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Modelling of Catalytical Bubbling Fluidized Bed on Pilot Scale

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Abstract

Crystalline melamine is a raw material for synthesizing of formaldehyde melamine resin. Formaldehyde melamine resin has been widely used in the industry. The simulation of fluidized reactor is a requirement of reactor design. To simulate the fluidized bed reactor is required that kinetic parameters (e.g. rate constant, k and reaction degree, n) and thermodynamic parameters (e.g. height, and minimum fluidization rate) to be known. The quantity of these parameters must be determine to synthesise melamine from urea (For both fixed bed reactor and fluidized bed reactor). They have been determined for both fixed bed and fluidized bed reactor in a pilot scale . Farshi (2002) has corrected these quantities for a two phases hydrodynamic model to simulate fluidized bed reactor. The results of these simulation and their comparison with the resulting experimental data from literature has been indicated that the results from the two phases model more properly matched with experimental data. Thus the two phases model is an appropriate model for simulation of gas-solid bubbling fluidized bed reactor.
The two phases model with some correction and the bubbles with the medium diameter that their diameter have been calculated using Mori and Wen equation (1975) are used in this paper.

Key words: formaldehyde melamine resin, simulation fluidized bed

Introduction:

Mathematical simulation of bubbled fluidized bed reactor is more complex than the simulation of fixed bed reactor. In order to simulate a fluidized bed reactor requires the understanding of the concepts of bed hydrodynamic (including bubble's movement, bubble's diameter, and bubble's rate) and the particle technology. [or the knowledge of bed hydrodynamic (including bubble's movement, bubble's diameter, and bubble's rate) and the particle technology have to be known.]

The models have been developed base on the fluidized bed hydrodynamic which are well known as hydrodynamic models. Many hydrodynamic models had been reviewed and finally, the two phases model [6] was selected to simulate the melamine bubbled fluidized bed reactor. Depending on the particle size, the type of model is varied for simulation of the bubbled fluidized reactor so that three phases and homogeneous phase models are used for small particle sizes and large particle sizes respectively [3].

For turbulent fluidized bed and fast fluidized bed shall select an appropriate model as well.

1- Simulation of solid-gas bubbled fluidized bed-the two phases model [6] :

The two phases model [6] with some correction and the study's results of the effects of different relations of bubble's diameter on the fluidized bed (the fraction of bed conversion) have been used to simulate the fluidized bed. The existence two phases model is valid for bubbling fluidized bed including group powders of A and B of Geldart's grouping (1973).

1-1- Assumptions of the two phases model [6] :

1-1-1- A dispersed bubble and a suspended continuous phase around the bubble form a two phases model.
1-1-2- Because is partially U>>U_{mf}, the distribution of gas flow in the suspended phase is small. Velocity limit $\frac{U_{mf}}{\varepsilon_{mf}}$ of gas velocity in the suspended phase and $\frac{U_d}{\varepsilon_d}$ of the suspended phase with porosity ε_d is sufficient.
1-1-3- Plug flow in both bubbled phase and suspended phase has been considered; gas axial distribution in the suspended phase will be more accurate, but a new parameter will involve the simulation which its quantity is unknown.
1-1-4- The bubbles are free of solid, for example, both heterogeneous catalytic reaction and solid-gas reaction progress in a suspended phase.
1-1-5- The variation of the gas volume rate has not been considered due to the reaction.
1-1-6- The effect of adsorption has been negligible.
1-1-7- The model has only considered the bubbling fluidization regime.
1-1-8- The reaction of above bubbling region (freeboard zone) has not been considered.
1-1-9- The model is considered for the powder groups of A and B of Geldart division. The Geldart's limit division is for particles:
A group:
$\rho_S < 1.4\ gr/cm^3, \quad d_P < 100\ \mu m$
B group:
$1.4 < \rho_S < 4 gr/cm^3, \quad 40\mu m < d_P < 500\mu m$

1-2- Material balance equations for solid-Gas fluidized bed reactor, two phase model, [6]:

Considering the assumptions of model, the material balance for the case of reactor volume Aydh for a element in bubbled and suspended phases; and also in the heterogeneous catalytic reaction, the following resulted equations are:
For bubbled phase:

$$\varepsilon_b \frac{\partial C_{bi}}{\partial t} = -\left(U - U_{m_f}(1-\varepsilon_b)\right)\frac{\partial C_{bi}}{\partial h} - K_{Gi} a_t (C_{bi} - C_{di}) \quad (1)$$

For dense phase:

$$(1-\varepsilon_b)\left(\varepsilon_{mf} + (1-\varepsilon_{mf})\varepsilon_i\right)\frac{\partial C_{di}}{\partial t} = -U_{mf}(1-\varepsilon_b)\frac{\partial C_{di}}{\partial h} + K_{Gi} a_t (C_{bi} - C_{di}) + (1-\varepsilon_b)(1-\varepsilon_{mf})\rho_s \sum_{J=1}^{M} \upsilon_{ij} r_j \quad (2)$$

In the steady state $\frac{\partial C_{bi}}{\partial t}$ and $\frac{\partial C_{di}}{\partial t}$ are zero and the following equations will be resulted:

$$\left(U - U_{mf}(1-\varepsilon_b)\right)\frac{\partial C_{bi}}{\partial h} = -K_{Gi} a_t (C_{bi} - C_{di}) \quad (3)$$

$$\frac{\partial C_{bi}}{\partial h} = \frac{-K_{Gi} a_t}{\left(U - U_{mf}(1-\varepsilon_b)\right)} (C_{bi} - C_{di})$$

$$-U_{mf}(1-\varepsilon_b)\frac{\partial C_{di}}{\partial h} + K_{Gi} a_t (C_{bi} - C_{di}) + (1-\varepsilon_b)(1-\varepsilon_{mf})\rho_s \sum_{J=1}^{\mu} \upsilon_{ij} r_j = 0$$

$$\Rightarrow \frac{\partial C_{di}}{\partial h} = \frac{K_{Gi} a_t}{U_{mf}(1-\varepsilon_b)}(C_{bi} - C_{di}) + \frac{(1-\varepsilon_b)(1-\varepsilon_{mf})}{U_{mf}(1-\varepsilon_b)} \rho_s \sum_{J=1}^{M} \upsilon_{ij} r_j \quad (4)$$

For a reaction that is J=1, the reaction rate equation for element I is:

$$r_f = k_{mj} C_{di}^{nr} \quad (5)$$

stoichiometric coefficient for primary material is considered one, then equation 4 can be written as:

$$\frac{\partial C_{di}}{\partial h} = \frac{K_{Gi} a_t}{U_{mf}(1-\varepsilon_b)}(C_{bi} - C_{di}) - \frac{(1-\varepsilon_b)(1-\varepsilon_{mf})}{U_{mf}(1-\varepsilon_b)} \rho_s k_m C_{di}^{n_r} \quad (6)$$

Considering relation k_i with k_{mi} and replacement in the equation 6 will be resulted:

$$k_i = \rho_S (1-\varepsilon) k_{mi} \quad (7)$$

$$\frac{\partial C_{di}}{\partial h} = \frac{K_{Gi} a_t}{U_{mf}(1-\varepsilon_b)}(C_{bi} - C_{di}) - \frac{k_i}{U_{mf}} C_{di}^{n_r} \quad (8)$$

Then the equations of 3 and 8 are the relations of concentration variations in the bubbled phase and suspended phase (dense phase):

$$\frac{\partial C_{bi}}{\partial h} = \frac{-K_{Gi} a_t}{\left(U - U_{mf}(1-\varepsilon_b)\right)}(C_{bi} - C_{di}) = f(C_{bi}, C_{di})$$

$$\frac{\partial C_{di}}{\partial h} = \frac{K_{Gi} a_t}{U_{mf}(1-\varepsilon_b)}(C_{bi} - C_{di}) - \frac{k_i}{U_{mf}} C_{di}^{n_r} = g(C_{bi}, C_{di})$$

Applying the conditional limits, the latter equation will be solved:
h=0 $C_{bi}=C_{di}=C_o$

Runge Kutta method is applied to solve the first differential equation using conditional limits, reactant concentration quantities on bubble & dense phases in each bed height is calculated according to above equation:

(9)

$$\text{Coverage} = \frac{C_b \times V_{bo}\,\varepsilon_b + C_d U_{mg}\,(1-\varepsilon_b)}{U}$$

Conversion of fluidized bed in each height of reactor are calculated using the following way:

$$x = 1 - \frac{Coverage}{Co}$$

1-3- Simulation parameters of fluidized bed-two phases model:

1-3-1- Bubble diameter, DB

The diameter of bubble is calculated using Mori and Wen equation (1991).

(10)

$$d_B = dBM - (dBM - dBo)\exp\left(\frac{-0.3h}{Dr}\right)$$

1-3-2- Bubble velocity, U_b

The velocities of an individual bubble and accumulated bubbles are calculated using Davidson and Harrison equations; the equations of 93 and 95 in the second chapter[2]. The velocity of bubbled phase is also obtained using the following equation:

$$U_b = 0.8\left(U - U_{mf}\right) \qquad (11)$$

This is an observer equation based on [6]; Werther and Schobler; and Hilligardt and Werther.

1-3-3- The volume fraction of bubble phase (ε_b)

The volume rate is the ratio of bubble volume to bed volume which will be calculated according to:

$$\varepsilon_b = \frac{A_b}{A} = \frac{U_b}{U_{b0}} \qquad (12)$$

1-3-4- The volume specified mass transfer area (at)

Existence equation in order to calculate the specified mass surface transfer between bubbled and suspended phases is :

$$a_t = 6\frac{\varepsilon_b}{d_b} \qquad (13)$$

1-3-5- Mass transfer coefficient between bubbled and suspended phases is calculated using the following equation:

$$k_{Gi} = \frac{U_{mf}}{3} + \sqrt{\frac{4D_i\varepsilon_{mf}U_{bo}}{\pi d_B}} \qquad (14)$$

where D_i is molecular diffusion coefficient, and U_{bo} is coagulated bubbled gas velocity.

1-3-6- The expanded bed height

The bed from the bed height will be expanded in the minimum of fluidity. Assumed that this expansion is because bubbles present in the media. In that case, the bed height will be calculated using the following equation;

$$H = \frac{H_{mf}}{1-\varepsilon_b} \qquad (15)$$

1-4- Simulation of catalytic fluidized bed reactor of melamine

The two phases simulation of Werther was introduced. The fluidized bed simulation has been done using the Werther model. Hydrodynamic factors of fluidized bed with internal diameter of 4.8 cm at 25°C for silicagel (400 g) as catalyst is calculated that are:

H_{mf}=54 cm, U_{mf}=2.94 cm/sec, W=400 g

Melamine will be synthesized from urea in the presence of silicagel, as catalyst in 380°C. Ammonia gas presents in the large amount in the reaction therefore the reaction fluid that can be assumed is ammonia. The minimum amounts of particle fluid velocity and bed height are partially varied with temperature.

The real minimum fluidization velocity will be calculated using the equations of Wen and Yu[5], and then the real U_{mf} will also be obtained.

The minimum amount of fluidization bed height will be obtained using the variation diagram of fluidization bed height versus velocity that will be;

U_{mf} = 2.344 cm/sec, H_{mf} = 53.75 cm

The minimum amount of the bed fluidization porosity will be obtained using the equation of Broadhurst Becker (2002) at 380°C is: $\varepsilon_{mf} = 0.425$

The amount of effective diffusion coefficient of cyanic acid with the molecular weight of 43 considering the effective diffusion coefficient of ozone (O_3) with the molecular weight of 46 will be:

$$D_e = 1\times10^{-5}\,m^2/s$$

Considering kinetic data of synthesis of melamine from urea have been obtained that the kinetic constant at 380°C is: K_{380^oC}=13.779

And the degree of reaction is: n = 0.4

Having all modeling parameters makes it possible to simulate the reaction.

Noting that the two phases model of Werther [6] has been introduced for all reaction degrees; the simulation has been done based on this model. In this case, the quantities of in put gas velocity have been selected based on fluidization regime.

Determination of fluidization regime in the simulation of fluidized bed reactor of Gas-solid:

The determination of hydro-dynamic and fluidization regime of fluidized bed is important. The simulation of fluidal bed reactor has been done for bubbled regime (bubbling fluidization) that is valid for this study. Also this simulation for other bubbling fluidization (before beginning of bubbling fluidization and turbulent fluidization) can be used with some rough estimation. In order to study the bubbling fluidization, the principles that had been explained in the section of 2[2] will be applied.

The quantities U*, d^*_p using the equations of 26,27 section 2[2] for the melamine fluidized will be calculated; then the bubbling fluidization using the figure 11, section 2[2] will be determine for 380°C, the fluid in the fluidized bed is assumed ammonia because its large amount; and based on the ammonia and silicagel particle properties. The quantities of d*p and U* will be calculated. In 380°C, the ammonia properties will be:

$$\mu_g = 2250\times10^{-7}\, g/(cm.\sec)$$

$$\rho_{g(O^oC)} = 0.7708 g/l,\ \rho_{g,(380^oC)} = 0.32224 g/l$$

For silicagel particles will have:

$$d_p = 212.88\times10^{-6} m = 212.88\times10^{-4} cm, \rho_S = 1.96\, gr/cc$$

The above quantities will be substituted in d*p and U* equations and the following quantities will be resulted:

d*p = 4.9039 , U*=6.217× 10^{-3} U

U (cm/sec)

The following quantities are resulted based on the velocity variations:

1) 4 cm/sec <U<28 cm/sec For fluidal bed fludization without bubbles

2) 28<U<140 For bubbling fluidal bed fluidization

3) 140<U<205 For bubbling fluidal bed fluidization and turbulent

4) 205<U<643 For turbulent fluidal bed fluidization

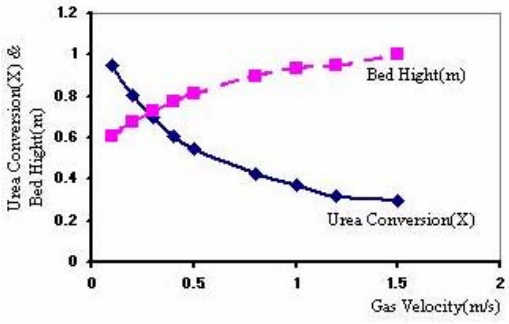
Thus the melamine catalytic fluidal bed in the range of 28<U<140 cm/sec is bubbling fluidal bed fluidization.

Table (1) indicated the variation of partial conversion of outlet urea based on gas velocity and bed height of fluidized bed using two phases model.

Table (1)

U(m/s)	X(two-phase)	(H_f) m
0.1	0.94	0.61
0.2	0.8	0.67
0.3	0.69	0.73
0.4	0.61	0.77
0.5	0.545	0.81
0.8	0.422	0.89
0.0	0.371	0.937
1.2	0.335	0.97
1.5	0.296	1.0
2.0	0.258	1.05

The figure 1 has been drawn using the resulted data from two phases model including the variation of partial conversion of urea and the fluidized bed height based on inlet gas at 380°C.

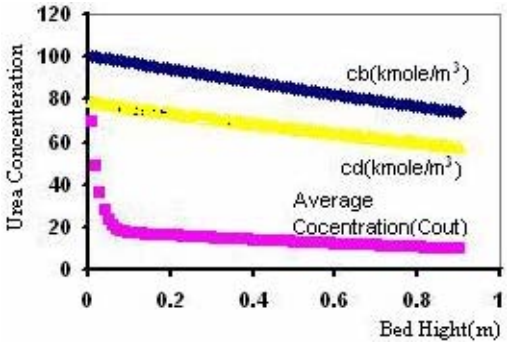


Fig(1)-two phase model results: urea conversion and bed height vs. gas velocity; u_{mf}=.0234m/s, H_{mf}=.5375m, D_r=0.041m,w=400g,emf=425,k=13.7798, n=.4,D_e=.00001 m/s2,

The figure 1 presents the variation of partial conversion quantities of outlet urea and fluidized bed height based on gas velocity using two phases model.

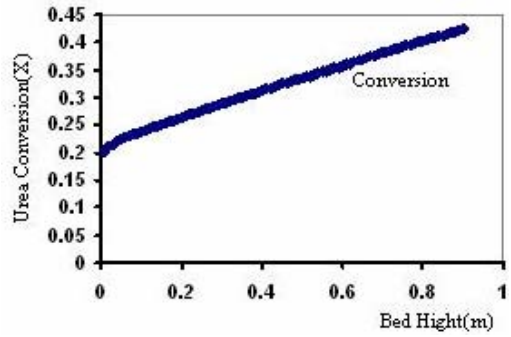
The model of outlet quantities including urea conversion, figure 3 and concentration in bubbling phase (Cb), concentration in suspended phase (Cd), figure 2 are drawn for gas velocity of 0.8 m/s versus fluidal bed height.

Figure 2: Presented the results of two phases model including the concentration in bubbling phase (Cb), and averaged the concentration in suspended phase (Cd) concentration (Cout) in 380°C versus the fluidized bed height.



Fig(2)-Two phase model results: phase concentration profile (bubble , dense and average) and urea conversion vs. bed height; d_r=4.1cm ,u=.8m/s, u_{mf}=.02344m/s, k= 13.7798, n=.4, T=380^{o}C, D_e=.00001m/s^2, H_{mf}=.5375m

Figure 3: Presented the results of two phases model including partial conversion of urea in 380^{o}C versus fluidized bed height.



Fig(3)- Two phase model results: urea conversion vs. bed height; d_r=4.1cm,u=.8m/s, u_{mf}=.02344m/s, k=13.4498,n=0.4,T=380oc, D_e=.00001m/s^2, H_{mf}=.5375m

Conclusion:

In order to simulate the fluidal bed reactor, understanding of the fluidized bed hydrodynamic concepts is a requirement. Understanding of fluidization and particle size is also other requirements that must be considered to select an appropriate model for fluidized bed reactor simulation. The three phases bubbling fluidized bed model for the small particles size (Geldart-A), the two phases bubbling fluidized bed model for averaged particles size (Geldart-B) and homogenous models for the large particle size are appropriate models. The reactor CSTR has been selected for fast fluidization, turbulent fluidization and N-Stages homogenous fluidization.

Consider that the bubbling fluidized bed fluidization is not applicable for the most industrial reactors. Application of the bubbling fluidized bed fluidization for melamine in the reactor with 4.8 cm diameter has been proven[2] .

The calculation fluidized bed hydrodynamic (the minimum amounts of fluidization velocity and fluidization height) and kinetic factors (k,n) are very important for this simulation. Modified two phases model [6] with the bubbles diameter calculated using [4] is appropriate model of simulation that has been selected in the case of bubbling fluidized bed [2] . Modified two phases model has been used to simulate the melamine bubbling fluidized bed reactor with particle size, 200 μ .

Nomenclature:

A, At: [m^2], cross-sectional area of reactor
Ab: [m^2], cross-sectional area of reactor occupied by bubble
Caverage: [kmole/m^3], reactant concentration (averaged over phases)
C_A: [kmole/m^3], reactant concentration component A
C_{Ab} : [kmole/m^3], reactant concentration in bubble phase component A
C_b : [kmole/m^3], reactant concentration in bubble phase
C_d : [kmole/m^3], reactant concentration in dense phase
C_{out} : [kmole/m^3], reactant concentration in outlet
D_b : [m], bubble diameter
D_b : [m], initial bubble diameter
D_{bM} : [m], maximum bubble diameter
H : [m], bed height
H_{mf} : [m], bed height at minimum fluidization
Km_i : [m^3/(kg s)], first order reaction rate constant
Kgi : [m /s], mass transfer coefficient
U. U_o : [m/s] , superficial fluidizing velocity
U_b : [m/s], superficial bubble phase velocity
U_{br} : [m/s], local bubble rise superficial velocity
U_{mf} : [m/s], superficial fluidizing velocity
μ : [kg/m.s. Gas viscosity
ρ_g : [kg/m^3], Gas density
ρ_S, ρ_P : [kg/m^3], solid, particle density
ε_{mf} :bed porosity at minimum fluidization
ε_b :local bubble gas hold up
ν_{ij} :Stoichiometric number of species i in reaction J

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