GENERALIZATION OF THE TWO-PHASE MODEL IN FLUIDIZED-BED CATALYTIC REACTOR

Tadashi MAMURO

Department of Chemical Engineering, Faculty of Textile Science & Technology, Shinshu University

1. Introduction

It is commonly understood that the fluidizing state of gas fluidized-bed may be classified into two types for gas flow pattern under a fluidizing condition, namely "particulate" and "aggregative" type.

In order to explain the performance of the fluidized-bed catalytic reactor by calculating of the conversion, various model have been proposed, and now, two-phase model is the most typical for aggregative type of fluidization.

While, in spite of proposing a number of types of the two-phase model, none of them are considered as the best model for good agreement of fluidized-bed behaviour.

For understanding of characteristics of the two-phase model and refering to develope of investigation of the more appropreate model, "generalized tow-phase model" is proposed in this work, which include all of types of two-phase model proposed previously. Then, various characteristics that the model itself has are analyzed mathematically. Similar attempt in a part of this work has been done by Muchi. [2]

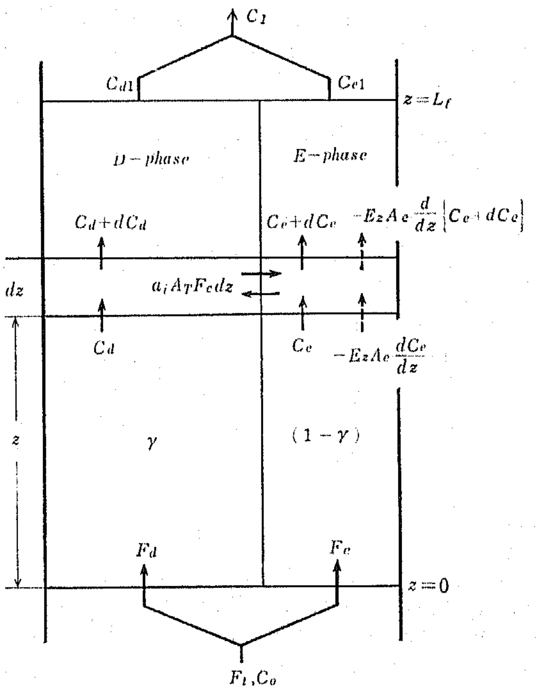

Fig. 1 Generalized two-phase model

2. Generalized two-phase model

It is considered that aggregative fluidized-bed consists of two phases, the bubble or lean phase and the emulsion or dense phase, and they make parallel two regions to the axis of bed as illustrated in **Fig. 1**.

Following analysis will be taken for the most general case of the system, that is, small amount of solid particles are present in bubble phase (dilute phase, D-phase) and large amount in emulsion phase (E-phase), so, the author designates this system as dilute-emulsion (D-E) type, while the system that none of solid particles are present in bubble phase, as bubble-emulsion (B-E) type.

The following restrictions are used for the analysis.

(**i**). In the bubble phase, a small amount of solid particles (γ fraction by weight or volume) are present, and the gas flow pattern in this phase is piston flow.

(**ii**). In the dense phase, a large amount of solid particles ($1-\gamma$ fraction) are present and the gas flow pattern in this phase follows the dispersion model in which dispersion coefficient can be adapted as the function of fluidizing characteristic parameters.

(**iii**). Considerable gas interchange occurs between the each phases, and the interchange rate per unit time per unit interfacial area of the two regions are independent of the axial distance.

(**iv**). First order or pseudo first order irreversible catalytic reaction proceeds according to the following rate equation.

$$-\frac{dn}{d\theta}=kW_sC \tag{1}$$

Taking the differential mass balances of reactant for each phase, follow ing simultaneous differential equations can be written.

D-phase :

$$\frac{dC_d}{dz}+\frac{a_iF_cA_T}{F_d}(C_d-C_e)+\frac{\gamma kW_s}{F_dL_f}C_d=0 \tag{2}$$

E-phase :

$$-\frac{A_eE_z}{F_e}\frac{d^2C_e}{dz^2}+\frac{dC_e}{dz}+\frac{a_iF_cA_T}{F_e}(C_e-C_d)+\frac{(1-\gamma)kW_s}{F_eL_f}C_e=0 \tag{3}$$

Following boundary conditions are determined for taking of differential mass balances of reactant at the top and bottom of each phase.

$$z=+0\quad\begin{cases} C_d=C_0 & (4)\\[4pt] \dfrac{dC_e}{dz}=-\dfrac{F_e}{A_eE_z}(C_0-C_e^0) & (5)\end{cases}$$

$$z=L_f\qquad \frac{dC_e}{dz}=0 \tag{6}$$

Solution of these fundamental simultaneous equations (2) and (3) under the boundary conditions (4), (5) and (6) is obtained using the Laplace transformation for concentrations of reactant C_e and C_d as a function of axial distance, z.

Putting $z=L_f$ on the solutions of C_e and C_d, effluent gas concentrations of each phase C_{e1} and C_{d1} are derived as follow.

$$\frac{C_{e1}}{C_0}=\sum_{j=1}^{3} A_j e^{\alpha j} \tag{7}$$

$$\frac{C_{d1}}{C_0}=\sum_{j=1}^{3} \frac{bA_j}{a+\alpha_j}(e^{\alpha_j}-e^{-a})+e^{-a} \tag{8}$$

where

$$A_1=(m/\lambda)\left[\{\alpha_1\alpha_2+(a+f)(m-\alpha_3)\}\alpha_2 e^{\alpha_2}-\{\alpha_3\alpha_1+(a+f)(m-\alpha_2)\}\alpha_3 e^{\alpha_3}\right]$$

$$A_2=(m/\lambda)\left[\{\alpha_2\alpha_3+(a+f)(m-\alpha_1)\}\alpha_3 e^{\alpha_3}-\{\alpha_1\alpha_2+(a+f)(m-\alpha_3)\}\alpha_1 e^{\alpha_1}\right]$$

$$A_3=(m/\lambda)\left[\{\alpha_3\alpha_1+(a+f)(m-\alpha_2)\}\alpha_1 e^{\alpha_1}-\{\alpha_2\alpha_3+(a+f)(m-\alpha_1)\}\alpha_2 e^{\alpha_2}\right]$$

$$\lambda=(\alpha_3-\alpha_2)(a+\alpha_1)\alpha_1^2 e^{\alpha_1}+(\alpha_1-\alpha_3)(a+\alpha_2)\alpha_2^2 e^{\alpha_2}+(\alpha_2-\alpha_1)(a+\alpha_3)\alpha_3^2 e^{\alpha_3}$$

α_1, α_2 and α_3 are real roots of the following complemental algebraical equation.

$$y^3+(a-m)y^2-m(a+g)y-m(ag-bf)=0 \tag{9}$$

a, b, f, g, and m are following dimensionless groups to be determined by operating conditions of fluidization, respectively.

$$a=(F_{cr}+\gamma X)/F_{dr}$$

$$b=F_{cr}/F_{dr}$$

$$f=F_{cr}/F_{er}$$

$$g=\{F_{cr}+(1-\gamma)X\}/F_{er}$$

$$m=u_e L_f/E_z=2U_e$$

$$X=kW_s/F_t$$

$$F_{cr}=a_i F_c A_T L_f/F_t$$

$$F_{dr}=F_d/F_t$$

$$F_{er}=F_e/F_t$$

Where X is a reactivity parameter, while F_{dr} and F_{er} are fractional flow rates of reactant gas in dilute and emulsion phase, respectively. The effluent gas concentration of reactant on a catalytic fluidized-bed can be obtained by equation (10) as assumed that the effluent gas of two phases are completely mixed, so

$$C_1=\frac{C_{e1}\,F_e+C_{d1}\,F_d}{F_t} \tag{10}$$

Then conversion η can be expressed by the following equation.

$$\eta = 1 - \frac{b}{1+(b/f)}\left[\sum_{j=1}^{3}\left(\frac{1}{a+\alpha_j}+\frac{1}{f}\right)A_j e^{\alpha_j} + \left\{\frac{1}{b}-\sum_{j=1}^{3}\frac{1}{a+\alpha_j}A_j\right\}e^{-a}\right] \tag{11}$$

3. Derivation of various types of the flow model

In order to determine various types of two phase model and to understand of their characteristics, E_z may be set limit to infinite or zero in the generalized two phase model (namely piston-incomplete mixed type, P-I type), and then extreme types of two-phase model are obtained as follow.

(1) $E_z \to \infty$ (P-M type) :

In this case, the flow pattern is piston type in the dilute phase, and it is complete mixed type in the emulsion phase, *i. e.*, P-M type. $E_z \to \infty$ means to set simultaniously limit to $\alpha_1 \to 0$, $\alpha_2 \to 0$, $\alpha_3 \to -a$ and $m \to 0$, so, to set the limits on equation (11), following is obtained as solution.

$$\eta = 1 - \frac{1}{1+(b/f)}\left[e^{-a} + \frac{b}{f}\cdot\frac{\{f(1-e^{-a})+a\}^2}{a^2(1+g)+bf(1-a-e^{-a})}\right] \tag{12}$$

(2) $E_z \to 0$ (P-P type) :

This case is both piston flows in dilute and in emulsion phase respectively, *i. e.*, P-P type. By similar treatment as above, setting $\alpha_1 \to \beta_1$, $\alpha_2 \to \beta_2$, $\alpha_3 \to +\infty$ and $m \to +\infty$, final form of η is obtained as follow.

$$\eta = 1 - \frac{1}{1+(b/f)}\cdot\frac{b/f}{\beta_1-\beta_2}\cdot\left[\frac{(a+f+\beta_1)^2}{a+\beta_1}e^{\beta_1} - \frac{(a+f+\beta_2)^2}{a+\beta_2}e^{\beta_2}\right] \tag{13}$$

where β_1 and β_2 are real roots of the following algeblaical equation

$$y^2 + (a+g)y + (ag-bf) = 0 \tag{14}$$

Each of equation (12) and (13) can also be derived by the basic equations which are established from each specialized model independently of the generalized two-phase model to put the differential mass balances as follow.

(1′) P-M type :

D-phase : the same to equation (2)

E-phase :

$$F_e(C_{e1}-C_0) + a_i F_c A_T \int_0^{L_f}(C_{e1}-C_d)\,dz + (1-\gamma)kW_s C_{e1} = 0 \tag{15}$$

boundary conditions :

$$\left.\begin{array}{ll} z=0 & C_d=C_0 \\ z=L_f & C_d=C_{d1} \\ z=0\sim L_f & C_e=C_{e1}\,\text{(constant for axial distance)} \end{array}\right\} \quad (16)$$

Solving the simultaneous differential equations (2) and (15) under the boundary conditions of equation (16), final form of η becomes completely accordant with equation (12).

(2'). P-P type :

D-phase: the same to equation (2).

E-phase :

$$\frac{dC_e}{dz}+\frac{a_iF_cA_T}{F_e}(C_e-C_d)+\frac{(1-\gamma)\,kW_s}{F_eL_f}C_e=0 \quad (17)$$

boundary conditions :

$$\begin{array}{lll} z=0 & C_d=C_e=C_0 & \\ z=L_f & C_d=C_{d1}, & C_e=C_{e1} \end{array} \quad (18)$$

Solving above equations, final form of η is completely conformed to equation (13).

(3). The equation derived from putting $\gamma=0$ on equation (11) means the situation that none of solid particles is present in bubble phase, namely B-E type. Furthermore, setting limit to infinite of parameter X on equation (11) we get

$$\lim_{\substack{\gamma\to 0\\ X\to\infty}} \eta = 1 - F_{dr}\, exp\{-F_{cr}/F_{dr}\} \quad (19)$$

While to set limit to infinite only X remaining $\gamma>0$ on equation (11), η approaches to unity, that is

$$\lim_{\substack{\gamma>0\\ X\to\infty}} \eta = 1 \quad (20)$$

On above calculations, it is considered that as X takes larger values, the conversion makes up to 100 % for D-E type, while the conversion makes up to certain value smaller than 100 % which is obtained by equation (19) for B-E type. Thus, when we takes up either B-E type or D-E type as more suitable model of fluidized-bed catalytic reactor, such a experimental system of reaction as large reation rate constant as possible, should be chosen to get large value of X. On the result of the experiment, it is guessed that if we get the value of η smaller than unity, B-E type are more suitable model for the system than D-E type, and numerical value of F_{cr} also will be evaluated by using equation (19).

4. Derivation of the homogeneous model

Setting limit to $\gamma \to 0$ and $F_{dr} \to 0$ and putting $u_e = u$ on the generalized two phase model, *i. e.*, equation (11) becomes

$$\eta = 1 - \frac{4P}{(1+P)^2 \, exp\{-U(1-P)\} - (1-P)^2 \, exp\{-U(1+P)\}} \tag{21}$$

where $$P = \sqrt{1+\frac{2X}{U}} = \sqrt{1+\frac{2k_1 L_f/u}{U}}$$

$$U = uL_f/2E_z$$

Equation (21) conforms to the homogeneous dispersion model derived by Dankwerts[1] and Yagi & Miyauchi[3]. Moreover, putting $\gamma = 0.5$ and $F_e = F_d$ on the P-P type, *i. e.*, equation (13), equation (22) which conforms to the case of piston flow in the homogeneous dispersion model can be derived as follow.

$$\eta = 1 - e^{-X} \tag{22}$$

In addition, putting $\gamma = 0$ and $F_d = 0$ in the P-M model, equation (23) is obtained.

$$\eta = 1 - 1/(1+X) \tag{23}$$

This equation conforms to the extreme case of complete mixed type in the homogeneous dispersion model.

5. Calculating procedure of η

In this section, following additional assumption is adopted, that the fractional void in the dense phase is maintained the void in the minimum fluidizing state regardless of any fluidizing condition. So, all excess volume of gas more than needful quantity to bring about the minimum fluidizing state flows into dilute phase. Then, net cross sectional area A_e which is concerned with dispersion of fluidizing gas in emulsion phase, can be expressed by equation (24).

$$A_e = \varepsilon_{mf}(1-\gamma)(L_{mf}/L_f) A_T \tag{24}$$

The fractions of gas flow rate in dilute and in emulsion phase are given by using equation (25).

$$\left.\begin{aligned} F_{dr} &= F_d/F_t = 1-(1-\gamma)(u_{mf} L_{mf}/u_0 L_f) \\ F_{er} &= F_e/F_t = (1-\gamma)(u_{mf} L_{mf}/u_0 L_f) \end{aligned}\right\} \tag{25}$$

In addition, put $u_e = u_{mf}$, mixing characteristic parameter m is expressed by following.

$$m = u_{mf} L_f / \varepsilon_{mf} E_z \tag{26}$$

So, conversion η can be calculated by substituting any suitable values for the parameters L_f, k, A_T, W_s, F_t, $a_i F_c$ (or F_{cr}), γ and E_z. In these, parameters W_s, k, A_T and F_t are operational variables, while L_f, F_{cr}, γ and E_z are determined experimentally as functions of an operating condition.

6. Influence of gas interchange rate F_{cr} on the conversion η

Numerical value of gas interchange rate F_{cr} is not yet determined clearly in a functional relation to operating conditions. However, following treatments are taken in equation (11) to make evident the influence of F_{cr} on the η.

(1) $F_{cr} \to 0$ in equation (11):

This case is no gas interchange occuring. Limiting value of η becomes

$$\eta = 1 - \left[F_{dr} \cdot exp\left(-\frac{\gamma X}{F_{dr}}\right) + F_{er} \cdot \frac{4P'}{(1+P')^2 \, exp\{-U_e(1-P')\} - (1-P')^2 \, exp\{-U_e(1+P')\}} \right] \tag{27}$$

where

$$P' = \sqrt{1 + \frac{2(1-\gamma)X}{F_{er} U_e}}$$

$$U_e = u_e L_f / 2E_z$$

and u_e has to be difined as $u_e = u_{mf}/\varepsilon_{mf}$.

The first and second terms in the bracket of the above equation, mean the conversion in D-phase and E-phase, respectively. Then, this equation gives the conversion for the case of the parallel connection of the two independent reactors, one of them is a piston flow reactor contained γW_s grams of catalyst with F_{dr} fraction of gas flow rate, and the other is a in complete mixed reactor contained $(1-\gamma)W_s$ grams of catalyst with F_{er} fraction of gas flow rate.

(2) $F_{cr} \to \infty$ in equation (11):

This case is of infinite gas interchange rate. To set limit for equation (11), final result of calculation becomes such equation that U_e/F_{er} is taken instead of U in equation (21). Therefore, when F_{cr} are very large value, two-phase model will be regarded as a homogeneous model, so, in this situation, E_z' corresponded with U' by the equation $U' \equiv u\ L_f/2E_z'$ can be looked upon as apparent dispersion coefficient assumed as a homogeneous dispersion field, because U_e/F_{er} can be regarded as a apparent mixing parameter U'. For such consideration, the following expression is given

$$U' \equiv \frac{U_e}{F_{er}} = \frac{u_0 L_f A_T}{2E_z A_e} = \frac{u L_f}{2E_z(A_e/\varepsilon A_T)} = \frac{u L_f}{2E_z'} \tag{28}$$

where ε is the average fractional void in a bed. Combining the equations (28) and (24), following relation is get,

$$E_z = \frac{1}{1-\gamma}\left\{1+\frac{(L_f/L_{mf})-1}{\varepsilon_{mf}}\right\}E_z' \tag{29}$$

Therefore, if F_{cr} could be made large enough, the dispersion coefficient of two-phase model E_z will be calculated by the apparent dispersion coefficient E_z' which is obtained by the experimental procedure similar to get a dispersion coefficient of the homogeneous fluidized-bed.[4)]

7. Calculation of η and discussions

Numerical values of η calculated with various sets of parameter are shown in **Fig.** 2, 3 and 4. The value of a fluidizing parameter $u_{mf}L_{mf}/u_0L_f$ is 0.25 in each curve.

The extreme types of two-phase model, P-P and P-M with respect to each of D-E and B-E types, and homogeneous type are together shown in **Fig.** 2. Increasing of F_{cr} on the both of the B-E and D-E types, P-P type approaches to the piston flow model in the homogeneous dispersion type, while P-M type does to the complete mixed model in the homogeneous

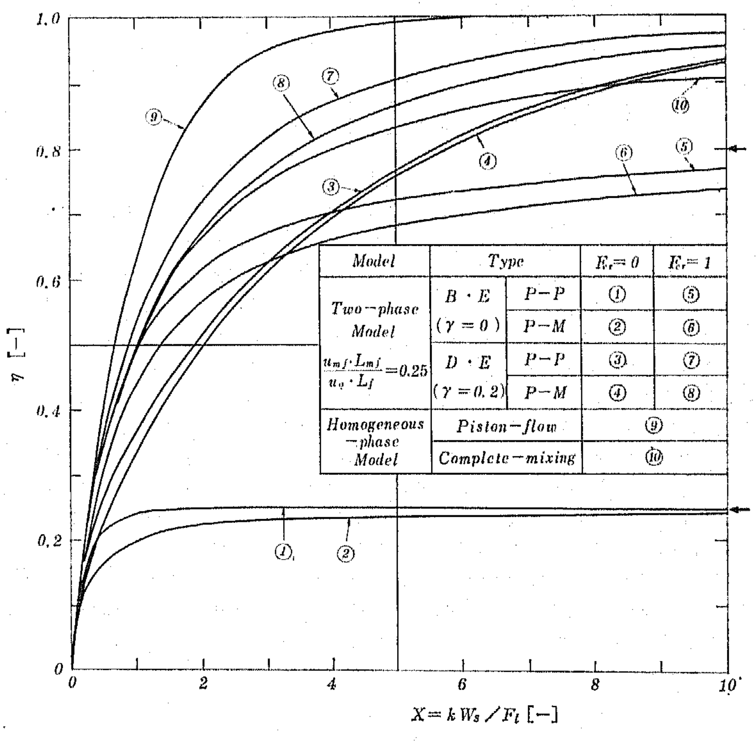

Fig. 2 η vs. X for two-phase and homogeneous-phase model dispersion type.

On the B-E type, as increasing of X, the curves close to the limiting value marked in the figure. As the tendency is remarkable in the range of small value of F_{cr}, η approaches to a fixed value independent of X. **Fig. 3-a** shows an example of the mixing effect in the emulsion phase at $\gamma = 0.1$ and $F_{cr}=1$. Effect of F_{cr} is shown in **Fig. 3-b** at $X=1$. Within the value of F_{cr} is small, η is affected sensitively with F_{cr} and γ, while in the large value of F_{cr} (more than about 2.5 at the P-M type), η approaches the limit value which is independent of F_{cr} and X. The values are indicated by the small arrows in **Fig. 3-b.**

To make evident of the mixing effect in emulsion phase, the difference of η s both in the P-P and in P-M type is appointed to a measure of degree of mixing. Therefore, the effect of E_z on η can be estimated by the ratio of such difference to η of P-P type as shown in **Fig. 4**. The effect of E_z is remarkable on a certain range of X, in other words, when reaction rate constant is very large or small, it is concluded so far as the two phase model

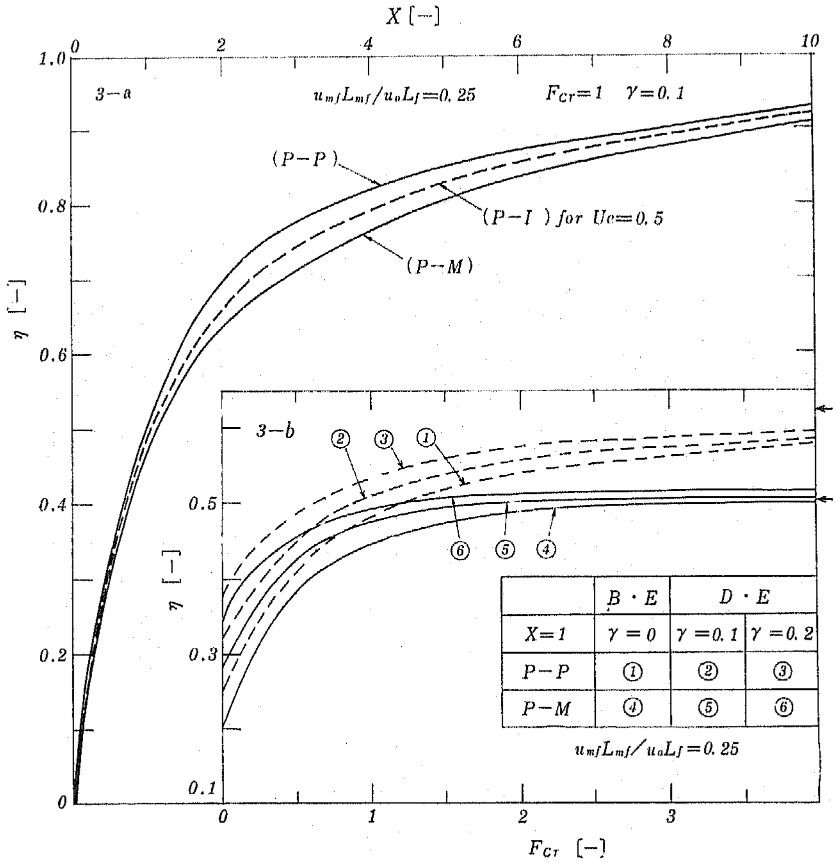

Fig. 3-a η vs. X for $\gamma=0.1$, $F_{cr}=1$
Fig. 3-b η vs. F_{cr} for $X=1$

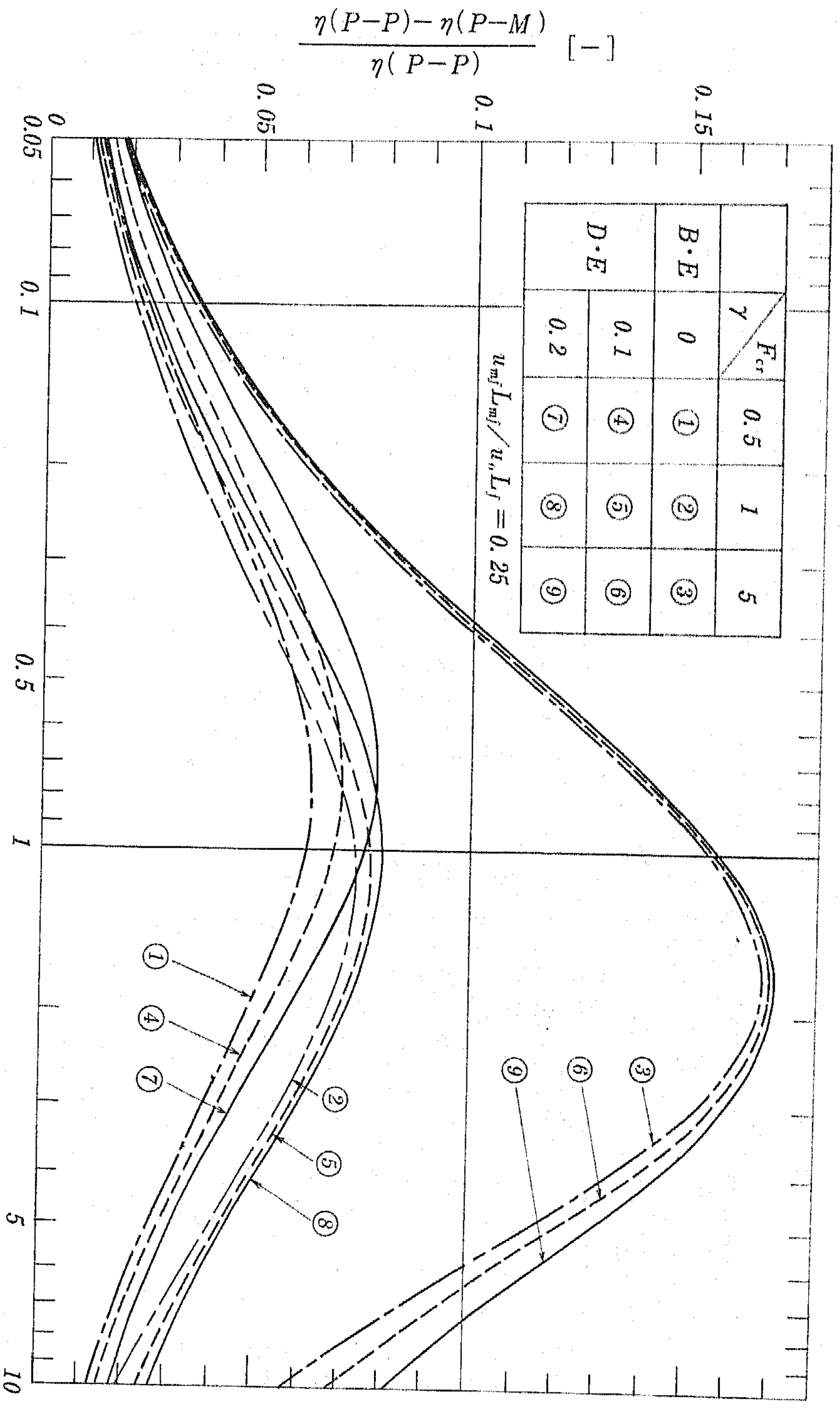

Fig. 4 Effect of parameter E_z for two-phase model

is adopted, that the suitable model of the fuidized-bed catalytic reator can be looked upon as P-P or P-M type, and the conversions of the both types approaches to the similar values to each other.

8. Conclusion

In order to explain conversion of a aggregative fluidized-bed catalytic reactor, generalized two phase model has been proposed by means of mathematical treatment. Then, various types of the model which were proposed previously by many investigators are all derived from the generalized two phase model, that is, B-E, D-E, P-P, P-M and homogeneous type.

For estimation of the effects of various parameters on the conversion, numerical calculation of conversion has been done and effects of important parameters F_{cr}, γ and X have been discussed by some illustrations. The characteristics of the two phase model has been clearly understood in this work.

Acknowledgment

The author is very grateful to Dr. Iwao Muchi for the instraction of this work.

Nomenclature

A_e	: effective cross sectional area for gas flow in emulsion phase	[cm^2]
A_T	: cross sectional area of fluidized-bed reactor	[cm^2]
a_i	: effective interfacial area between dilute and emulsion phases per unit volume of bed	[cm^2/cm^3]
B-E	: (Bubble-Emulsion)	
C_d, C_e	: concentration of gaseous reactant in dilute and emulsion phases, respectively	[mol/cm^3]
C_{d1}, C_{e1}	: concentration of gaseous reactant at the top of dilute and emulsion phases, respectively	[mol/cm^3]
C_0 C_1	: concentration of gaseous reactant at the inlet and outled of fluidized-bed reactor, respectively	[mol/cm^3]
C_e^0	: concentration of gaseous reactant at the bottom of emulsion phase	[mol/cm^3]
D-E	: (Dilute-Emulsion)	
E_z	: longitudinal dispersion coefficient of gas	[cm^2/sec]
E_z'	: apparent longitudinal dispersion coefficient of gas regarded aggregative fluidized-bed as a particulate fluidized-bed	[cm^2/sec]
F_c	: gas interchange rate per unit interfacial area	[cm^3/cm^2·sec]
F_d, F_e	: volumetric gas flow rate through dilute and emulsion phases, respectively	[cm^3/sec]
F_{cr}, F_{dr}, F_{er}	: ratio of $a_iF_cA_TL_f$, F_d and F_e to F_t, respectively	[–]
F_t	: volumetric flow rate of total gas in fluidized-bed reator	[cm^3/sec]
k	: first order reaction rate constant	[cm^3/g-(cat)·sec]
k_1	: first order reaction rate constant $= kW_s/V_g$	[1/sec]
L_{mf}	: bed height in minimum fluidization state	[cm]
L_f	: fluidized-bed height	[cm]
n	: moles of reactant	[mol]

P-I	: (Piston-Incomplete mixing)		
P-M	: (Piston-Complete mixing)		
P-P	: (Piston-Piston)		
U	$= uL_f/2E_z$		[–]
U_e	$= u_eL_f/2E_z$		[–]
U'	$= U_e/F_{er}$		[–]
u	: average gas velocity in particulate fluidized-bed		[cm/sec]
u_e	: average gas velocity in emulsion phase		[cm/sec]
u_0	: superficial gas velocity		[cm/sec]
u_{mf}	: minimum fluidization velocity		[cm/sec]
V_g	: total volume of gas in fluidized-bed reactor		[cm^3]
W_s	: total mass of catalyst in fluidized-bed reator		[g]
X	$= kW_s/F_t$ (reactivity parameter)		[–]
z	: axial distance of bed		[cm]
γ	: catalyst fraction in dilute phase		[–]
ε	: average fractional void in particulate fluidized-bed		[–]
ε_{mf}	: average fractional void in minimum fluidization state		[–]
η	: conversion		[–]
θ	: time		[sec]

Literature cited

1) Dankwerts, P. V. : *Chem. Eng. Sci.* 2, 1 (1953)
2) Muchi, I. : *Kagaku-kikai-gijutsu.* No. 16 (1964) Kagaku-Dojin.
3) Yagi, S. and T. Miyauchi : *Kagaku-kogaku* (*Chem. Eng., Japan*) 19, 507 (1955)
4) Muchi, I., T. Mamuro and K. Sasaki : *Kagaku-kogaku* (*Chem. Eng., Japan*) 25, 747 (1961)