r \cdot \Delta \rho - N_{A_x}^\delta \cdot A_\rho}{\Delta r} \right] + \eta_{\text{int}} \cdot \left( - r_{\text{kin}}(C_{A_y}) \right) \cdot (1 - \epsilon_{\text{fb}}) \cdot \rho_p = 0
\] (2.23)

Taking the limit as \( \Delta z \) and \( \Delta r \) approach zero leads to:

\[
\frac{\partial N_{A_x}^\delta \cdot A_x}{\partial z} + \frac{1}{r} \cdot \frac{\partial}{\partial r} \left( r \cdot N_{A_x}^\delta \right) + \eta_{\text{int}} \cdot \left( - r_{\text{kin}}(C_{A_y}) \right) \cdot (1 - \epsilon_{\text{fb}}) \cdot \rho_p = 0
\] (2.24)

Equation (2.24) as it stands has three dependent variables, the concentration, \( C_x \), the axial flux \( N_{A_x}^\delta \), and the radial flux \( N_{A_x}^\delta \). In order to remove this problem, Chen et al. [8] suggests using a Fick’s First Law approach combining the dispersion coefficient for the solid pellets with the mean concentration of component A inside the pellet. They then convincingly shows that this approach works for protein adsorption in liquid-solid particulate fluidized beds.
This leads to

\[
N_z^{\ast} = -D_z^{\ast} \frac{\partial \bar{C}_A}{\partial z}
\]

\[
N_r^{\ast} = -D_r^{\ast} \frac{\partial \bar{C}_A}{\partial r}
\]

(2.25)

Where \( \bar{C}_A \) is the mean concentration of A inside the pellet (see equation (2.26)) \([\text{mol} / \text{m}^3]\)

\( D_z^{\ast} \) is the radial dispersion coefficient for the solid \([\text{m}^2 / \text{s}]\)

\( D_r^{\ast} \) is the radial dispersion coefficient for the solid \([\text{m}^2 / \text{s}]\)

The mean concentration of A inside the pellet can be calculated from equation (2.26) when the concentration profile inside the pellet has been determined as described in [9].

\[
\bar{C}_A = \frac{1}{V_p} \int \int C_A(V) dV_p
\]

Which for a spherical pellet yields

\[
\bar{C}_A = \frac{3}{4 \cdot \pi \cdot L_p^3} \int_{0}^{L_p} \int_{0}^{2\pi} \int_{0}^{\pi} C_f(\theta, \phi, z) \cdot z^2 \cdot \sin \phi \cdot dz \cdot d\phi \cdot d\theta
\]

\[
= \frac{3}{L_p^3} \int_{0}^{L_p} (C_f(z) \cdot z^2) \, dz
\]

(2.26)

Where \( L_p \) is the radius of the catalyst pellet \([\text{m}]\)

\( V_p \) is the volume of the catalyst pellet \([\text{m}^3]\)

Inserting equations (2.25) into the molar balance (2.24) yields:

\[
\frac{\partial}{\partial z} \left( -D_z^{\ast} \frac{\partial \bar{C}_A}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( -D_r^{\ast} \frac{\partial \bar{C}_A}{\partial r} \right) + \eta_{int} \cdot (-r_{int}(C_{A}\phi)) \cdot (1 - \epsilon_{fl}) \cdot \rho_p = 0
\]

(2.27)

which can be reshaped into the final equation for the solid phase molar balance for a particulate liquid-solid fluidized bed:

\[
- D_z^{\ast} \frac{\partial^2 \bar{C}_A}{\partial z^2} - D_r^{\ast} \frac{\partial^2 \bar{C}_A}{\partial r^2} - D_r^{\ast} \frac{\partial \bar{C}_A}{\partial r} + \eta_{int} \cdot (-r_{km}(C_{A}\phi)) \cdot (1 - \epsilon_{fl}) \cdot \rho_p = 0
\]

(2.28)
with the boundary conditions:

\[
\begin{align*}
\left. \frac{\partial \bar{C}_A}{\partial z} \right|_{z = 0} &= 0 \\
\left. \frac{\partial \bar{C}_A}{\partial z} \right|_{z = L_{flb}} &= 0 \\
\left. \frac{\partial \bar{C}_A}{\partial r} \right|_{r = 0} &= 0 \\
\left. \frac{\partial \bar{C}_A}{\partial r} \right|_{r = R_{flb}} &= 0
\end{align*}
\]

(2.29)

### 2.3.2.2 Solid Phase Totally Mixedness Model for a Particulate Fluid Bed

If it is assumed that the solid phase is totally mixed the mass balance for the solid phase becomes:

\[
k_r \cdot a_{cat} \cdot \left( C_A - C_{As} \right) = \eta_{int} \cdot (-r_{kin}(C_{As})) \cdot (1 - \varepsilon_{mb}) \cdot \rho_p
\]

(2.30)

### 2.4 Dispersion coefficients for Particulate Liquid-Solid Fluidized Beds

The dispersion coefficient in particulate liquid solid-fluidized beds is a complex function of fluid flow conditions, fluid transport properties and solid particle size and shape. Even so sets of semi-empirical correlations exist that describe the available experimental data well. Research within particulate fluidization though has not been given the same attention as has fixed bed reactors. Therefore the knowledge in the field of particulate fluidized beds has not matured to the same degree. With the advent of liquid-solid fluidized beds for protein purification, biohydrogen production and biotechnology in general, this situation is most likely to be remedied in the coming years. For the time being the correlations presented here seems the most promising though more complete correlations are likely to appear in the near future.

#### 2.4.1 Yun-Yao-Lin’s Correlation for the Liquid Axial Dispersion in Particulate Liquid-Solid Fluidized Beds

Yun et al [10] have arrived at the following correlation describing the axial dispersion in particulate liquid-solid fluidized beds

\[
\frac{D_r \cdot \rho_f}{\mu_r} = 13.2 \cdot (Re_p \cdot \varepsilon_{mb})^{0.65} \cdot \beta_r^{-0.05}
\]

(2.31)

where  
\( u_{flb} \) is the superficial velocity in the fluid bed  
\[ \frac{m}{s} \]

\( Re_p \) is the particle Reynolds number defined in equation (1.25) with \( u \) equal to \( u_{flb} \)

\( \beta_r \) is the relative energy dissipation rate given by equation (2.32).
The relative energy dissipation rate $\beta_r$ can be calculated by

$$\beta_r = \frac{32 \cdot u_{\text{fluid}}}{d_p^2 \cdot (\rho_p - \rho_{\text{fluid}}) \cdot (1 - \epsilon_{\text{fb}}) \cdot \epsilon_{\text{fb}} \cdot g \cdot \mu_{\text{fluid}}} + 32 \cdot u_{\text{fluid}}$$  \hspace{1cm} (2.32)

It should be noted that the correlation is only valid for spherical pellets and the data available was in the range $0.03 \leq Re_p \leq 0.5$ and $0.66 \leq \epsilon_{\text{fb}} \leq 0.9$.

### 2.4.2 Correlation for the Liquid Radial Dispersion in Particulate Liquid-Solid Fluidized Beds

No correlation has been found describing the radial liquid dispersion in particulate liquid-solid fluidized beds.

### 2.4.3 Asif-Petersen’s Correlation for the Solid Axial Dispersion in Particulate Liquid-Solid Fluidized Beds

According to Patel et al [11] the most accurate correlation describing the solid axial dispersion in particulate liquid-solid fluidized beds are the correlation of Asif and Petersen:

$$P_{e_z}^* = 0.113 \cdot \left( \frac{u_{\text{term}}}{u_{\text{fb}} - u_{\text{fb,min}}} \right)^{2.141} \cdot Fr_{\text{fb}}$$  \hspace{1cm} (2.33)

where $Fr_{\text{fb}}$ is the Froude number defined in equation (2.34)

$P_{e_z}^*$ is the fluid bed axial Peclet number for the solid defined in equation (2.35)

The fluid bed Froude number is given by

$$Fr_{\text{fb}} = \frac{u_{\text{fb}}^2 \cdot \rho_{\text{fluid}}}{(\rho_p - \rho_{\text{fluid}}) \cdot g \cdot d_p}$$  \hspace{1cm} (2.34)

and the fluid bed axial Peclet number by

$$P_{e_z}^* = \frac{D_{z}^*}{u_{\text{fluid}} \cdot d_p}$$  \hspace{1cm} (2.35)

### 2.4.4 Correlation for the Solid Radial Dispersion in Particulate Liquid-Solid Fluidized Beds

No correlation has been found describing the radial solid dispersion in particulate liquid-solid fluidized beds.
2.5 Mass Transfer Coefficients in Particulate Liquid-Solid Fluidized Beds

In order to use any of the mass balance models for particulate liquid-solid fluidized beds the mass transfer coefficient needs to be known. According to Chen et al [8] the correlation that describes the available data best is

\[
Sh = 2 + 1.5 \cdot (1 - \epsilon_{\text{bed}}) \cdot Re_p^{1/2} \cdot Sc^{1/3}
\]  
(2.36)

Where \( Re_p \) is the particle Reynolds number defined in equation (1.25) with \( u = u_{\text{flb}} \)

\( Sc \) is the Schmidt number given by equation (1.26)

\( Sh_{\text{flb}} \) is the Sherwood number given by equation (2.37)

The Schmidt number is defined as

\[
Sc = \frac{\mu_l}{\rho_{\text{fluid}} \cdot D_{A,l}}
\]  
(1.26)

where \( D_{A,l} \) is the diffusivity of component A in the liquid \( \left[ \frac{m^2}{s} \right] \)

and the fluid bed Sherwood number as

\[
Sh_{\text{flb}} = \frac{k_l \cdot d_p}{D_{A,l}}
\]  
(2.37)

2.6 Bubbling Gas-Solid Fluidization

In general gas fluidized beds behave very differently from liquid fluidized. If the superficial gas velocity of a gas-solid fluidized bed increases just a little above the minimum fluidization velocity \( u_0 \) the relatively well ordered hydrodynamics of the particulate fluidized bed breaks down. Depending on the particle size and density, to a lesser intend the gas properties, and to a large intent superficial gas velocity and gas dispenser design, the fluid bed will behave as either a bubbling fluidized bed, a slugging fluidized bed, a turbulent fluidized bed or a sprouting bed. How a gas-solid fluidized bed behaves influence the design equations used to predict the behavior of the bed. Kunii and Levenspiel [6] have based on reported experiences with a large number of gas-solid fluidized beds developed the fluidization regime plot shown in figure 2.5. The figure is based on the dimensionless terminal pellet velocity defined as

\[
\frac{1}{\text{Re}_{\text{term}}} \cdot \left(\frac{4}{3} \cdot \frac{Re_{\text{term}}}{C_D}\right)^{1/3}
\]  
(2.38)

and the dimensionless pellet diameter defined as

\[
d_p^* = Ar^{1/3}
\]  
(2.39)
For heterogeneous catalyzed reactions the engineer is normally able to choose the fluidization regime and can choose pellet size and gas velocity accordingly. For heterogeneously catalyzed gas phase reactions when particulate fluidization cannot be achieved the next best choice is the bubbling fluidized bed. Thus this is the fluidization regime sought after and the one that will be described in some detail in the following sections. For other fluidization regimes the reader is referred to Kunii and Levenspiel [6] and Kwauk [12].

2.6.1 Basic Fluid Dynamics of Bubbling Gas-Solid Fluidization

Surprisingly much more information and knowledge is available on bubbling fluidization than for particulate fluidization. This is mainly because gas-solid fluidization has been in the forefront in an industry based on petrochemicals and coal chemistry. Even so the first 20 years most fluid bed design had to be based on cautious scale up from lab-scale through many steps of pilot plants to the final full scale fluid bed. The main reason for this was, that the fluid dynamic behavior of bubbling fluid beds were poorly understood. The main breakthrough came in 1963 with Davidson and Harrison’s ground breaking theoretical modeling of a single gas bubble’s behavior in a particulate fluid bed. Based on their theoretical model, described in [13], they described in detail the expected behavior of a gas bubble. A description that, after minor improvements, have been verified experimentally in numerous experiments [6].

Figure 2.5 Grace-plot for fluidization regimes as modified by Kunii and Levenspiel [6].
A single bubble moving through an otherwise particulate fluidized bed behaves as indicated in figure 2.6. The gas bubble is formed at the gas dispersion device at the bottom of the fluid bed. The initial bubble size depends on the geometry and configuration of this dispenser. How the bubble behaves as it rises through the bed depend on the flow regime. In it’s most developed form the gas bubble consist of the gas bubble proper, a particle cloud around the bubble and a particle wake. The gas bubble is not totally void of catalyst particles but contains only a minor fraction of the total amount of catalyst pellets in the bed. Thus only a minor part of the reactant conversion happens in the bubble. The gas bubble do though exchange matter with the cloud phase, the wake phase and, sometimes only indirectly, with the particulate phase, which in bubbling fluid beds, in order to avoid confusion, often is termed the emulsion phase. It is therefore important not only to be able to describe the bubble phase but also the cloud, wake and emulsion phase.

The particles are transported upward in the fluid bed in the bubble phase and in the wake phase while they flow downward in the emulsion and cloud phase. Normally the gas in the emulsion phase will travel upward in the fluid bed, but if the fraction of gas in the bubble phase is large enough, backmixing can occur through the emulsion phase. Depending on the relative velocity of the gas in the bubble phase and the emulsion phase a cloud phase will form as shown in figure 2.7.

Figure 2.6 Gas bubble geometry in gas-solid fluidized bed after Butt [14].
Figure 2.7 Gas bubble behavior dependence on the relative gas velocity in the emulsion and bubble phase. \( u_{br} \) is the gas bubble velocity, \( u_f \) the emulsion gas velocity [6].

If the bubble velocity is slower than the emulsion gas velocity no cloud will form. Here the emulsion gas rises faster than the bubble. The emulsion gas may therefore short cut through the bubble phase where the pressure drop caused by the gas flow is lower. The emulsion gas enters the bubble at the bottom and leaves at the top. A small annular ring of recycling gas though does exist inside the bubble.

If the bubble velocity is larger than the emulsion gas velocity a cloud forms around the bubble. Gas still enters through the bottom of the bubble as the pressure drop inside the bubble is lower than in the emulsion phase. The gas leaves the top of the bubble it is forced aside by the fast rising bubble and returns to the bottom to be recycled through the bubble. It is this recycling gas that forms the cloud phase.

For industrial applications more than one bubble in the fluidized bed will be present at the same time. The behavior predicted by Davidson and Harrison still holds except for the fact that bubbles coalesce as they move toward the top of the bed leading to larger individual bubbles as they near the top. When setting up design equations for a bubbling fluidized bed all these findings have to be included in order to model the fluid bed height, diameter and conversion properly. Furthermore suitable correlations have to be found as well to predict the size of bubble, cloud, wake and emulsion phase.
2.6.2 Mass Balances for a Bubbling Gas-Solid Fluid bed - The K-L model

Taken the complexity of the fluid dynamics it is not surprising that numerous models for bubbling fluidized beds have been setup. The one most favored by chemical engineers is the Kunii-Levengiel three phase model or K-L model for short. The model somewhat crudely divide the bed into three continuous phases as seen in figure 2.8

![Figure 2.8 Idealization of the K-L model. a. true bubbling fluidized bed. b. K-L model for setting up mass balances over the bed.](image)

The basic assumption is that each phase behaves as a plug flow reactor and that transfer of matter between each phase can be described using a transfer coefficient. Furthermore the wake phase and the cloud phase is treated as one phase. Based on this the steady state molar balance for the bubble phase is

\[
\Delta m_{\text{in}} + \Delta m_{\text{generated}} = \Delta m_{\text{out}} + \Delta m_{\text{accumulated}}
\]

\[
\frac{A_{zb}}{J_z} \cdot \Delta z \cdot \Delta t + \frac{\eta_{gb}}{J_z} \cdot \Delta z \cdot \Delta t + \frac{C_{Ab}}{J_z} \cdot \Delta z \cdot \Delta t = 0
\]

Where

- \( A_{zb} \) is the axial cross sectional area taken up by the bubble phase at length \( z \) in the gas fluidized bed \([m^2]\)
- \( a_b \) is the bubble surface area per volume of fluidized bed \([m^2/m^3]\)
- \( C_{Ab} \) is the molar concentration of component A in the bubble phase \([mol/m^3]\)
- \( C_{Ac} \) is the molar concentration of component A in the cloud/wake phase \([mol/m^3]\)
- \( k_{gb} \) is the mass transfer coefficient for component A between bubble and cloud/wake phase \([m/s]\)
- \( u_b \) is the bubble velocity in the fluid bed \([m/s]\)
- \( z \) is the axial position \([m]\)
- \( \Delta t \) is the small control time interval over which the molar balance is setup \([s]\)
- \( \Delta z \) is the small control axial length interval over which the molar balance is setup \([m]\)
- \( \eta_{gb} \) is the efficiency factor for the catalyst pellet, including internal and external mass transfer limitations in the bubble phase
The total bubble phase volume, though not the size of the individual bubbles, are taken to be constant independent of the position in the bed. Therefore $A_{zb}$ cancels out and equation (2.40) can be restated as:

$$\frac{u_b \cdot C_{Ab}}{\Delta z} \frac{1}{1 + \Delta z} - u_b \cdot C_{Ab} \frac{1}{\Delta z} + \eta_{Gb} \cdot (-r_{kin}(C_{Ab})) \cdot (1 - \epsilon_{bub}) \cdot \rho_p + k_{gb} \cdot a_b \cdot (C_{Ab} - C_{Ac}) = 0$$ \hspace{1cm} (2.41)

Taking the limit as $\Delta z$ goes towards zero this leads to:

$$u_b \cdot \frac{dC_{Ab}}{dz} = \eta_{Gb} \cdot r_{kin}(C_{Ab}) \cdot (1 - \epsilon_{bub}) \cdot \rho_p - k_{gb} \cdot a_b \cdot (C_{Ab} - C_{Ac})$$ \hspace{1cm} (2.42)

In modeling of bubbling fluidization instead of the porosity the volumetric volume of catalyst per volume of bubble is often used:

$$\gamma_b = \frac{\text{volume of catalyst in bubble phase}}{\text{volume of bubble phase}} = 1 - \epsilon_{bub}$$ \hspace{1cm} (2.43)

Where $\gamma_b$ is volume fraction of catalyst per volume of gas bubble in the bubble phase.

Furthermore the mass transfer coefficient $k_{gb}$ and the bubble surface area per volume $a_b$ is from an experimental point of view statistically correlated and difficult to determine independently. Therefore they are combined into a single transfer coefficient:

$$K_{bc} = k_{gb} \cdot a_b$$ \hspace{1cm} (2.44)

Where $K_{bc}$ is the bubble-cloud interchange coefficient $[\text{s}^{-1}]$

The mass balance for the bubble phase thus become:

$$u_b \cdot \frac{dC_{Ab}}{dz} = \gamma_b \cdot \eta_{Gb} \cdot r_{kin}(C_{Ab}) \cdot \rho_p - K_{bc} \cdot (C_{Ab} - C_{Ac})$$ \hspace{1cm} (2.45)
Similarly a steady state molar balance for the cloud/wake phase can be setup:

\[
\begin{align*}
\text{In} & \quad + \quad \text{Generated} = \\
& u_c \cdot A_{zc} \cdot C_{Ac} \cdot \Delta t + k_{gb} \cdot a_b \cdot A_{zb} \cdot \Delta z \cdot \left( C_{Ab} - C_{Ac} \right) \cdot \Delta t + \eta \cdot r_{km}(C_{Ac}) \cdot \left( 1 - \epsilon_{cloude} \right) \cdot \rho_p \cdot A_{zc} \cdot \Delta z \cdot \Delta t \\
& \text{Out} + \quad \text{accumulated} \\
& u_c \cdot A_{zc} \cdot C_{Ac} \cdot \Delta z + k_{gb} \cdot a_b \cdot A_{zc} \cdot \Delta z \cdot \left( C_{Ac} - C_{Ac} \right) \cdot \Delta t + 0
\end{align*}
\]

(2.46)

Where  

\- \( A_{zc} \) is the axial cross sectional area taken up by the cloud/wake phase at length \( z \) [m²]  
\- \( a_c \) is the cloud/wake emulsion surface area per volume of fluidized bed \( \frac{m^2}{m^3} \)  
\- \( C_{Ac} \) is the molar concentration of component A in the emulsion phase \( \frac{mol}{m^3} \)  
\- \( k_{ge} \) is the mass transfer coefficient for component A between cloud/wake and emulsion phase \( \frac{m}{s} \)  
\- \( u_c \) is the cloud/wake velocity in the fluid bed \( \frac{m}{s} \)  
\- \( \eta_{Gcw} \) is the efficiency factor for the catalyst pellet, including internal and external mass transfer limitations in the cloud/wake phase

The total cloud/wake phase volume is taken to be constant independent of the position in the bed leading to:

\[
\frac{u_c \cdot C_{Ac} |_{z+\Delta z} - u_c \cdot C_{Ac} |_z}{\Delta z} + \eta_{Gcw} \cdot \left( - r_{km}(C_{Ac}) \right) \cdot \left( 1 - \epsilon_{cloude} \right) \cdot \rho_p \cdot k_{ge} \cdot a_c \cdot \left( C_{Ac} - C_{Ac} \right) - k_{gb} \cdot a_b \cdot \frac{A_{zh}}{A_{zc}} \cdot \left( C_{Ab} - C_{Ac} \right) = 0
\]

(2.47)

Taking the limit as \( \Delta z \) goes towards zero this leads to:

\[
u_c \cdot \frac{dC_{Ac}}{dz} = etasubGcw \cdot r_{km}(C_{Ac}) \cdot \left( 1 - \epsilon_{cloude} \right) \cdot \rho_p - k_{gb} \cdot a_b \cdot \frac{A_{zh}}{A_{zc}} \cdot \left( C_{Ab} - C_{Ac} \right) + k_{gb} \cdot a_b \cdot \frac{A_{zh}}{A_{zc}} \cdot \left( C_{Ab} - C_{Ac} \right)
\]

(2.48)

Just as for the bubble phase for the cloud and wake phase instead of the porosity the volumetric volume of catalyst per volume of bubble is often used:

\[
\gamma_c = \frac{\text{volume of catalyst in cloud/wake phase}}{\text{volume of bubble phase}}
\]

(2.49)

Where  \( \gamma_c \) is volume fraction of catalyst per volume of gas bubble in the cloud or wake phase.

As the cloud/wake porosity is defined per volume cloud/wake a conversion between cloud/wake volume and bubble volume is needed.
To this purpose the volume fractions $f_w$ and $f_c$ is defined:

$$
\begin{align*}
  f_w &= \frac{\text{volume of wake phase}}{\text{volume of bubble phase}} \\
  f_c &= \frac{\text{volume of cloud phase}}{\text{volume of bubble phase}}
\end{align*}
$$

(2.50)

Where $f_c$ is volume fraction of cloud per volume of gas bubble in the bed. $f_w$ is volume fraction of wake per volume of gas bubble in the bed.

This makes it possible to describe the cloud/wake porosity as

$$
1 - \varepsilon_{\text{cloud}} = \frac{\gamma_c}{f_w + f_c}
$$

(2.51)

Further as the height of the bed is the same for each phase the ratio between the cross sectional area of the cloud/wake phase and the bubble phase can be expressed by

$$
\frac{A_{\text{cc}}}{A_{\text{bc}}} = \frac{L \cdot A_{\text{cc}}}{L \cdot A_{\text{bc}}} = \frac{\text{volume of bubble phase}}{\text{volume of wake and cloud phase}} = \frac{1}{f_w + f_c}
$$

(2.52)

If finally the molar transfer coefficient $k_{gc}$ and the cloud/wake surface area per volume $a_c$ together with the volume fraction of cloud and wake for convenience is expressed as a single interchange coefficient:

$$
K_{\text{bc}} = k_{gc} \cdot a_c \cdot (f_w + f_c)
$$

(2.53)

Where $K_{\text{bc}}$ is the cloud-emulsion interchange coefficient $[s^{-1}]$

The molar balance for the cloud/wake phase can be expressed as:

$$
\frac{dC_{Ac}}{dz} = \frac{\gamma_c}{f_w + f_c} \cdot \eta \cdot r_{\text{kin}}(C_{Ab}) \cdot \rho_p - \frac{K_{gc}}{f_w + f_c} \cdot (C_{Ac} - C_{As}) + \frac{K_{bc}}{f_w + f_c} \cdot (C_{Ab} - C_{Ac})
$$

(2.54)
Finally the molar balance over the emulsion phase at steady state is:

\[
\begin{align*}
\text{In} + \text{Generated} &= \text{Out} + \text{accumulated} \\
&= u_e \cdot A_{ze} \cdot C_{Ae} \big|_z \cdot \Delta t + k_{ge} \cdot a_e \cdot A_{ze} \cdot \Delta z \cdot \left(C_{Ac} - C_{Ac}\right) \Delta t + \eta_e \cdot r_{kin}(C_{Ac}) \cdot \left(1 - \epsilon_{\text{emulsion}}\right) \cdot \rho_p A_{ze} \cdot \Delta z \cdot \Delta t \\
&+ \eta_e \cdot r_{kin}(C_{Ac}) \cdot \left(1 - \epsilon_{\text{emulsion}}\right) \cdot \rho_p A_{ze} \cdot \Delta z \cdot \Delta t + 0
\end{align*}
\]

(2.55)

Where \( A_{ze} \) is the axial cross sectional area taken up by the emulsion phase at length \( z \) [m²]

\( u_e \) is the velocity of the gas in the emulsion phase [m/s]

\( \eta_e \) is the efficiency factor for the catalyst pellet, including internal and external mass transfer limitations in the emulsion phase.

The total emulsion phase volume is taken to be constant independent of the position in the bed leading to:

\[
\frac{u_e \cdot C_{Ac} \big|_z \cdot \Delta z}{\Delta z} - \frac{u_e \cdot C_{Ac} \big|_{z + \Delta z}}{\Delta z} + \eta_e \cdot (-r_{kin}(C_{Ac})) \cdot \left(1 - \epsilon_{\text{emulsion}}\right) \cdot \rho_p - k_{ge} \cdot a_e \cdot A_{ze} \cdot \left(C_{Ac} - C_{Ac}\right) = 0
\]

(2.56)

Taking the limit as \( \Delta z \) goes toward zero this leads to:

\[
\left. u_e \right|_z \cdot \frac{dC_{Ac}}{dz} = \eta_e \cdot r_{kin}(C_{Ac}) \cdot \left(1 - \epsilon_{\text{emulsion}}\right) \cdot \rho_p + k_{ge} \cdot a_e \cdot a_b \cdot \frac{A_{ze}}{A_{ze}} \left(C_{Ac} - C_{Ac}\right)
\]

(2.57)

Again instead of the porosity the volumetric volume of catalyst per volume of gas bubble is often used:

\[
\gamma_e = \frac{\text{volume of catalyst in emulsion phase}}{\text{volume of bubble phase}}
\]

(2.58)

Where \( \gamma_e \) is volume fraction of catalyst per volume of gas bubble in the emulsion phase.

and again a conversion between emulsion volume and bubble volume is needed:

\[
f_e = \frac{\text{volume of emulsion phase}}{\text{volume of bubble phase}}
\]

(2.59)

Where \( f_e \) is volume fraction of emulsion per volume of gas bubble in the bed.

making it possible to describe the emulsion porosity as

\[
1 - \epsilon_{\text{emulsion}} = \frac{\gamma_e}{f_e}
\]

(2.60)
The ratio between the cross sectional area of the emulsion phase and the cloud/wake phase can of cause be expressed by

\[
\frac{A_{ze}}{A_{ze}} = \frac{L \cdot A_{ze}}{L \cdot A_{ze}} = \frac{\text{volume of wake and cloud phase}}{\text{volume of emulsion phase}} = \frac{\text{volume of bubble phase}, \text{volume of wake and cloud phase}}{\text{volume emulsion phase}, \text{volume of bubble phase}} = \frac{f_w + f_c}{f_c}
\]  

(2.61)

This lead to the following mass balance for the emulsion phase:

\[
u_e \cdot \frac{dC_{Ae}}{dz} = \frac{\gamma_e}{f_c} \cdot \eta_1 \cdot r_{kin}(C_{Ae}) \cdot \rho_p + \frac{K_{ce}}{f_c} \cdot (C_{Ac} - C_{Ae})
\]  

(2.62)

The total set of mass balances to be solved therefore are:

\[
\frac{dC_{Ab}}{dz} = \frac{\gamma_b}{u_b} \cdot \eta \cdot \gamma \cdot g \cdot b \cdot \rho_p \cdot r_{kin}(C_{Ab}) - \frac{K_{bc}}{u_b} \cdot (C_{Ab} - C_{Ac})
\]

\[
\frac{dC_{Ac}}{dz} = \frac{\gamma_c}{(f_w + f_c)} \cdot \eta_g \cdot \gamma \cdot g \cdot c \cdot \rho_p \cdot r_{kin}(C_{Ac}) \cdot \frac{K_{ce}}{(f_w + f_c)} \cdot (C_{Ac} - C_{Ae}) + \frac{K_{bc}}{(f_w + f_c)} \cdot u_c \cdot (C_{Ab} - C_{Ac})
\]

\[
\frac{dC_{Ae}}{dz} = \frac{\gamma_e}{f_c} \cdot \eta_1 \cdot r_{kin}(C_{Ae}) \cdot \rho_p + \frac{K_{ce}}{f_c} \cdot u_e \cdot (C_{Ac} - C_{Ae})
\]  

(2.63)

with the boundary conditions:

\[
\begin{array}{ll}
\forall: & z = 0: \quad C_{Ab} = C_{Ae0} \\
& z = 0: \quad C_{Ac} = C_{Ae0} \\
\end{array}
\]

(2.64)

or

\[
\begin{array}{ll}
z = 0: \quad C_{Ac} = C_{Ae0} & \text{if } u_e \text{ is positive} \\
\frac{dC_{Ae}}{dz} = 0 & \text{if } u_e \text{ is negative}
\end{array}
\]
2.7 Correlations for Bubbling Gas-Solid Fluid Bed Properties

The properties on which most of the correlations used for predicting properties in the K-L model are based, are the bubble velocity, the bubble velocity relative to the emulsion velocity, the minimum fluidization velocity and the emulsion velocity. The description of correlations will therefore begin with correlations for these individual velocities.

2.7.1 Correlations for Bubble and Emulsion velocities

The minimum fluidization velocity $u_{\text{min}}$ can still be found from equation (2.4).

The rise velocity relative to the emulsion phase for a single bubble $u_{br}$ can be estimated from [6]

$$u_{br} = 0.711 \cdot \sqrt{g \cdot d_b} \quad \text{if} \quad \frac{d_b}{d_i} < 0.125$$

$$u_{br} = 0.711 \cdot \sqrt{g \cdot d_b} \cdot 1.2 \cdot \exp \left( -1.49 \cdot \frac{d_b}{d_i} \right) \quad \text{if} \quad 0.125 < \frac{d_b}{d_i} < 0.6$$

$$u_{br} = \text{if} \quad \frac{d_b}{d_i} > 0.6 \text{ the bed will behave as a slugging bed, not a bubbling bed}$$

Where   $d_i$ is the diameter of a single bubble [m]

$u_{br}$ is the bubble rise velocity relative to the fluid in the fluid bed $[\text{m/s}]$

The bubble diameter can be estimated as described in section 2.7.2.

The bubble velocity in a bubbling fluid bed $u_b$ depends on the fluid bed diameter. For small diameter fluid beds equation (2.66) can be used [6] for Geldart A, B and D particles.

$$u_b = u_{sfb} - u_{\text{min}} + u_{br} \quad (2.66)$$

Where $u_{sfb}$ is the superficial feed gas velocity $[\text{m/s}]$

For larger diameter fluid beds equation (2.67) should be used for Geldart A particles [6]:

$$u_b = 1.55 \cdot (u_{sfb} - u_{\text{min}} + 14.1 \cdot (d_b + 0.005)) \cdot d_{fb}^{0.32} + u_{br} \left[ \text{m/s} \right] \quad d_{fb} < 1 \text{ [m]} \quad (2.67)$$

Where $d_b$ and $d_{fb}$ has to have the unit [m] as equation (2.67) is not dimensionless.

and equation (2.68) for Geldart B particles [6]:

$$u_b = 1.6 \cdot (u_{sfb} - u_{\text{min}} + 1.13 \cdot d_b^{0.5}) \cdot d_{fb}^{1.35} + u_{br} \left[ \text{m/s} \right] \quad d_{fb} < 1 \text{ [m]} \quad (2.68)$$

Where $d_b$ and $d_{fb}$ has to have the unit [m] as equation (2.68) is not dimensionless.
Equations (2.67) and (2.68) have only been tested for fluid bed diameters below 1 meter, but until further data emerges they will have to do also for larger beds. As wall effects will be of less importance for large beds this will most likely not lead to any major error. When to substitute (2.66) for either (2.67) or (2.68) can be determined by first calculating \( u_b \) from (2.67) or (2.68) respectively and then compare this value with the value calculated from (2.66). When the value of \( u_b \) calculated by either (2.67) or (2.68) becomes smaller than the that found from (2.66), equation (2.66) should be used [6].

The cloud and wake velocity in a bubbling fluid bed \( u_c \) is equal to the bubble velocity \( u_b \) as the cloud and wake are attached to the bubble.

The emulsion velocity in a bubbling fluid bed \( u_e \) can for Geldart A and small Geldart AB particles be estimated from (2.69)

\[
\left( \frac{u_e}{u_{fb,min}} \right)^{0.7} = \left( \frac{\varepsilon_{emulsion}}{\varepsilon_{fb,min}} \right)^3 \left( \frac{1 - \varepsilon_{fb,min}}{1 - \varepsilon_{emulsion}} \right) \tag{2.69}
\]

and for larger Geldart B and Geldart D particles from (2.70)

\[
u_e = \frac{1}{3} (u_{fb} - u_{fb,min}) + u_{fb,min} \tag{2.70}
\]

The emulsion porosity can be found as described in section 2.7.4.

### 2.7.2 Correlations for the Bubble Diameter

The gas bubble diameter in a fluid bed depends both of the geometry of distributor from where the gas is injected and on the distance the gas bubble has travelled. A thorough discussion on distributor construction is given in [6]. The main purpose of the dispenser is to ensure that the injected gas is well distributed across the bed. In laboratory scale fluid beds this is insured by injecting the gas through a porous plate at the bottom of the bed. This gives an ideal gas distribution in the bed. Unfortunately for mechanical reasons this arrangement can not be used in larger beds, partly because lack of strength but also because the porous plate will expand at the high temperatures normally encountered in gas fluidized bed operation. In full scale operations therefore perforated plates, valve plates (commonly called tuyeres) or pipe grids and spargers as known from distillation columns are used.

The initial bubble diameter, \( d_{b0} \) depends on the arrangement of these spargers and the number of gas inlet orifices per unit area.

The number of gas inlets per area can be calculated as

\[
N_{or} = \frac{1}{L_{or}^2} \quad \text{for a square array of orifices} \tag{2.71}
\]

\[
N_{or} = \frac{2}{\sqrt{3} \cdot L_{or}^2} \quad \text{for a triangle array of orifices}
\]

Where \( L_{or} \) is the distance between the individual orifices [m]

\[
N_{or} \text{ is the number of orifices per area } \left[ \frac{1}{m^2} \right]
\]
For low gas velocities the bubbles initial rise as individual bubbles. For larger gas velocities the adjacent gas bubbles coalesce as soon as they leave the orifices. Therefore the bubble diameter must be estimated differently depending on the gas velocity and the distance between the orifices [6]:

\[
\begin{align*}
\frac{d_{b0}}{g} &= 0.0130 \left( \frac{u_0 - u_{\text{min}}}{N_{or}} \right)^{0.4} \quad \text{for } d_{b0} \leq L_{or} \\
\frac{d_{b0}}{g} &= 0.0278 \left( u_0 - u_{\text{min}} \right)^2 \quad \text{for } d_{b0} > L_{or}
\end{align*}
\]  

(2.72)

Where \( \frac{d_{b0}}{g} \) is the bubble diameter in SI-units, \( u_0 \) is the superficial gas velocity, \( u_{\text{min}} \) is the minimum fluidization velocity, \( N_{or} \) is the number of orifices, \( L_{or} \) is the distance between the orifices, and \( g \) is the acceleration due to gravity.

For porous plate distributors the distance between the orifices is not well defined, but the distance \( L_{or} \) will be smaller than the bubble diameter \( d_{b0} \), thus (2.72) can still be used. As the gas bubbles move up through the bed they tend to coalesce into larger bubbles. These larger bubbles might split up again into smaller bubbles. In this way the bubble size will increase until an equilibrium is reached where bubble splitting and bubble coalescence cancels out. This bubble equilibrium size is the maximum size bubble size that might be reached in a fluid bed, depending on the fluid bed height. For Geldart type A, B and D particles the bubble size can be calculated using the Choi-Son-Kim method [15].

According to Choi et al [15] the bubble splitting frequency can be estimated as

\[
f_s^* = 6.47 \cdot 10^{-4} \left( \frac{u_{\text{eff}}}{u_{\text{fb,min}}} \right)^{0.454} \frac{g}{u_{\text{fb,min}}}
\]

(2.73)

Where \( f_s^* \) is the bubble splitting frequency in \( \text{s}^{-1} \).

From this the equilibrium bubble diameter can be estimated as

\[
d_{b,\text{eq}} = 6.729 \cdot \frac{u_{\text{eff}}}{f_s^*} \left( 1 - \left( \frac{u_{\text{eff}}}{u_{\text{fb,min}}} \right)^{-0.380} \right)
\]

(2.74)

Based on the equilibrium bubble size the bubble size as a function of distance over the distributor can be estimated iteratively from [15]:

\[
d_b = \left( \sqrt{d_{b0}} - \frac{z}{a_{fb}} + \frac{b_{fb}}{2} \ln \left( \frac{d_{b0} - d_{b,\text{eq}}}{d_b - d_{b,\text{eq}}} \right) + \sqrt{d_{b,\text{eq}}^2} \ln \left( \frac{\sqrt{d_{b0}} - \sqrt{d_{b,\text{eq}}}}{\sqrt{d_b} - \sqrt{d_{b,\text{eq}}}} \right) \right)^2
\]

(2.75)

Where \( a_{fb} \) is a constant found from equation (2.76) \( \text{m}^{0.5} \)

\( b_{fb} \) is a constant found from equation (2.77) \( \text{m}^{0.5} \).
With

\[ a_{fb} = 4.266 \cdot \frac{\sqrt{g}}{f^*} \]  

(2.76)

and

\[ b_{fb} = 1.406 \cdot \frac{u_{sfb} - u_{fb,\text{min}}}{\sqrt{g}} \]  

(2.77)

2.7.3 Bubble Voidage Fraction, Cloud, Wake and Emulsion Volume to Bubble Volume in Bubbling Fluidized Beds

The voidage fraction of the bed taken up by gas bubbles can for slow moving bubbles be estimated from

\[ \delta = \frac{u_{sfb} - u_{fb,\text{min}}}{u_b + 2 \cdot u_{fb,\text{min}}} \text{ for } u_b < u_e \]  

(2.78)

Where \( \delta \) is the bubble voidage fraction in the fluidized bed.

For intermediate bubbles with thick overlapping clouds there are no general correlations but the bubble velocity will be somewhere in between the two limiting values given by (2.79)

\[ \delta = \frac{u_{sfb} - u_{fb,\text{min}}}{u_b + u_{fb,\text{min}}} \text{ for } u_b = \frac{u_{fb,\text{min}}}{\epsilon_{fb,\text{min}}} \]

\[ \delta = \frac{u_{sfb} - u_{fb,\text{min}}}{u_b - u_{fb,\text{min}}} \text{ for } u_b = 5 \cdot \frac{u_{\text{min}}}{\epsilon_{fb,\text{min}}} \]  

(2.79)

For fast bubbles the voidage fraction can be found from 2.80.

\[ \delta = \frac{u_{sfb} - u_{fb,\text{min}}}{u_b - u_{fb,\text{min}}} \text{ for } u_b > 5 \cdot \frac{u_{fb,\text{min}}}{\epsilon_{fb,\text{min}}} \]  

(2.80)

The cloud to bubble volume can be found from

\[ f_c = \frac{3}{u_{br} \cdot \epsilon_{fb,\text{min}} - 1} \]  

(2.81)
The wake to bubble volume is determined from figure 2.9.

![Figure 2.9 Wake volume to bubble volume \( f_w \) as a function of particle properties, after [6].](image)

The emulsion to bubble volume not including the wake and cloud phase is

\[
    f_e = 1 - (1 + f_w + f_b) \cdot \delta
\]  

(2.82)

2.7.4 Correlations for Porosity and Solid volume Fractions in Bubbling Fluidized Beds

Equation (2.12) also holds for bubbling fluidized beds with minor expansions

\[
    L_{flb, min} \cdot (1 - \epsilon_{flb, min}) = L_{min} \cdot (1 - \epsilon_{min}) = L_{flb} \cdot (1 - \epsilon_{flb})
\]  

(2.83)

Where

- \( L_{flb, min} \) is the bed height at minimum bubbling fluidization [m]
- \( \epsilon_{flb, min} \) is the porosity of the fluidized bed at minimum bubbling

The porosity at minimum fluidization and bubbling fluidization has to be determined experimentally, but for spherical pellets the values are typically between 0.4 and 0.5.
The porosity of the emulsion phase is nearly equal to:

\[
\begin{align*}
\epsilon_{\text{emulsion}} &= \epsilon_{\text{fb,min}} \quad \text{for Geldart A particles} \\
\epsilon_{\text{emulsion}} &= \epsilon_{\text{fb,min}} \quad \text{for Geldart B and D particles}
\end{align*}
\]  

As the porosity at minimum bubbling can be difficult to determine it is often substituted with the minimum fluidization velocity.

The mean porosity of the fluidized bubbling bed can be estimated as from (2.83), (2.84) and one of the equations 2.78-2.80:

\[
\epsilon_{\text{fb}} = 1 - (1 - \epsilon_{\text{fb,min}}) \cdot (1 - \delta)
\]  

The solid volume to bubble volume fraction in the bubble phase is not well established, partly because it is so low, that it for most applications is considered unimportant. Experimental evidence points to a value between 0.001 and 0.01 based on which a safe guess is

\[
\gamma_b = 0.005
\]  

The solid volume in cloud/wake to bubble volume can be found from

\[
\gamma_c = (1 - \epsilon_{\text{fb,min}}) \cdot (f_w + f_c)
\]  

And finally the solid volume to bubble volume in the emulsion phase can be found as

\[
\gamma_e = \frac{(1 - \epsilon_{\text{fb,min}}) \cdot (1 - \delta)}{\delta} \cdot (1 - \gamma_b - \gamma_c)
\]

### 2.7.5 Correlations for transfer coefficients in Bubbling Fluidized Beds

The bubble-cloud interchange coefficient can be estimated from Equation (2.88) [6]:

\[
K_{bc} = 4.5 \cdot \left( \frac{u_{\text{fb,min}}}{d_b} \right) + 5.85 \cdot \left( \frac{\sqrt{D_i} \cdot g^{0.25}}{d_b^{1.25}} \right)
\]

The cloud-emulsion interchange coefficient can be estimated as [6]:

\[
K_{ce} = 6.77 \cdot \sqrt{\frac{D_i \cdot \epsilon_{\text{fb,min}} \cdot u_{br}}{d_b^2}}
\]
3. Models for Gas-Liquid Reactors

Reactions where the reactants are immiscible are notoriously difficult to model in detail. This in turn leads to difficulties during reactor design and scale-up. Non the less many industrially important chemicals are produced from reactants that cannot form miscible solutions. Depending on if the reactants are two immiscible liquids, like methanol and long chained fatty acids in biodiesel production, or a gas and a liquid like in hydrothermal cracking of heavy hydrocarbons to light fuels, the optimal reactor design will differ. This section will deal with gas-liquid and solid catalysed gas-liquid reactions only. For design of liquid-liquid reactions the reader for the time being is referred to other standard literature [1, 5, 16].

As the basic design options useful for gas-liquid reactions to some extend differ from those possible for solid catalysed gas-liquid reactions the designs will be presented separately, followed by an example on how a reactor can be modelled.

3.1 Basic Reactor Designs for Gas-Liquid Reactions

The main concern when designing reactors for gas-liquid reactions is to ensure sufficient contact between the gas and the liquid to ensure a fast reaction without spending too much energy in the mixing process. Depending on which step in the reaction that is rate determining, i.e., the transport of gas to the liquid interface, the transport of dissolved gas from the liquid phase to the liquid bulk phase or the actual chemical reaction, different reactor designs are optimal. Figure 3.1 shows, without being an exhaustive list, the most common reactor configurations for gas-liquid reactions.

![Figure 3.1. Tower and tank contactors (reactors) for gas-liquid reactions [6].](image)

How to choose between the individual reactors is not a simple task, some general rules of thumb based on the approximate flow pattern in the reactors and the mass transfer and reaction rates though can be given:

**Flow patterns:**

Irrigated packed beds and Static mixers: Gas and liquid flow behaves more or less as plug flow. Some axial and radial dispersion should be expected. The ratio between gas and liquid feed rates can only be chosen within specific limits as described for distillation, stripper and absorption columns [1, 16].
Plate towers: Gas phase behaves as a plug flow. Liquid phase can, at least for small column diameters, be modelled as a perfectly mixed flow on each tray. For very large trays a dispersion model might be more appropriate.

Staged bubble tower: Gas and liquid phase is best modelled as a tank-in-series model with each stage being modelled as a CSTR.

Spray-Towers: Gas phase behaves as plug flow. Each liquid drop behaves as a batch reactor with individual residence time in the column. Some liquid drop coalescence might be expected so a residence time distribution model for the liquid phase might lead to more accurate predictions of conversion than a pure plug flow model.

Bubble tank: Gas behaves as plug flow, liquid phase as mixed flow.

Agitated bubble tank: Both gas and liquid phase might behave as mixed flow, depending on how vigorously the two phases are mixed.

Mass transfer, solubility and kinetic considerations:
For liquid droplets in a gas phase the mass transfer from gas to liquid is usually high and mass transfer in the liquid phase will dominate over gas phase mass transfer.
For gas bubbles in a liquid phase the mass transfer from gas to liquid is usually low and mass transfer in the gas phase will dominate over liquid phase mass transfer.
If the gases are very soluble in the liquid, gas transfer controls.
If the reaction is very slow, gas and liquid mass transfer limitations are unimportant.

Selecting the reactor configuration:
If the liquid-to-gas flow rate of the feed cannot be kept within the operation limits for tower reactors (spray, irrigated beds, static mixers, plate towers, bubble columns) use tank reactors.
If gas phase mass transfer dominates, bubble columns should not be used.
If liquid phase mass transfer dominates, spray towers should not be used.
If liquid phase reaction dominates use tank reactors.

Based on these simple rules, a preliminary design can be chosen and tested in pilot scale. This can then form basis for further modelling and finally scale-up to full industrial size.

3.2 Basic Reactor Designs for Solid Catalysed Gas-Liquid Reactions
When designing reactors for solid catalysed gas-liquid reactions it is of utmost importance to ensure sufficient contact between the gas and liquid, and between the catalyst and the gas saturated liquid phase. This enables a fast reaction without spending too much energy on the mixing process. As for pure gas-liquid reactions depending on which step in the reaction that is rate determining different reactor designs are optimal. In solid catalysed gas-liquid reactions the transport of gas to the liquid interphase, the transport of dissolved gas from the liquid phase to the liquid bulk phase is followed by the transport to the solid catalyst surface into the catalyst where the actual chemical reaction takes place. All of these steps can be rate determining.
Figure 3.2 shows, without being an exhaustive list, the most common reactor configurations for gas-liquid-solid reactions.
Flow patterns:
Co-current and counter-current packed beds: Gas and liquid flow behaves more or less as plug flow. Some axial and radial dispersion should be expected. The ratio between gas and liquid feed rates in counter-current beds can only be chosen within specific limits as described for distillation, stripper and absorption columns [1, 16]. In trickle beds and counter-current beds the catalyst pellets are normally totally wetted by the liquid phase. For co-current beds where the liquid is blown through by the gas this is not the case.

Slurry columns: Each gas bubble behaves as a batch reactor with individual residence time in the column. Some bubble coalescence might be expected so a residence time distribution model for the gas phase might lead to more accurate predictions of conversion than a pure plug flow model. The liquid phase behaves as a plug flow with some dispersion.

Three phased fluidized bed: Depending on the liquid to gas feed ratio the reactor can be modelled as a bubbling fluidized gas-solid bed with wetted catalyst pellets or specific models have to be sought out in the literature.

Agitated slurry tank: Gas, liquid and solid phase might behave as mixed flow, depending on how vigorously the two phases are mixed.

Mass transfer, solubility and kinetic considerations:
For liquid wetted catalysts suspended in a gas phase the mass transfer from gas to liquid is usually high and mass transfer in the liquid phase will dominate over gas phase mass transfer.
For gas bubbles in a liquid phase the mass transfer from gas to liquid is usually low and mass transfer in the gas phase will dominate over liquid phase mass transfer.
If the gases are very soluble in the liquid, gas transfer controls.
If the reaction is very slow, gas and liquid mass transfer limitations are unimportant.
Selecting the reactor configuration:
If internal mass transfer in the catalyst pellets dominates use small pellets suspended in either a gas-solid fluidized reactor or a liquid slurry reactor.
If the liquid-to-gas flow rate of the feed cannot be kept within the operation limits for three phase packed bed reactors (counter-current or co-current) use gas-fluidized beds or slurry tank reactors.
If gas phase mass transfer dominates, slurry tanks should not be used.
If liquid phase mass transfer dominates, wetted gas-solid fluidized beds should not be used.
If liquid phase reaction dominates use tank reactors.

Based on these simple rules, a preliminary design can be chosen and tested in pilot scale. This can then form basis for further modelling and finally scale-up to full industrial size.

3.3 Design Equations for Counter-Current for Solid Catalysed Gas-Liquid Reactors
As an example the design equations for counter-current packed bed reactors will be developed for solid catalysed gas-liquid reactions. The basic mass transfer considerations are sketched in figure 3.3.

When designing reactors for solid catalysed gas-liquid reactions it is of utmost importance to ensure sufficient contact between the gas and liquid, and between the catalyst and the gas saturated liquid phase. The theoretical description of the transport from the bulk gas phase to the bulk liquid phase can be described either by the Higbie penetration theory or the film layer theory. For turbulent flow the penetration theory probably comes closest to the truth, for laminar flow the two-layer film theory is probably more correct. As the film layer theory gives the easiest math and the findings of penetration theory can be included through the correlations for the mass transfer coefficients the two-film theory will be used when deriving the molar balances used in the design equations.

The basic design of a counter-current packed bed gas-liquid reactor is a kin to a packed column for absorption or stripping. The packing in the reactor being the catalyst material in the shape of randomly packed spherical solids, Rashig rings etc. or as structured packing like KataPak (Sulzer Chemtech). The diameter of the column is decided by the operating conditions of the column. The operation has to be carried out below the flooding point and the gas-liquid feed ratio has to be adjusted accordingly as described in detail in [1, 16]. The pressure drop through the column is similarly calculated as for packed columns [1, 16].
The main difference between packed columns and packed bed counter current gas-liquid reactors is in the molar balances which now have to include chemical reactions in the catalyst. The bulk flow of gas and liquid is assumed to follow a plug flow like behaviour with the liquid totally wetting the catalyst surface. According to the two-film layer theory the reactant gas therefore first has to diffuse through a stagnant gas film layer, dissolve into the liquid and diffuse into the liquid bulk before finally reaching the catalyst pellet surface, from where it can diffuse into the pellet pores to finally react on the catalyst. The basic mass transfer over the film layer can be described using a driving force, the difference in concentration, and a mass transfer coefficient. At the gas-liquid interphase the absorption is assumed to happen instantaneously, wherefore a local equilibrium between gas and liquid exists. Based on these assumptions the molar balance for the gas phase becomes:

\[
\begin{align*}
\text{In} & + \text{Generated} = \text{Out} + \text{ac} \\
\epsilon_{glt} \cdot u_{sg} \cdot A_z \cdot \Delta t & + 0 = u_{sg} \cdot \epsilon_{glt} \cdot A_z \cdot C_A^g|_{z+\Delta z} \cdot \Delta t + k_g \cdot a_h \cdot A_z \cdot \Delta z \cdot \left( C_A^g - C_{A|z}^g \right) \Delta t + 0 \\
\end{align*}
\]

Where  
- \( A_z \) is the reactor axial cross sectional area at length \( z \) [m²]  
- \( a_h \) is the hydraulic surface area between gas and liquid per volume reactor \( \left[ \frac{m^2}{m^3} \right] \)  
- \( C_A^g \) is the gas phase concentration of A \( \left[ \frac{mol}{m^3} \right] \)  
- \( C_{A|z}^g \) is the gas phase concentration of A at the gas-liquid interphase \( \left[ \frac{mol}{m^3} \right] \)  
- \( k_g \) is the mass transfer coefficient for component A between gas and liquid interphase \( \left[ \frac{m}{s} \right] \)  
- \( u_{sg} \) is the superficial gas velocity \( \left[ \frac{m}{s} \right] \)  
- \( \epsilon_{glt} \) is the gas bed porosity excluding both liquid and solid from the void of the bed.

The column cross sectional area and the gas bed porosity is normally constant. The gas velocity though might change with column height. This leads to

\[
\epsilon_{glt} \cdot u_{sg} \cdot \left( C_A^g|_{z+\Delta z} - C_A^g|_{z} \right) \Delta z + k_g \cdot a_h \cdot \left( C_A^g - C_{A|z}^g \right) = 0 
\]

which by letting \( \Delta z \) go towards zero leads to:

\[
\frac{d(u_{sg} \cdot C_A^g)}{dz} = k_g \cdot a_h \cdot \frac{\epsilon_{glt}}{\Delta z} \cdot \left( C_A^g - C_{A|z}^g \right) 
\]
The equilibrium condition between the gas phase and the liquid phase can be described by a distribution coefficient, that is not necessarily a Henry’s law constant the strict sense of the word, but never the less can be found from thermodynamics [17]:

\[ C_{Al}^g = K_A \cdot C_{Al}^l \]  

(3.4)

Where \( C_{Al}^l \) is the liquid phase concentration of A at the gas-liquid interphase \( \text{mol m}^{-3} \)

\( K_A \) is the dimensionless distribution coefficient for A between gas and liquid.

As the gas velocity cannot in general be assumed constant since liquid might evaporate, vapour condense and product not be present in the gas phase. Therefore it is often more appropriate to use the gas flux as the variable than the gas concentration:

\[ N_A^g = u_{fg} \cdot C_A^g \]  

(3.5)

Where \( N_A^g \) is the gas phase flux of A \( \text{mol m}^{-2} \text{s} \)

For the gas phase concentration the flux can then be substituted using that

\[ C_A^g = y_A^g \cdot C_{tot} = \frac{N_A^g}{R \cdot T} \sum_{i=1}^{N_l} Z_i \cdot P \]  

(3.6)

Where \( R \) is the universal gas constant 8.314 \( \text{Pa m}^3 \text{mol}^{-1} \text{K}^{-1} \)

\( Z_i \) is the compressibility factor, 1 for ideal gases, else calculable as described in [17].

\( y_A^g \) is the gas phase molecular fraction of A.

When equations (3.4) to (3.6) is entered into the molar balance (3.3) this yields the gas phase design equation

\[ \frac{dN_A^g}{dz} = \frac{k_{fg} \cdot a_h}{\varepsilon_{gref}} \left( K_A \cdot C_{Al}^l - \frac{N_A^g}{R \cdot T} \sum_{i=1}^{N_l} Z_i \cdot P \right) \]  

(3.7)
The molar balance for the liquid flow is similar except that it includes the reaction rate term:

\[
\begin{align*}
\text{In} & \quad + \quad \text{Generated} & \quad = \\
\left[ u_{ls} \cdot (\epsilon_{gl} - \epsilon_{glr}) \cdot A_z \cdot C_A^I \right]_{z + \Delta z} & \quad + \quad \sum_{i} \left[ C_A^I - C_A \right] \Delta t + k_i \cdot a_h \cdot A_z \cdot \sum_{i} \left[ C_A^I - C_A \right] \Delta z \cdot \Delta t = \\
\text{Out} & \quad + \quad \text{ac} & \quad + \quad u_{ls} \cdot (\epsilon_{gl} - \epsilon_{glr}) \cdot A_z \cdot C_A^I \left[ z \right] \Delta t + 0
\end{align*}
\] (3.8)

Where \( C_A^I \) is the liquid phase concentration of A \( \left[ \text{mol} \right] \),
\( u_{ls} \) is the superficial liquid velocity \( \left[ \frac{\text{m}}{\text{s}} \right] \),
\( \epsilon_{gl} \) is the particulate bed porosity void of gas and liquid.

The column cross sectional area and the gas bed porosity is normally constant. The liquid velocity though might change with column height. This leads to

\[
\left( \epsilon_{glr} - \epsilon_{gl} \right) \cdot \frac{u_{ls} \cdot C_A^I_{z + \Delta z} - u_{ls} \cdot C_A^I_{z}}{\Delta z} + \eta \cdot r_A (C_A^I) \cdot \rho_p \cdot (1 - \epsilon_{gl}) + k_i \cdot a_h \cdot \left( C_A^I - C_A \right) = 0
\] (3.9)

which by letting \( \Delta z \) goes towards zero leads to:

\[
\frac{d \left( u_{ls} \cdot C_A^I \right)}{dz} = - \frac{1 - \epsilon_{gl}}{\left( \epsilon_{gl} - \epsilon_{glr} \right)} \cdot r_A (C_A^I) \cdot \rho_p - \frac{k_i \cdot a_h}{\left( \epsilon_{gl} - \epsilon_{glr} \right)} \cdot \left( C_A^I - C_A \right)
\] (3.10)

Just as for the gas phase the liquid velocity cannot in general be assumed constant since liquid might evaporate, vapour condense and product may not be present in the liquid phase. Therefore it is often more appropriate to use the liquid flux as the variable than the gas concentration:

\[
N_A^I = u_{ls} \cdot C_A^I
\] (3.11)

Where \( N_A^I \) is the gas phase flux of A \( \left[ \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right] \).
Similarly to gas phase concentration the liquid concentration can be substituted by the liquid flux using that

\[ C_A^f = y_A^f \cdot C_{\text{tot}} = \frac{N_A^f}{\sum_{i=1}^{n} N_i^f \cdot V_M^f} \cdot \frac{1}{V_M^f} \]  

(3.12)

Where \( V_M^f \) is the total liquid molecular volume, calculable as described in [17] \( \text{mol/m}^3 \)

\( y_A^f \) is the liquid phase molecular fraction of A.

If the liquid density is nearly constant during the reaction, as is often the case, equation (3.12) can be simplified as

\[ C_{\text{tot}}^f = \frac{1}{V_M^f} = \frac{\rho_f}{\sum_{i=1}^{n} N_i^f \cdot M_{wi}} \]  

(3.13)

Where \( M_{wi} \) is the total molecular weight of component i \( \text{kg/mol} \)

\( \rho_f \) is the liquid density \( \text{kg/m}^3 \)

This inserted into (3.12) leads to

\[ C_A^f = \frac{N_A^f}{\sum_{i=1}^{n} N_i^f \cdot M_{wi}} \cdot \rho_f \]  

(3.14)

When equations (3.11) and (3.14) is entered into the molar balance (3.10) the liquid phase design equation appears

\[ \frac{dN_A^f}{dz} = -\frac{(1 - \varepsilon_{\text{gl}})}{\varepsilon_{\text{gl}} - \varepsilon_{\text{glt}}} \cdot \eta_A \cdot \left( \frac{N_A^f}{\sum_{i=1}^{n} N_i^f \cdot M_{wi}} \cdot \rho_f \right) \cdot \rho_p - \frac{k_f \cdot a_h}{\varepsilon_{\text{gl}} - \varepsilon_{\text{glt}}} \cdot \left( \frac{C_{\text{Ai}} - \frac{N_A^f}{\sum_{i=1}^{n} N_i^f \cdot M_{wi}} \cdot \rho_f}{\sum_{i=1}^{n} N_i^f \cdot M_{wi}} \right) \]  

(3.15)

The design equations for a counter-current reactor for solid catalysed gas-liquid reactions therefore is:

\[ \frac{dN_A^g}{dz} = \frac{k_f \cdot a_h}{\varepsilon_{\text{glt}}} \left( K_A \cdot C_{\text{Ai}}^g - \frac{N_A^g}{\sum_{i=1}^{n} N_i^g \cdot R \cdot T} \cdot Z_{\varepsilon} \cdot \rho_f \right) \]  

\[ \frac{dN_A^f}{dz} = -\frac{(1 - \varepsilon_{\text{gl}})}{\varepsilon_{\text{gl}} - \varepsilon_{\text{glt}}} \cdot \eta_A \left( \frac{N_A^f}{\sum_{i=1}^{n} N_i^f \cdot M_{wi}} \cdot \rho_f \right) \cdot \rho_p - \frac{k_f \cdot a_h}{\varepsilon_{\text{gl}} - \varepsilon_{\text{glt}}} \cdot \left( \frac{C_{\text{Ai}} - \frac{N_A^f}{\sum_{i=1}^{n} N_i^f \cdot M_{wi}} \cdot \rho_f}{\sum_{i=1}^{n} N_i^f \cdot M_{wi}} \right) \]  

(3.16)
with the boundary conditions:

\[
N_{A0}^g = u_{g0} \cdot C_{A0}^g \text{ at } z = 0
\]
\[
N_{A0}^l = u_{l0} \cdot C_{A0}^l \text{ at } z = L
\]

(3.17)

Where \( u_{g0} \) is the superficial gas velocity at the gas entrance to the reactor \( \frac{\text{m}}{\text{s}} \)

\( u_{l0} \) is the superficial liquid velocity at the liquid entrance to the reactor \( \frac{\text{m}}{\text{s}} \)

### 3.4 Parameter Correlations for Counter-Current for Solid Catalysed Gas-Liquid Reactors

Correlations for the parameters entering into the model for counter current reactors exist in numerous versions, mostly based on experiments with gas-liquid absorbers or strippers. The most accurate correlations at present seems to be the ones from Billet and Schultes. A thorough description of these correlations with data for a vast number of different packings is given in [16]. The reader is therefore referred to this textbook.
4. Symbols

\( A_r \) is the radial cross sectional area at radius \( r \) (fixed bed see figure (1.1), liquid fluid bed see figure (2.4)) \( [m^2] \)

\( A_z \) is the axial cross sectional area at radius \( r \) (fixed bed see figure (1.1), liquid fluid bed see figure (2.4)) \( [m^2] \)

\( A_{zb} \) is the axial cross sectional area taken up by the bubble phase at length \( z \) in the gas fluidized bed \( [m^2] \)

\( A_{zc} \) is the axial cross sectional area taken up by the cloud/wake phase at length \( z \) \( [m^2] \)

\( A_{ze} \) is the axial cross sectional area taken up by the emulsion phase at length \( z \) \( [m^2] \)

\( \text{Ar} \) is the Archimedes number defined in equation (2.5)

\( a_b \) is the bubble surface area per volume of fluidized bed \( \left[ \frac{m^2}{m^3} \right] \)

\( a_{flb} \) is a constant found from equation (2.76) \( [m^{0.5}] \)

\( a_c \) is the cloud/wake emulsion surface area per volume of fluidized bed \( \left[ \frac{m^2}{m^3} \right] \)

\( a_{caf} \) is the outer catalyst surface area per volume of fluidized bed \( \left[ \frac{m^2}{m^3} \right] \)

\( a_h \) is the hydraulic surface area between gas and liquid per volume reactor \( \left[ \frac{m^2}{m^3} \right] \)

\( B \) is a constant defined by equation (1.39)

\( b \) is a shape factor as given in table 1.2.

\( b_{flb} \) is a constant found from equation (2.77) \( [m^{0.5}] \)

\( C_A \) is the molar concentration of component A \( \left[ \frac{mol}{m^3} \right] \)

\( C_{Ab} \) is the molar concentration of component A in the bubble phase \( \left[ \frac{mol}{m^3} \right] \)

\( C_{Ac} \) is the molar concentration of component A in the cloud/wake phase \( \left[ \frac{mol}{m^3} \right] \)

\( C_{Ae} \) is the molar concentration of component A in the emulsion phase \( \left[ \frac{mol}{m^3} \right] \)

\( C_{AS} \) is the molar concentration of component A at the catalyst pellets outer surface \( \left[ \frac{mol}{m^3} \right] \)

\( C_{A0} \) is the molar concentration of component A in the feed to the reactor \( \left[ \frac{mol}{m^3} \right] \)

\( C_D \) is the Cunningham factor given by equation (2.7)

\( C_{\text{Fluid}} \) is molar heat capacity of the fluid feed mixture \( \left[ \frac{J}{kg \cdot K} \right] \)

\( C_{\text{perf}} \) is the specific heat capacity of the fluid mixture \( \left[ \frac{J}{kg \cdot K} \right] \)

\( C_{\text{tot}} \) is the total molar concentration of the fluid \( \left[ \frac{mol}{m^3} \right] \)

\( C_A^g \) is the gas phase concentration of A \( \left[ \frac{mol}{m^3} \right] \)
Symbols

$C_{Al}$ is the gas phase concentration of A at the gas-liquid interphase $\left[ \frac{\text{mol}}{\text{m}^3} \right]$.

$C_{Ai}$ is the liquid phase concentration of A at the gas-liquid interphase $\left[ \frac{\text{mol}}{\text{m}^3} \right]$.

$C_{A}^f$ is the liquid phase concentration of A $\left[ \frac{\text{mol}}{\text{m}^3} \right]$.

$\bar{C}_{A}$ is the mean concentration of A inside the pellet (see equation (2.26)) $\left[ \frac{\text{mol}}{\text{m}^3} \right]$.

$D_{A,ij}$ is the diffusivity of component A in the liquid $\left[ \frac{\text{m}^2}{\text{s}} \right]$.

$D_{ij}$ is the diffusivity of component i in j $\left[ \frac{\text{m}^2}{\text{s}} \right]$.

$D_{rls}$ is the radial dispersion coefficient in the fixed bed $\left[ \frac{\text{m}^2}{\text{s}} \right]$.

$D_{rlb}$ is the liquid radial dispersion coefficient $\left[ \frac{\text{m}^2}{\text{s}} \right]$.

$D_{rls}$ is the axial dispersion coefficient in the fixed bed $\left[ \frac{\text{m}^2}{\text{s}} \right]$.

$D_{rlb}$ is the liquid axial dispersion coefficient $\left[ \frac{\text{m}^2}{\text{s}} \right]$.

$D_r^s$ is the radial dispersion coefficient for the solid $\left[ \frac{\text{m}^2}{\text{s}} \right]$.

$D_z^s$ is the radial dispersion coefficient for the solid $\left[ \frac{\text{m}^2}{\text{s}} \right]$.

$d_b$ is the diameter of a single gas bubble in a fluidized [m].

$d_{b,eq}$ is the equilibrium diameter of a single gas bubble in a fluidized [m] as defined in equation (2.74).

$d_{in}$ is the diameter of the internal fixed bed diameter [m].

$d_{mb}$ is the bed diameter [m].

$d_p$ is the characteristic length of the catalyst pellet [m].

$d_p^*$ is the dimensionless pellet diameter defined in equation (2.39).

$Fr_{flb}$ is the Froude number defined in equation (2.34).

$f_c$ is volume fraction of cloud per volume of gas bubble in the bed defined in equation (2.50).

$f_e$ is volume fraction of emulsion per volume of gas bubble in the bed defined in equation (2.59).

$f_w$ is volume fraction of wake per volume of gas bubble in the bed defined in equation (2.50).

$f_*^c$ is the bubble splitting frequency $\left[ \frac{1}{\text{s}} \right]$.

$g$ is the gravitational constant 9.84 $\left[ \frac{\text{m}}{\text{s}^2} \right]$.

$H_{\text{tot}}$ is the molar enthalpy of fluid mixture $\left[ \frac{\text{J}}{\text{mol}} \right]$.

$H_{m}^{\text{tot}}$ is the specific enthalpy of the fluid mixture $\left[ \frac{\text{J}}{\text{kg}} \right]$. 
### Symbols

- \( h_{r,\text{radiation}} \) is the axial heat radiation transfer coefficient given by equation (1.35) \( \frac{W}{m^2\cdot K} \)
- \( h_{r,\text{radiation}} \) is the radial heat radiation transfer coefficient given by equation (1.41) \( \frac{W}{m^2\cdot K} \)
- \( J_r \) is the the radial heat flux \( \frac{J}{m^2\cdot s} \)
- \( J_z \) is the the axial heat flux \( \frac{J}{m^2\cdot s} \)
- \( K_A \) is the dimensionless distribution coefficient for A between gas and liquid defined in equation (3.4).
- \( K_{bc} \) is the bubble-cloud interchange coefficient \( [s^{-1}] \) given by equation (2.44).
- \( K_{ce} \) is the cloud-emulsion interchange coefficient \( [s^{-1}] \) given by equation (2.53).
- \( k_g \) is the mass transfer coefficient for component A between gas and liquid interphase \( \frac{m}{s} \)
- \( k_{gb} \) is the mass transfer coefficient for component A between bubble and cloud/wake phase \( \frac{m}{s} \)
- \( k_{gc} \) is the mass transfer coefficient for component A between cloud/wake and emulsion phase \( \frac{m}{s} \)
- \( k_f \) is the mass transfer coefficient for component A across the film layer around the catalyst pellet \( \frac{m}{s} \)
- \( L_{flb} \) is the fluid bed height [m]
- \( L_{flb,\text{min}} \) is the height of the bed at minimum fluidization [m]
- \( L_{flb,\text{minb}} \) is the bed height at minimum bubbling fluidization [m]
- \( L_{fix} \) is the length of the fixed bed reactor as defined in figure 1.1 [m]
- \( L_{ot} \) is the distance between the individual orifices [m]
- \( L_P \) is the radius of the catalyst pellet [m]
- \( L_0 \) is the height of the fluid bed at rest [m]
- \( M_{wi} \) is the total molecular weight of component i \( \frac{kg}{mol} \)
- \( \dot{n} \) is the mass flow of the fluid \( \frac{kg}{s} \)
- \( m_{flb,\text{cat}} \) is the total amount of catalyst in the bed [kg]
- \( N_{Ar} \) is the radial dispersive flux of component A \( \frac{mol}{m^2\cdot s} \)
- \( N_{Az} \) is the axial dispersive flux of component A \( \frac{mol}{m^2\cdot s} \)
- \( N_{or} \) is the number of orifices per area \( \frac{1}{m^2} \)
Symbols

\( N_A^g \) is the gas phase flux of A in a gas-liquid reactor \( \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \)

\( N_A^r \) is the radial dispersive flux of component A with the pellet \( \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \)

\( N_A^a \) is the axial dispersive flux of component A with the pellet \( \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \)

\( N_A^f \) is the gas phase flux of A \( \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \)

\( \text{Nu}_{\text{radiation}} \) is the radiation Nusselt number as given by equation (1.34).

\( n_{\text{fix}} \) is an exponent \( n \) found from equation (1.32)

\( n_{\text{flb}} \) is an exponent to be found from experiments or estimated from equation (2.13).

\( P \) is the the total pressure \( \text{[Pa]} \)

\( P_0 \) is the the total pressure at the entrance to the reactor \( \text{[Pa]} \)

\( \Theta (\text{Re}_p) \) the likelihood that a molecule diffuses into the fixed bed is found from the formulas given in table 1.1.

\( \text{Pe}_{\text{fluid}} \) is the fluid Peclét number as stated in table 1.1.

\( \text{Pe}_f \) is the fluid bed axial Peclét number for the solid defined in equation (2.35)

\( \text{Pr}_{\text{fluid}} \) is the Prandtl number defined by equation (1.37)

\( R \) is the universal gas constant 8.314 \( \frac{\text{Pa} \cdot \text{m}^3}{\text{mol} \cdot \text{K}} \)

\( R_{\text{fix}} \) is the internal radius of the fixed bed reactor tube as defined in figure 1.1 \( \text{[m]} \)

\( R_{\text{flb}} \) is the internal radius of the fluid bed tube \( \text{[m]} \)

\( \text{Re} \) is the Reynolds number defined in equation (1.25)

\( \text{Re}_{\text{p,term}} \) is the Reynolds number for the pellet terminal fall velocity as stated in equation (2.9)

\( r \) is the radial position (fixed bed see figure (1.1), liquid fluidbed see figure (2.4)) \( \text{[m]} \)

\( r_A \) is the kinetic rate of formation of component A \( \frac{\text{mol}}{\text{kg cat} \cdot \text{s}} \)

\( \text{Sc} \) is the Schmidt number defined in equation (1.26)

\( \text{Sh}_{\text{flb}} \) is the fluid bed Sherwood number given by equation (2.37)

\( T \) is the temperature \( \text{[K]} \)

\( T_0 \) is the feed temperature \( \text{[K]} \)

\( T_W \) is the reactor wall temperature \( \text{[K]} \)

\( u \) is the superficial velocity in the reactor \( \frac{\text{m}}{\text{s}} \)

\( u_b \) is the bubble velocity in the fluid bed \( \frac{\text{m}}{\text{s}} \)

\( u_{br} \) is the bubble rise velocity relative to the fluid in the fluid bed \( \frac{\text{m}}{\text{s}} \)

\( u_c \) is the cloud/wake velocity in the fluid bed \( \frac{\text{m}}{\text{s}} \)

\( u_e \) is the velocity of the gas in the emulsion phase \( \frac{\text{m}}{\text{s}} \)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$u_{\text{fix}}$</td>
<td>velocity in the fixed bed</td>
<td>m/s</td>
</tr>
<tr>
<td>$u_{\text{flb}}$</td>
<td>fluid velocity in the fluid bed</td>
<td>m/s</td>
</tr>
<tr>
<td>$u_{\text{g0}}$</td>
<td>superficial gas velocity at the gas entrance to the reactor</td>
<td>m/s</td>
</tr>
<tr>
<td>$u_{\text{fix}}$</td>
<td>velocity in the fixed bed</td>
<td>m/s</td>
</tr>
<tr>
<td>$u_{\text{flb}}$</td>
<td>superficial fluidization velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>$u_{\text{flb, min}}$</td>
<td>superficial minimum fluidization velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>$u_{\text{lg}}$</td>
<td>superficial gas velocity in a gas liquid reactor</td>
<td>m/s</td>
</tr>
<tr>
<td>$u_{\text{lf}}$</td>
<td>superficial liquid velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>$u_{\text{lf0}}$</td>
<td>superficial liquid velocity at the liquid entrance to the reactor</td>
<td>m/s</td>
</tr>
<tr>
<td>$u_{\text{term}}$</td>
<td>terminal fall velocity or maximum fluidization velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>$u_{*}$</td>
<td>dimensionless terminal pellet velocity defined in equation (2.38)</td>
<td></td>
</tr>
<tr>
<td>$V_{M}^{\text{t}}$</td>
<td>total liquid molecular volume, calculable as described in [17]</td>
<td>mol/m$^3$</td>
</tr>
<tr>
<td>$V_{P}$</td>
<td>volume of the catalyst pellet</td>
<td>m$^3$</td>
</tr>
<tr>
<td>$V_{\text{flb}}$</td>
<td>volumetric feed flow</td>
<td>m$^3$/s</td>
</tr>
<tr>
<td>$y_{\text{A}}^{\text{g}}$</td>
<td>gas phase molecular fraction of A</td>
<td></td>
</tr>
<tr>
<td>$y_{\text{A}}^{\text{l}}$</td>
<td>liquid phase molecular fraction of A</td>
<td></td>
</tr>
<tr>
<td>$Z_c$</td>
<td>compressibility factor</td>
<td></td>
</tr>
<tr>
<td>$z$</td>
<td>axial position (fixed bed see figure (1.1))</td>
<td>m</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>first root in the Bessel function $J_0(x)$ which is approximately 2.405.</td>
<td></td>
</tr>
<tr>
<td>$\beta_r$</td>
<td>relative energy dissipation rate given by equation (2.32).</td>
<td></td>
</tr>
<tr>
<td>$\gamma_b$</td>
<td>volume fraction of catalyst per volume of gas bubble in the bubble phase given by equation (2.43).</td>
<td></td>
</tr>
<tr>
<td>$\gamma_c$</td>
<td>volume fraction of catalyst per volume of gas bubble in the cloud or wake phase given by equation (2.49).</td>
<td></td>
</tr>
<tr>
<td>$\gamma_e$</td>
<td>volume fraction of catalyst per volume of gas bubble in the emulsion phase given by equation (2.58).</td>
<td></td>
</tr>
<tr>
<td>$\Delta H_{\text{fA}}$</td>
<td>molar enthalpy of reaction based on component A</td>
<td>J/mole of A</td>
</tr>
<tr>
<td>$\Delta P_{\text{ll}}$</td>
<td>pressure drop over the perforated plate</td>
<td>Pa</td>
</tr>
<tr>
<td>$\Delta r$</td>
<td>small control radial width interval over which the molar balance is setup (fixed bed see figure (1.1))</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>small control time interval over which the molar balance is setup</td>
<td>s</td>
</tr>
<tr>
<td>$\Delta z$</td>
<td>small control axial length interval over which the molar balance is setup (fixed bed see figure (1.1))</td>
<td>m</td>
</tr>
</tbody>
</table>
\( \delta \) is the bubble voidage fraction in the fluidized bed.

\( \varepsilon_{e_{mi}} \) is the emissivity of the catalyst pellet, 0 for black, 0.5 for gray and 1 for white bodies.

\( \varepsilon_{fix} \) is the porosity of the fixed bed, typically around 0.4 to 0.5.

\( \varepsilon_{gel} \) is the fluid bed porosity.

\( \varepsilon_{gel} \) is the fluid bed porosity at rest.

\( \varepsilon_{gel, min} \) is the bed porosity at minimum fluidization.

\( \varepsilon_{gel, min} \) is the porosity of the fluidized bed at minimum bubbling.

\( \varepsilon_{gpm} \) is the particulate bed porosity void of gas and liquid.

\( \varepsilon_{gel} \) is the gas bed porosity excluding both liquid and solid from the void of the bed.

\( \eta_{G} \) is the efficiency factor for the catalyst pellet, including internal and external mass transfer limitations.

\( \eta_{Gb} \) is the efficiency factor for the catalyst pellet, including internal and external mass transfer limitations in the bubble phase.

\( \eta_{Gcw} \) is the efficiency factor for the catalyst pellet, including internal and external mass transfer limitations in the cloude/wake phase.

\( \eta_{Ge} \) is the efficiency factor for the catalyst pellet, including internal and external mass transfer limitations in the emulsion phase.

\( \eta_{int} \) is the internal efficiency factor for the catalyst pellet, excluding external mass transfer limitations.

\( \lambda_{er}^{0} \) is defined by equation (1.27).

\( \Phi_{S} \) is the sphericity of the catalyst pellet.

\( \lambda_{er}^{0} \) is the effective radial conductance of the fixed bed at zero flow \( \left[ \frac{J}{m \cdot K \cdot s} \right] \).

\( \lambda_{ex}^{0} \) is the effective axial heat conductance of the fixed bed at zero flow \( \left[ \frac{J}{m \cdot K \cdot s} \right] \).

\( \lambda_{ex, conductance}^{0} \) is the effective axial pure heat conductance of the fixed bed at zero flow \( \left[ \frac{J}{m \cdot K \cdot s} \right] \).

\( \lambda_{ex, radiation}^{0} \) is the axial heat transport by radiation in the fixed bed at zero flow \( \left[ \frac{J}{m \cdot K \cdot s} \right] \).

\( \lambda_{fluid} \) is the heat conductance of the fluid \( \left[ \frac{J}{m \cdot K \cdot s} \right] \).

\( \lambda_{p} \) is the heat conductance of pellet \( \left[ \frac{J}{m \cdot K \cdot s} \right] \).

\( \lambda_{zfix} \) is the axial thermal conductivity \( \left[ \frac{J}{m \cdot s \cdot K} \right] \).

\( \lambda_{rfix} \) is the radial thermal conductivity \( \left[ \frac{J}{m \cdot s \cdot K} \right] \).

\( \mu_{fluid} \) is viscosity of the fluid mixture \( \left[ \frac{kg}{m \cdot s} \right] \).

\( \rho_{fib} \) is the fluid bed density \( \left[ \frac{m}{g^{2}} \right] \).

\( \rho_{fluid} \) is the density of the fluid \( \left[ \frac{kg}{m^{3}} \right] \).

\( \rho_{l} \) is the liquid density \( \left[ \frac{kg}{m^{3}} \right] \).
\( \rho_p \) is the pellet density \( \frac{\text{kg}}{\text{m}^3} \).

\( \tau_{\text{fix}} \) is the radial tortuosity factor for the fixed bed as given in table 1.1.

\( \tau_{\text{efix}} \) is the axial tortuosity factor for the fixed bed as given in table 1.1.

\( \Theta \) is defined by equation (1.40).
5. Literature


9. K.V. Christensen *Notes for X-CAT\textsuperscript{1}Heterogeneous Catalysis,* University of Southern Denmark, Odensen, 2009.


