LIQUID-PHASE MASS TRANSFER COEFFICIENT AND GAS HOLDUP IN A PACKED-BED COCURRENT UP-FLOW COLUMN

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Packed-bed cocurrent up-flow reactors gave better results than conventional trickling flow reactors in hydrodesulfurization of heavy oil. To find the characteristics of this up-flow type reactor, liquid-phase mass transfer coefficient, gas-liquid interfacial area and gas holdup in a column packed with 0.1, 0.28 or 0.43 cm glass beads were studied using the oxidation reaction of sodium sulfite.

Experiments were carried out at a reaction temperature of 20°C. Superficial liquid and gas velocities based on empty column, u_l and u_g, were 1～6 and 0.5～6 cm/sec, respectively, for any size of glass beads. With the values of u_l and u_g, glass beads bed remained stationary, expanded or fluidized.

Stagnant gas holdup was observed under the condition of $u_l < u_{lmf}$ (minimum fluidization liquid velocity).

It was found that the stagnant gas holdup was almost ineffective on mass transfer. Volumetric mass transfer coefficient, k_La, and gas-liquid interfacial area, a, were well correlated with dynamic gas holdup, ε_{gd}, which was a difference between total and stagnant gas holdups. When $u_l < u_{lmf}$, the correlation was represented in a simple equation of $k_La = f_p\varepsilon_{gd}$ (f_p: constant depending on particle size, d_p).

k_La was found to be mainly affected by gas-liquid interfacial area. Larger packing particles gave larger values of k_La. They were larger than those in bubble columns when $d_p \geqq 0.28$ cm and smaller when $d_p = 0.1$ cm.

1. Introduction

Fixed-bed cocurrent up-flow reactors have been applied in hydrodesulfurization of heavy oil[3-5,7] and have given better results[4,7] in sulfur removal than have conventional cocurrent down-flow reactors. Up-flow arrangement has been found to be more effective than the down-flow arrangement either in temperature control[7] or in keeping catalyst life long[8] in hydrodesulfurization but very little has been reported about the characteristics of this reaction system such as gas-liquid mixing, mass transfer of gas into liquid and heat transfer across the reaction zone, some of which are estimated to have caused the better results mentioned above.

In this paper, mass transfer coefficient, gas-liquid interfacial area and gas holdup in the reaction system of air and sodium-sulfite aqueous solution in a glass beads packed column will be presented.

2. Experimental

2. 1 Apparatus

The schematic diagram of the experimental apparatus is shown in **Fig. 1**. The cylindrical column (A), made of transparent methacrylic resin, was 5 cm in inside diameter and 2 m in length. The column was put on a scale (H) so that gas holdup could be measured by weight under the operating conditions. Particle bed was supported by a wire screen at the bottom of the column. Gas and liquid were fed into

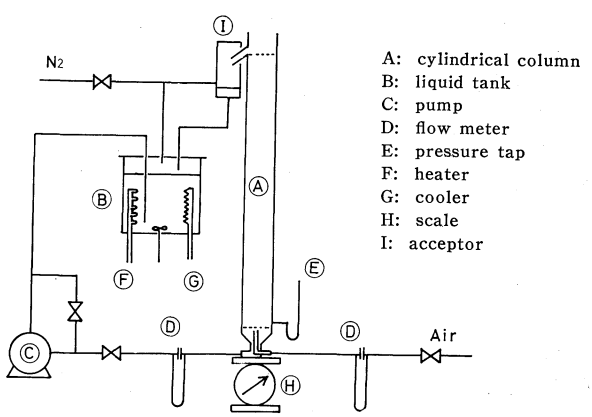

Fig. 1 Schematic diagram of the apparatus

Received May 16, 1975.
Presented at the 40th Annual Meeting of The Soc. of Chem. Engrs., Japan, at Nagoya, April 1975.

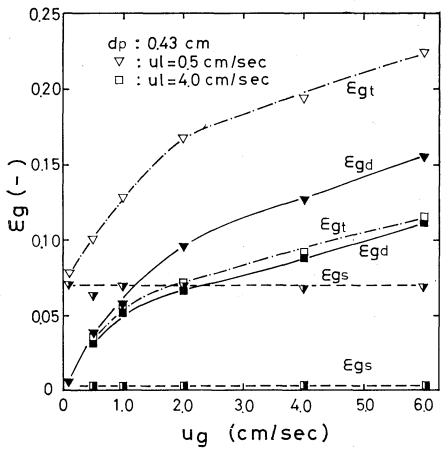

Fig. 2 Relations between gas holdups and superficial gas velocity

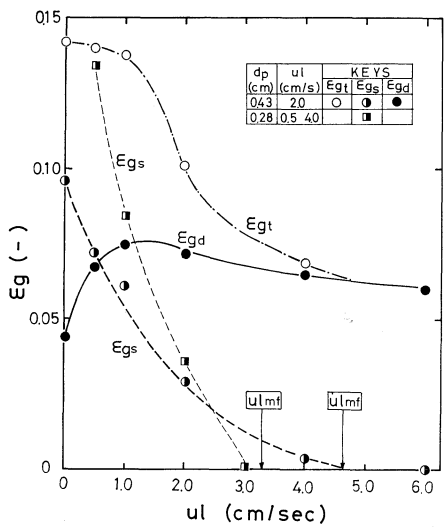

Fig. 3 Relations between gas holdups and superficial liquid velocity

the column through a concentric double-tube nozzle (0.3 and 1.2 cm I.D.) just below the screen. Another wire screen was located at the top of the column to prevent particles from floating out of it.

The liquid tank (B) and the acceptor (I) were sealed with nitrogen to prevent sodium-sulfite aqueous solution from being in contact with air.

2. 2 Procedures

Experiments were carried out at a reaction temperature of 20°C and superficial gas and liquid velocities based on empty column, u_g and u_l, were 0.5～6 and 1～6 cm/sec, respectively. Average diameters of packing particles were 0.1, 0.28 and 0.43 cm. The volume fraction occupied by particles in the column changed with the values of u_l and u_g, because bed expansion varied with them.

To measure the values of liquid-phase volumetric mass transfer coefficients, 0.385 mol/l of Na_2SO_3 aqueous solution as liquid reactant and 10^{-6} mol/l of $CuSO_4$ as catalyst were used. In the oxidation reaction under this liquid condition, the value of reaction factor, β, was very close to 1. To measure the values of gas-liquid interfacial area, a, 0.5×10^{-3} mol/l of $CoCl_2$ was used as catalyst to keep the value of β over 3.

Apparent reaction rate was obtained by the decrease of Na_2SO_3 concentration with time which was measured by iodometry of remaining Na_2SO_3 in liquid samples withdrawn at the mid-point of the reactor. The value of volumetric mass transfer coefficient, k_La, was obtained from Eq. (2) on the assumption that oxygen concentration in the liquid bulk was zero when $\beta=1$.

$$N_{O_2}=k_La(C_{O_2i}-C_{O_2l}) \tag{1}$$

$$k_La=\frac{1}{2}\frac{V_l}{V_r}\frac{dC_{SO_3}}{dt}/C_{O_2i} \quad (\beta=1) \tag{2}$$

The value of the interfacial area was obtained using the following equation under the condition that β was over 3 and oxygen concentration in the liquid bulk was zero.

$$a=\frac{1}{2}\frac{V_l}{V_r}\frac{dC_{SO_3}}{dt}\frac{1}{\sqrt{kD_fC_{SO_3}}\,C_{O_2i}} \quad (\beta>3) \tag{3}$$

Therefore the mass transfer coefficient, k_L, was calculated with k_La from Eq. (2) and a from Eq. (3).

The gas holdups were measured by weighing the column under the following conditions:

(x) gas was flowing at a given superficial velocity,
(y) gas feed was stopped and no gas was flowing, but stagnant bubbles were still in the bed and
(z) all the stagnant gas was expelled and no more gas remained in the column,

while the liquid was flowing at a given superficial velocity in any case. Thus the gas holdup was calculated by the following equations:

Total gas holdup: $$\varepsilon_{gt}=\frac{g_c(Wz-Wx)}{g\rho_lV_r} \tag{4}$$

Stagnant gas holdup: $$\varepsilon_{gs}=\frac{g_c(Wz-Wy)}{g\rho_lV_r} \tag{5}$$

3. Results and Discussion

3. 1 Stagnant gas holdup

In the column packed with glass beads of average diameter, d_p, of 0.43 and 0.28 cm, "stagnant" gas bubbles were observed during operation. These bubbles stayed in the column after gas feed had been shut off while liquid was kept flowing at given superficial velocities. The holdup of these stagnant bubbles is defined here as "stagnant gas holdup, ε_{gs}".

As shown in **Fig. 2**, stagnant gas holdup is found to have a constant value independent of u_g and to vary with d_p. ε_{gs} decreases with increasing u_l approaching zero at the minimum fluidization velocity, u_{lmf}, corresponding to each d_p as shown in **Fig. 3**.

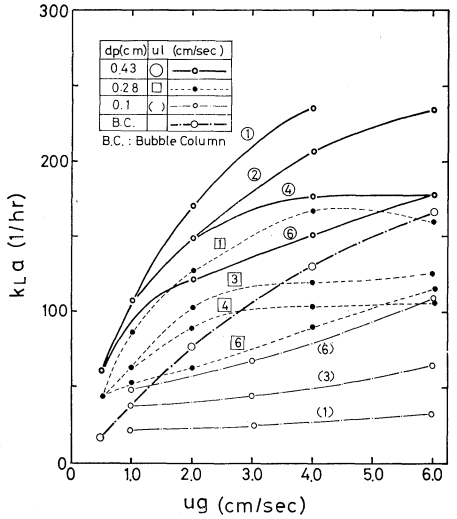

Fig. 4 Relations between k_La and u_g as functions of u_l and particle size

When u_l is larger than u_{lmf} (4.3 cm/sec for d_p= 0.43 cm and 3.0 cm/sec for d_p=0.28 cm), no stagnant gas holdup is observed. In the case of the smallest particles (d_p=0.1 cm), ε_{gs} was not observed under the experimental conditions of this work.

The difference between total gas holdup, ε_{gt}, and ε_{gs} is defined here as "dynamic gas holdup, ε_{gd}", which decreases slightly with increasing u_l and increases with increasing u_g, which can be seen in Figs. 2 and 3.

3. 2 Liquid-phase volumetric mass transfer coefficients

As shown in **Fig. 4**, volumetric mass transfer coefficient, k_La, generally increases with increasing u_g. Under the same operating conditions, larger packing particles give a larger value of k_La. Where d_p=0.43 and 0.28 cm, a smaller value of u_l is found to give a larger value of k_La. In the case of d_p=0.1 cm, a larger value of u_l gives a larger value of k_La. These phenomena are considered to be caused by the relations among u_l, ε_{gd}, a and average bubble diameter, d_b, which will be discussed later.

The values of k_La in a bubble column containing no particles under the conditions of u_l=0 and u_g= 1~6 cm/sec are from 20 to 160 hr^{-1}, as shown in Fig. 4. This agrees well with the results of Yoshida *et al.*[9], i.e. 20~150 hr^{-1} in 7.7 cm I.D. bubble column under the same operating conditions. These values of k_La are larger than 20~110 hr^{-1} of d_p=0.1 cm, almost the same as 40~170 hr^{-1} of d_p=0.28 cm and smaller than 40~240 hr^{-1} of d_p=0.43 cm in the packed column. This shows that particles of very small size have a negative effect on k_La and that larger ones have a positive effect on it under the experimental conditions of this work.

The relations between k_La and ε_{gt} are shown in **Figs. 5, 6**, and **7**. As shown in Fig. 5, where the values of u_l are smaller than the u_{lmf} corresponding to d_p=0.43 cm, the relations between k_La and ε_{gt} are

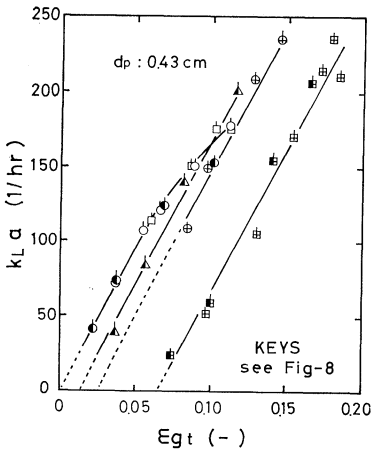

Fig. 5 Relations between k_La and total gas holdup as a function of u_l for d_p=0.43 cm

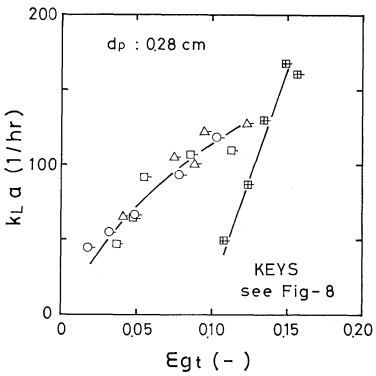

Fig. 6 Relations between k_La and total gas holdup as a function of u_l for d_p=0.28 cm

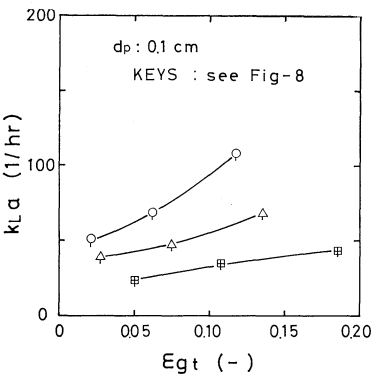

Fig. 7 Relations between k_La and total gas holdup as a function of u_l for d_p=0.1 cm

given in parallel straight lines having different intercepts with u_l. The values of ε_{gt} of these intercepts agree with the values of ε_{gs} of corresponding u_l in Fig. 3.

In the case where u_l is larger than or very close to the u_{lmf}, when particles are in fluidized state or nearly fluidizing, the values of k_La are found to be in a linear correlation with ε_{gt} in the range of ε_{gt} below 0.06. However, in the range of larger ε_{gt}, gradual deviation from the linear line is observed.

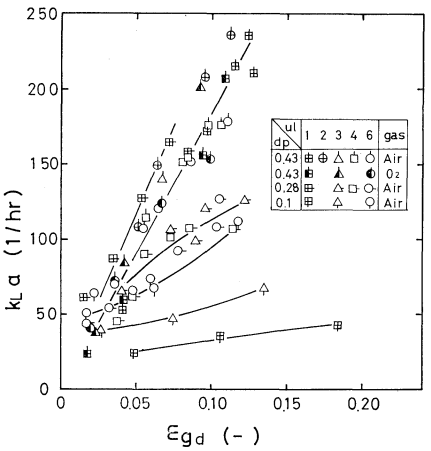

Fig. 8 Relations between k_La and dynamic gas holdup as functions of u_l and d_p

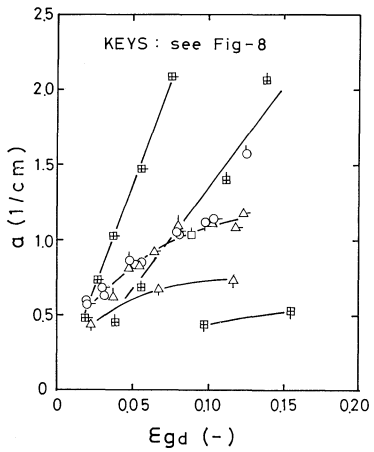

Fig. 9 Relations between interfacial area and dynamic gas holdup as functions of u_l and d_p

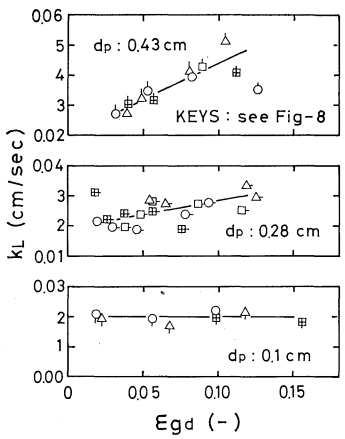

Fig. 10 Relations between k_La and dynamic gas holdup as a function of u_l

Similar phenomena are observed with d_p=0.28 cm, as shown in Fig. 6. In this case, the relation between k_La and ε_{gt} when $u_l>u_{lmf}$ is given in a clear curve independent of u_l. When d_p=0.1 cm, the relations between k_La and ε_{gt} are given in curves different with u_l, as shown in Fig. 7. In this case, u_l is larger than the u_{lmf} of the corresponding particles, and all the particles are well fluidized at any value of u_l in this work.

In explanation of the phenomena shown in Figs. 5 and 6, two hypotheses may be considered:

(1) As the stagnant gas bubbles stay too long in the column, they may be too poor in oxygen partial pressure to contribute to oxygen mass transfer.

(2) k_La of stagnant gas bubbles may be negligibly small compared with that of dynamic gas bubbles and its contribution to mass transfer may not be important.

To substantiate the first hypothesis, pure oxygen was used in place of air. But as shown in Fig. 5, no difference between pure oxygen and air in k_La-ε_{gt} correlation was observed. Another trial to clarify the phenomena was made. It was a plot of k_La against dynamic gas holdup, ε_{gd}, which gave better correlations for d_p=0.43 and 0.28 cm as shown in **Fig. 8**. In the case of d_p=0.43 cm, the relation between k_La and ε_{gd} is given as a straight line independent of u_l when $u_l<u_{lmf}$. When $u_l>u_{lmf}$, the deviation of k_La-ε_{gd} curve from the straight line is so small that all the k_La-ε_{gd} correlations are apparently on a single straight line passing the origin. In the case of d_p=0.28 cm, the straight line corresponding to u_l=1, which kept away from the origin in Fig. 6, passes it in Fig. 8. Curves in Fig. 8 are all the same as those in Figs. 6 and 7, because in this case, $\varepsilon_{gd}=\varepsilon_{gt}$ where $u_l>u_{lmf}$.

From Figs. 5, 6 and 8, it is probably proper to adopt the second hypothesis. Therefore, dynamic gas holdup can be the only effective gas holdup, and a simple correlation between k_La and ε_{gd} under the condition of $u_l<u_{lmf}$ is represented by the following equation:

$$k_La=f_p\varepsilon_{gd} \quad (u_l<u_{lmf}) \tag{6}$$

in which f_p is a constant dependent on d_p.

3. 3 Gas-liquid interfacial area

As shown in **Fig. 9**, the relation between gas-liquid interfacial area, a, and ε_{gd} is found to be almost the same in appearance as that of k_L-ε_{gd}. This suggests that k_La is mainly affected by a with regard to any value of d_p within the experimental conditions of this work. The value of a corresponding to u_l=1 of d_p=0.28 cm is larger than that of d_p=0.43 cm. This may be attributable to the difference in bubble diameter, d_b, in both cases, as is shown later.

3. 4 Mass transfer coefficients

Mass transfer coefficient, k_L, as a function of ε_{gd} is shown in **Fig. 10**, which was calculated using Eqs. (2) and (3). As shown in the figure, k_L is found to be almost independent of u_l. It is also found that k_L increases with ε_{gd} for d_p=0.43 cm, slightly increases

with ε_{gd} for d_p=0.28 cm and is almost constant with ε_{gd} for d_p=0.1 cm. These phenomena are considered to have close reference to the difference in extent of bed expansion which varies with d_p. But in any case, the variation of k_L under the experimental conditions of this work is so small that it does not have much influence on k_La as a.

The approximate values of k_L for d_p=0.43, 0.284 and 0.1 cm were 0.035, 0.025 and 0.02 cm/sec, respectively, which agrees well with the results of Calderbank *et al.*[2] and of Tadaki *et al.*[6]. These values are ten times larger than those ranging from 0.001 to 0.003 cm/sec given by Akehata *et al.*[1] in mass transfer from a stationary single bubble under the same condition of u_l as that of this work. It may be supposed that the value of k_L in mass transfer from stagnant bubbles does not differ much from that in mass transfer from a stationary single bubble. Therefore, it can be recognized that the contribution of stagnant gas holdup to mass transfer is negligibly small compared with that of dynamic gas holdup.

3. 5 Average bubble diameter

Average bubble diameter, d_b, was calculated by Eq. (7) as a hypothetical value assuming bubbles to be spheres and taking ε_{gd} as gas holdup.

$$d_b=6\varepsilon_{gd}/a \tag{7}$$

i) When d_p=0.43 cm d_b has a constant value of approximately 0.4 cm almost independent of u_l and ε_{gd}, as shown in **Fig. 11**. This suggests that the increase in ε_{gd} makes linear increase in number of bubbles of the same size, which results in a linear relation between a and ε_{gd} as shown in Fig. 9.

ii) When d_p=0.28 cm d_b has a constant value of approximately 0.2 cm almost independent of ε_{gd} under the condition of u_l=1 cm/sec ($<u_{lmf}$), as shown in Fig. 11. This value of d_b is smaller than that of d_p=0.43 cm, which must be due to the difference in size of vacant spaces surrounded by the particles of both sizes. This is the reason for the difference in the value of a of d_p=0.43 and 0.28 cm in the case of $u_l<u_{lmf}$, as shown in Fig. 9. In this case, the linear correlation between a and ε_{gd} shown in Fig. 9 results from the linear correlation between number of bubbles of the same size and ε_{gd}, as it was in the case of d_p=0.43 cm.

When $u_l>u_{lmf}$, d_b is found to increase linearly with ε_{gd} independent of u_l ranging from 0.2 to 0.66 cm/sec. This suggests that a does not increase linearly with ε_{gd}, as shown in Fig. 9.

iii) When d_p=0.1 cm d_b is found to increase with ε_{gd} and to decrease with u_l, as shown in Fig. 11. This suggests that consolidation of bubbles is promoted by increase in ε_{gd} and is retarded by increase in u_l in a fully fluidized system of fine particles.

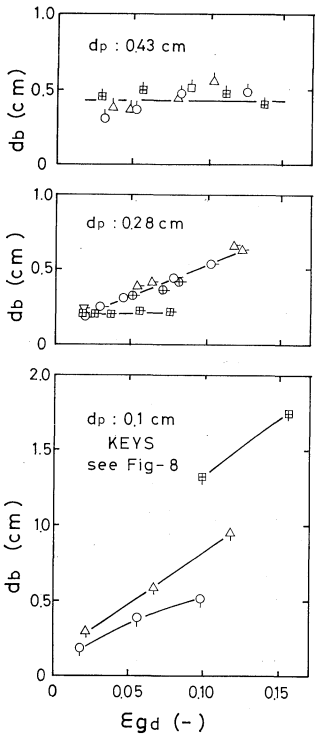

Fig. 11 Relations between bubble diameter and dynamic gas holdup as a function of u_l

The relation of d_b with a is similar to that of d_p= 0.28 cm when $u_l>u_{lmf}$ except for the contribution of u_l.

4. Conclusion

Liquid-phase volumetric mass transfer coefficient, gas-liquid interfacial area and gas holdup in a packed-bed cocurrent up-flow column were observed using the oxidation reaction of sodium sulfite, and studies were made of the mutual relations among them and also of liquid-phase mass transfer coefficient and average bubble diameter in relation to them.

Stagnant gas holdup, ε_{gs}, was observed under the condition of $u_l<u_{lmf}$, which decreased with u_l and was almost independent of u_g. It was found that the contribution of ε_{gs} to mass transfer was negligibly small.

Volumetric mass transfer coefficient, k_La, and gas-liquid interfacial area, a, were well correlated with dynamic gas holdup, ε_{gd}, which was the difference between total and stagnant gas holdups. The value of k_La was found to be mainly affected by a.

The value of mass transfer coefficient, k_L, was found to be independent of u_l, slightly increasing with ε_{gd} for d_p=0.43 and 0.28 cm, but almost constant with ε_{gd} for d_p=0.1 cm. It was also found that k_L was larger when d_p was larger.

Acknowledgment

The authors wish to express their appreciation to Mr. K.

Iigima of Kanagawa University (now of Showa Sangyo Co., Ltd.) for his contribution in experimental work and to Dr. H. Yoshitome of National Chemical Laboratory For Industry for giving them many helpful comments and suggestions regarding this paper.

Nomenclature

a	=	interfacial area per unit vol. of reactor	[cm^2/cm^3]
$C_{O_2 i}$	=	equilibrium concentration of O_2 at gas-liquid interface	[mol/l]
$C_{O_2 l}$	=	concentration of O_2 in the liquid phase	[mol/l]
C_{SO_3}	=	concentration of Na_2SO_3 in the liquid phase	[mol/l]
D_f	=	diffusion coefficient of O_2 in the liquid phase	[cm^2/sec]
f_p	=	constant dependent on particle size	[—]
k	=	chemical reaction constant	[l/mol·sec]
k_L	=	liquid-phase mass transfer coefficient	[cm/sec]
N_{O_2}	=	absorption rate of O_2 with chemical reaction	[mol/l·sec]
t	=	time	[sec]
u_g, u_l	=	superficial gas and liquid velocity	[cm/sec]
u_{lmf}	=	minimum fluidization velocity of liquid	[cm/sec]
V_l	=	total liquid volume	[l]
V_r	=	reactor volume	[l]
Wx,Wy,Wz	=	weight of column in the state of x,y,z	[G]
β	=	reaction factor	[—]
$\varepsilon_{gd},\varepsilon_{gs},\varepsilon_{gt}$	=	dynamic, stagnant, total gas holdup	[—]
ρ_l	=	density of liquid	[g/cm^3]

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