Nomenclature

a	= specific surface area of particles	[1/cm]
a_{mf}	= specific surface area of naphthalene particles	[1/cm]
B	= coefficient of Eq. (4)	[cm ^{1/2}]
C_b	= concentration of naphthalene gas in bubble phase	[g-mole/cc]
C_{cal}	= calculated concentration of naphthalene gas at the outlet gas	[g-mole/cc]
C_{ob}	= measured concentration of naphthalene gas at the outlet gas	[g-mole/cc]
C_s	= saturated concentration of naphthalene gas	[g-mole/cc]
D	= diffusion coefficient	[cm ² /sec]
D_B	= bubble size in the bed	[cm]
D_p	= average particle size	[cm]
F_o	= gas interchange coefficient	[1/sec]
f	= the volume ratio of naphthalene particle to glass beads	[—]
g	= gravitational acceleration	[cm/sec ²]
k_f	= gas-particle mass transfer coefficient in bubble phase	[cm/sec]
L	= expanded bed height	[cm]
L_{mf}	= bed height at the minimum fluidization gas velocity	[cm]
Q	= volume flow rate of the secondary air	[cc/sec]
Q_{mf}	= volume flow rate of the primary air	[cc/sec]
S	= cross sectional area	[cc/sec]
r_B	= bubble radius	[cm]
$r_{c,eff}$	= effective cloud radius	[cm]
$r_{c,max}$	= maximum cloud radius	[cm]
U	= superficial gas velocity	[cm/sec]
U_b	= bubble rising velocity	[cm/sec]

U_{bb}	= bubble rising velocity based on fixed axis	[cm/sec]
$\bar{U}_{bb}$	= average bubble rising velocity based on fixed axis	[cm/sec]
U_{mf}	= the minimum fluidization gas velocity	[cm/sec]
V_b	= volume of single gas bubble in the bed	[cc]
V	= volume flow rate of gas per unit nozzle	[cc/sec]
Z	= distance from the gas inlet nozzles	[cm]
α	= the ratio of cloud volume to bubble volume	[—]
ε_{mf}	= void fraction of fluidized bed at U_{mf}	[—]
θ	= angle measured round bubble	[—]
ρ	= density of gas	[g/cc]
μ	= viscosity of gas	[g/cm-sec]

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CATALYTIC CRACKING OF METHYLCYCLOHEXANE OVER SILICA ALUMINA CATALYST IN GAS FLUIDIZED BED*

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This paper presents a simulation model to predict the reaction performance of a fluidized bed from the operating conditions. The simulation model was derived from the observation of bubble behavior, and was developed in a form which can elucidate the conversion and selectivity with catalyst fouling. The model was applied to methylcyclohexane cracking data, and unknown parameters in the model were estimated by a non-linear regression technique. It was confirmed that the model is applicable to the performance of a fluidized bed reactor.

Introduction

The fluidized bed reactor is widely applied to catalytic reactions because of the advantages of uniform temperature, but there is low conversion of chemical

reaction, mainly caused by the gas by-passing through the bed. Considerable evidence for the two-phase model has appeared in the literature^{1,7,10,13}, and it is known that gas interchange between the two phases influences conversion and selectivity. Rowe *et al.*¹⁶ proposed a model in which a rising bubble is surrounded by a cloud of circulating gas, and some interchange occurs between the cloud and dense phases. Kobayashi *et al.*⁹ reported a two-phase model describing the gas interchange between the cloud phase involving a cloud-wake overlap and dense phase. Fryer and Potter², and Kunii and Levenspiel¹⁰ ad-

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vanced a model involving an upward flow of solids with the bubbles. Furthermore, Kunii *et al.*¹⁰ advanced a correlation of successive gas interchange among bubbles cloud-wake and dense phase according to the Davidson and Harrison theory¹¹ and the Higbie-type penetration model¹⁵. Despite numerous studies, there has been no unequivocal model to predict the performance of chemical reaction in the fluidized bed.

The purpose of this study is to give the formulation of an adequate model to elucidate the conversion and selectivity of catalytic cracking with catalyst fouling in the fluidized bed reactor. In a recent paper²³, the authors proposed a model for the kinetics of methylcyclohexane (MCH) cracking in a fixed bed reactor. In the present study, MCH cracking in the fluidized bed was investigated and bubble behavior was observed. On the basis of the kinetics of MCH cracking in the fixed-bed reactor, a simulation model based on the bubble behavior was advanced. From this model, unknown parameters such as gas interchange coefficient and cloud-wake volume fraction to bubble volume were evaluated by a nonlinear regression technique, and were studied for the operating conditions.

1. Experimental

1.1 Reagent, experimental apparatus and catalyst

MCH employed as the sample of cracking reaction was obtained from a commercial source and purified by distillation.

A flow sheet of the experimental apparatus is shown in Fig. 1. Two different sizes of reactors made of quartz tube were used, one of them being 4.51 cm ϕ $\times$ 40 cm and the other 5.21 cm ϕ $\times$ 50 cm. The gas distributor was a sintered porous plate of -60+80 mesh fraction of quartz particles.

The cracking catalyst (Shokubai Kasei Co.) used consisted of 75 wt% silica and 25 wt% alumina, and was sifted out in the range of -150+170 mesh fractions and then calcined in an air stream for 3 hours at 600°C. The particle density (ρ_p) was 0.836 g/cc and bulk density (ρ_B) was 0.475 g/cc.

For the measurement of temperature of the catalyst bed and the bath of fluidized alumina particles, an alumel-chromel thermocouple was used, as shown in Fig. 1.

1.2 Measurement of bed expansion and rising bubble size

The incipient fluidization velocity (u_{mf}) was observed by measuring pressure drop in the stream of N₂-MCH mixture at 470°C, 500°C and 530°C.

The bed expansion during fluidization was measured by visual observation through the transparent quartz wall at the same temperature conditions, and the bed height at the incipient fluidizing conditions (L_{mf}) was also measured.

To study the bubble behavior in the fluidized bed, the bubble frequency was measured by means of a capacitance probe, as illustrated in detail in Fig. 2, at

Fig. 1 Flow sheet of experimental apparatus

Fig. 2 Electric capacitance probe to measure bubble size

various bed heights and flow rates in the temperature range of 30–650°C in both N₂ and N₂-MCH streams. On the other hand, the shape and size of rising bubbles were photographed through the quartz tube wall.

The rate of solid mixing was measured according to Talmor and Benenati²¹. The bed was prepared in two layers—a layer of coked catalyst (black) above a layer of fresh catalyst (white), and was fluidized with N₂ stream at 500°C. The bed was uniformly mixed after 15 seconds at $3.5u_{mf}$. It was ascertained that the fluidized bed behaved as completely mixed state.

1.3 Measurement of MCH conversion and product yield in fluidized bed cracking

The reactor with passage of nitrogen gas was placed in the bath of fluidized alumina particles used as thermomedium. After the temperature of catalyst bed reached equilibrium, the stream of N₂-MCH mixture

Fig. 3 Bubble volume fraction vs. $(u_o - u_{mf})/u_{mf}$

Fig. 4 Bubble size vs. u_o/u_{mf} with parameter of temperature

(50 mol% MCH) was passed through the reactor to start the cracking reaction. The feed MCH flow rate was controlled by microfeeder. The exit products were condensed through a cooler condenser, and the condensed mixture was subjected to gas chromatographic analysis using a DC-550 column. Uncondensed gaseous products were led to the gas chromatograph directly and analyzed using an alumina+squalane column. The difference of gas density between inlet and outlet was found to be negligible.

The coked catalyst was withdrawn by sucking, and the weight of coke formed on the catalyst was measured by means of a thermogravimetric balance. The experimental conditions are summarized in Table 3.

2. Experimental Results

2.1 Incipient fluidization velocity and bed expansion

The value of u_{mf} gradually decreased with increasing temperature, as shown in Table 3, but a bed voidage at the incipient fluidization (ϵ_{mf}) kept a uniform value at various bed heights and temperatures. The bubble volume fraction (ϵ_b) was calculated based on the measurement of L_{mf} and L_f in the N_2 -MCH stream, and is represented by Eq.(1) as a result of the slope of these linear plots as shown in Fig. 3.

$$\epsilon_b = \frac{L_f - L_{mf}}{L_f} = 0.115 \left(\frac{u_o - u_{mf}}{u_{mf}} \right)^{0.5} L_c^{-0.5} \quad (\text{unit: CGS}) \quad (1)$$

The results were compared with the value of ϵ_b for an

Fig. 5 An example of plots of conversion and yield vs. process time

ozone decomposition in a fluidized bed according to Orcutt *et al.*¹³⁾

2.2 Determination of bubble size

Assuming that the bubble frequency (n) has a uniform value across any horizontal plane, the bubble size (d_b) would be evaluated according to the Kunii and Levenspiel formula¹⁰⁾, i.e.,

$$d_b = \frac{1.5u_b}{n} \cdot \frac{u_o - u_{mf}}{u_b - u_{mf}} \approx \frac{1.5}{n} (u_o - u_{mf}) \quad (2)$$

Bubble frequency measured with N_2 -MCH stream closed to that of N_2 stream only, and the d_b calculated from bubble frequency agreed reasonably well with that of the photograph. The values of d_b decrease with increasing temperature, as shown in Fig. 4, and were found about one half the value of the empirical formula of Kobayashi *et al.*⁸⁾ at room temperature, where the ratio of wake volume to bubble volume was taken to be 0.47 according to the data (glass sphere) of Rowe and Partridge¹⁷⁾. These facts may be illustrated with the drop in viscosity of the fluidized bed according to Mii *et al.*¹²⁾. The d_b was also found to vary linearly with the axial distance (Z) from a gas distributor. As a result, the empirical formula of d_b is approximately expressed by Eq.(3), obtained from Fig. 4.

$$d_b = \frac{0.00142Z + 0.0233}{(T \times 10^{-3})^{1.21}} \cdot \left(\frac{u_o}{u_{mf}} \right) + 0.08 \quad (\text{unit: CGS}) \quad (3)$$

The difference in respective ϵ_b and d_b for each different size of reactor was found to be negligible.

2.3 MCH conversion and product yield in fluidized bed

The products of MCH cracking in the fluidized bed were hydrogen, C_1 - C_6 hydrocarbons, aromatic compounds, etc. The main products were propane, propylene, butanes and butenes, and were similar to those in a fixed-bed reactor²³⁾.

Fig. 6 An example of plots of olefins and paraffins vs. MCH conversion with parameter of static bed height

Fig. 7 An example of plots of olefins and paraffins vs. MCH conversion with parameter of gas flow rate

In **Fig. 5**, MCH conversion, olefins ($C_3 + C_4$) and paraffins ($C_3 + C_4$) yields decrease with increasing coke deposit and decreasing temperature, and these results are rather lower than expected, based on the fixed bed. **Figures 6 and 7** show the yield of olefins and paraffins based on the MCH conversion at various values of L_c and u_o , respectively. As shown in these figures, it can be seen that the selectivity for olefins production (olefins yield/ MCH conversion) increased with lower bed height and with higher flow rate, and that the decay of catalyst activity resulted in the lowering of olefins yield. On the other hand, the selectivity of paraffins showed an approximately uniform value. It will be suggested that the maximum yield of olefins may be attained by adjusting the operating conditions.

3. Mathematical Formulation of Model

3.1 Kinetic model and two-phase model

In the previous work²³⁾, the reaction mechanism of MCH cracking was investigated in a small-scale fixed-bed reactor. The kinetics was reported by the reaction model shown in **Fig. 8**. The rate constant of each step and an activity factor indicating catalyst fouling are given in **Table 1**.

In recent research, bubble behavior in the fluidized bed was made clear theoretically and experimentally by Davidson and Harrison¹⁾, Rowe *et al.*¹⁶⁾ and Kunii and Levenspiel¹⁰⁾. However, these rigorous mathematical models may be impracticable for the simulation of such a complicated reaction system as MCH cracking with catalyst fouling as shown in **Fig. 8**²³⁾.

For the development of the simulation model for the fluidized bed based on bubble behavior, the following simplifying assumptions are made:

1) The fluidized bed consists of the bubble phase with wake solids and the dense phase, in which interstitial gas flows at incipient state.

where $k_M = k_1 + k_2 + k_3$

Olefins : Propylene + Butenes

Paraffins : Propene + Butanes

Fig. 8 MCH cracking model²³⁾

Fig. 9 Model to account for gas interchange between bubble phase and dense phase

Table 1 Reaction rate constants and parameters for a small-scale fixed bed²³⁾

$k_M = \exp(25.8 - 38500/RT)\phi$	[sec ⁻¹]	(4)
$k_1 = \exp(24.8 - 39100/RT)\phi$	[sec ⁻¹]	(5)
$k_2 = \exp(25.2 - 42300/RT)\phi$	[sec ⁻¹]	(6)
$k_4 = \exp(-5.15 + 7000/RT)$	[sec ⁻¹]	(7)
$k_5 = \exp(-5.87 + 3360/RT)$	[sec ⁻¹]	(8)
$\alpha = \exp(10.5 - 18600/RT)$	[g-cat/mg-coke]	(9)
$\phi = 1/(1 + \alpha n_c)$	[—]	(10)

2) The bubble phase consists of the bubble and wake surrounded by a spherical cloud. The cloud volume is negligibly small compared with the wake volume, and the solids in the cloud are ignored. The cloud volume, therefore, is lumped together with the wake volume. This assumption^{2,10,11)} is supported where u_o/u_{mf} is large, as shown in Table 3.

3) Finite interchange of gases occurs between the bubble and dense phases, and the main transfer resistance exists between cloud boundary and dense phase.

4) The gas composition in the bubble with cloud-wake is uniform.

5) The average of size and velocity of the rising bubbles are given over the whole bed.

6) The voidage distribution is uniform over the whole bed.

7) The voidage in the cloud-wake is equal to that of incipient bed.

A sketch of the bubble model is illustrated in **Fig. 9**.

3.1.1 Gas velocity According to the Kunii and Levenspiel hypothesis¹⁰⁾, the upward velocity of gas

through the dense phase (u_e) is given by subtracting the downward velocity of solids in dense phase (u_s) from the upward velocity of the gas at incipient state (u_f).

$$u_e = u_f - u_s = \frac{u_{mf}}{\varepsilon_{mf}} - u_s \quad (11)$$

The rising velocity of cloud-wake (u_c) is assumed to be equal to that of rising bubble (u_b).

Consequently, u_o is shown by Eq.(12) from the summation of gas flow in each phase.

$$u_o = \varepsilon_b u_b (1 + \delta_w \varepsilon_{mf}) + \varepsilon_{mf} \{1 - \varepsilon_b (1 + \delta_w)\} u_e \quad (12)$$

(cloud-wake and bubble phase) (dense phase)

where δ_w can be defined as Eq.(13) in this study.

$$\delta_w = \frac{\text{volume of cloud-wake around a bubble}}{\text{volume of a bubble}} \quad (13)$$

The amount of the downward flowing solids in the dense phase is equal to that of the upflowing solids in the cloud-wake, and the relation is given by Eq.(14).

$$\{1 - \varepsilon_b (1 + \delta_w)\} u_s = \varepsilon_b \delta_w u_b \quad (14)$$

Combining Eqs.(11) and (12) with Eq.(14),

$$u_o = \varepsilon_b u_b + \{1 - \varepsilon_b (1 + \delta_w)\} u_{mf} \quad (15)$$

if $u_o \gg \varepsilon_b (1 + \delta_w) u_{mf}$, the average velocity of rising bubbles is approximated by Eq.(16).

$$u_b = \frac{u_o - u_{mf} + \varepsilon_b (1 + \delta_w) u_{mf}}{\varepsilon_b} \sim \frac{u_o - u_{mf}}{\varepsilon_b} \quad (16)$$

3.1.2 Material balance Two assumptions are made to derive a material balance for each component.

1) The gas interchange coefficient between bubble and dense phases per unit of bubble volume is uniform through the bed.

2) The cracking system is in a pseudo-steady state because the individual product traverses the bed so quickly relative to catalyst fouling at a definite process time.

With these two assumptions, we may then derive the following simplified ordinary differential equations for an element of the bed height (dZ) and of the unit cross-sectional area in both phases.

i) MCH(M) balance

For the bubble phase,

$$-u_1 \frac{dC_{Mc}}{dZ} = K_{cM} (C_{Mc} - C_{Me}) + k_{rM} \gamma_c C_{Mc} \quad (17)$$

For the dense phase,

$$-u_2 \frac{dC_{Me}}{dZ} = K_{cM} (C_{Me} - C_{Mc}) + k_{rM} \gamma_e C_{Me} \quad (18)$$

ii) Olefins (A) balance

For the bubble phase,

$$-u_1 \frac{dC_{Ac}}{dZ} = K_{cA} (C_{Ac} - C_{Ae}) + \gamma_c \{ -k_{r1} C_{Me} + (k_{r4} + k_{r5}) C_{Ac} \} \quad (19)$$

For the dense phase,

$$-u_2 \frac{dC_{Ae}}{dZ} = K_{cA} (C_{Ae} - C_{Ac}) + \gamma_e \{ -k_{r1} C_{Me} + (k_{r4} + k_{r5}) C_{Ae} \} \quad (20)$$

3) Paraffins (B) balance

For the bubble phase,

$$-u_1 \frac{dC_{Bc}}{dZ} = K_{cB} (C_{Bc} - C_{Be}) - \gamma_c (k_{r2} C_{Mc} + k_{r4} C_{Ac}) \quad (21)$$

For the dense phase,

$$-u_2 \frac{dC_{Be}}{dZ} = K_{cB} (C_{Be} - C_{Bc}) - \gamma_e (k_{r2} C_{Me} + k_{r4} C_{Ae}) \quad (22)$$

where

$$u_1 = u_b (1 + \delta_w \varepsilon_{mf}) \quad (23), \quad u_2 = \{1 - \varepsilon_b (1 + \delta_w)\} \cdot \frac{u_e \varepsilon_{mf}}{\varepsilon_b} \quad (24)$$

$$\gamma_c = (1 - \varepsilon_{mf}) \delta_w \quad (25), \quad \gamma_e = (1 - \varepsilon_{mf}) \{1 - \varepsilon_b (1 + \delta_w)\} / \varepsilon_b \quad (26)$$

4) Coke formation

Assuming that the solids within the bed are completely mixed, the rate of coke formation per unit weight of catalyst is written as

$$\frac{dn_c}{d\theta} = k_{r5} (\nu_1 \gamma_c \bar{C}_{Ac} + \nu_2 \gamma_e \bar{C}_{Ae}) \quad (27)$$

where

$$\bar{C}_{Ac} = \frac{1}{L_f} \int_0^{L_f} C_{Ac} dZ, \quad \bar{C}_{Ae} = \frac{1}{L_f} \int_0^{L_f} C_{Ae} dZ \quad (28)$$

ν_1 and ν_2 are the conversion factors for the coke formation based on the process time, namely,

$$\nu_1 = 1000 L_f f_M / (u_1 W) \quad (29)$$

$$\nu_2 = 1000 L_f f_M \varepsilon_b / [u_{mf} \{1 - \varepsilon_b (1 + \delta_w)\} W] \quad (30)$$

Boundary conditions are:

$$i) \text{ at } Z=0, \text{ for } \theta \geq 0, C_{Mj}=1.0, C_{Aj}=C_{Bj}=0 \quad (j=c, e) \quad (31)$$

$$ii) \text{ for } Z>0, \text{ at } \theta=0, n_c=0 \quad (32)$$

3.2 Evaluation of model parameters

Before applying the mathematical model to the experimental data, the model could be further simplified. It is said that the upward velocity of gas in the dense phase (u_e) is negligibly small where u_o/u_{mf} is large^{7,10}. By using Eqs.(11), (14) and (15), u_e/u_{mf} can be expressed as

$$\frac{u_e}{u_{mf}} = \frac{1}{\varepsilon_{mf}} - \frac{\delta_w (u_o - u_{mf})}{[1 - \varepsilon_b (1 + \delta_w)] u_{mf}} \quad (33)$$

Under the experimental conditions (i.e., u_o/u_{mf} being 3.5–12.1) as shown in Table 3, Eq.(33) gives $u_e/u_{mf} \simeq 0$ for $u_o/u_{mf}=3.8$, $u_e/u_{mf}=-0.05$ – -0.11 for $u_o/u_{mf}=7.0$ – 12.1 , from the assumption of δ_w being 0.5.

From the calculations, it is found that our experimental conditions are almost in the region in which downflow of gas in the dense phase takes place, and that the values of u_e are negligibly smaller than those of u_{mf} . It is therefore reasonable to assume u_e as zero under the experimental conditions as shown in Table 3.

To evaluate the model parameters of K_{ci} ($i=M, A$)

and δ_w , six simultaneous differential equations from Eq.(17) to Eq.(22) could be solved analytically based on u_e being zero, and the solutions are given in **Table 2**, where the values of $C_i(L_f)$ represent the product concentrations at the top of the bed and are considered to be equal to those of bubble phase.

The evaluation procedures were performed as follows. At first, the values of $C_i(L_f)$ in Table 2 were calculated using the coke content corresponding to $\theta=4$ min., and the rate of coke formation in a

Table 2 Solutions of Eqs. (17)–(22) at $u_e=0$

1) MCH
$$C_M(L_f) = \exp(-DL_f) \quad (34)$$

2) Olefins
$$C_A(L_f) = P \left\{ \exp(-DL_f) - \exp\left(-\frac{FL_f}{u_1}\right) \right\} \quad (35)$$

3) Paraffins
$$C_B(L_f) = \frac{(Q+SP)}{Du_1} \left\{ 1 - \exp(-DL_f) \right\} - \frac{SP}{P} \left\{ 1 - \exp\left(-\frac{FL_f}{u_1}\right) \right\} \quad (36)$$

where

$$D = \frac{k_{rM}(\gamma_e E + \gamma_c)}{u_1}, \quad E = \frac{K_{cM}}{K_{cM} + \gamma_e k_{rM}} \quad (37)$$

$$F = \frac{K_{cA}(k_{r4} + k_{r5})(\gamma_c + \gamma_e) + \gamma_c \gamma_e (k_{r4} + k_{r5})^2}{K_{cA} + \gamma_e (k_{r4} + k_{r5})} \quad (38)$$

$$G = \gamma_c k_{r1} + \frac{\gamma_e K_{cA} k_{r1} E}{K_{cA} + \gamma_e (k_{r4} + k_{r5})} \quad (39)$$

$$P = \frac{G}{F - Du_1} \quad (40)$$

$$Q = \gamma_e k_{r2} E + \gamma_c k_{r2} + \frac{\gamma_e^2 k_{r1} k_{r4} E}{K_{cA} + \gamma_e (k_{r4} + k_{r5})} \quad (41)$$

$$S = \gamma_c k_{r4} + \frac{\gamma_e K_{cA} + k_{r4}}{K_{cA} + \gamma_e (k_{r4} + k_{r5})} \quad (42)$$

definite process time ($\Delta n_c / \Delta \theta$) was calculated from Eq.(27). Consequently, the coke content corresponding to $\theta + \Delta \theta$ should be shown by $n_c + \Delta n_c$. These procedures were repeated for the calculation of objective function (ϕ) as expressed in Eq.(43) until the final value of process time was reached.

$$\phi = \sum_{j=1}^5 \sum_{i=M, A}^3 \omega_i (C_{i, \text{exp}} - C_{i, \text{cal}})^2 + \omega_c \sum_{j=1}^5 (n_{c, \text{exp}} - n_{c, \text{cal}})^2 \quad (43)$$

where the suffix “i,exp” and “i,cal” are used to denote the experimental and calculated values, respectively; the values of ω_i and ω_c are weighting factors and were chosen to evaluate the ϕ exactly for all experimental data as shown in **Table 3**.

The model parameters can be estimated according to the non-linear regression technique, modifying the method developed by Sobol^[20]. The model parameters evaluated are tabulated in Table 3.

3.3 Rearrangement of model parameters with operating conditions

By considering the bubble velocity and bubble size governing the interchange coefficient, the following relation was derived by dimensional analysis.

$$\frac{K_{ci} \bar{d}_b}{u_b} = \beta_i \left(\frac{D_{Gi}}{u_b \bar{d}_b} \right)^m \quad (i=M, A) \quad (44)$$

where $\bar{d}_b$ is the average size of bubbles along the bed height and is given by using Eq.(3).

$$\bar{d}_b = \frac{1}{L_f} \int_0^{L_f} d_b dZ \quad (45)$$

where D_{Gi} ($i=M, A$) is the molecular diffusivity in a

Table 3 Experimental conditions and the results of estimated parameters

	Run	u_0^{***} [cm/sec]	L_c [cm]	L_f [cm]	ε_b [—]	$\bar{d}_b$ [cm]	K_{cM} [sec ⁻¹]	K_{cA} [sec ⁻¹]	δ_w [—]
Temp. = 470°C	12	1.04	5.0	7.0	0.11	0.22	0.71	1.08	0.43
u_{mf} = 0.300*	13	1.04	10.0	13.6	0.10	0.24	0.71	0.87	0.55
D_{GM} = 0.373**	14	1.04	20.0	25.8	0.05	0.29	0.86	3.16	0.53
D_{GA} = 0.527**	19	2.09	5.0	7.8	0.20	0.37	0.34	0.46	0.53
ε_{mf} = 0.55	20	2.09	10.0	14.7	0.16	0.42	0.23	0.13	0.43
	21	2.09	20.0	26.9	0.09	0.50	0.55	0.66	0.53
	30	3.12	10.0	14.8	0.17	0.59	0.44	0.53	0.50
	28	3.12	20.0	27.8	0.11	0.72	1.76	2.09	0.50
Temp. = 500°C	11	1.04	5.0	7.0	0.11	0.23	1.14	1.36	0.50
u_{mf} = 0.270*	10	1.04	10.0	13.6	0.10	0.25	0.08	0.95	0.53
D_{GM} = 0.386**	9	1.04	20.0	25.8	0.05	0.30	1.06	2.50	0.43
D_{GA} = 0.546**	6	2.09	5.0	7.8	0.20	0.38	0.76	0.90	0.53
ε_{mf} = 0.55	7	2.09	10.0	14.7	0.17	0.44	0.74	0.88	0.50
	8	2.09	20.0	26.9	0.09	0.53	1.16	1.38	0.53
	15	3.12	5.0	7.9	0.21	0.54	0.58	0.69	0.50
	17	3.12	20.0	27.4	0.11	0.76	0.68	0.30	0.45
Temp. = 530°C	35	1.04	5.0	7.0	0.11	0.23	1.80	2.14	0.50
u_{mf} = 0.257*	36	1.04	10.0	13.6	0.10	0.26	0.73	0.87	0.53
D_{GM} = 0.438**	37	1.04	20.0	25.8	0.05	0.30	1.70	1.89	0.43
D_{GA} = 0.620**	34	2.09	5.0	7.8	0.20	0.39	1.04	2.19	0.43
ε_{mf} = 0.55	23	2.09	10.0	14.7	0.16	0.44	1.55	1.83	0.55
	22	2.09	20.0	26.9	0.09	0.53	1.53	1.82	0.53
	31	3.12	5.0	7.9	0.21	0.56	3.29	3.91	0.55
	33	3.12	20.0	27.4	0.10	0.76	1.46	0.28	0.43

weighting factors: $\omega_1=0.02$, $\omega_2=\omega_3=1.0$, $\omega_c=0.00024$
unit: * cm/sec, ** cm²/sec *** at reaction temperature

Fig. 10 Plot of $(K_{ci}\bar{d}_b)/u_b$ vs. $D_{Gi}/(u_b\bar{d}_b)$

binary N_2 -component i system and was estimated according to Reid and Sherwood¹⁵⁾.

From the plots of $(K_{ci}\bar{d}_b)/u_b$ vs. $D_{Gi}/(u_b\bar{d}_b)$ in Fig. 10, the values of m , β_M and β_A in Eq.(44) were 0.5, 0.088 and 0.088, respectively. The evaluated value of δ_w showed in 0.43–0.55 and its average value of δ_w was 0.53. In Figs. 5–7, the solid lines represent the curves calculated using these parameters.

4. Discussion of the Results

4.1 Relation between bed expansion and bubble size

An estimation of ε_b based on the two-phase model has been made by Orcutt *et al.*¹³⁾, Davidson and Harrison¹⁾, Kato and Wen⁷⁾. Orcutt *et al.*¹³⁾ evaluated an effective bubble size by the following relation.

$$\varepsilon_b = \frac{u_o - u_{mf}}{u_o - u_{mf} + 0.711\sqrt{gd_b}} \quad (46)$$

Kato and Wen⁷⁾ confirmed that Eq.(46) may be applied for the bed expansion data published by numerous workers. However, Toei *et al.*²²⁾ reported that the rising velocity of bubbles varied along bed height. Godart *et al.*⁴⁾ found that the rising velocity of many bubbles is many times greater than that of a single isolated bubble. In the present data relating to bed expansion, the ε_b values calculated from Eq.(46) deviated from those observed at lower flow rate of gas and lower bed height. It was found in the present work that there existed many bubbles of fine size, less than 2–3 mm diameter, in the neighborhood of the gas distributor. On the other hand, Geldert *et al.*³⁾ reported that the voidage in the dense phase was quite large compared with that of the incipiently fluidized bed at low gas flow rates. Furthermore, the solid flow may be influenced by an electrostatic effect and wall effect. It may therefore be considered that Eq.(46) is not always applicable to estimate the bed expansion from operating conditions.

4.2 Availability of simulation model

The evaluated values of K_{cM} and K_{cA} using a simulation model for MCH cracking lay in less than about one to ten times those calculated from the empirical formula published in the literature^{1,10)}. Despite numerous studies of the transport properties of the fluidized bed, little is known concerning these proper-

Table 4 Comparison of solutions between rigorous and simplified model ($\theta=4$ min.)

Run	u_o/u_{mf} [—]		MCH [*]	Olefins [*]	Paraffins [*]
11	3.47	R:	0.40	0.039	0.082
		S:	0.40	0.034	0.087
10	3.47	R:	0.23	0.039	0.114
		S:	0.25	0.032	0.117
9	3.47	R:	0.17	0.030	0.136
		S:	0.17	0.032	0.140
12	4.06	R:	0.60	0.027	0.053
		S:	0.59	0.020	0.060
13	4.06	R:	0.63	0.018	0.090
		S:	0.59	0.018	0.091

[*]: [g-component/g-feed]

R: rigorous solution ($u_e \neq 0$), $\delta_w = 0.53$

S: simplified solution ($u_e = 0$), $\delta_w = 0.53$

ties at high temperature¹²⁾. In addition, the behavior of fluidized bed involving chemical reaction may show complicating features. Shaw *et al.*¹⁷⁾ reported according to the Orcutt model¹³⁾ that the calculated selectivity in n -butane hydrogenolysis deviated from observations because of the reaction kinetics involving desorption and surface reaction. Partridge and Rowe¹⁴⁾ pointed out that the reaction performance of large-size solids was much more effective than that of small size. Hovmand and Davidson⁶⁾ also reported that the estimated performance of an ozone decomposition deviated from observations with increasing reaction rate. From the facts above-mentioned, it was considered that the gas interchange coefficient showed a low value apparently because various factors such as size of solids¹⁴⁾, order of reaction rate⁶⁾, adsorption/desorption of reactants on the catalyst^{18,19)}, a lack of reactant in the dense phase¹⁸⁾, etc. However, the parameters calculated from Eq.(44) were useful in predicting the conversion and selectivity of MCH cracking in the fluidized-bed reactor.

On the other hand, the authors assumed the gas velocity in the dense phase as zero to formulate the simplified model as described previously. For the operating conditions of gas flow at which $u_e \approx 0$ according to Eq.(33), Eqs.(17)–(22) were resolved numerically according to the Runge-Kutta-Gill method to obtain rigorous predictions for the conversion and selectivity, and the calculated results are shown in Table 4. The predictions from the simplified model solution almost agreed with those of the rigorous solutions. This indicates that the simplified model is adequate to predict the fluidized-bed performance of MCH cracking.

Conclusion

The catalytic cracking of MCH was carried out using silica alumina catalyst in a fluidized bed, and the bubble size and bed expansion were measured. The product distribution was influenced by the bed height, flow rate and catalyst activity. A simulation model is proposed from the observation of bubble behavior, in a

form which can predict the conversion and selectivity with catalyst fouling. Applying the model to experimental data, unknown parameters (K_{cM} , K_{cA} , δ_w) have been estimated by non-linear regression technique and have been rearranged with operating conditions. The present model is effective in simulating the performance of MCH cracking in a fluidized-bed reactor.

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Nomenclature

C_{ic}	= weight fraction of component i in the bubble phase ($i=M, A, B$)	[g-component/g-feed MCH]
C_{ie}	= weight fraction of component i in the dense phase ($i=M, A, B$)	[g-component/g-feed MCH]
D_T	= bed diameter	[cm]
f_M	= feed rate of methylcyclohexane	[g/min]
g	= acceleration of gravity	[cm/sec ²]
K_{ci}	= gas interchange coefficient of component i between bubble phase and dense phase ($i=M, A, B$)	[sec ⁻¹]
k_j	= reaction rate constant for a fixed bed	[sec ⁻¹]
k_{rj}	= rate constant based on volume of solid ($j=1, 2, 3, 4, 5, M$) $k_{rj}=k_j/(1-\epsilon_c)$	[sec ⁻¹]
L_c	= static bed height	[cm]
L_f	= bed height of a fluidized bed	[cm]
n_c	= coke content on catalyst	[mg-coke/g-cat]
R	= gas constant = 1.987	[cal/g-mol·°K]
T	= absolute temperature	[°K]
u_b	= velocity of bubble rising through a bed	[cm/sec]
u_o	= superficial gas velocity based on empty bed	[cm/sec]
W	= weight of catalyst	[g]
α	= a constant as expressed in Eq.(9)	[g-cat/mg-coke]
γ_c	= ratio of solid in the cloud-wake to volume of bubbles in the bed	[—]
γ_e	= ratio of solid in the dense phase to volume of bubbles in the bed	[—]
ϵ_c	= voidage in a packed bed = 0.452	[—]

θ	= process time	[min]
ϕ	= activity factor	[—]

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