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# Chemical and Catalytic Reaction Engineering

## *Practical 10 – a.a. 2023-2024*


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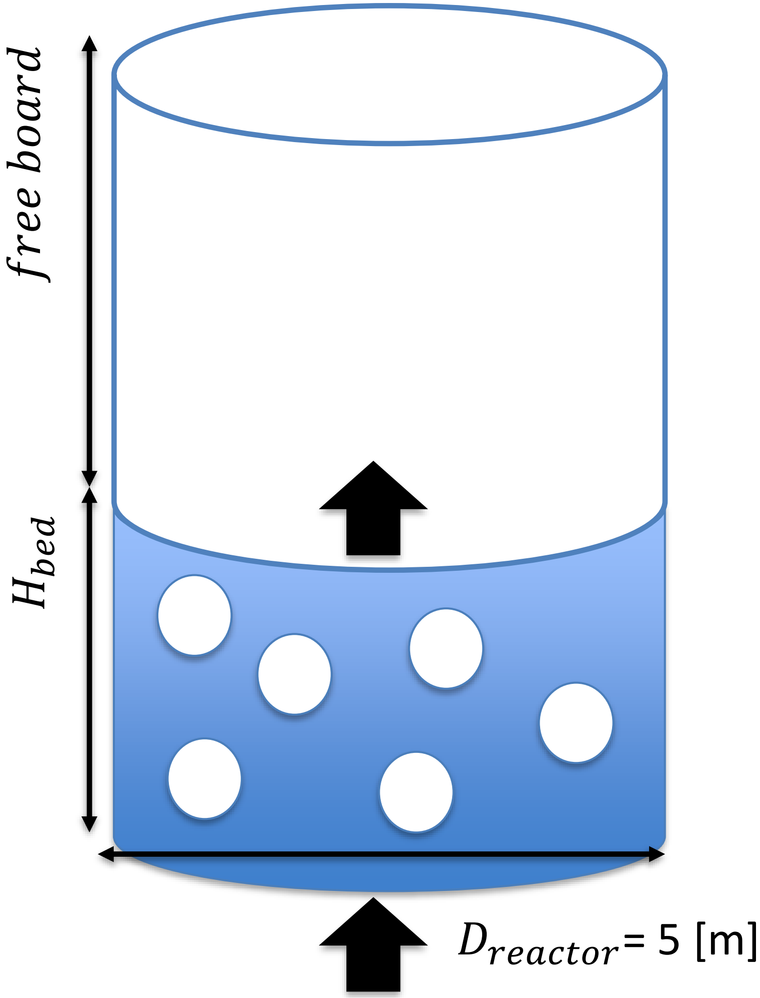
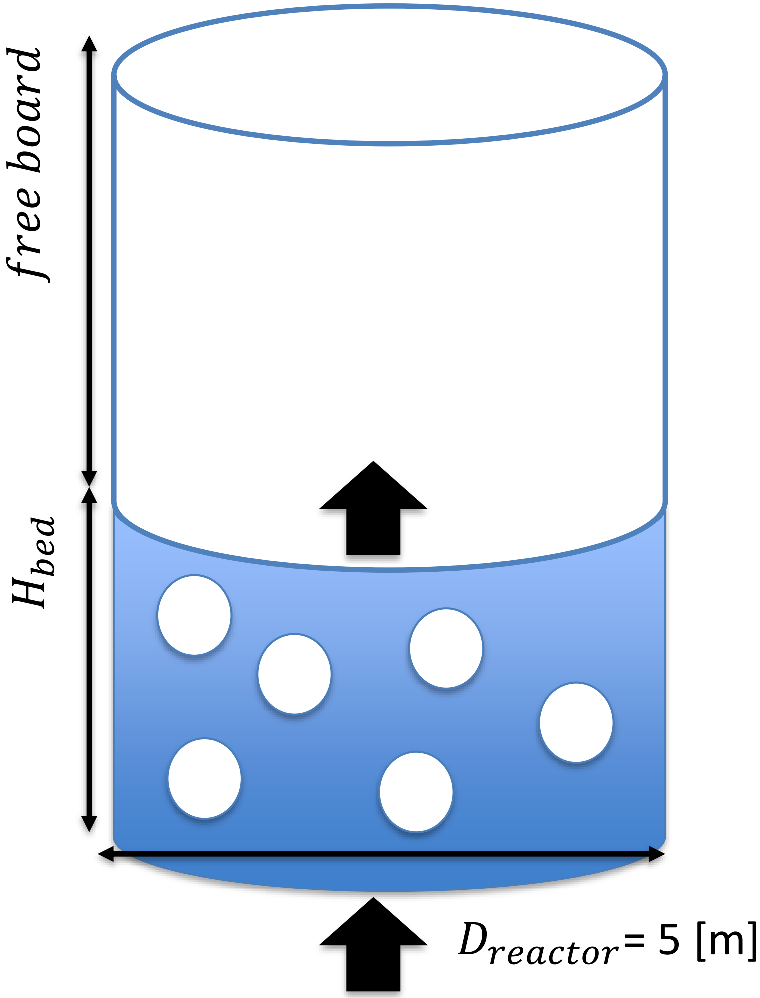
# Case of study: Maleic Anhydride synthesis from n-butane.



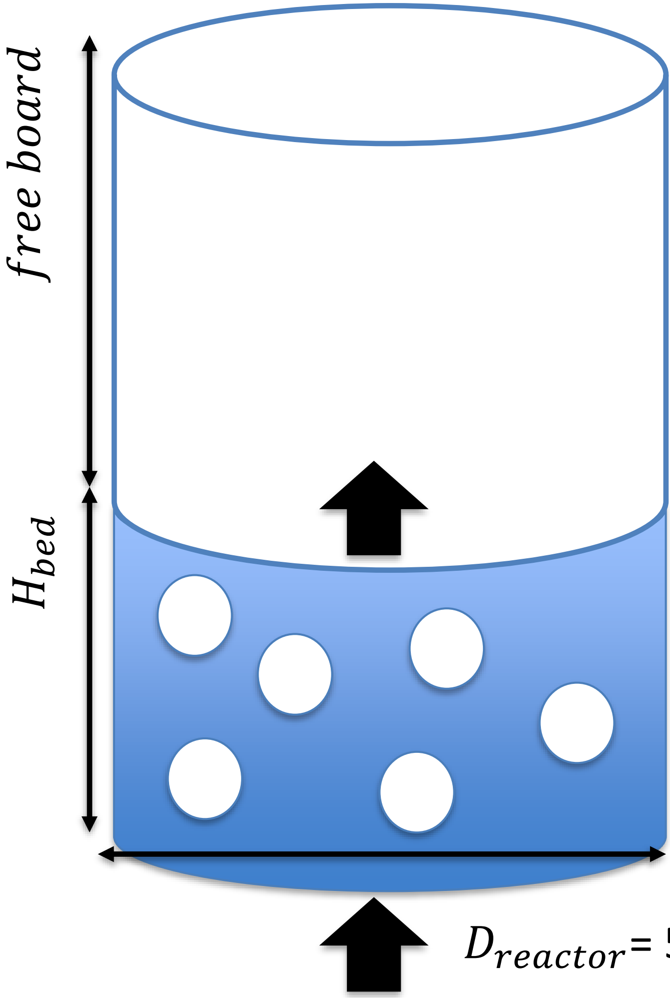

- With **Geldart A particles** there is a **homogeneous fluidization** at the minimum fluidization velocity and then the bubbles are formed when the **bubbling velocity** is reached
- Inside the gas-solid region there could be **cooling elements**
- In order to **model fluidized bed reactors**, the rise of the bubbles has to be taken into account
- **In fixed bed reactors,** the **bed geometry is fixed** for all the process. Whereas, in **fluidized reactors** the **bed expansion** depends on the gas velocity. The terminal velocity has to be considered as well.

# Case of study: Maleic Anhydride synthesis from n-butane.




- These particles act as a **third body** allowing to operate slightly above the **flammability limit**. This reduces the **separation costs**
- The minimum fluidization velocity strongly depends on the particle diameter. For **Geldart A** particles the order of magnitude for the Umf is **mm/s**
- With **Geldart A particles** two possible scenarios can take place. The first one is that the gas flow rate through the bubble phase is much higher than the one through the emulsion. The second case could be that the two gas flow rate are comparable

# Case of study: Maleic Anhydride synthesis from n-butane.




$D_{reactor}$= 5 [m]

**Operating Conditions**

$T_{inlet} = 430\ [°C]$

$\Delta P_{fluid} = 0.135\ [bar]$

$P_{outlet} = 101325\ [Pa]$

$U_0 = 25\ \left[\frac{cm}{s}\right]$

$\frac{n_{butane}}{air}\left[\frac{v}{v}\right] = 0.04(LFL\ 0.018)$

**Catalyst properties**

$\rho_{cat} = 1.2\ \left[\frac{g}{cm^3}\right]$

$d_p = 125\ [\mu m]$

$\varepsilon_{mf} = 0.42\ [-]$

$m_{cat} = 27.318\ [ton]$

**Gas properties**

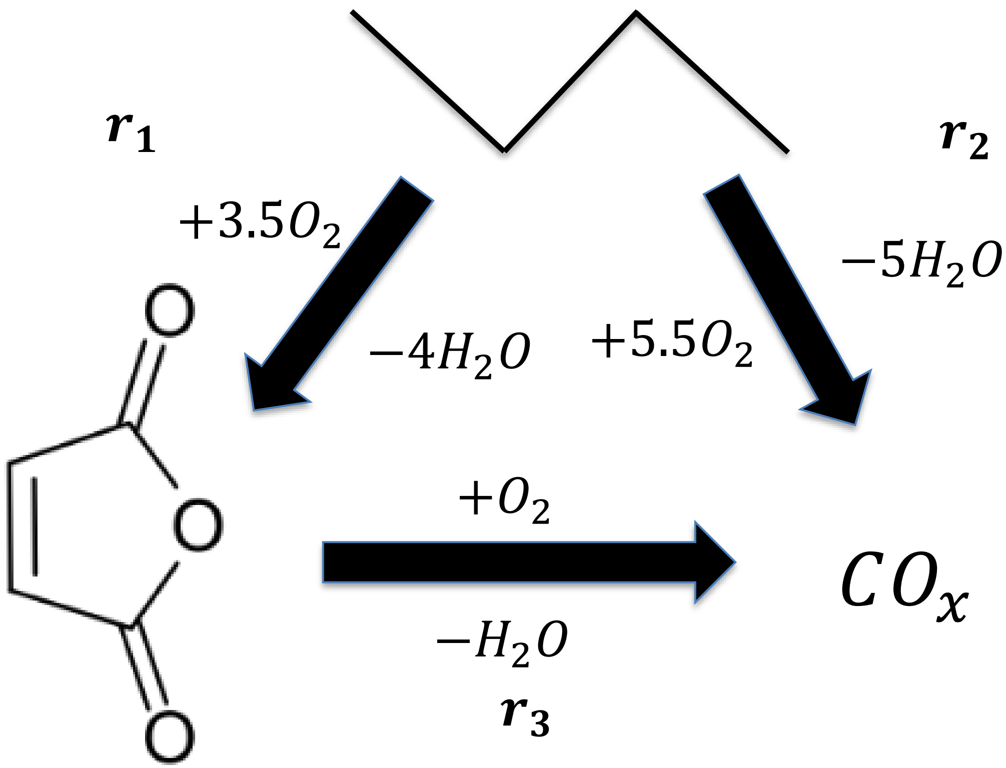
$\mu = 3.28 \cdot 10^{-5}\ [Pa \cdot s]$

$\mathfrak{D} = 3 \cdot 10^{-5}\ [m^2/s]$

**Synthesis Reaction**

$C_4H_{10} + 3.5O_2 \rightarrow C_4H_2O_3 + 4H_2O$

# Maleic Anhydride synthesis from n-butane: kinetic scheme.




$$r_1 = k_1 \cdot \frac{p_{n-but}^{0.54}}{1 + K_{MA} p_{MA}}$$

$$r_2 = k_2 \cdot p_{n-but}^{0.54}$$

$$r_3 = k_3 \cdot \frac{p_{MA}}{(1 + K_{MA} p_{MA})^2}$$

For the detailed kinetic parameters have a look to the matlab files related to this practical

# Kunii-Levenspiel Fluidized Bed 1D Model: check of the fluidization regime

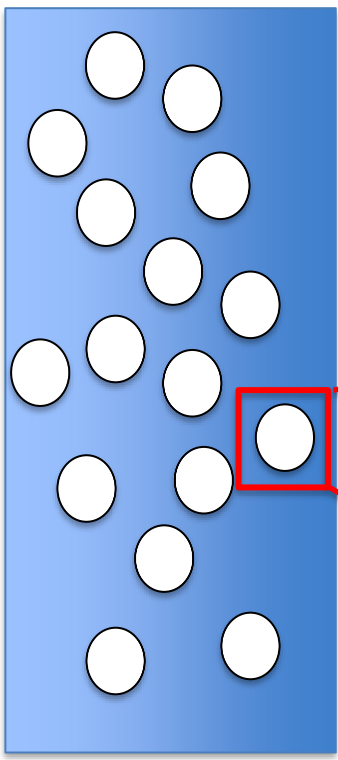
- The **minimum fluidization void fraction** has been experimentally obtained by fluidizing a small pilot scale reactor. In particular a value of **0.42** has been found
- The **minimum bubbling velocity** can be computed with the following empirical correlation proposed by Geldart and Abrahamsen:

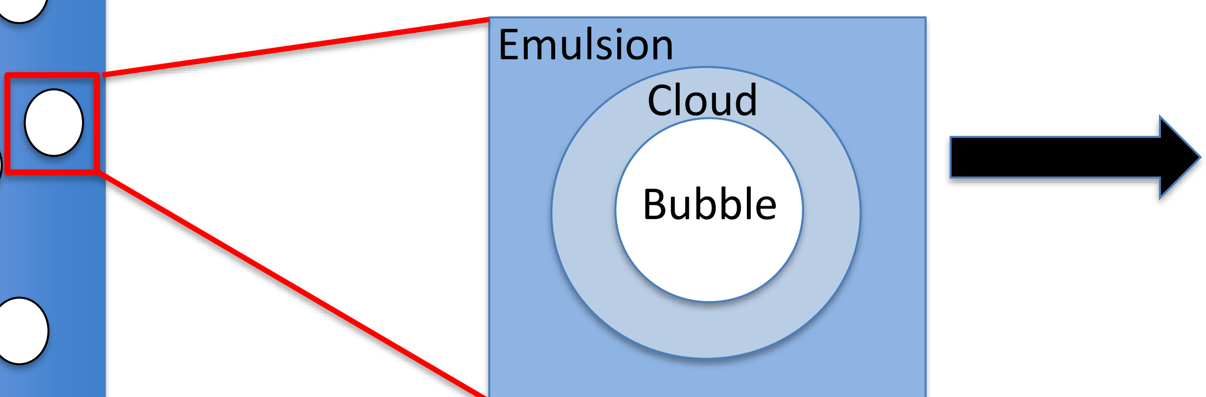
$$\frac{U_{mb}}{U_{mf}} = 2300 \cdot \frac{\rho_g^{0.13}\mu^{0.52}}{d_p^{0.8}\left[\left(\rho_{cat} - \rho_g\right)g\right]^{0.93}} = 2.13 \longrightarrow U_{mb} = 1.1 \left[\frac{cm}{s}\right]$$

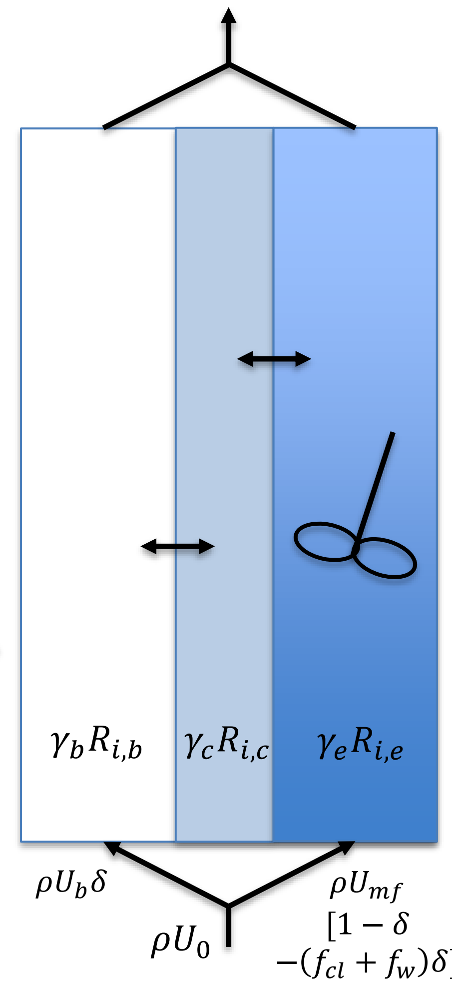
The cloud, wake and emulsion regions are approximated to be at minimum fluidization void fraction and velocity, since the operating velocity is relevantly higher, and it is experimentally easier to characterize minimum fluidization

# Kunii-Levenspiel Fluidized Bed 1D Model.

- The fluidized bed is constituted by **<u>spherical Geldart A particles</u>** and is operated in bubbling mode.
- The bubble rise velocity is higher with respect to the velocity of the gas percolating through the emulsion at minimum fluidization conditions. Hence, the bubbles are surrounded by thin clouds of recirculating gas.
- The wakes of the bubbles are considered one region together with cloud.

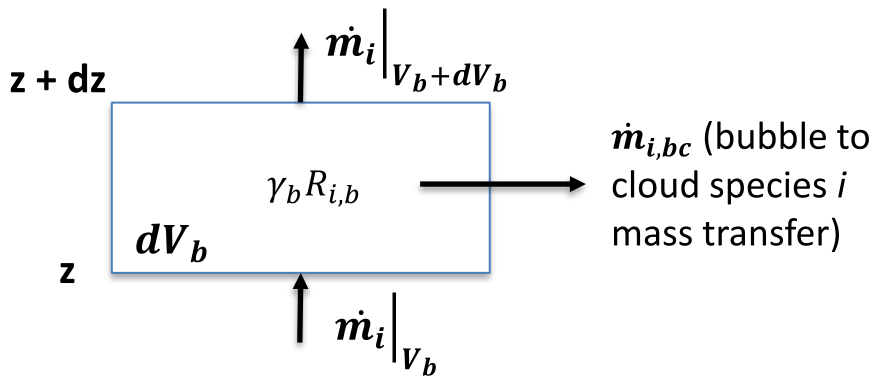


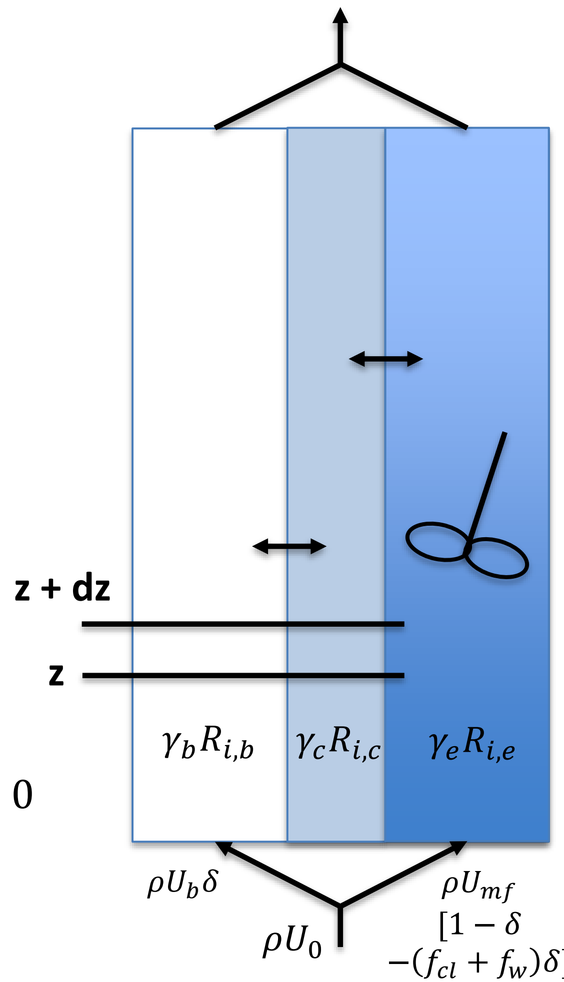



<u>where $\delta$ is the fraction of bubble</u>

## BUBBLE REGION SPECIES i MASS BALANCE



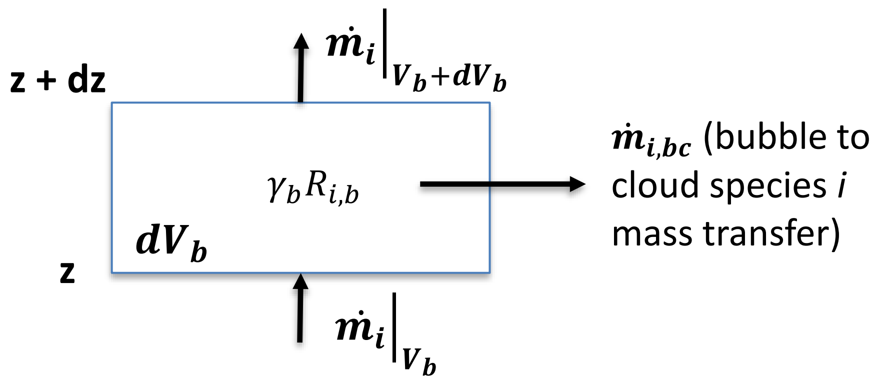

$$IN - OUT + PROD = \cancel{ACC} = 0$$

$$\dot{m}_i\Big|_{V_b} - \dot{m}_i\Big|_{V_b+dV_b} - \dot{m}_{i,bc} + R_{i,b}\gamma_b dV_b = 0$$

$$\dot{m}_i\Big|_{V_b} - \left(\dot{m}_i\Big|_{V_b} + \frac{d\dot{m}_i}{dV_b}dV_b\right) - K_{i,bc}\rho(\omega_{i,b}-\omega_{i,c})dV_b + R_{i,b}\gamma_b dV_b = 0$$

$$-\frac{d\dot{m}_i}{dV_b} - K_{i,bc}\rho(\omega_{i,b}-\omega_{i,c}) + R_{i,b}\gamma_b = 0$$

## BUBBLE REGION SPECIES i MASS BALANCE

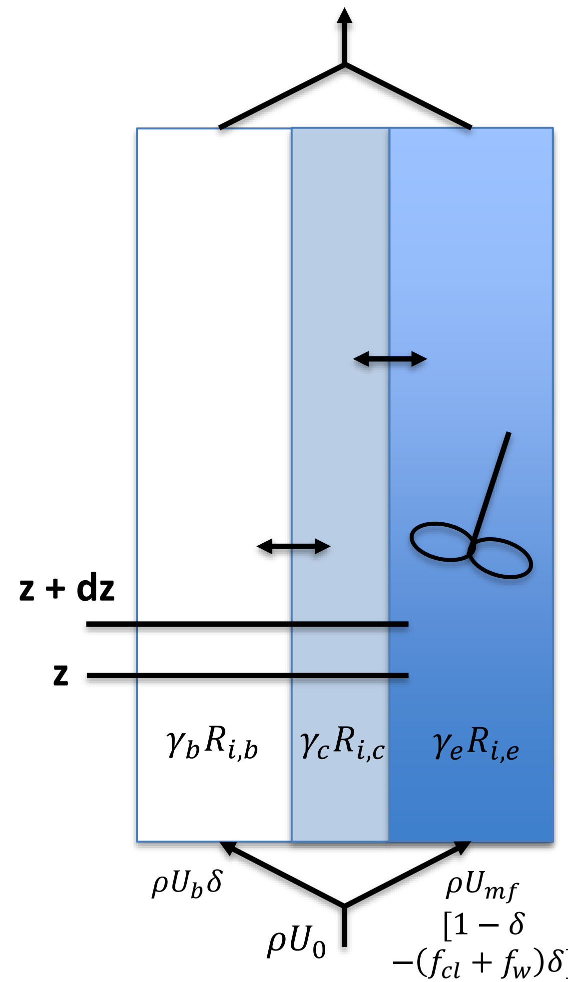



$$-\frac{d\dot{m}_i}{dV_b} - K_{i,bc}\rho\left(\omega_{i,b} - \omega_{i,c}\right) + R_{i,b}\gamma_b = 0$$

$$-G_b A_b \frac{d\omega_{i,b}}{A_b dz} - K_{i,bc}\rho\left(\omega_{i,b} - \omega_{i,c}\right) + R_{i,b}\gamma_b = 0$$

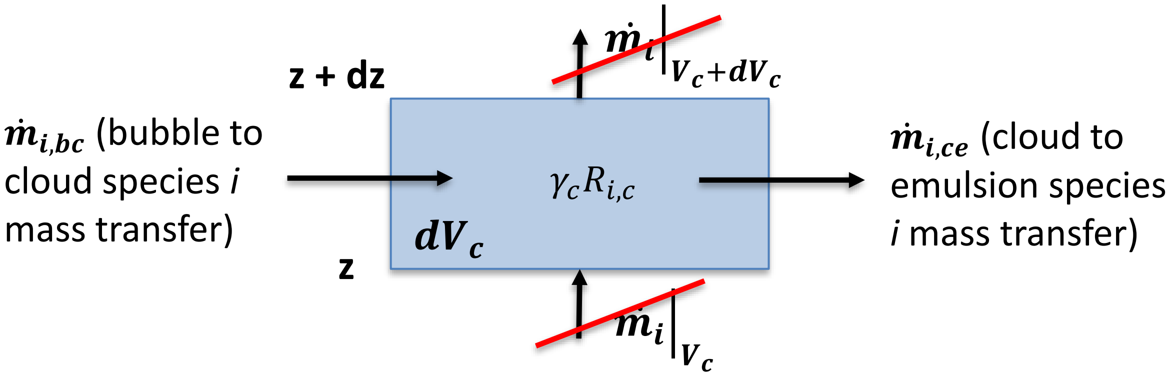
$$\boxed{-G_b \frac{d\omega_{i,b}}{dz} - K_{i,bc}\rho\left(\omega_{i,b} - \omega_{i,c}\right) + R_{i,b}\gamma_b = 0}$$

With $G_b = \rho U_b$



# Kunii-Levenspiel Fluidized Bed 1D Model.

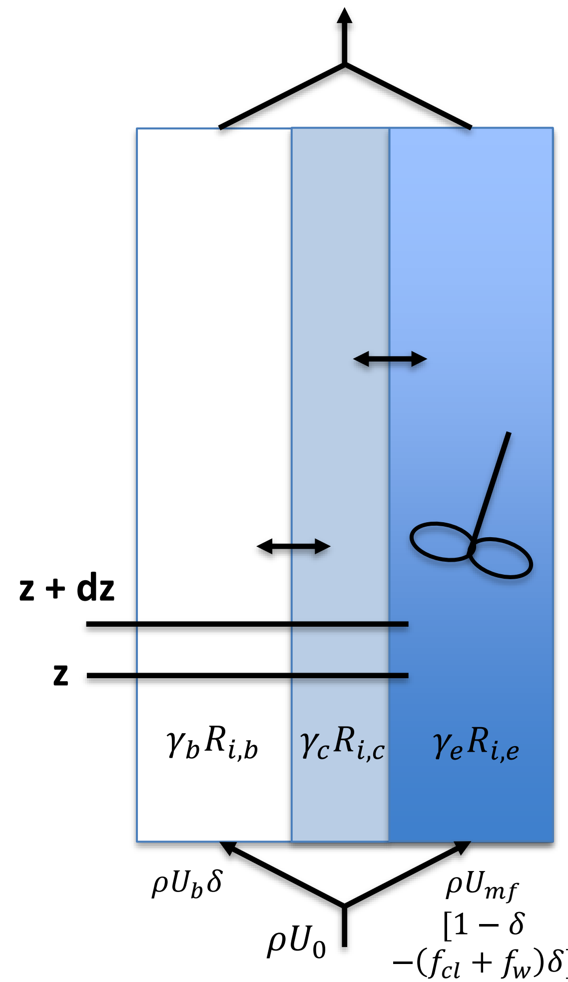
## CLOUD REGION SPECIES i MASS BALANCE




$$IN - OUT + PROD = \cancel{ACC} = 0$$

$$K_{i,bc}\rho(\omega_{i,b} - \omega_{i,c})dV_b - K_{i,ce}\rho(\omega_{i,c} - \omega_{i,e})dV_b + R_{i,c}\gamma_c dV_b = 0$$

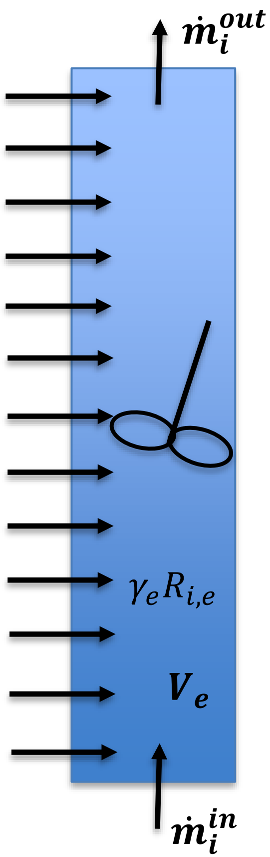
$$\boxed{\boldsymbol{K_{i,bc}\rho(\omega_{i,b} - \omega_{i,c}) - K_{i,ce}\rho(\omega_{i,c} - \omega_{i,e}) + R_{i,c}\gamma_c = 0}}$$



# Kunii-Levenspiel Fluidized Bed 1D Model.

## EMULSION REGION SPECIES i MASS BALANCE

$\sum \dot{\boldsymbol{m}}_{\boldsymbol{i,ce}}$ (cloud to emulsion species *i* mass transfer)




$$IN - OUT + PROD = \cancel{ACC} = 0$$

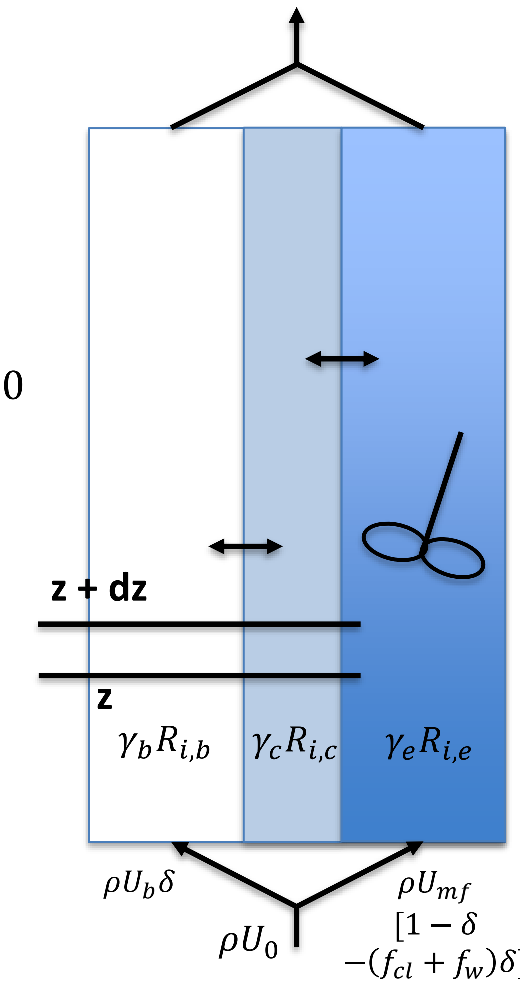
$$\dot{m}_i^{in} + \int \dot{m}_{i,ce} dV_b - \dot{m}_i^{out} + \gamma_e R_{i,e} V_b = 0$$

$$G_e \frac{A_e}{A_b}(\omega_i^{in} - \omega_{i,e}) + \int \dot{m}_{i,ce} dz + \gamma_e R_{i,e} H_{bed} = 0$$

with $$\frac{A_e}{A_b} = \frac{V_e}{V_b} = \frac{V_r - V_b - \frac{V_{cl} + V_w}{V_b} V_b}{V_r} \cdot \frac{V_r}{V_b} = \frac{1 - \delta - (f_{cl} + f_w)\delta}{\delta}$$

with $G_e = \rho U_{mf}$

$$\boxed{\boldsymbol{G_e}\left[\frac{\boldsymbol{1 - \delta - (f_{cl} + f_w)\delta}}{\boldsymbol{\delta}}\right](\boldsymbol{\omega_i^{in} - \omega_{i,e}}) + \int \boldsymbol{K_{c,e}(\omega_{i,c} - \omega_e)dz + \gamma_e R_{i,e} H_{bed} = 0}}$$



# Kunii-Levenspiel Fluidized Bed 1D Model.

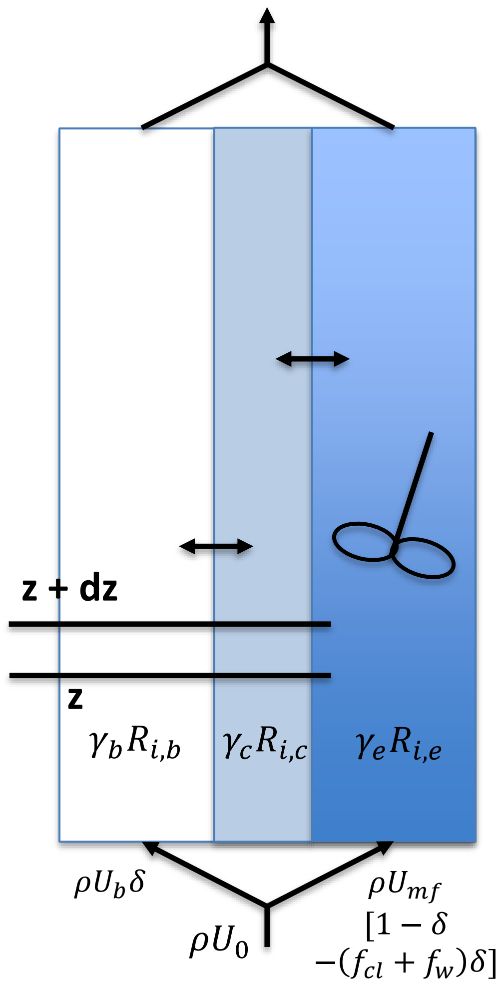
## MODEL TO BE SOLVED FOR EACH SPECIES IN THE SYSTEM

$$-G_b \frac{d\omega_{i,b}}{dz} - K_{i,bc}\rho(\omega_{i,b} - \omega_{i,c}) + R_{i,b}\gamma_b = 0$$

$$K_{i,bc}\rho(\omega_{i,b} - \omega_{i,c}) - K_{i,ce}\rho(\omega_{i,c} - \omega_{i,e}) + R_{i,c}\gamma_c = 0$$

$$G_e \left[\frac{1 - \delta - (f_{cl} + f_w)\delta}{\delta}\right] (\omega_i^{in} - \omega_{i,e}) + \int K_{i,ce}\rho(\omega_{i,c} - \omega_{i,e})dz + \gamma_e R_{i,e} H_{bed} = 0$$

Temperature gradients are considered negligible thanks to mixing

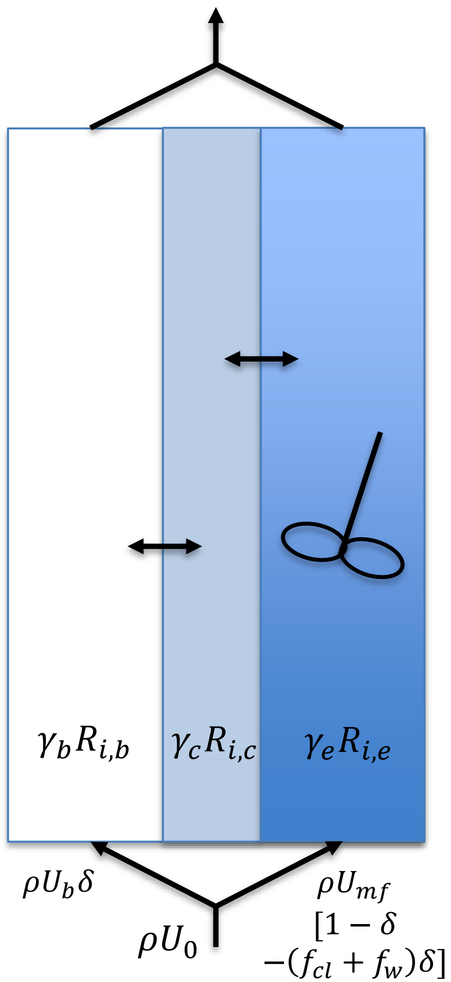


# Computation of Gb, $\delta$ and Hbed.

**To compute the specific mass flow rate in the bubbles region, we need to compute first the bubble rise velocity**. Davidson and Harrison proposed that the rise velocity of a bubble in a swarm of bubbles is the combination between the **excess gas velocity** and the **rise velocity of a single bubble**:

$$U_b^* = \left(U_0 - U_{mf}\right) + U_{br} \qquad \text{where} \qquad U_{br} = 0.711(gd_b)^{0.5}$$

- Thus, the diameter of the bubble should be computed. In case of Geldart A particles, the diameter of the bubbles is roughly constant with height, since it rapidly increases and reaches a steady value just above the gas distributor. In our case a maximum **bubble diameter of 5 cm** has been found from experimental tests in a small pilot reactors and it can be considered constant scaling from pilot to industrial scale reactor.
- Considering that Umf is equal to 0.48 cm/s and $U_0$ is equal to 25 cm/s, **we have a bubble rise velocity of 74.31 cm/s.**
- Considering that the gas tends to recirculate around the bubble, **the gas velocity $U_b$ in the bubble region can be considered equal to the bubble rise velocity.**



# Computation of Gb, $\delta$ and Hbed.

By performing a mass balance at the inlet of the fluidized bed, we can compute the volumetric fraction of bubbles in the bed:

$$U_0 = U_b\delta + U_{mf}[1 - \delta - (f_{cl} + f_w)\delta]$$

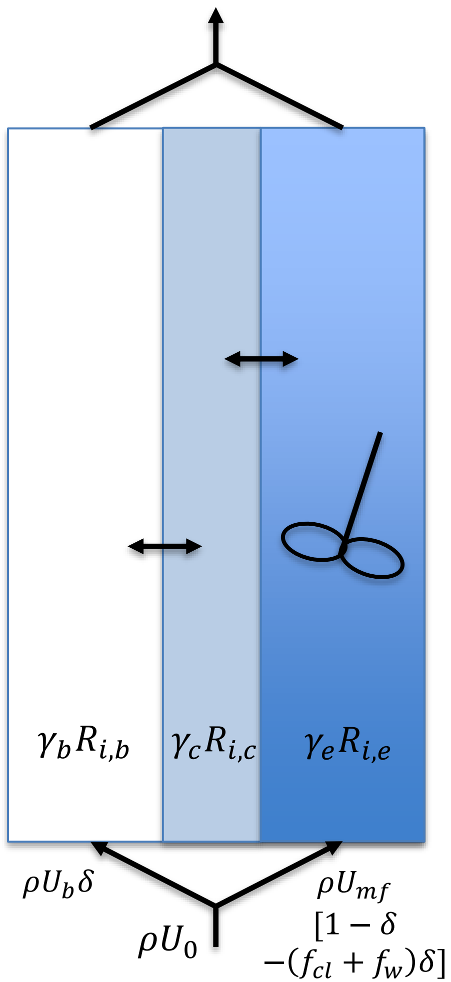
$$\delta = \frac{U_0 - U_{mf}}{U_b - [1 + (f_{cl} + f_w)]U_{mf}}$$

Hence, the bubble volumetric fraction is a function of the characteristic and operating velocities of the fluidized bed and of the ratio between cloud and wake volumes with respect to bubble volume

Kunii and Levenspiel proposed the following expression to compute the cloud to bubble volume ratio:

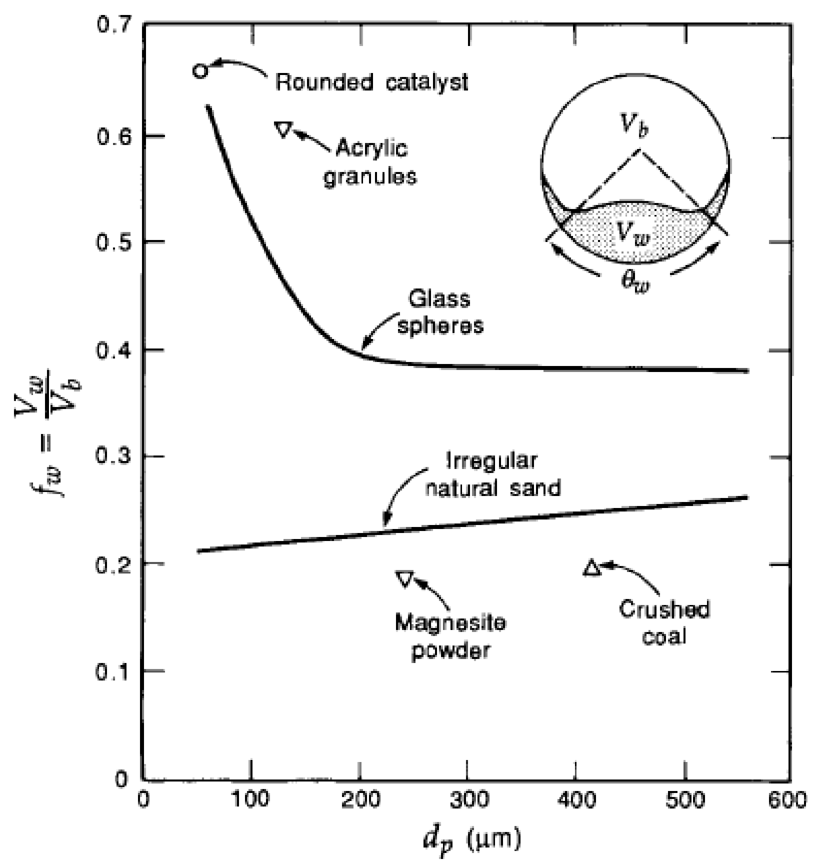
$$f_{cl} = \frac{V_{cl}}{V_b} = \frac{3\left(\frac{U_{mf}}{\varepsilon_{mf}}\right)}{U_b - \left(\frac{U_{mf}}{\varepsilon_{mf}}\right)}$$

which leads to 0.0468 in our case



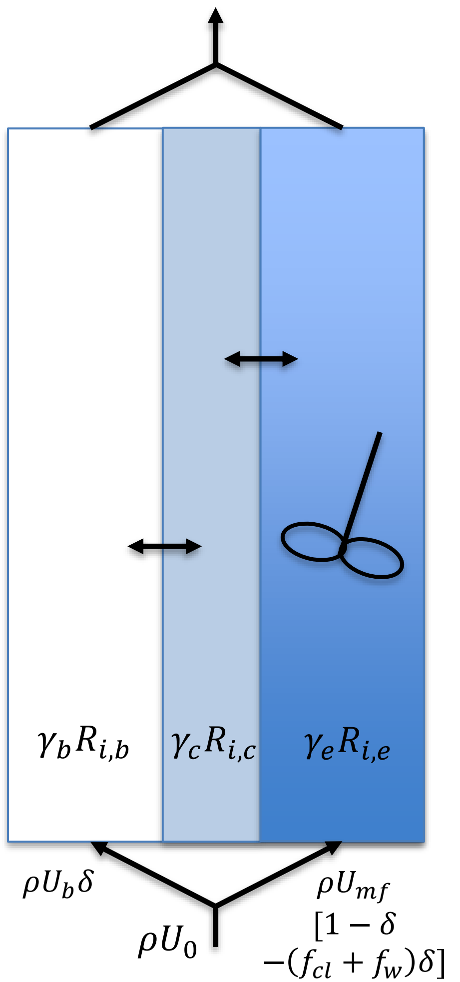
# Computation of Gb, $\delta$ and Hbed.

With respect to the wake to bubble volume ratio, the following plot has been experimentally obtained by Rowe and Partridge:




- By assuming that the VPO catalytic particles of 125 µm mechanically behaves like «irregular natural sand», **we can graphically derive a fw value of about 0.2**

- This value, combined with the cloud to bubble one, leads to a **bubble fraction of 0.3326**



# Computation of Gb, $\delta$ and Hbed.

Once the bubble volume fraction is known, the average solid fraction in the fluidized bed can be obtained performing the mass balance on the catalyst mass in the reactor:

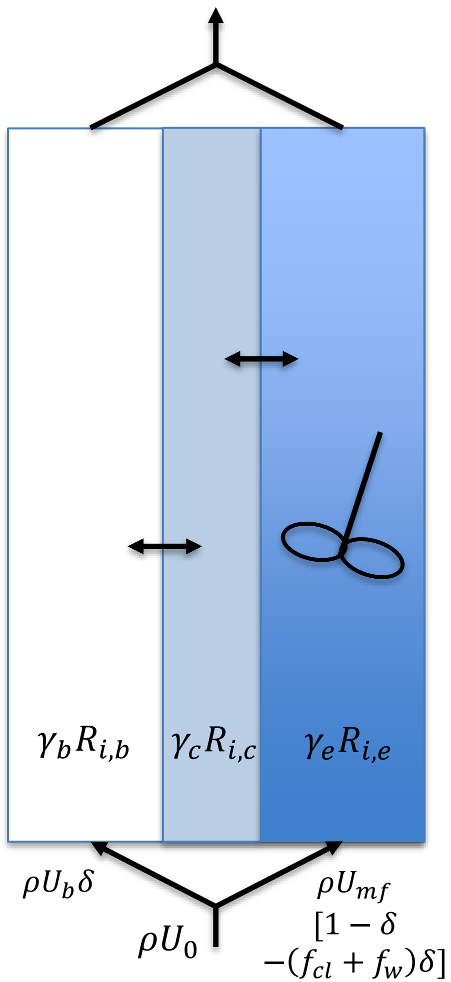
$$\rho_{cat} V_r (1-\varepsilon_{bed}) = \rho_{cat} V_r \delta \gamma_b + \rho_{cat} V_r (1-\delta)(1-\varepsilon_{mf})$$

$$(1-\varepsilon_{bed}) = \delta \gamma_b + (1-\delta)(1-\varepsilon_{mf})$$

If the average solid fraction in the fluidized bed is known, we can compute the average bed height, since the reactor diameter (i.e. 5 m) is known:

$$\rho_{cat} A_r H_{bed} (1-\varepsilon_{bed}) = m_{cat}$$

However, since the average solid fraction in the bed is also a function of the volumetric fraction of solid particles in the bubble region, this value must be also computed



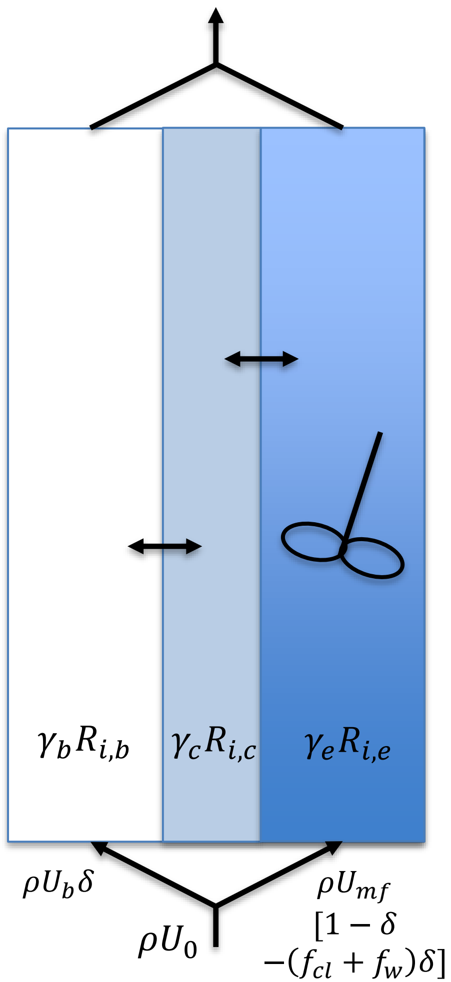
# Computation of the ratio of the volume of solid particles among the three regions with respect to bubble region volume.

It has been found experimentally **the ratio between the volume of solid particles in the bubbles and the bubbles volume** is between 0.01 and 0.001. Thus, in absence of precise information ir is usually fixed at 0.005:

$$\gamma_b = \frac{volume\ of\ particles\ in\ bubbles}{volume\ of\ bubbles} = 0.005\ [-]$$

Leading to an average solid fraction of the bed of 0.3887 and the following fluidized bed height:

$$H_{bed} = \frac{m_{cat}}{\rho_{cat} A_r (1 - \varepsilon_{bed})} = 3\ [m]$$



# Computation of the ratio of the volume of solid particles among the three regions with respect to bubble region volume.

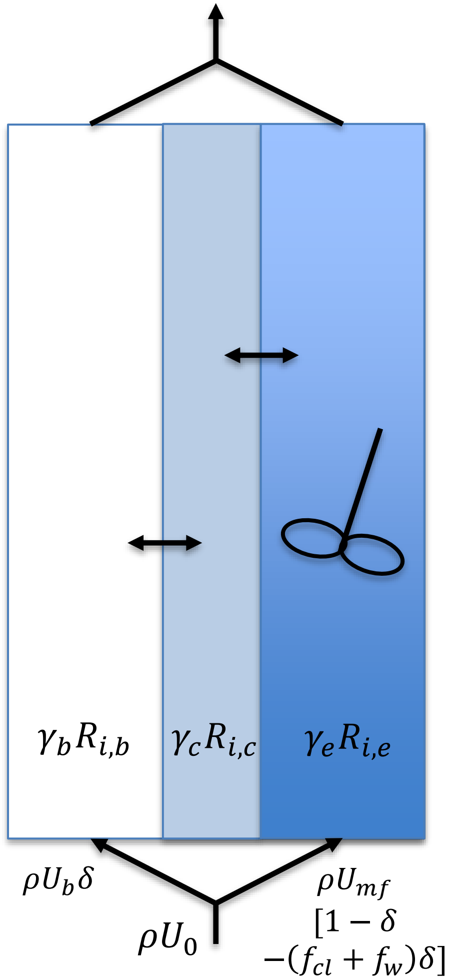
With respect to **the ratio between particle volume in cloud+wake region and the volume of the bubbles** , it can be computed as:

$$\gamma_c = \frac{volume\ of\ cloud+volume\ of\ wakes}{volume\ of\ bubbles} \cdot \frac{volume\ of\ particles\ in\ cloud\ and\ wakes}{volume\ of\ cloud+volume\ of\ wakes}$$
$$= (f_{cl} + f_w)(1 - \varepsilon_{mf}) = 0.1431\ [-]$$

Finally, the following expression can be used to **compute the volume of solid particles in the emulsion with respect to the volume of bubble region**:

$$\delta(\gamma_c + \gamma_e) = (1 - \varepsilon_{mf})(1 - \delta)$$

$$\frac{V_{bubbles}}{V_{fluidized\ bed}} \cdot \frac{V_{p\ in\ cloud+wakes} + V_{p\ in\ emulsion}}{V_{bubbles}}$$
$$= \frac{V_{p\ in\ cloud+wakes+emulsion}}{V_{cloud+wakes+emulsion}} \cdot \frac{V_{cloud+wakes+emulsion}}{V_{fluidized\ bed}}$$



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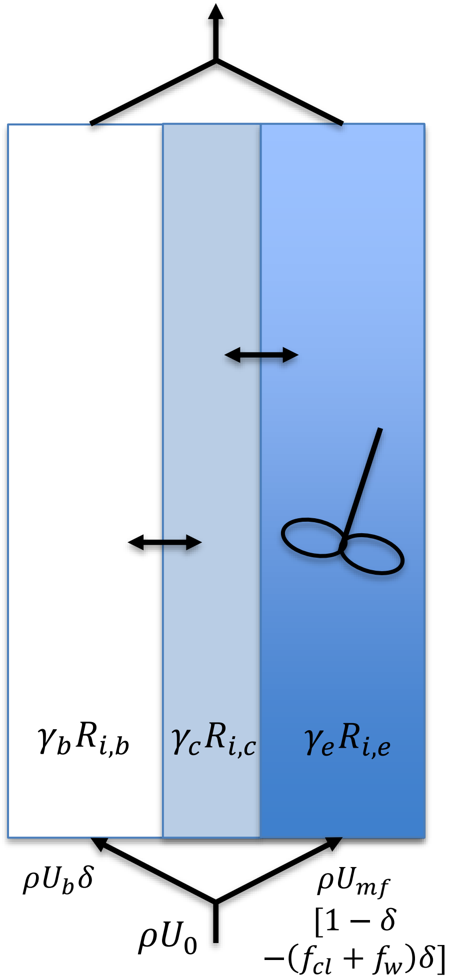
$$= (f_{cl} + f_w)(1 - \varepsilon_{mf}) = 0.1431\ [-]$$

Finally, the following expression can be used to **compute the volume of solid particles in the emulsion with respect to the volume of bubble region**:

$$\delta(\gamma_c + \gamma_e) = (1 - \varepsilon_{mf})(1 - \delta)$$

$$\gamma_e = \frac{(1 - \varepsilon_{mf})(1 - \delta)}{\delta} - \gamma_c = 1.016\ [-]$$



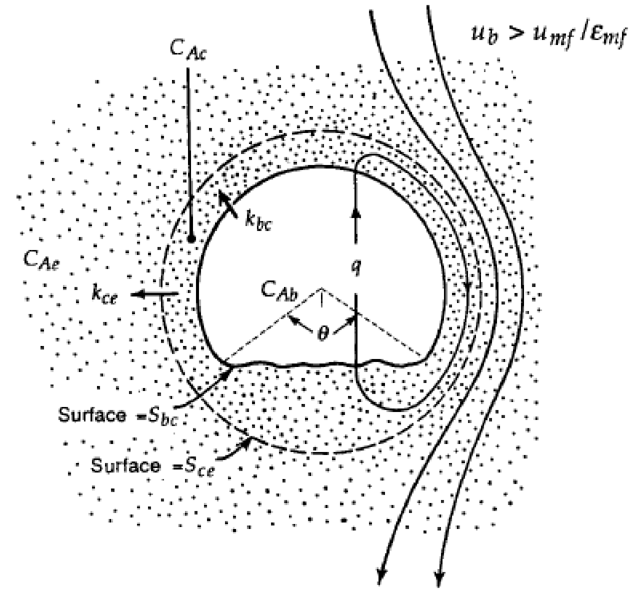
# Mass Transfer Coefficients.

## Bubble to Cloud Mass Transfer Coefficient

$$K_{i,bc} = 4.5\left(\frac{U_{mf}}{d_b}\right) + 5.85\left(\frac{D_i^{0.5} g^{0.25}}{d_b^{5/4}}\right)$$

convective contribution

diffusive contribution



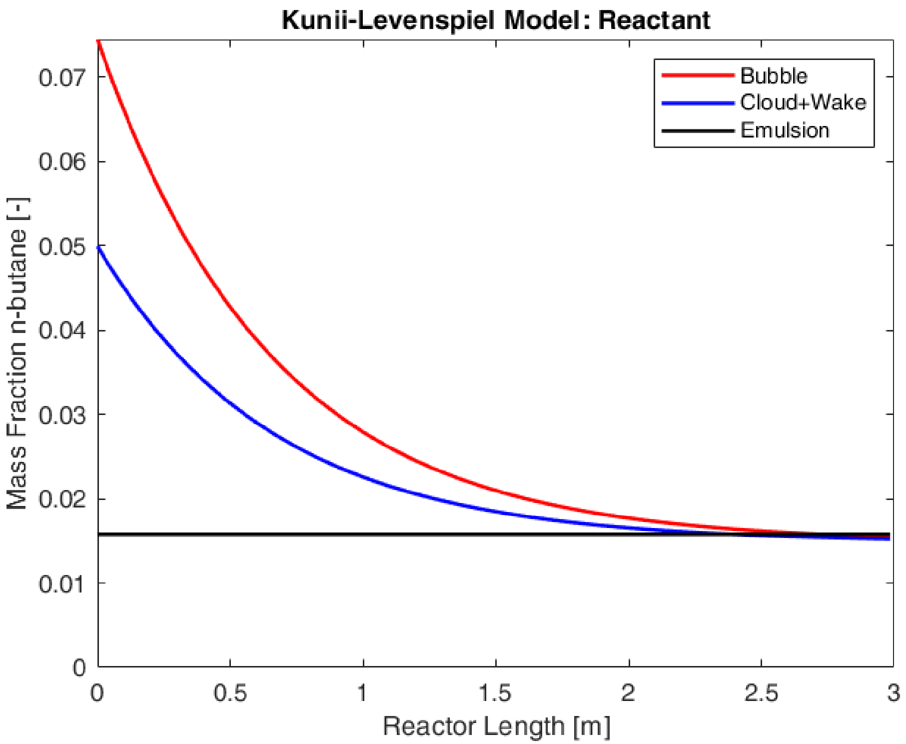

## Cloud to Emulsion Mass Transfer Coefficient

$$K_{ce} = 6.77\left(\frac{\varepsilon_{mf} D_{AB} U_b}{d_b^3}\right)^{0.5}$$

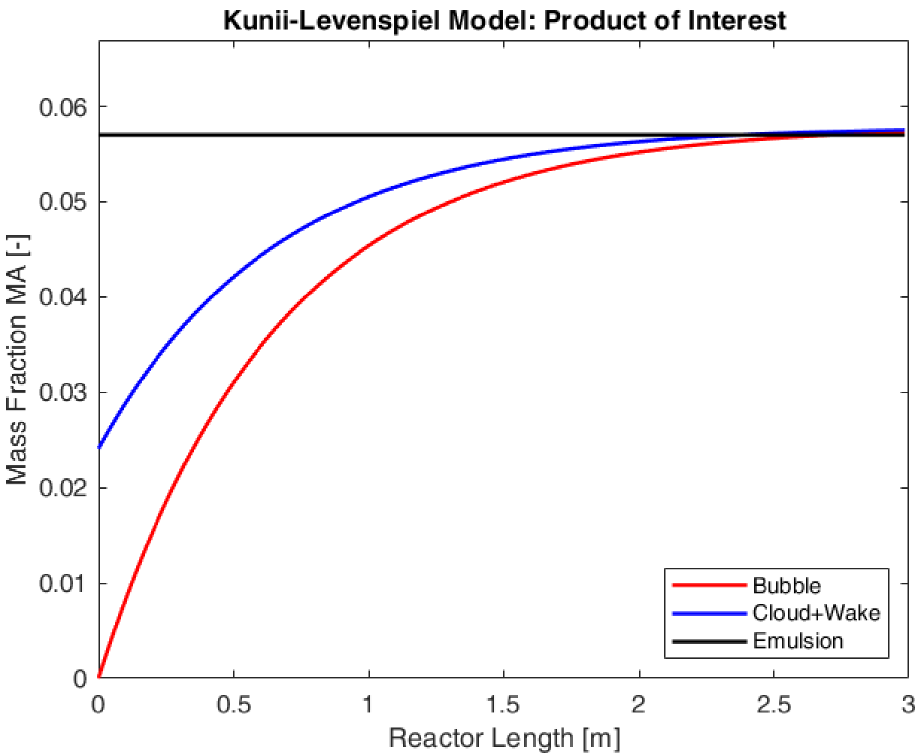
diffusive contribution

gas to particle mass transfer resistances are neglected for all the three regions due to the fine size of the particles

# Results.

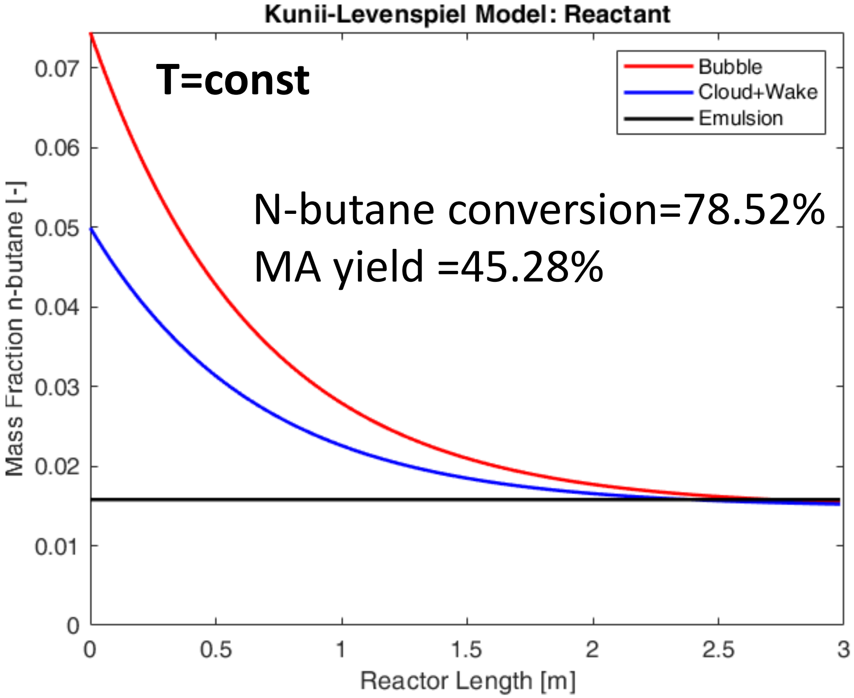


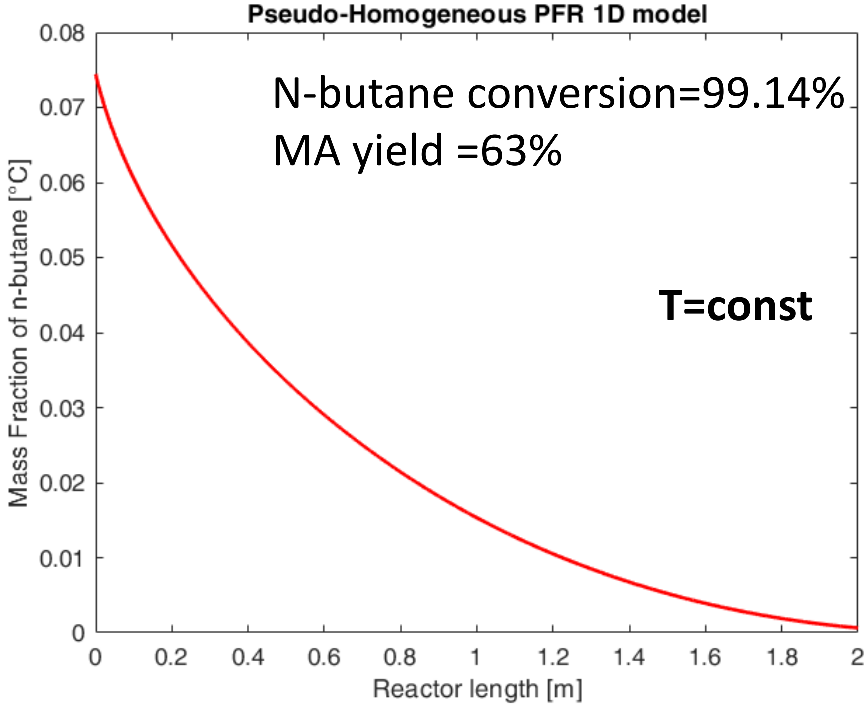
Kunii-Levenspiel Model: Reactant
Bubble
Cloud+Wake
Emulsion
Mass Fraction n-butane [-]
Reactor Length [m]
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0.5
1
1.5
2
2.5
3

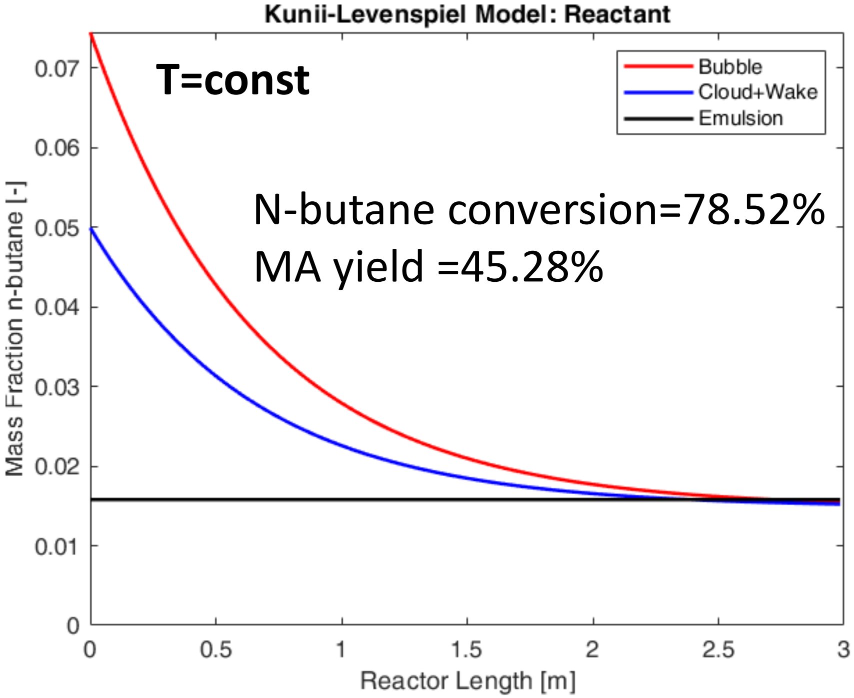
Kunii-Levenspiel Model: Product of Interest
Bubble
Cloud+Wake
Emulsion
Mass Fraction MA [-]
Reactor Length [m]
0.06
0.05
0.04
0.03
0.02
0.01
0
0.5
1
1.5
2
2.5
3

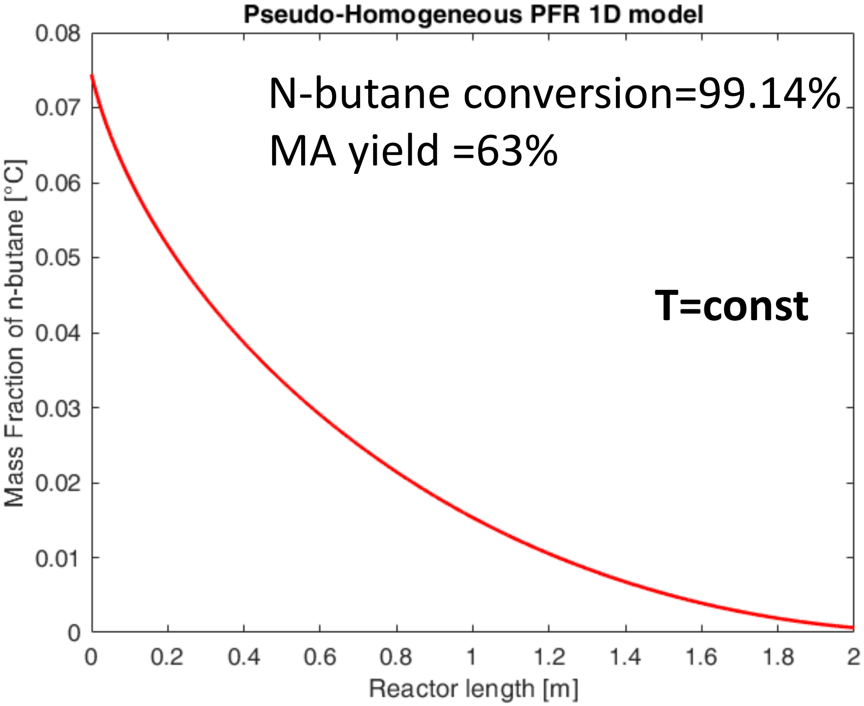
# Results.


Kunii-Levenspiel Model: Reactant
T=const
Bubble
Cloud+Wake
Emulsion
N-butane conversion=78.52%
MA yield =45.28%
Mass Fraction n-butane [-]
Reactor Length [m]
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.5
1
1.5
2
2.5
3


Pseudo-Homogeneous PFR 1D model
N-butane conversion=99.14%
MA yield =63%
T=const
Mass Fraction of n-butane [°C]
Reactor length [m]
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2

# Results.




As expected, a fixed bed run with the same G0 and the same catalyst inventory, presents a higher conversion of n-butane with respect to the fluidized bed. However, the fixed bed cannot be run isothermally at that temperature and cannot be run above the LFL. Thus, the fluidized bed reactor allows for higher operating temperatures and a more concentrated outlet stream reducing the separation costs