

ANALYSIS OF THE REMOVAL OF H₂S WITH IMPREGNATED ACTIVATED CARBON

Tan Xiaoyao (谭小耀)*, Wu Diyong (吴迪镛) and Yuan Quan (袁权)

Dalian Institute of Chemical Physics, Academia Sinica, Dalian 116012, China

Abstract A general mathematical model with its governing equations in dimensionless forms has been developed to describe the removal of hydrogen sulfide with impregnated activated carbon. An approximate relationship between the sulfur capacity and the reaction time in a single carbon pellet is obtained, and criterion to ascertain the rate controlling step of the process can then be deduced. In the meantime, the choice of the appropriate oxygen concentration and the principle to be followed are also described.

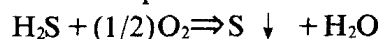
Keywords desulfurization, impregnated activated carbon, hydrogen sulfide

1 INTRODUCTION

The removal of H₂S through catalytic oxidation with activated carbon has been found to be economically feasible and is particularly suitable for removing H₂S in low concentrations^[1-4]. The sulfur capacity and desulfurizing rate can be greatly increased by the addition of an impregnating agent^[5, 6]. We have studied the mechanism^[7], and found that this process is mainly due to the oxidation of H₂S by the polarized oxygen molecules and active oxygen atoms in the adsorptive water film with the result of formation of elemental sulfur, which gradually deposits on the pores of activated carbon. The impregnating agent serves to a better environment for the catalytic oxidation and a higher alkalinity on the water film, as well as acting as a catalyst itself. In the course of desulfurization, the reaction rate decreases with the formation of elemental sulfur because the active sites are covered by sulfur and the resistance to mass transfer increases with decreases in porosity. In this paper, we have analyzed the process with taking these two factors into consideration. The results obtained can be used as the bases for experimental design and industrial application. Furthermore, they may also be used for analyzing the process of deactivation of catalyst because of the formation of a solid product.

2 MODEL EQUATIONS

Generally speaking, the desulfurization process follows to the following pattern



The following basic assumptions have been made for the modeling procedure:

- (1) The activated carbon particle is spherical in form with a radius of R_p ;
- (2) Reaction heat is negligible, *i.e.* the desulfurization process is isothermal;
- (3) The reaction occurs only in the adsorptive water film, and the kinetics may be

described by that formulated in reference [7];

(4) The diffusivities of H₂S and O₂ are independent of their concentrations;

(5) There exists an equilibrium between the gas phase and the adsorptive water film, and Henry's law is being obeyed;

(6) Liquid mass transfer can be neglected compared to gas mass transfer.

Then the mass balance equations for A, B and S inside a carbon pellet may be expressed as

$$\varepsilon_p[(1-f)\frac{\partial c_{i,g}}{\partial t} + f\frac{\partial c_{i,l}}{\partial t}] = \frac{D_{i,g}}{R^2} \frac{\partial}{\partial R} (R^2 \frac{\partial c_{i,g}}{\partial R}) - r_i \rho_1 \quad (i=A, B) \quad (1)$$

$$dW_s/dt = 10^{-3} M_{sR} \quad (2)$$

with boundary and initial conditions

$$t > 0, R = 0, \frac{\partial c_{i,g}}{\partial R} = 0; R = R_p, D_{i,g} \frac{\partial c_{i,g}}{\partial R} = k_{f,i}(c_{i,0} - c_{i,g}) \quad (3a)$$

$$t = 0, c_{i,g} = 0, W_s = 0 \quad (3b)$$

where A,B,S stand for H₂S, O₂ and elemental sulfur respectively.

The equation of desulfurization kinetics may be described as^[7]

$$r_A = [k_1 k_2 W_{s,\infty} c_{A,g} c_{B,g} / (1 + k_2 c_{B,g})] \cdot (1 - W_s / W_{s,\infty})^2 \quad (4)$$

Since the porosity decreases with the formation of elemental sulfur during the course of the reaction, the effective diffusivity also decreases with increases in the sulfur capacity. According to the random pore model, the effective diffusivity is given by

$$D_{i,g} = D_{i,g}^0 (1-f)^2 (1 - \beta W_s)^2 \quad (5)$$

Obviously, β would be subjected to the following constraint

$$\beta W_{s,\infty} \leq 1 \quad (6)$$

The overall sulfur capacity may be written as

$$W_t = \int_0^{R_p} 4\pi R^2 (W_s \rho_1) dR / \frac{4}{3} \pi R_p^3 \rho_1 \quad (7)$$

By defining the dimensionless variables and parameters as follows

$$X_i = c_{i,g} / c_{i,0}, \eta = R / R_p, \tau = (D_{A,g} / R_p^2) t, X_s = W_s / W_{s,\infty} \quad (8a)$$

$$\beta_A = (1-f)^2 (1 - \beta W_{s,\infty} X_s)^2, \alpha_i = \varepsilon_p (1-f + f K_{H,i}) \quad (8b)$$

$$\delta_s = 10^{-3} M_s c_{A,0} / \rho_1 W_{s,\infty}, \Phi_A = R_p \sqrt{\rho_1 k_1 W_{s,\infty} / D_{A,g}^0}, Sh_i = k_{f,i} R_p / D_{i,g} \quad (8c)$$

$$\lambda_B = k_2 c_{B,0}, \gamma_K = D_{B,g}^0 / D_{A,g}^0, \gamma_C = c_{A,0} / 2c_{B,0} \quad (8d)$$

we may rewrite the model Eqs. (1) and (2) in dimensionless form as

$$\alpha_A \frac{\partial X_A}{\partial \tau} = \beta_A \left(\frac{2}{\eta} \frac{\partial X_A}{\partial \eta} + \frac{\partial^2 X_A}{\partial \eta^2} \right) - \Phi_A^2 \frac{\lambda_B X_A X_B}{1 + \lambda_B X_B} (1 - X_s)^2 \quad (9)$$

$$\alpha_B \frac{\partial X_B}{\partial \tau} = \beta_A \gamma_K \left(\frac{2}{\eta} \frac{\partial X_B}{\partial \eta} + \frac{\partial^2 X_B}{\partial \eta^2} \right) - \gamma_C \Phi_A^2 \frac{\lambda_B X_A X_B}{1 + \lambda_B X_B} (1 - X_S)^2 \quad (10)$$

$$\frac{dX_S}{d\tau} = \delta_s \Phi_A^2 \frac{\lambda_B X_A X_B}{1 + \lambda_B X_B} (1 - X_S)^2 \quad (11)$$

with boundary conditions

$$\eta = 0, \quad \frac{\partial X_i}{\partial \eta} = 0; \quad \eta = 1, \quad \frac{\partial X_i}{\partial \eta} = \frac{Sh_i}{\beta_i} (1 - X_i) \quad (12)$$

The overall sulfur capacity in dimensionless form is given as

$$X_t = W_t/W_{S,\infty} = 3 \int_0^1 X_S \eta^2 d\eta \quad (13)$$

The model system consists of a group of nonlinear partial differential equations, and thus they have to be solved numerically. In this paper, the difference method is used for the radius variable

$$\frac{\partial X_i}{\partial \eta} = \frac{1}{2\Delta\eta} (X_{i,j+1} - X_{i,j-1}) \quad (14)$$

$$\frac{\partial^2 X_i}{\partial \eta^2} = \frac{1}{\Delta\eta^2} (X_{i,j+1} - 2X_{i,j} + X_{i,j-1}) \quad (j=1, 2, \dots, N) \quad (15)$$

Substituting Eqs. (14) and (15) into the governing Eqs. (9) – (11), they can be transformed into a set of ordinary differential equations. Consequently, the model can be solved with the Runge-Kutta method of changing time step length. N is usually chosen as 8 to attain sufficient calculation accuracy.

3 ASYMPTOTIC BEHAVIOR AND APPROXIMATE SOLUTION

3.1 Kinetics control

When the overall rate is controlled by chemical kinetics, the reactant concentration is uniform throughout the pellet, and $X_A = X_B = 1$. Under these conditions, the sulfur capacity can be directly obtained by integrating Eq.(11)

$$X_t = \lambda_B \delta_s \Phi_A^2 \tau / [(1 + \lambda_B) (1 + \delta_s \Phi_A^2 \tau)] \quad (16)$$

3.2 External diffusion control

When the process is controlled by external diffusion, the overall desulfurization rate equals to the rate of mass transfer from main stream to the surface of the carbon particle, while sulfur deposits uniformly within the carbon pellet. When the external diffusion of A is the sole resistance, the overall rate may be expressed as

$$dX/d\tau = 3\delta_s Sh_A \quad (17)$$

Integrating the above equation gives

$$X_t = 3\delta_s Sh_A \tau \quad (18a)$$

Similarly, when there exists only the external diffusion resistance of B, then

$$X_t = 3\delta_s \gamma_K Sh_B \tau / \gamma_C \quad (18b)$$

3.3 Internal diffusion control

If the reaction rate is rapid enough in contrast to the diffusion process, it may be considered that the reaction occurs only at a certain interface inside the carbon pellet. As the reaction proceeds, elemental sulfur deposits only on the interface approaching the maximum sulfur capacity, and the reaction interface would shift gradually to center of the pellet.

When the overall rate is solely controlled by the internal diffusion of A, $X_s = 1$ in the whole outer reaction area where the reaction rate is zero. Such case may be described by the following governing equation

$$\alpha_A \frac{\partial X_A}{\partial \tau} = \beta'_A \left(\frac{2}{\eta} \frac{\partial X_A}{\partial \eta} + \frac{\partial^2 X_A}{\partial \eta^2} \right) \quad (19)$$

with boundary conditions

$$\eta = \eta_c, X_A = 0; \quad \eta = 1, X_A = 1 \quad (19a)$$

where

$$\beta'_A = (1-f)^2 (1 - \beta W_{S,\infty})^2 \quad (19b)$$

In addition, the amount of mole A diffused should equal to that of the elemental sulfur formed at the reaction interface, and may be readily formulated as

$$\frac{d\eta_c}{d\tau} = -\delta_s \beta'_A \left. \frac{\partial X_A}{\partial \eta} \right|_{\eta=\eta_c} \quad (20)$$

with initial condition

$$\tau = 0, \eta_c = 1 \quad (20a)$$

Solving Eq(19) by the variable separation method gives the local concentration of A at any time inside the pellet as

$$X_A = \frac{2}{\eta} \sum_{n=1}^{\infty} \frac{(-1)^n}{n\pi} \exp\left[-\left(\frac{n\pi}{1-\eta_c}\right)^2 \frac{\beta'_A}{\alpha_A} \tau\right] \sin\left[\frac{n\pi(\eta-\eta_c)}{1-\eta_c}\right] + \frac{\eta-\eta_c}{\eta(1-\eta_c)} \quad (21)$$

Combining Eq.(21) with Eq.(20) gives

$$\frac{d\eta_c}{d\tau} = \frac{-\delta_s \beta'_A}{\eta_c(1-\eta_c)} \left\{ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left[-\left(\frac{n\pi}{1-\eta_c}\right)^2 \frac{\beta'_A}{\alpha_A} \tau\right] \right\} \quad (22)$$

The sulfur capacity related to η_c can be calculated by

$$X_t = 1 - \eta_c^3 \quad (23)$$

Therefore, the overall reaction rate can be obtained by combining Eq.(22) with Eq.(23)

$$\frac{dX_t}{d\tau} = \frac{3\delta_s \beta'_A \eta_c}{(1-\eta_c)} \left\{ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left[-\left(\frac{n\pi}{1-\eta_c}\right)^2 \frac{\beta'_A}{\alpha_A} \tau\right] \right\} \quad (24)$$

Applying the quasi-steady state condition $\partial X_A / \partial \tau \approx 0$, Eq.(24) reduces into a solution in

the form of ordinary function

$$\begin{aligned}\tau &= \frac{1}{\delta_s \beta_A'} \left(\frac{1}{6} - \frac{1}{2} \eta_c^2 + \frac{1}{3} \eta_c^3 \right) \\ &= \frac{1}{\delta_s \beta_A'} \left[\frac{1}{2} - \frac{1}{3} X_t - \frac{1}{2} (1 - X_t)^{2/3} \right]\end{aligned}\quad (25)$$

Comparing Eq.(24) with Eq.(25), we can conclude that the bigger the value of β_A'/α_A , the more the possibility to use the quasi-steady state condition. Fig. 1 shows the desulfurization rate curves from Eq. (24) and (25) at different values of β_A'/α_A respectively. We can see that sulfur capacity may be calculated with Eq.(25) when $\beta_A'/\alpha_A \geq 0.005$.

On the other hand, when the reaction is controlled only by the internal diffusion of B, we may also obtain the reaction time corresponding to a certain overall sulfur capacity

$$\tau = \frac{\gamma_C}{\delta_s \gamma_K \beta_A'} \left[\frac{1}{2} - \frac{1}{3} X_t - \frac{1}{2} (1 - X_t)^{2/3} \right] \quad (26)$$

3.4 Approximate solution

Sohn and Szekely^[8, 9] have derived an approximate solution for a general non-catalytic gas-solid reaction process. It is stated that the time required to attain a certain conversion equals approximately to the sum of the time required to attain the same conversion in every separate controlling step. Applying this concept to our desulfurization reaction system, we can calculate the reaction time required to attain a certain amount of sulfur capacity X_t from the following expression

$$\delta_s \tau \approx \left(\frac{\gamma_C}{3\gamma_K Sh_B} + \frac{1}{3Sh_A} \right) X_t + \frac{1 + \lambda_B}{\Phi_A^2 \lambda_B} \frac{X_t}{1 - X_t} + \left(\frac{1}{\beta_A'} + \frac{\gamma_C}{\gamma_K \beta_A'} \right) \left[\frac{1}{2} - \frac{1}{3} X_t - \frac{1}{2} (1 - X_t)^{2/3} \right] \quad (27)$$

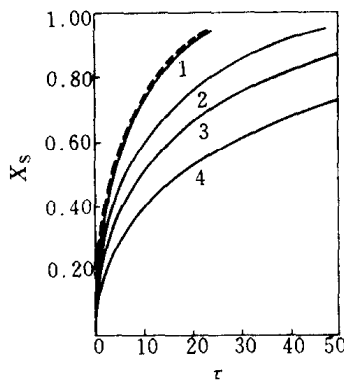


Figure 1 Plot of X_s against time at different values of β_A'/α_A ($\delta_s = 0.01$, $\beta_A = 0.5$)
 β_A'/α_A : 1- 5×10^{-3} ; 2- 1×10^{-3} ; 3- 5×10^{-4} ; 4- 1×10^{-4} ;
 ---- solution to Eq.(25)

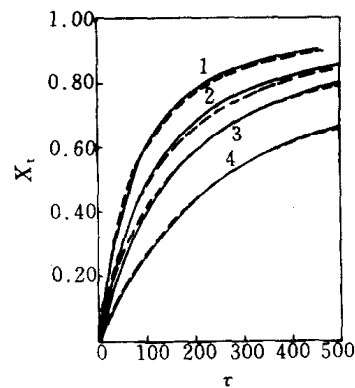


Figure 2 Comparison of numerical solution with approximate solution
 ($\alpha = 2$, $\gamma_g = 10$, $Sh = 1$, $f = 0.5$, $\delta_s = 0.01$)
 — numerical solution; ---- approximate solution
 1- $\lambda_B = 1$, $\gamma_K = 2$, $\gamma_C = 1$; 2- $\lambda_B = 0.5$, $\gamma_K = 2$, $\gamma_C = 1$;
 3- $\lambda_B = 5$, $\gamma_K = 1$, $\gamma_C = 0.1$; 4- $\lambda_B = 0.2$, $\gamma_K = 1$, $\gamma_C = 0.5$

Fig.2 shows the comparison of the results from numerical solution with approximate solution. It may be readily seen from the figure that they are in excellent agreement under all conditions. That is to say, Eq.(27) can give a satisfactory representation of the exact solution.

3.5 Criterion for process control

It is noted from the approximate solution [expressed by the Eq.(27)] that the time required for attaining a certain amount of sulfur capacity consists of three parts: the time under the control of external diffusion, the time under the control of internal diffusion and the time under the control of reaction kinetics. Apparently, the importance of each step may be readily evaluated by the relative values of the three time terms. Assuming that the step which contributes 95% of the time to the overall reaction time ($X_t=0.5$) is the controlling step, then we can readily draw the following conclusions.

When $\gamma_w < 0.25$, external diffusion may be negligible, and when $\gamma_s < 3$, internal diffusion may be negligible. But, when $\gamma_s \geq 1050$, the process is controlled by internal diffusion where

$$\gamma_w = \left(\frac{\gamma_C}{3\gamma_K Sh_B} + \frac{1}{3Sh_A} \right) / \left(\frac{1+\lambda_B}{\Phi_A^2 \lambda_B} \right), \quad \gamma_s = \left(\frac{1}{\beta_{A'}} + \frac{\gamma_C}{\gamma_K \beta_{A'}} \right) / \left(\frac{1+\lambda_B}{\Phi_A^2 \lambda_B} \right) \quad (28)$$

4 EFFECT OF OXYGEN CONCENTRATION ON THE DESULFURIZING PROCESS

Generally speaking, increases in oxygen concentration favor the desulfurizing rate. But it will lead to the problem of excess O_2 in the product gas. Moreover, the effect of increasing O_2 concentration on improving desulfurization rate is not very significant when $\lambda_B \gg 1$. Therefore, we expect to find a criterion for the optimization of the O_2 concentration.

As mentioned above, the desulfurization process is zero order with respect to O_2 when the O_2 concentration is excessively higher than the H_2S concentration. For this case, the process is independent of oxygen concentration. The lower the concentration of O_2 , the greater will be the effect of it on the process, and also the less the sulfur capacity will be. We here define the ratio of them as oxygen effect factor, which is denoted by ζ_0 .

$$\zeta_0 = W_t / W_{t,0} = \int_0^1 W_s \eta^2 d\eta / \int_0^1 W_{s,0} \eta^2 d\eta \quad (29)$$

where $W_{s,0}$ is the sulfur capacity when the process is independent of oxygen concentration. Accordingly, the value of ζ_0 reflects the extent of effect of O_2 concentration on the reaction.

Substituting Eq.(29) into Eq.(27) gives the expression of effective oxygen factor in relation to other variables as

$$\frac{X_t/\zeta_0}{3Sh_A} + \frac{1}{\Phi_A^2} \frac{X_t}{\zeta_0 - X_t} + \frac{1}{\beta_{A'}} \left[\frac{1}{2} - \frac{1}{3} X_t/\zeta_0 - \frac{1}{2} (1 - X_t/\zeta_0)^{2/3} \right] =$$

$$\left(\frac{\gamma_C}{3\gamma_K Sh_B} + \frac{1}{3Sh_A}\right)X_t + \frac{1+\lambda_B}{\Phi_A^2 \lambda_B} \frac{X_t}{1-X_t} + \frac{1+\gamma_C/\gamma_K}{\beta_A'} \left[\frac{1}{2} - \frac{1}{3}X_t - \frac{1}{2}(1-X_t)^{2/3}\right] \quad (30)$$

$$\left(\frac{\gamma_C}{3\gamma_K Sh_B} + \frac{1}{3Sh_A}\right)X_t + \frac{1+\lambda_B}{\Phi_A^2 \lambda_B} \frac{X_t}{1-X_t} + \frac{1+\gamma_C/\gamma_K}{\beta_A'} \left[\frac{1}{2} - \frac{1}{3}X_t - \frac{1}{2}(1-X_t)^{2/3}\right] \quad (30)$$

Variation in oxygen concentration would lead to changes in the values of γ_C and λ_B , and in turn influences value of ζ_0 . Figs. 3 and 4 are the relationships between oxygen effect factor ζ_0 with γ_C and λ_B respectively. It is noted that the effect of oxygen on the desulfurization process is greatest at the beginning of the reaction, and the effect of kinetic parameter γ_C is greater than that of the concentration parameter λ_B .

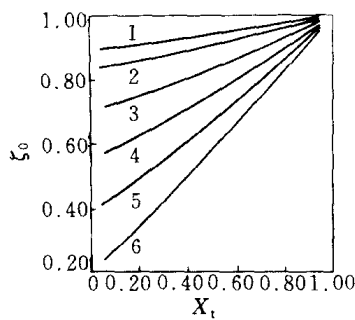


Figure 3 Effect of λ_B on ζ_0

($Sh_A=Sh_B=1$, $\beta_A'=1$, $\Phi_A=1$, $\gamma_K=1$, $\gamma_C=0.2$)
 λ_B : 1-10; 2-5; 3-2; 4-1; 5-0.5; 6-0.2

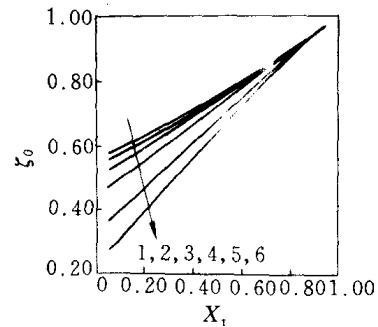


Figure 4 Effect of γ_C on ζ_0

($Sh_A=Sh_B=1$, $\beta_A'=1$, $\Phi_A=1$, $\gamma_K=1$, $\lambda_B=0.2$)
 γ_C : 1-0.2; 2-0.5; 3-1; 4-2; 5-5; 6-10

5 CONCLUSIONS

- (1) A desulfurization process can be described with quasi-steady state when $\beta_i'/\alpha_i > 0.005$.
- (2) External diffusion may be negligible when $\gamma_w < 0.25$.
- (3) Internal diffusion may be negligible when $\gamma_s < 3$, but when $\gamma_s \geq 1050$, the process is controlled by internal diffusion.
- (4) The effect of oxygen concentration on desulfurization process is most outstanding at the early stages of the reaction. The suitable O₂ concentration may be ascertained by the oxygen effect factor determined by Eq.(30).
- (5) Sulfur capacity within a single carbon pellet can be calculated through an approximate solution to Eq.(27).

NOMENCLATURE

$c_{i,0}$	initial concentration, mol · L ⁻¹
$c_{i,g}$	gas concentration, mol · L ⁻¹
$D_{i,g}$	gas effective diffusivity, cm ² · min ⁻¹
$D_{i,g}^0$	gas effective diffusivity without water film and elemental sulfur, cm ² · min ⁻¹ .
f	ratio of the volume fraction of water film to the total pore volume
$K_{H,i}$	Henry constant of gas-liquid equilibrium
k_1	reaction rate constant, ml · g ⁻¹ · min ⁻¹

k_2	adsorptive constant of O_2 , $L \cdot mol^{-1}$
$k_{f,i}$	coefficient of external mass transfer, $cm \cdot min^{-1}$
M_s	molecular weight of sulfur ($M_s=32$), $g \cdot mol^{-1}$
N	total number of difference point
R	radius variable, cm
R_p	radius of carbon particle, cm
r_i	reaction rate, $mmol \cdot g^{-1} \cdot min^{-1}$
Sh_i	Sherwood number ($Sh_i = k_{f,i} R_p / D_{i,g}^0$)
t	reaction time, min
W_s	mass of sulfur formation in one gram of activated carbon
$W_{s,\infty}$	maximum mass of sulfur formed in one gram of activated carbon
W_t	averaged sulfur capacity over the whole carbon pellet
X_i	dimensionless gas concentration
X_s, X_t	dimensionless sulfur capacity
$\alpha_i, \beta_i, \delta_s$	dimensionless variables defined by Eq.(8)
β	volume parameter of deposited sulfur
β_A'	parameter defined by Eq.(19b)
γ_K, γ_C	parameters defined by Eq.(8d)
γ_g	modified Thiele number ($\gamma_g = \Phi_A / \beta_A'$)
γ_w, γ_s	parameters defined by Eq. (28)
ϵ_p	porosity
ζ_0	effect factor of oxygen
η	dimensionless radius
η_c	dimensionless radius of reaction interface
λ_B	dimensionless parameter for adsorptive O_2
ρ_l	density of impregnated carbon, $g \cdot ml^{-1}$
τ	dimensionless time
Φ_A	Thiele number ($\Phi_A = R_p \sqrt{\rho k_1 W_{s,\infty} / D_{A,g}^0}$)

Subscripts

A	hydrogen sulfide
B	oxygen
g	gas phase
i	A or B
j	serial number of difference point
L	liquid phase
S	sulfur

REFERENCES

- 1 Ghosh, T. K. and Tollefson, E. L., *Can. J. Chem. Eng.*, **64** (6), 960 (1986).
- 2 Sreeramamurthy, R. and Menon, P.G., *J. Cat.*, **37**(2), 287 (1975).
- 3 Steijns, M. and Mars, P., *Ind. Eng. Chem. Prod. Res. Dev.*, **16**(1), 35 (1977).
- 4 Coskun, I. and Tollefson, E. L., *Can. J. Chem. Eng.*, **58**(1), 72 (1980).
- 5 Hiroshi Ikeda, Hideki Asaba and Yasushi Takeuchi, *J. Chem. Eng. Jap.*, **21**(1), 91 (1988).
- 6 Turk, A., Sakalls, E. and Lessuck, J., *et al.*, *Environ. Sci. Technol.*, **23**(10), 1242 (1989).
- 7 Tan X. Y., Ph D. thesis, Dalian Institute of Chemical Physics, Academia Sinica, Dalian (1995).
- 8 Sohn, H. Y. and Szekely, J., *Chem. Eng. Sci.*, **29**(2), 630 (1974).
- 9 Sohn, H. Y. and Szekely, J., *Chem. Eng. Sci.*, **27**(4), 763 (1972).