Analysis of Fluidization Quality of a Fluidized Bed with Staged Gas Feed for Reactions Involving Gas-Volume Reduction

Takami Kai, Mitsunobu Furukawa, Tsutomu Nakazato, Toshio Tsutsui, and Kei Mizuta
Dept. of Chemical Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

Mitsuyuki Nakajima
Ishikawajima Plant Engineering & Construction Co., Ltd., 3-3-3 Harumi, Chuo-ku, Tokyo 104-0053, Japan

DOI 10.1002/aic.12169

A significant defluidization occurs when carrying out reactions involving a decrease in gas volume in a fluidized catalyst bed. The cause of this phenomenon is a decrease in the gas velocity in the emulsion phase below the minimum fluidization velocity. Fluidization quality is improved by a staged gas feed when hydrogenation of CO_2 is carried out. To evaluate the experimental results, two parameters are introduced; gas-volume reduction rate and gas-volume ratio. Fluidization quality and defluidization zone are indicated as a map using these parameters. The vertical distributions of these parameters are calculated using a reactor model to obtain operating lines. The calculation shows that fluidization quality can be improved by operating the reactor by avoiding the operating lines of the defluidization zone in the map. For this purpose, it is required to control the gas-volume ratio at a level near unity and maintain the gas-volume reduction rate below 0.01/s. © 2010 American Institute of Chemical Engineers *AIChE J,* 56: 2297–2303, 2010

Keywords: fluidized bed, fluidization, chemical reactors, methanation, defluidization, volume decrease

Introduction

Many industrial gas phase reactions involve a volume change that influences their conversion and selectivity. The effects of volume change on conversion in fluidized bed reactor models have been reported by some researchers.[1–6] In addition, volume change can influence the hydrodynamic behavior of fluidized beds. Abba et al.[6] have pointed out the possibility of defluidization as a consequence of volume reduction, and in fact a large decrease in fluidization quality has been reported for hydrogenations of CO_2 in a fluidized catalyst bed.[2] The pressure fluctuation increased and large numbers of catalyst particles were occasionally entrained from the bed without being trapped by a cyclone in the freeboard. From the signal pattern of pressure fluctuations measured at the bed bottom, the presence of channeling and slugging was also inferred.

Recently, using glass reactors, phenomena occurring in the bed have been directly observed[7,8] during hydrogenation of CO_2. The emulsion phase was defluidized and a packed bed was formed and then lifted through the column like a moving piston. This part then collapsed from its bottom, causing large pressure fluctuations. Sometimes, however, it was lifted without breakup and large numbers of catalyst particles were entrained from the bed.

In the emulsion phase, the gas decreases when the gas is consumed by reactions and the gas consumed is not completely compensated for by gas flow from bubbles. In this

---

Correspondence concerning this article should be addressed to T. Kai at t.kai@cen.kagoshima-u.ac.jp.

case, the gas drag force becomes too small to balance the gravitational and buoyancy forces acting on the particles in the emulsion phase. Consequently, a part of the bed cannot be fluidized, thus causing defluidization.

This indicates that the fluidized bed is intrinsically inadequate for reactions involving a decrease in gas volume. This has not been properly recognized in the half century since the fluid bed catalytic cracker was firs constructed. Because cracking reaction is accompanied by volume increase, good fluidization is easily established. In the application of fluidized beds to other reactions, however, many engineers have depended on symptomatic treatments to deal with incomprehensible phenomena.

In addition, some process developments probably ended in failure when the reactions involved a large decrease in gas volume. Fischer-Tropsch synthesis, the production of liquid hydrocarbons from CO and H_2, is one such reaction that involves a decrease in gas volume. The mole number of this reaction reduces to half of the initial mole number when the conversion is high. The process developed using fluidized catalyst beds in Brownsville (TX, USA) in the latter 1940s and early 1950s had never been in industrial operation.[9] The engineers observed defluidization of sticky solids and made strenuous efforts to avoid this problem.

In reactions involving a decrease in gas volume, the volume decreases faster with an increasing rate. That is, defluidization is greater for higher reaction rates. However, however, the influence of the reaction rates is insignificant when the extent of the reduction is small. The extent of the reduction is affected by the stoichiometric relation of the reaction and the content of inert gas in the feed. Go et al.[10] have reported that the total flow, which was 60% inert gas, was needed to avoid defluidization and maintain the stable fluidization state in the oxidation stage of two-step oxychlorination of ethylene.

For the hydrogenation of CO_2, defluidization can be avoided with a two-staged feed of CO_2 gas.[11] This occurs because the concentration of CO_2 decreases, especially near the bottom inlet, and the gas-volume reduction rate remains below the critical value throughout the bed. In addition, the gas-volume ratio is controlled at a level near unity, lessening the influence of a gas-volume decrease. Fluidization quality is further improved by increasing the height of the secondary gas inlet. The relationship between the gas-volume reduction rate and gas-volume ratio is given as a map, which shows that good fluidization can be maintained by avoiding the operating lines of the defluidization zone in the map.

To design the reactor that provides good fluidization, it is essential to understand the mechanism of poor fluidization and predict the necessary condition for good fluidization. Thus, it is important to quantitatively analyze the tendency described above. In this study, we analyze the experimental data published elsewhere[11] based on the vertical distribution of the parameters. In the previous study,[8] the gas-volume reduction rate and ratio were obtained at the reactor inlet. We calculate the vertical distribution of these parameters by simulation using experimental conversions, compare these results with the observed fluidization quality, and then discuss the criteria needed to maintain good fluidization conditions.

Index for Evaluation

A previous study[8,12] proposed two important parameters for reactions involving a decrease in the gas volume: the gas-volume reduction rate and gas-volume ratio. When a large amount of inert gas is added to the reactant, the gas-volume reduction is small even if the reaction proceeds to completion. The same effect is obtained using an excess of one of the reactants. In these cases, fluidization quality is only marginally affected by the gas-volume reduction rate; therefore, the gas-volume ratio is the more important parameter.

When the reaction,

$$aA + bB \rightarrow cC + dD, \tag{1}$$

is carried out at constant pressure and temperature, the relative gas volume changes with the conversion x_A:

$$\eta_x = 1 + \varepsilon_A x_A, \tag{2}$$

where ε_A is the expansion factor and δ_A is the expansion per mole of the reference component A. They are defined as

$$\varepsilon_A = y_{A0}\delta_A, \tag{3}$$

$$\delta_A = (-a - b + c + d)/a. \tag{4}$$

The parameter η_x is the relative gas volume based on the gas volume at the reactor inlet. When conversion is 100%, η_x is minimized and the following equation is obtained:

$$\eta = 1 + \varepsilon_A. \tag{5}$$

The minimum volume ratio based on the gas volume at x_A becomes

$$\eta^* = \frac{1 + \varepsilon_A}{1 + \varepsilon_A x_A}. \tag{6}$$

We call this parameter the gas-volume ratio.

Figure 1 shows the relationship between conversion and the gas-volume ratio for the methanation of CO_2:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{7}$$

When this reaction is carried out from a feed of stoichiometric composition and CO_2 is the key component (A component in Eq. 1), y_{A0} is 0.2 and δ_A is –2; consequently, ε_A is –0.4. Therefore, from Eq. 5, η^* at x_A=0 is 0.6. Thus, when inert gases are not present, after all reactants convert to products at constant pressure and temperature, the gas volume decreases to 60% of the initial reactant volume. As conversion increases, η^* also increases, reaching unity when the conversion reaches 100%.

Differentiating Eq. 2 with respect to time, we obtain the gas-volume reduction rate $-r_v$ based on the initial gas volume:

$$-r_V = -\varepsilon_A \frac{dx_A}{dt} \tag{8}$$

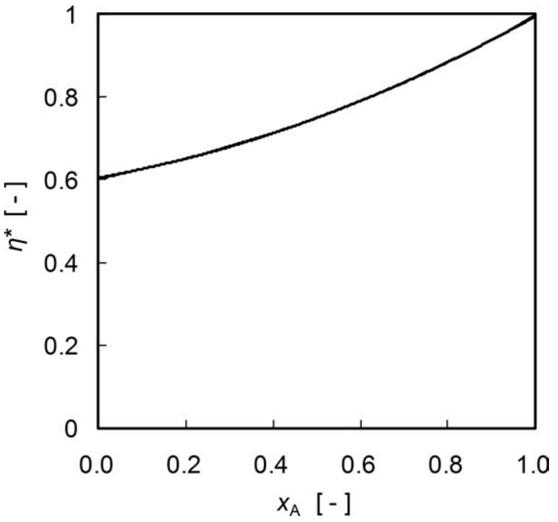

Figure 1. Relationship between CO_2 conversion and gas-volume ratio.

This parameter, used in a previous study,[8] is proportional to the reaction rate; therefore, the gas-volume reduction rate based on the volume at conversion x_A becomes

$$-r_V^* = \frac{-\varepsilon_A}{1+\varepsilon_A x_A}\frac{dx_A}{dt}. \tag{9}$$

This parameter is based on a bed volume composed of bubble and emulsion phases. Considering the bubble gas holdup ε_b and the voidage in the emulsion phase ε_{fe}, we obtain the gas-volume ratio based on the gas volume in the emulsion phase as

$$-r_{Ve}^* = \frac{-r_V^*}{(1-\varepsilon_b)\varepsilon_{fe}}. \tag{10}$$

This equation is based on the assumption that there is no radial distribution of reactant concentration in the emulsion phase. In the present study, we use the value obtained from Eq. 9, although the value based on the emulsion-phase volume is two to three times larger. As the vertical distribution of ε_b and ε_{fe} are difficult to measure in the present study, Eq. 10 is used for the analysis. In addition, the reaction mainly proceeds around bubbles in the emulsion phase when the reaction rate is high. Therefore, even Eq. 10 cannot correctly evaluate the gas-volume reduction rate, and Eq. 9 is sufficient to describe the phenomena.

Experimental

The experimental setup employed a glass column as a reactor to allow observation of the internal walls of the reactor. The inner diameter and length of the column were 50 mm and 1.5 m, respectively. A transparent electrical resistance material was coated on the outer surface of the column to serve an electrical heater. The average diameter of catalyst particles was 56 μm and the bed density was 600 kg m^{-3}. The catalyst support material was porous γ-alumina. The metal loading was 20 wt % for Ni and 10 wt % for La_2O_3.

The initial settled bed height was 0.4 m. The feed gas consisted of H_2 and CO_2 and did not contain any inert components. The superficial gas velocity at the reactor inlet was 0.05 m s^{-1} with all gases supplied from the bottom. CO_2 was fed from both the bottom and a secondary gas nozzle, while H_2 was fed only from the bottom. Glass beads 700 μm in diameter were packed in the bottom of the column and the fluidizing gas was distributed by this glass bead bed. The secondary inlet was made of stainless steel with 3-mm outer diameter—its height was varied. The ratio of H_2 to total CO_2 in the feed to the reactor was stoichiometric. The experiments details are described elsewhere.[8,11]

The reaction rate was measured in a fixed bed microreactor, 6.0 mm diameter. The expression for the reaction rate was based on the previously proposed equation:[13]

$$r = \frac{kP_{H_2}^{1/2}P_{CO_2}^{1/3}}{(1+K_{H_2}P_{H_2}^{1/2}+K_{CO_2}P_{CO_2}^{1/2}+K_{H_2O}P_{H_2O})^2}. \tag{11}$$

The temperature dependence of the rate constant and equilibrium constants in Eq. 11 are described by Arrhenius equations:

$$k = k_a \exp(-E/RT), \tag{12}$$

$$K = K_a \exp(-\Delta H/RT). \tag{13}$$

The effective activation energy, E, and the effective enthalpy of adsorption, ΔH, were obtained from the experimental results, as shown in Table 1. The constants in Eq. 11 were determined using these values for each temperature. Only the value of k_a was determined from the analysis of the results in fluidized beds. Figure 2 shows the relationship between conversion and the gas-volume reduction rate at 473 K. The gas-volume reduction rate was normalized by the rate at the reactor inlet. As shown in the figure, the gas-volume reduction rate decreased sharply with increasing conversion. When the conversion was 0.5, the gas-volume reduction rate was 35% of that at the reactor inlet.

Results and Discussion

Evaluation of the fluidization quality

Time series schematic pictures of defluidization have been presented in previous papers.[8,12] When carrying out the

Table 1. Apparent Energy of Activation and Enthalpy of Adsorption

k_a (mol kg $Pa^{-5/6}$ s^{-1})	K_{H_2} ($Pa^{-1/2}$)	K_{CO_2} ($Pa^{-1/2}$)	K_{H_2O} (Pa^{-1})
3.98×10^{-1}	3.08×10^{-8}	8.41×10^{-7}	2.14×10^{-7}
E (J mol^{-1})	ΔH_{H_2} (J mol^{-1})	ΔH_{CO_2} (J mol^{-1})	ΔH_{H_2O} (J mol^{-1})
5.45×10^4	-4.61×10^4	-3.67×10^4	-2.39×10^4

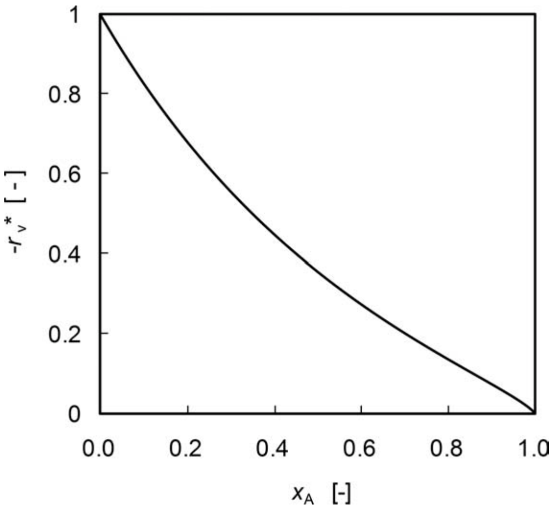

Figure 2. Relationship between CO_2 conversion and gas-volume reduction rate at 473 K.

reaction in a fluidized bed, the bed divided into two sections at a height of around 200 mm. The length of the upper defluidized section was about 150 mm. Its voidage was smaller than that of the settled bed and it was lifted through the column by the gas flow. The lower part was fluidized after the separation. Under these conditions, the gas supply from the bubble phase could not compensate for the gas consumption in the emulsion phase.

If the force balance on particles is lost due to a decrease in gas velocity in the emulsion phase, the voidage in the emulsion phase reduces and the apparent viscosity of the phase increases. As a result, gases cannot rise as bubbles and form channels. When the gas-volume reduction rate increases further, the emulsion phase contracts and even channels cannot be formed. Consequently, the defluidized part formed a fixed bed and was lifted through the column like a moving piston.

On the basis of direct observation, we classified the fluidization quality into three regions: A (good fluidization), B (poor fluidization), and C (defluidization). Channeling was observed in region B and defluidization in region C.

Map of the fluidization quality

Figure 3 shows a plot of the relationship between the gas-volume reduction rate and gas-volume ratio for all experimental runs, along with the fluidization quality. A similar map was shown using values at the reactor inlet in a previous paper.[8] In the present study, however, the averaged values through the bed were plotted. Defluidization was observed in the runs shown by closed circles. It was easy to generate defluidization with a high gas-volume reduction rate; when the gas-volume reduction ratio was above 0.9, however, defluidization could be avoided even if the gas-volume reduction rate was high. The figure shows that defluidization occurred when the gas-volume reduction rate exceeded 0.01/s and the gas-volume ratio was below 0.9.

Good fluidization was observed in the runs indicated by the open circles. Good fluidization quality could be achieved by maintaining the gas-volume reduction rate below 0.01/s throughout the bed. The gas-volume reduction rate can be decreased by decreasing the reaction rate; however, is not desirable for industrial reactors because it produces low conversion.

Effect of temperature

The reaction rate and gas-volume reduction rate increase with temperature. When the reactant gases were fed only from the bottom, and the temperature was raised to 483 K, channeling was observed. In addition, the defluidized part of the bed sometimes formed a packed bed that was lifted through the column. This moving part gradually collapsed from the bottom at this temperature. Although the fluidization quality was basically poor under these conditions, the phenomenon occurred only intermittently once or twice during a period of 100 s. When the temperature was raised to 493 K, defluidization occurred frequently but the moving part did not collapse. In this case, the gas supply was stopped to prevent particle entrainment from the reactor.

Figure 4 shows the vertical change in the gas-volume reduction rate, $-r_v^*$, when all reactants were fed from the bottom. The overall reaction rate was calculated using a simple piston-flow reactor model. The vertical change was determined from the experimental conversion value. Therefore, the values at $z/L_f = 0$ and $z/L_f = 1$ were directly obtained. Because no fluidized bed model can estimate the vertical concentrations correctly, we used a piston-flow reactor model. Thus, the lines in this figure might not exactly correspond to the vertical profile of concentrations in the emulsion and bubble phases. However, the concentrations at both the inlet and outlet of the reactor were measured values, and the actual distribution curve for the concentration will be concave. Therefore, the calculated line connecting the two end points is a sufficient approximation.

Good fluidization was observed at 463 K. In this case, the gas-volume reduction rate was below 0.01/s throughout the bed. In contrast, defluidization was sometimes observed at

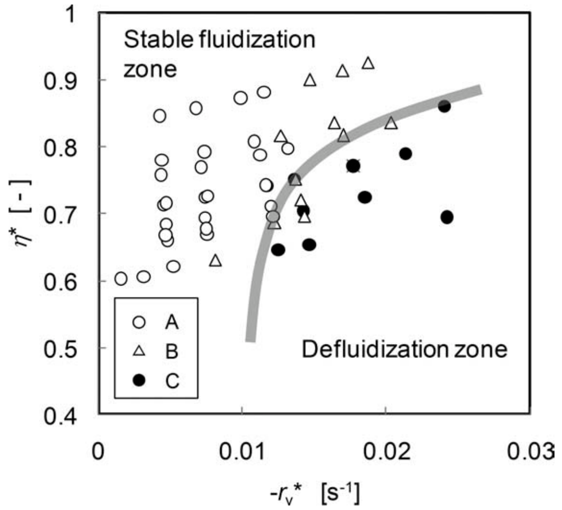

Figure 3. Effect of gas-volume reduction rate and gas-volume ratio on fluidization quality when reaction gases were supplied from only the bottom.

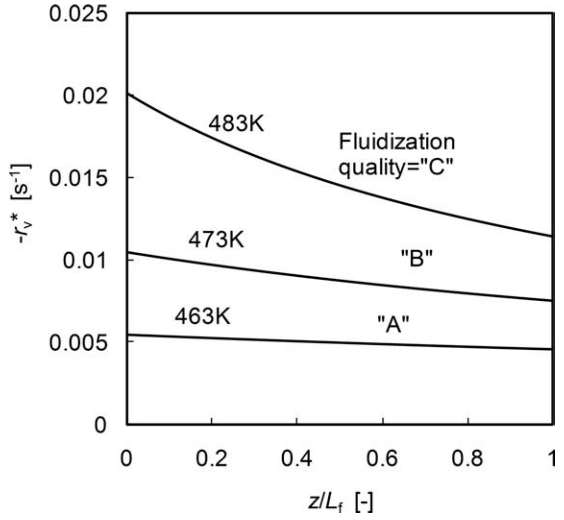

Figure 4. Axial distribution of gas-volume reduction rate when reaction gases were supplied from only the bottom.

483 K. At this temperature, the reduction rate exceeded 0.01/s throughout the bed, suggesting that the possibility of formation of defluidization increases with an increase in the length of the region having a gas-volume reduction rate in excess of 0.01/s.

Figure 5 shows operating lines constructed according to the relationship between the gas-volume reduction rate and gas-volume ratio. The gas-volume reduction rate decreases with increasing bed height, while the gas-volume ratio increases with bed height. Because the gas-volume reduction rate is 0/s and gas-volume ratio is unity when the conversion is 100%, the curve postpones toward this point. The right and left ends of each operating line indicates the experimental values at the reactor inlet and outlet, respectively. This line is independent of the axial distribution of concentration, and depends on the end values. The lines in Figure 5 are outside of the defluidization zone and show that defluidization can be avoided by decreasing the temperature. However, at low temperature, conversion is low at this bed height and gas velocity.

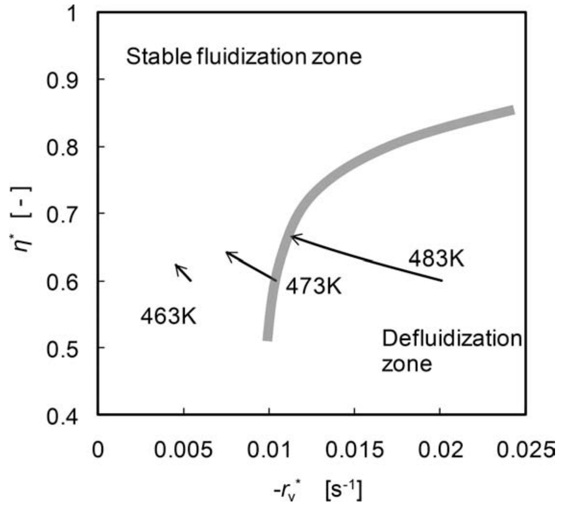

Figure 5. Effect of temperature on the operating lines when reaction gases were supplied from only the bottom.

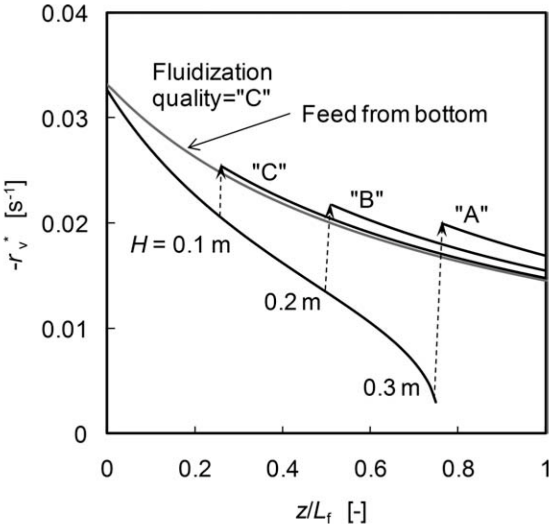

Figure 6. Effect of the height of the secondary inlet on the vertical distribution of gas-volume reduction rate at 493 K when R_D=0.75.

Effect of the secondary-inlet height

One of the reactants, CO_2, was fed from both the bottom and a secondary gas nozzle. Fluidization quality increased when the height of the secondary inlet, H, was raised.[11] Figure 6 shows the vertical change of the gas-volume reduction rate when H was changed at 493 K and 25% of the total CO_2 was fed from the bottom. The rest of CO_2 was fed from the secondary inlet, making the ratio of the feed from the secondary gas inlet, R_D, 0.75. The line for $H = 0$ was the calculation when the reactant mixture was fed only from the bottom.

The gas-volume reduction rate at the inlet was 0.032/s, and independent of H. The conversion calculated using the parameters given in Table 1 is given in Table 2. As the conversion decreased with increasing H, the gas-volume reduction rate at the reactor outlet increased slightly with increasing H. Because the CO_2 concentration of the reactant gas fed from the bottom was low for the two-staged feed, most CO_2 reacted and the gas-volume reduction rate sharply decreased just below the secondary gas inlet when $H = 0.3$ m.

Good fluidization was observed when H was 0.3 m, whereas defluidization was observed when H was 0.1 m. As the reaction rate was not influenced by gas composition, the gas-volume reduction rates at the inlet were almost the same for single and stage feeds. The gas-volume reduction rate

Table 2. Effect of H on Conversion when T = 493 K and R_D = 0.75

H (m)	0	0.1	0.2	0.3
x_A (%)	39.6	38.9	37.0	33.1

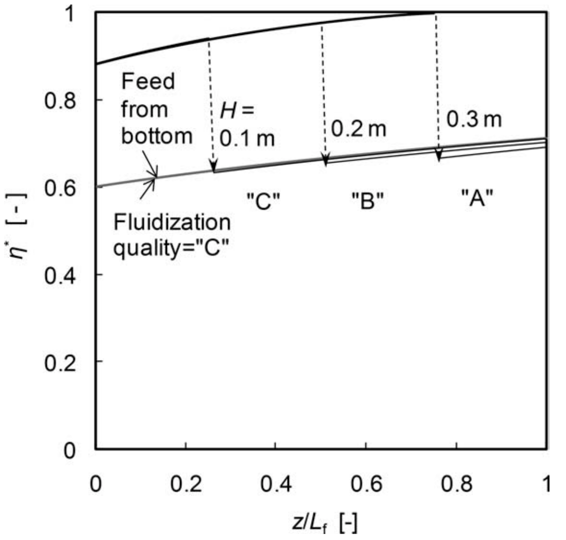

Figure 7. Effect of the height of the secondary inlet on the vertical distribution of gas-volume ratio at 493 K when R_D=0.75.

was high and above 0.01/s in the lower part of the bed. Figure 7 shows that the gas-volume ratio in this region was large (about 0.88), and therefore, the fluidization quality in this region was good. When *H* was 0.1 m, the gas-volume reduction rate increased and the gas-volume ratio decreased to about 0.6 when CO_2 was introduced from the secondary inlet, indicating that defluidization was easily induced. In contrast, when *H* was 0.3 m, the gas-volume ratio was held high in the greater part of the bed as shown in Figure 7, and defluidization did not occur. The region where the gas-volume ratio was about 0.65 and the gas-volume reduction rate was >0.01/s was short. In addition, since the movement of particles and bubbles is vigorous near the bed surface, defluidization was not induced. Miyauchi et al.[14] showed that the contact efficiency between the gas in bubbles and catalyst particles was high in this region.

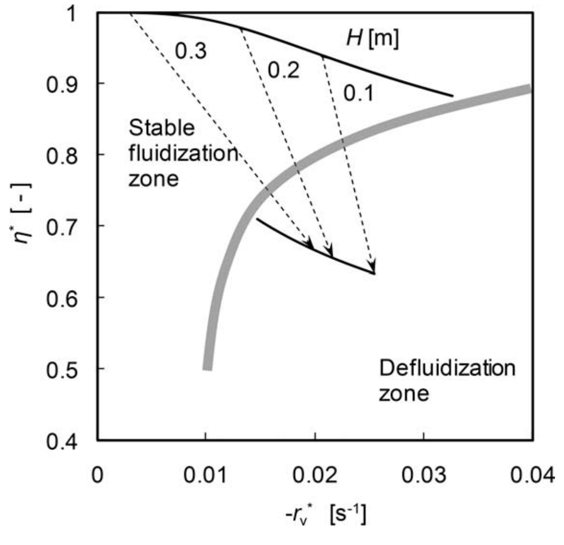

Figure 8. Effect of the height of the secondary inlet on the operating lines at 493 K when R_D=0.75.

Figure 8 shows the operating lines for the two-staged feed. The operating lines below and above the secondary inlet differed. Although the initial point was the same for all conditions, the endpoints corresponding to the reactor outlet, were slightly different. Because hydrogen was stoichiometrically excessive below the secondary inlet, the gas-volume ratio almost reached unity. Increasing the level of the secondary inlet decreased the gas-volume reduction rate after the second feed. Although the operating line was involved in the defluidization zone, it was short, as described above, and this prevented defluidization when *H* was 0.3 m.

Effect of the carbon dioxide distribution ratio

The effect of the CO_2 distribution ratio between the bottom and the secondary inlet on fluidization quality was investigated. According to a previous study,[11] the fluidization quality increased with increasing R_D. However, the effect of the distribution ratio on the fluidization was not large. Figure 9 shows the relationship between the gas-volume reduction rate and gas-volume ratio. The level of the secondary inlet was 0.2 m and the temperature was 493 K. As the composition of the feed gas supplied from the bottom was different between the two cases, the parameters drew different lines below the secondary inlet.

When R_D was 0.25, the lower part of the bed was involved in the defluidization zone. As the gas-volume reduction rate decreased and the gas-volume ratio increased when R_D was increased, fluidization quality improved in the lower part of the bed for higher R_D. In this case, however, the ratio of the CO_2 supplied from the secondary inlet was high, hence the gas-volume reduction rate increased and the gas-volume ratio decreased above the secondary inlet. Figure 9 shows that the region below the secondary inlet was not involved in the defluidization zone when R_D was 0.75, but a wider region was involved in the defluidization zone above the secondary inlet. When R_D was changed, the operating line of either the lower or upper part of the bed was involved in the defluidization zone. Therefore, the effect of the distribution ratio on the fluidization quality was small.

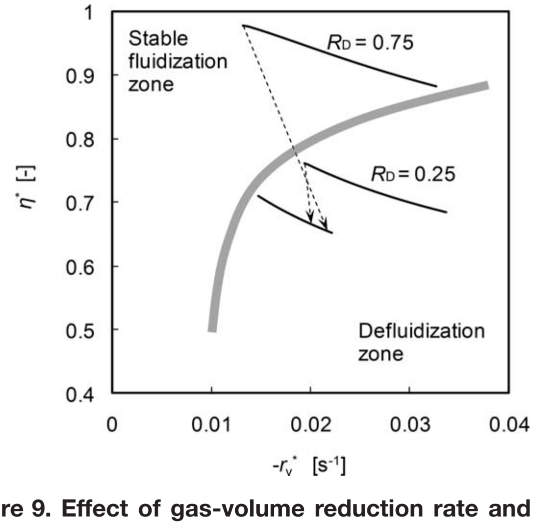

Figure 9. Effect of gas-volume reduction rate and gas-volume ratio on fluidization quality at 493 K when H = 0.2 m.

Conclusions

Significant defluidization occurred when carrying out the hydrogenation of CO_2 in a fluidized catalyst bed. The cause of this phenomenon is a decrease in the gas velocity in the emulsion phase. The defluidization zone is indicated as a map using two parameters: the gas-volume reduction rate and the gas-volume ratio. Defluidization can be avoided by feeding CO_2 into the bed from both the bottom and a secondary inlet. The improvements from staged feeding were analyzed using the vertical distribution of the values of parameters based on experimental results. Good fluidization could be maintained by controlling the operating line drawn by the parameters not involved in the defluidization zone. When the CO_2 feed is staged, the fluidization quality can be improved by decreasing the gas-volume reduction rate and controlling the gas-volume ratio at a level near unity. Good fluidization quality can be maintained by keeping the gas-volume reduction rate below 0.01/s. There are some approaches besides staged feeding method for improving the fluidization quality for this kind of reaction. For this purpose, the map and operating lines proposed in the present study are useful in studying the operating conditions.

Acknowledgments

This work is supported in part by the Iwatani Naoji Foundation's Research. We also acknowledge financial support from a Grant-in-Aid for Scientific Research (B) (No. 21360389), Ministry of Education, Culture, Sports, Science and Technology, Japan.

Notation

a, b, c, d = stoichiometric coefficients in Eq. 1
E = effective Arrhenius activation energy, kJ mol^{-1}
H = height of secondary gas-inlet, m
ΔH = effective enthalpy of adsorption, kJ mol^{-1}
k = reaction rate constant in Eq. 2, mol m^{-3} s^{-1} $Pa^{-5/6}$
KH_2 = equilibrium constant in Eq. 2, $Pa^{-1/2}$
KCO_2 = equilibrium constant in Eq. 2, $Pa^{-1/2}$
KH_2O = equilibrium constant in Eq. 2, Pa^{-1}
L_f = bed height of fluidized bed, m
PH_2 = partial pressure of H_2, Pa
r = reaction rate, mol m^{-3} s^{-1}
r_0 = reaction rate at reactor inlet, mol m^{-3} s^{-1}
$-r_v$ = relative gas-volume reduction rate at inlet, s^{-1}
$-r^*_v$ = relative gas-volume reduction rate, s^{-1}
$-r^*_{ve}$ = relative gas-volume reduction rate based on gas volume in emulsion phase, s^{-1}
R = gas constant, J K^{-1} mol^{-1}
R_D = ratio of CO_2 supplied from secondary gas-inlet
t = time, s
T = temperature, K
x_A = CO_2 conversion
y_{A0} = initial molar ratio of CO_2
z = coordinate of bed height, m

Greek letters

ε_A = expansion factor ($=\delta_A\ y_{A0}$)
ε_b = averaged gas-bubble holdup
ε_{fe} = volume fraction of gas in emulsion
δ_A = expansion per mole of reference component A [$=(-a - b + c + d)/a$]
η = ratio of gas volume at $x_A = 1$ to that at $x_A = 0$
η^* = ratio of gas volume at $x_A = 1$ to that at $x_A = x_A$
η_x = ratio of gas volume at $x_A = x_A$ to that at $x_A = 0$

Subscripts

a = Arrhenius pre-exponential factor
CO_2 = carbon dioxide
H_2 = hydrogen
H_2O = water

Literature Cited

1. Irani RK, Kulkarni BD, Doraiswamy LK. Analysis of fluid bed reactors for reactions involving a change in volume. *Ind Eng Chem Fundam.* 1980;19:424–428.
2. Kai T, Furusaki S. Methanation of carbon dioxide and fluidization quality in a fluid bed reactor—the influence of a decrease in gas volume. *Chem Eng Sci.* 1987;42:335–339.
3. Shiau CY, Lin CJ. Analysis of volume change effects in a fluidized bed catalytic reactor. *J Chem Technol Biotechnol.* 1993;56:295–303.
4. Tafreshi ZM, Opoku-Gyamfi K, Adesina AA. A two-phase model for variable-density fluidized bed reactors with generalized nonlinear kinetics. *Can J Chem Eng.* 2000;78:815–826.
5. Adris AM, Lim CJ, Grace JR. The fluidized-bed membrane reactor for steam methane reforming: model verification and parametric study. *Chem Eng Sci.* 1997;52:1609–1622.
6. Abba LA, Grace JR, Bi HT. Variable-gas-density fluidized bed reactor model for catalytic processes. *Chem Eng Sci.* 2002;57:4797–4807.
7. Kai T, Nishie K. Takahashi T, Nakajima M. Effect of decrease in gas volume due to reactions on the fluidization quality in a fluidized catalyst bed. *Kagaku Kogaku Ronbunshu (in Japanese).* 2004;30:256–261.
8. Kai T, Toriyama K, Nishie K, Takahashi T, Nakajima M. Effect of volume decrease on fluidization quality of fluidized catalyst beds. *AIChE J.* 2006;52:3210–3215.
9. Squires AM. Contributions toward a history of fluidization. Proceedings of joint meeting of Chemical Industry and Engineering Society of China and American Institute of Chemical Engineers. Beijing, China, September 20–22, 1982:322–353.
10. Go KS, Kim Y, Son SR, Kim SD. 1,2-dichloroethane production by two-step oxychlorination reactions in a fluidized bed reactor. *Chem Eng Sci.* 2009;65:499–503.
11. Kai T, Furukawa M, Toriyama K, Takahashi T, Nakajima M. Elimination of defluidization caused by reactions involving a volume reduction in a fluidized catalyst bed and improvement of fluidization by two-stage feeding. *J Chem Eng Jpn.* 2009;42:733–738.
12. Kai T, Toriyama K, Takahashi T, Nakajima M. Defluidization caused by the reaction involving a volume reduction in a fluidized catalyst bed and improvement of the fluidity by internals. *Kagaku Kogaku Ronbunshu (in Japanese).* 2008;34:351–357.
13. Kai T, Takahashi T, Furusaki S. Kinetics of the methanation of carbon dioxide over a supported Ni-La_2O_3 catalyst. *Can J Chem Eng.* 1988;66:343–347.
14. Miyauchi T, Furusaki S, Morooka S, Ikeda Y. Transport phenomena and reaction in fluidized catalyst beds. *Adv Chem Eng.* 1981;11:276–448.

Manuscript received July 21, 2009, and revision received Nov. 2, 2009.