EFFECT OF PARTICLES IN BUBBLES ON FLUIDIZED BED MASS AND HEAT TRANSFER KINETICS

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Experiments in bubbling fluidized beds show that gases which adsorb on solids experience up to ten times more rapid bubble-emulsion interchange than do nonadsorbing gases. We propose that the very small fraction of solids dispersed in and passing through the bubbles are the vehicle for this behavior.

A theory is developed which shows that the enhancement in the overall bubble-emulsion interchange coefficient is strongly dependent on the value of the gas-solid adsorption equilibrium constant. The enhancement predictions from theory are then compared with values reported in the literature.

This mass transfer phenomenon is then extended to gas-solid heat transfer in fluidized beds. The results indicate that the particles dispersed in bubbles usually play the dominant role in the heat interchange between bubble gas and emulsion gas.

In a previous paper⁹⁾ we considered the phenomenon of bubble emulsion interchange of nonadsorbing gases in bubbling fluidized beds. However, a number of workers^{2,3,11,13,14)} have measured this interchange using gases which are adsorbed by the bed solids, and have found an enhancement in the interchange. This paper presents an explanation for these findings, as well as a comparison of prediction with experimental findings.

Experimental Findings

Most workers measured the extent of gas interchange between bubble and emulsion by injecting

tracer gas into a rising gas bubble, and then following its disappearance as the bubble rose in the bed. We summarize these findings here.

Wakabayashi and Kunii¹⁴⁾ injected single bubbles of humid air into a 0.2 m ID bed of 145 μm micro-spherical catalyst fluidized by dry air, obtaining values of the interchange coefficient of

$$K_{be} = 10\text{--}15 \text{ s}^{-1} \quad \text{for } \bar{d}_b = 0.04\text{--}0.11 \text{ m}$$

This range of K_{be} values was several times larger than for nonadsorbed tracer gas.

Toei *et al.*¹³⁾ sampled the composition of bubbles containing Freon-12 tracer in a two-dimensional bed of active 161–252 μm alumina catalyst, finding interchange coefficients

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Fig. 1. Experimental values for the bubble-emulsion transfer coefficient, from Morooka¹⁰. Silica-alumina FCC catalyst, $\bar{d}_p = 59 \mu\text{m}$, bulk density $= 960 \text{ kg/m}^3$, $u_{mf} = 0.0012 \text{ m/s}$, $d_t = 0.12$ and 0.19 m , $L_f \cong 2 \text{ m}$, $u_o = 0.06\text{--}0.23 \text{ m/s}$

$$k_{be} = 2\text{--}4 \times 10^{-2} \text{ m} \cdot \text{s}^{-1} \quad \text{for } \bar{d}_b = 0.06\text{--}0.11 \text{ m}$$

Rietema *et al.*³⁾ injected hydrocarbon tracer gas into 0.18 m and 0.90 m ID beds of spent $66 \mu\text{m}$ cracking catalyst, and their results can be summarized as follows:

$$d_t = 0.18 \text{ m}, u_o = 0.2 \text{ m} \cdot \text{s}^{-1}, d_b = 0.05\text{--}0.07 \text{ m}$$

tracer gas: methane, ethane, ethene, propane

$$k_{be} = 0.8\text{--}1.2 \times 10^{-2} \text{ m} \cdot \text{s}^{-1}$$

$$d_t = 0.9 \text{ m}, u_o = 0.3 \text{ m} \cdot \text{s}^{-1}$$

Tracer gas	Methane	Ethane	Ethene	Propane
d_b (m)	0.1 0.15	0.1 0.15	0.1 0.15	0.1 0.15
k_{be} ($\text{m} \cdot \text{s}^{-1}$)	2.7 2.8	2.6 3.3	3.0 4.3	3.9 5.5×10^{-2}

———— increase in adsorption ———>

This table of results shows larger values of k_{be} for more adsorbing tracer gases. In addition, larger bubbles with adsorbing tracer gas gave larger k_{be} values, which is just the reverse of what was found for nonadsorbing tracer gas.

Bohle and van Swaaij²⁾ carried out similar experiments in a 0.105 m ID bed of $70 \mu\text{m}$ silica-alumina particles. Their findings indicate that k_{be} with adsorbing propane tracer is just about double that for helium tracer. The adsorption equilibrium constant for propane was reported to be $m = 7.07$, while helium was found to be hardly adsorbed.

Pulse-response measurements were used by Morooka *et al.*¹⁰⁾ to study bubble-emulsion gas interchange. On the basis of the two-region model they determined the volumetric mass transfer coefficient, $a_b k_{be}$. Their data are shown in Fig. 1. This figure also shows the findings of Yamazaki and Miyauchi¹⁵⁾ calculated from measured temperature differences between bubble and emulsion in the bed.

Figure 1 clearly shows the strong effect of the adsorption equilibrium constant m of tracer gas on FCC catalyst. The values of m for the various gases

used as tracer are reported as follows:

Tracer gas	Helium	CO ₂	Freon 12	Freon 22
m (—)	0.6	2–4	7–10	13–17

Gas Interchange between Bubble and Emulsion

The mass transfer coefficient k_d^* for a single spherical particle of diameter d_p moving through a fluid at a relative velocity u is given by Froessling⁴⁾ as

$$Sh^* = \frac{k_d^* d_p \gamma}{\mathcal{D}} = 2 + 0.6 Re_p^{1/2} Sc^{1/3} \quad (1)$$

First consider the vaporization or sublimation of substance A from all the particles in a bubbling fluidized bed. Since the flow of gas in the emulsion is small, and even slowly downward in some situations, let us ignore its contribution to the total flow of gas through the bed. Thus we assume that fresh gas enters the bed only as bubbles, and at steady state the measure of the rate of sublimation of A is given by the increase of C_A with height in the bubble phase.

In addition, let us assume that equilibrium is rapidly established between C_A at the particle surface and its surroundings. Then, since particles rapidly enter and leave the rising clouds, and since C_A in the emulsion only changes slowly with time, all this leads to the conclusion that at any level in the bed C_A at the particle surface, in the emulsion, and in the cloud are close to equal, or $C_{Ap} = C_{Ae} = C_{Ac}$. Thus in terms of the interchange coefficient for mass transfer between bubble and emulsion, $K_d (\text{s}^{-1})$, we may write

$$\frac{1}{V_b} \frac{dN_A}{dt} = u_b \frac{dC_A}{dz} = K_d (C_{Ap} - C_{Ab}) \quad (2)$$

Now K_d represents the addition of A to the bubble gas from two sources, as follows:

$$K_d = \left(\begin{array}{l} \text{added from particles} \\ \text{dispersed in bubbles} \end{array} \right)$$

$$\begin{aligned}
& + \left(\text{transferred across the} \right. \\
& \quad \left. \text{bubble-cloud boundary} \right) \\
& = \gamma_b a' k_d^* + K_{bc} \\
& = \gamma_b \frac{6(Sh^*)}{\phi_s d_p^2 y} + K_{bc} \quad (\text{s}^{-1}) \quad (3)
\end{aligned}$$

In this expression K_{bc} represents the transfer across the bubble-cloud boundary of A which is present in the gas alone. From a previous paper⁹) it is found to be given by

$$K_{bc} = 4.5 \left(\frac{u_{mf}}{d_b} \right) + 5.85 \left(\frac{\mathcal{D}^{1/2} g^{1/4}}{d_b^{5/4}} \right) \quad (4)$$

In Eq. (3) γ_b is the volume fraction of particles dispersed in the bubble phase. A number of research groups^{1,5,6,12}), using a variety of measurement techniques, have clearly confirmed the existence of these particles. However, the value of γ_b is still uncertain, the best estimates today being in the range of $\gamma_b = 0.001$ – 0.01 .

Although this volume fraction of solids is very small, it is important to realize that the mass of solids in bubbles is not small, being in the range of 1 to 10 times that of the bubble gas. So, even though γ_b is very small, the first term in Eq. (3) can become important in beds of fine particles.

According to the development in our earlier articles^{7,9}), the two different measures of interchange rate between bubble and emulsion are related as follows:

$$a_b k_{be} = \delta K_d \cong \frac{u_o}{u_b} K_d \quad (5)$$

Effect of Adsorption on the Interchange Coefficient

Equation (3) cannot be used directly for adsorbing and desorbing gases because in these processes one has an additional mode of transport of A from phase to phase, namely as adsorbed material on the carrier particles which move from phase to phase. Let us develop the equations to account for this added factor.

Consider a bubble containing tracer A of concentration C_{Ab} passing up a bed of adsorbing particles, as shown in Fig. 2. In general, for a typical particle in the emulsion we may write

$$C_{As} = m C_{Ap} \quad (6)$$

where C_{As} is the concentration of tracer A within the particle which is in equilibrium with tracer gas of concentration C_{Ap} bathing the particle. As with the nonadsorbing case, we again assume the same concentration of tracer in emulsion and cloud at any level in the bed, or

$$C_{Ap} = C_{Ae} = C_{Ac} \quad (7)$$

Fig. 2. Notation used in deriving the expression which accounts for the take-up of tracer A from bubble gas by solids passing through the bubbles

Now focus attention on a particle of sphericity ϕ_s passing through the bubble. The transfer of tracer A from bubble gas to particle is given by

$$\left(\text{accumulation of A} \right) = \left(\text{transfer of A} \right) \\ \left(\text{in the particle} \right) \quad \left(\text{from bubble gas} \right)$$

or

$$\left(\frac{\pi}{6} d_p^3 \right) dC_{As} = \left(\frac{\pi d_p^2}{\phi_s} \right) k_d^* (C_{Ab} - C_{Ap}) dt \quad (8)$$

At time $t=0$ when the particle just enters the bubble

$$C_{Ap} = C_{Ac} \quad (9)$$

Integrating Eq. (8) with this condition gives

$$\frac{C_{Ab} - C_{Ap}}{C_{Ab} - C_{Ac}} = \exp \left(- \frac{6k_d^*}{m\phi_s d_p} t \right) \quad (10)$$

For a random stay with mean residence time $\bar{t}_p$, the residence time distribution of particles in the bubble is given by

$$E(t) = \frac{1}{\bar{t}_p} \exp \left(- \frac{t}{\bar{t}_p} \right) \quad (11)$$

Thus the mean concentration of tracer A at the surface of a particle just leaving the bubble and reentering the emulsion is $\bar{C}_{Ap}$, given by

$$C_{Ab} - \bar{C}_{Ap} = \int_0^\infty (C_{Ab} - C_{Ap}) E(t) dt \quad (12)$$

Combining the above three equations and integrating then give

$$C_{Ab} - \bar{C}_{Ap} = \frac{C_{Ab} - C_{Ac}}{1 + 6k_d^* \bar{t}_p / m\phi_s d_p} \quad (13)$$

Tracer A goes from bubble gas to the emulsion phase via two paths: capture by solids passing through the bubble, and by transfer across the bubble-cloud interface, or

$$K_d (C_{Ab} - C_{Ac}) = \frac{\gamma_b}{\bar{t}_p} (m \bar{C}_{Ap} - m C_{Ac}) + K_{bc} (C_{Ab} - C_{Ac}) \quad (14)$$

Substituting Eqs. (1) and (13) into (14) and simplifying

gives

$$K_d = \gamma_b \frac{6(Sh^*)\mathcal{D}}{\phi_s d_p^2 \gamma} \eta_d + K_{bc} \quad (15)$$

where the fitted adsorption efficiency factor, because $\bar{t}_p$ is unknown, is

$$\eta_d = \frac{1}{1 + \alpha/m} \quad \text{with} \quad \alpha = \frac{6k_d^* \bar{t}_p}{\phi_s d_p} \quad (16)$$

An examination of eq. (15) shows that the gas interchange between bubble and emulsion can be greatly enhanced by adsorption of tracer gas A by the particles which pass through the rising bubbles. For example, the data of Wakabayashi and Kunii¹⁴⁾ are well fitted by the above expression by taking $\gamma_b \eta_d = 4 \times 10^{-4}$, as shown below:

$\bar{d}_b$ (m)	0.04	0.06	0.08	0.11
K_d measured (s^{-1})	11–16	9–18	8–14	7–11
K_d calculated, with $\gamma_b \eta_d = 0$	5	3	2	1.6
K_d calculated, with $\gamma_b \eta_d = 4 \times 10^{-4}$	13	12	12	11

These numbers show that one can explain the increased bubble-emulsion interchange by accounting for the gases transported from phase to phase as adsorbed material in the solids which pass through the bubbles.

The findings of Rietema and his collaborators³⁾, that adsorbing gas interchange is more rapid in large bubbles as opposed to nonadsorbing gases, can be explained as follows: the more frequent and vigorous splitting and coalescence of larger bubbles should result in larger γ_b , the quantity which is the prime factor in enhancing interchange of adsorbing gas. Hence interchange increases.

For nonadsorbing gases the K_{bc} term in Eq. (3) dominates, and Eq. (4) shows that K_{bc} decreases with increase in bubble size, so one would expect a decrease in overall bubble-emulsion interchange with increase in bubble size for nonadsorbing gases.

Interpretation of the Data in Fig. 1

To analyze the reported data shown in Fig. 1, we use the following values:

$$\begin{aligned} u_{mf} &= 1.2 \times 10^{-3} \text{ m} \cdot \text{s}^{-1}, & u_o &= 0.4 \text{ m} \cdot \text{s}^{-1}, \\ u_b &= 1.2 \text{ m} \cdot \text{s}^{-1} \\ \mathcal{D} &= 7 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1} \end{aligned}$$

From the extremes in Fig. 1, experiments show the following:

For nonadsorbing particles ($m=0$) $a_b k_{be} = 1 \text{ s}^{-1}$

For highly adsorbing particles ($m \rightarrow \infty$) $a_b k_{be} = 18 \text{ s}^{-1}$

In general, for any value of the adsorption equilibrium constant, Eq. (5) with Eq. (15) gives

$$\begin{aligned} a_b k_{be} &= \frac{u_o}{u_b} \gamma_b \frac{6(Sh^*)\mathcal{D}}{\phi_s d_p^2 \gamma} \eta_d + \frac{u_o}{u_b} K_{bc} \\ &= M \eta_d + \frac{u_o}{u_b} K_{bc} \end{aligned} \quad (17)$$

Let us first find the bubble size which fits the nonadsorbing extreme, $m=0$. Here Eq. (5) with Eqs. (16) and (4) gives

$$\begin{aligned} a_b k_{be} &= \frac{u_o}{u_b} K_{bc} \\ &= \frac{u_o}{u_b} \left[4.5 \left(\frac{u_{mf}}{d_b} \right) + 5.85 \left(\frac{\mathcal{D}^{1/2} g^{1/4}}{d_b^{5/4}} \right) \right] \end{aligned}$$

and on replacing values from above,

$$1 = \frac{40}{120} \left[4.5 \frac{0.0012}{d_b} + 5.85 \frac{(7 \times 10^{-5})^{1/2} (9.8)^{1/4}}{d_b^{5/4}} \right]$$

from which we get

$$d_b = 0.06 \text{ m} \quad \text{and} \quad K_{bc} = 3 \text{ s}^{-1}$$

Next, for strongly adsorbing particles $m \rightarrow \infty$, Eq. (16) gives $\eta_d = 1$, hence Eq. (17) gives

$$a_b k_{be} = M + \frac{u_o}{u_b} K_{bc}$$

Again, replacing values from above gives

$$18 = M + \frac{40}{120} (3.0) \quad \text{or} \quad M = 17$$

Finally, consider some intermediate condition, say $\alpha=100$ and $m=10$. Then the adsorption efficiency, from Eq. (16) is

$$\eta_d = \frac{1}{1 + 100/10} = 0.091$$

By choosing different values for α and m we draw the lines shown in Fig. 1. These lines seem to be consistent with the reported data.

Heat Transfer between Bubble and Emulsion Phase

Consider bubbling beds of fine particles in which bubbles are surrounded by thin clouds and where just about all the gas passes through the bed as bubbles. If we consider the transfer of heat by gas flow alone across the bubble-cloud boundary then it can be shown, see (7), that the heat flow expression analogous to K_{bc} is given by

$$H_{bc} = 4.5 \left(\frac{u_{mf} \rho_g C_g}{d_b} \right) + 5.85 \frac{(k_g \rho_g C_g)^{1/2} g^{1/4}}{d_b^{5/4}} \quad (18)$$

However, the particles passing through the bubbles also carry heat across the bubble-cloud boundary, and in calculations similar to Eqs. (7) to (16), we can show that the overall heat transfer coefficient is given by

$$H_{\text{total}} = \gamma_b \frac{6(Nu^*)k_g}{\phi_s d_p^2} \eta_h + H_{bc}, \quad \left[\frac{W}{m^3 \text{ bubble} \cdot K} \right] \quad (19)$$

where

$$\eta_h = \frac{1}{1 + 6(Nu^*)k_g t_p / \phi_s d_p^2 \rho_s C_s} \quad (20)$$

Finally, let us estimate the value of the adsorption efficiency for heat transfer, η_h . For mass transfer Eqs. (1) and (16), with m and with $y \cong 1$ give

$$\eta_d = \left[1 + \frac{6(Sh^*)}{Sc} \cdot \frac{\mu}{\rho_g} \cdot \frac{t_p}{\phi_s d_p^2} \right]^{-1} \quad (21)$$

while for heat transfer Eq. (20) gives

$$\eta_h = \left[1 + \frac{\rho_g C_g}{\rho_s C_s} \left(\frac{6(Nu^*)}{Pr} \cdot \frac{\mu}{\rho_g} \cdot \frac{t_p}{\phi_s d_p^2} \right) \right]^{-1} \quad (22)$$

But from the analogy between heat and mass transfer we have

$$\frac{Sh^*}{Sc} \cong \frac{Nu^*}{Pr} \quad (23)$$

Combining Eqs. (21), (22) and (23) then give

$$\eta_h \cong \left[1 + \alpha \left(\frac{\rho_g C_g}{\rho_s C_s} \right) \right]^{-1} \quad (24)$$

However, $\rho_g C_g / \rho_s C_s \cong 10^{-3}$, and for fine particles $\alpha \cong 20-100$. Thus

$$\eta_h = \frac{1}{1 + (20-100)10^{-3}} = 0.98-0.91 \quad (25)$$

This rough estimate shows that for heat transfer we can reasonably assume that $\eta_h = 1$. Numerical calculations of Eq. (19) with $\eta_h = 1$ indicates that the particles dispersed within and passing through the bubbles are the main vehicle for transferring heat from bubble gas to the dense bed. This is particularly so for fine-particle systems with intermediate to large bubble sizes. For numerical calculations see (8).

Conclusion

The theory developed in this paper matches the experimental findings of a number of workers by showing that gases which are adsorbed by the bed solids experience a larger bubble-emulsion interchange rate than do nonadsorbing gases. The particles with their adsorbed gases which rain through the bubbles are found to be the cause of this enhancement.

An extension of this theory to heat transfer

phenomena leads to the conclusion that the primary mechanism for heat interchange between bubble and emulsion is not the flow of gas across the bubble-cloud boundary, but the absorption of heat by the particles which traverse the bubble.

Nomenclature

$d' = 6/\phi_s d_p$	= specific surface area of solids	$[m^2 \cdot m^{-3}]$
a_b	= area of bubble interface per bed volume	$[m^2 \cdot m^{-3}]$
C_{Ab}, C_{Ac}, C_{Ae}	= concentration of A in bubble, cloud and emulsion phase, respectively	$[mol \cdot m^{-3}]$
C_{Ap}	= concentration of A in equilibrium at the external surface of solid	$[mol \cdot m^{-3}]$
C_{As}	= concentration of A within solid	$[mol \cdot m^{-3}]$
C_g, C_s	= specific heat of gas and solid, respectively	$[J/kg \cdot K]$
$\mathcal{D}$	= diffusivity	$[m^2 \cdot s^{-1}]$
d_b	= bubble size	$[m]$
d_t	= diameter of bed	$[m]$
$E(t)$	= residence time distribution function	$[s^{-1}]$
g	= acceleration of gravity	$[m \cdot s^{-2}]$
H_{bc}	= heat transfer coefficient per bubble volume	$[W \cdot m^{-3} \cdot K^{-1}]$
H_{total}	= total heat transfer coefficient per bubble volume, Eq. (19)	$[W \cdot m^{-3} \cdot K^{-1}]$
K_{bc}, K_{be}	= volume-based interchange coefficient between bubble and cloud, and bubble and emulsion, respectively	$[s^{-1}]$
K_d	= interchange coefficient for mass transfer defined in Eq. (3)	$[s^{-1}]$
k_{be}	= mass transfer coefficient between bubble and emulsion	$[m \cdot s^{-1}]$
k_d^*	= mass transfer coefficient on the solid surface	$[m \cdot s^{-1}]$
k_g	= thermal conductivity of gas	$[W \cdot m^{-1} \cdot K^{-1}]$
L_f	= height of fluidized bed	$[m]$
m	= adsorption equilibrium constant, Eq. (6)	$[-]$
N_A	= quantity of component A	$[mol]$
$Nu^* = h^* d_p / k_g$	= Nusselt number of a single particle	$[-]$
$Pr = C_g \mu / k_g$	= Prandtl number	$[-]$
$Re_p = d_p u \rho_g / \mu$	= Reynolds number	$[-]$
$Sc = \mu / \rho_g \mathcal{D}$	= Schmidt number	$[-]$
Sh^* , Eq. (1)	= Sherwood number at a single particle	$[-]$
t	= time	$[s]$
$\bar{t}_p$	= average residence time of a particle in a gas bubble	$[s]$
u_b	= bubble rise velocity	$[m \cdot s^{-1}]$
u_o	= superficial gas velocity	$[m \cdot s^{-1}]$
u_{mf}	= minimum fluidization velocity	$[m \cdot s^{-1}]$
V_b	= volume of a bubble	$[m^3]$
y	= logarithmic mean fraction of inert or nondiffusing component	$[-]$
z	= distance upward	$[m]$
α , Eq. (16)	= parameter representing the rate of mass transfer from single particles	$[-]$
γ_b	= volume fraction of particles dispersed in bubbles	$[-]$
δ	= volume fraction of bubble phase in the bed	$[-]$
ε_{mf}	= void fraction of the bed at minimum fluidization	$[-]$
η_d	= adsorption efficiency	$[-]$
η_h	= heat adsorption efficiency	$[-]$

μ	= viscosity of gas	$[\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}]$
ρ_g, ρ_s	= density of gas and solid, respectively	$[\text{kg} \cdot \text{m}^{-3}]$
ϕ_s	= sphericity of particles	[—]

Literature Cited

- 1) Aoyagi, M. and D. Kunii: *Chem. Eng. Comm.*, **1**, 191 (1974).
- 2) Bohle, W. and W. P. M. van Swaaij, in *Fluidization*, J. F. Davidson and D. L. Keairns eds., Cambridge University Press, p. 167, New York, 1978.
- 3) Drinkenburg, A. A. H. and K. Rietema: *Chem. Eng. Sci.*, **28**, 259 (1973); K. Rietema and J. Hoebink, in *Fluidization Technology*, vol. 1, D. L. Keairns ed., p. 279, Hemisphere, Washington, D.C., 1975.
- 4) Froessling, N.: *Gerland Beitr. Geophys.*, **52**, 170 (1938).
- 5) Hiraki, I., K. Yoshida and D. Kunii: *Kagaku Kogaku*, **29**, 846 (1965).
- 6) Kobayashi, H., F. Arai and T. Chiba: *Kagaku Kogaku*, **29**, 858 (1965).
- 7) Kunii, D. and O. Levenspiel: *I. E. C. Proc. Des. Dev.*, **7**, 481 (1968).
- 8) Kunii, D. and O. Levenspiel: *Fluidization Engineering*, 2nd Ed., Butterworth, Boston, (1991).
- 9) Kunii, D. and O. Levenspiel: *J. Chem. Eng. Japan*, **24**, 138 (1991).
- 10) Morooka, S., M. Nishinaka and Y. Kato: *Kagaku Kogaku Ronbunshu*, **2**, 71 (1976).
- 11) Szekely, J.: *Proc. Symp. on Interaction between Fluids and Particles*, Inst. Chem. Engrs., p. 197, June 1962.
- 12) Toei, R., R. Matsuno, H. Ishi and H. Kojima: *Kagaku Kogaku*, **29**, 851 (1965); R. Toei and R. Matsuno, in *Proc. Intern. Symp. on Fluidization*, A. A. H. Drinkenburg ed., p. 271, Netherlands University Press, Amsterdam, 1967.
- 13) Toei, R. Matsumo, H. Miyakawa, K. Nishiya and Y. Komagawa: *Kagaku Kogaku*, **32**, 565 (1968); *J. Chem. Eng. Japan*, **5**, 273 (1972).
- 14) Wakabayashi, T. and D. Kunii: *J. Chem. Eng. Japan*, **4**, 226 (1971).
- 15) Yamazaki, M. and T. Miyauchi: *J. Chem. Eng. Japan*, **4**, 324 (1971).