Benzaldehyde Oxidation Catalyzed by the Wall of a Tubular Bubble Column Reactor

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The development of a tubular wall reactor using a heterogenized homogeneous catalyst was reported in a previous paper (Kuo and Chou, 1987). In this study, the characteristics and mathematical modeling of a heterogenized homogeneous catalytic reaction in a continuous tubular wall bubble column are developed and compared with the experimental data.

In the past few years, many investigations concerning the mathematical simulation of reactions occurring heterogeneously or homogeneously have been reported (Dang, 1983). Numerous researchers (Solomon and Hudson, 1967; Nigam, 1982; Lawrence and Shaeiwitz, 1983) analytically or experimentally considered the first- and second-order reactions of heterogeneous or homogeneous reaction systems in tubular reactors. Oxidation of aldehydes using a heterogenized homogeneous catalyst is usually a series of free radical reactions that are initiated by the free radicals, which are in turn initiated at the surface of the heterogenized homogeneous catalyst. Then, the free radical diffuses to the bulk solution where propagation and termination reactions occur (Kuo and Chou, 1987; Chou and Lee, 1985; Hwang and Chou, 1987). It is of interest to investigate this type of reaction in a continuous process.

Bubble column reactors have been widely used in the chemical industry (Danckwerts, 1970; Saunby and Kiff, 1976). Usually, the reactors proposed have different shapes, such as a tubular column, a mechanically agitated column, a spray column, and so on (Schumpe et al., 1979; Laurent and Charpentier, 1983; Sharma, 1983; Darde et al., 1985). Tubular bubble column reactors require a relatively complex model to describe the changes in the concentrations of the species. The compartment model and the dispersion flow model are two models usually proposed to describe this reactor (Wen and Fan, 1975). It is generally accepted that two-phase dispersion models adequately describe the flow dynamics, axial mixing, and transport phenomena in a tubular contactor (Shioya et al., 1978; Hagberg and Krupa, 1975). In recent years a number of studies and reviews have been made on hydrodynamics in aqueous and organic systems (Shah et al., 1982, 1985; Godbole et al., 1984; Charpentier, 1981). There are few studies concerning the hydrodynamic characteristics of the oxygen-acetone system in the homogeneous flow regime, which is one of the purposes of this paper.

A plug-flow model with radial and axial dispersion was developed to simulate the design of the continuous process of the tubular wall bubble column that is lined with heterogenized homogeneous catalyst. The model is presented below, and experimental results are correlated with the theoretical analysis.

Experimental Procedure

The experimental runs were carried out in a glass bubble column lined with a Co-type ion exchange membrane as catalyst (Kuo and Chou, 1987). The column was a double pipe as shown in Figure 1a. The inner tube of the column was a 2.7 cm in dia. and 135 cm in height, with a glass sintered disperser at the bottom of the tube. Eight sample ports were drilled through the wall of the inner tube at a series of 15 cm intervals from the bottom to the top of the tube for sampling and injecting or receiving dye tracer. Two pressure taps were made to measure the liquid height and were needed to calculate gas holdup. The annulus space between inner and outer tubes was filled with circulating water at constant temperature to keep the reaction isothermal. This column is the tubular reactor, *D*, in the overall set-up shown in Figure 1b.

The relative gas holdup in the liquid was determined using a manometric method. Measurement of the axial dispersion coefficient was made as follows. At the beginning of a run, the acetone solution, which contained a small amount of benzaldehyde and oxygen, was fed and adjusted at a desired flow rate. When the flow was at steady state, an impulse signal of 1 mL of dye tracer was injected from sampling port 5 in each run. Immediately the (LDC/Milton) UV/VIS detector with a recorder was started and operated until a complete response curve of sampling port 6 was obtained.

To carry out the runs of benzaldehyde oxidation, a sample

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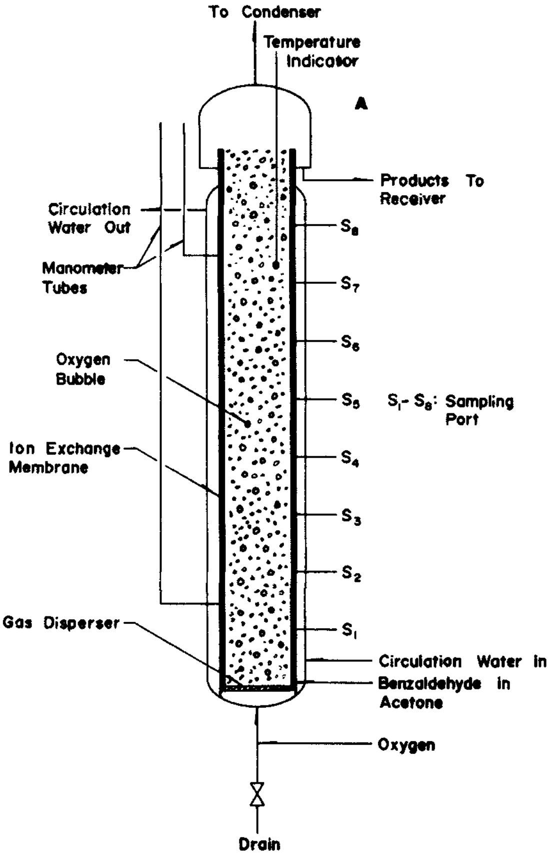


Figure 1a. Details of tubular wall bubble column.

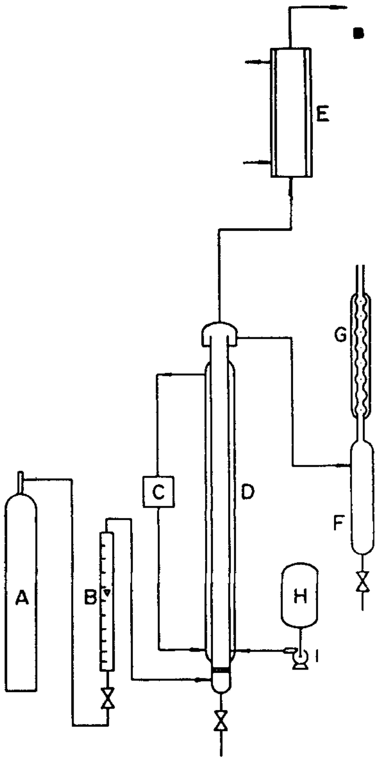


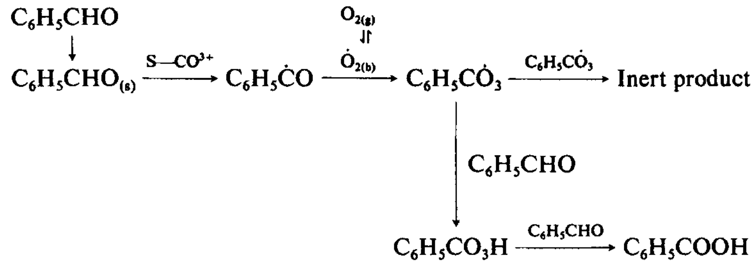
Figure 1b. Experimental set-up.

A. Oxygen cylinder	F. Product receiver
B. Gas flowmeter	G. Condenser
C. Thermostat	H. Feed tank
D. Tubular reactor	I. Metering pump
E. Overhead condenser	T. Temperature indicator

was periodically taken and analyzed until the concentration of perbenzoic acid was found to be constant. Then, samples were taken from the sampling ports along the axial direction of the bubble reactor. The method of analysis of samples was reported in a previous paper (Kuo and Chou, 1987).

Theoretical Analysis

The oxidation of benzaldehyde to form perbenzoic acid and benzoic acid using heterogenized homogeneous cobalt ion as catalyst in a semibatch tubular wall reactor has been studied by Kuo and Chou (1987). The main reaction scheme is as follows:



$$\begin{tikzcd}
C_6H_5CHO \arrow[d] & & & \\
C_6H_5CHO_{(s)} \arrow[r, "S—CO^{3+}"] & C_6H_5\dot{C}O \arrow[r, "\overset{O_{2(g)}}{\overset{\rightleftharpoons}{\dot{O}_{2(b)}}}"] & C_6H_5C\dot{O}_3 \arrow[r, "C_6H_5C\dot{O}_3"] \arrow[d, "C_6H_5CHO"] & \text{Inert product} \\
 & & C_6H_5CO_3H \arrow[r, "C_6H_5CHO"] & C_6H_5COOH
\end{tikzcd}$$

where (s), (g), and (b) respectively denote solid phase, gas phase, and bulk solution.

Since the reaction of free radical $C_6H_5\dot{C}O$ with O_2 to form free radical $C_6H_5C\dot{O}_3$ is very rapid, the free radical $C_6H_5C\dot{O}_3$ is dominant in the bulk solution. The reaction steps of benzaldehyde oxidation as shown in the above scheme can be reduced to the following five major reactions:

$$C_6H_5CHO_{(s)} + S—Co^{3+} \xrightarrow{k_i} C_6H_5\dot{C}O + S—Co^{2+} + H^+ \quad (1)$$

$$C_6H_5\dot{C}O + O_{2(b)} \xrightarrow{k_g} C_6H_5C\dot{O}_3 \quad (2)$$

$$C_6H_5C\dot{O}_3 + C_6H_5CHO \xrightarrow{k_p} C_6H_5CO_3H + C_6H_5\dot{C}O \quad (3)$$

$$C_6H_5CO_3H + C_6H_5CHO \xrightarrow{k_c} 2\,C_6H_5COOH \quad (4)$$

$$C_6H_5C\dot{O}_3 + C_6H_5C\dot{O}_3 \xrightarrow{k_t} \text{inert products} \quad (5)$$

Based on the dispersion model (Parulekar and Ramkrishna, 1984), the oxidation of benzaldehyde in a tubular bubble column with complete mixing in the radial direction and at steady state can be expressed in dimensionless form:

$$1/Pe\, d^2C_b/dZ^2 - dC_b/dZ - \epsilon_l S(k_pC_fC_b + k_cC_pC_b) = 0 \quad (6)$$

$$1/Pe\, d^2C_p/dZ^2 - dC_p/dZ + \epsilon_l S(k_pC_fC_b - k_cC_pC_b) = 0 \quad (7)$$

$$1/Pe\, d^2C_a/dZ^2 - dC_a/dZ + \epsilon_l S(k_cC_pC_b) = 0 \quad (8)$$

The boundary conditions are

$$C_{bo} = C_b(0) - 1/Pe(dC_b/dZ)_o \quad (9)$$

$$C_p(0) = 1/Pe(dC_p/dZ)_o \quad (10)$$

$$C_a(0) = 1/Pe(dC_a/dZ)_o \quad (11)$$

$$(dC_b/dZ)_1 = (dC_p/dZ)_1 = (dC_a/dZ)_1 = 0 \quad (12)$$

where

$$C_b = c_b/c_{bo} \qquad Z = z/L$$

$$C_f = c_f/c_{bo} \qquad S = c_{bo}L/U$$

$$C_p = c_p/c_{bo} \qquad Pe = UL_o/De$$

$$C_a = c_a/c_{bo}$$

The terms c_b, c_p, c_f, and c_a are the concentrations of benzaldehyde, perbenzoic acid, perbenzoyl free radical, and benzoic acid, respectively. c_{bo} indicates the initial concentration of benzaldehyde.

Substituting the termination rate of free radical $C_6H_5\dot{C}O_3$, $2k_t\,[C_6H_5\dot{C}O_3]^2$, occurring in the bulk solution, the dispersion of free radical $C_6H_5\dot{C}O_3$ in the tubular bubble column becomes

$$Dr(d^2C_f/dR^2 + 1/R\, dC_f/dR) + (2Ro^2k_tc_{bo}C_f^2) = 0 \quad (13)$$

with the following boundary conditions:

$$(C_f)_1 = C_{fs} \quad (14)$$

$$(dC_f/dR)_o = 0 \quad (15)$$

where $C_{fs} = c_{fs}/c_{bo}$. c_f and c_{fs} indicate the concentration of free radical $C_6H_5\dot{C}O_3$ in the bulk solution and on the surface of the wall of tubular reactor, respectively.

To obtain the concentration profile of perbenzoic acid C_p in the reactor, Eq. 7 should be solved. Since Eq. 7 contains parameters ϵ_l and Pe, rate constants k_c and k_p, and concentration variables C_f and C_b, solving Eqs. 6, 7, and 13 with the boundary conditions given by Eqs. 9, 10, 12, 14, and 15 is necessary.

Results and Discussion

The relationship between gas holdup and superficial gas velocity in pure acetone or in a solution of benzaldehyde dissolved in acetone was found to be as shown in Figure 2. The results indicate that the gas holdup varies almost linearly with gas flow velocity. The gas holdup in acetone solvent is smaller than that in 1.0M or 2.0M benzaldehyde in acetone solution when the gas velocity is above 38 cm/min. Increasing the concentration of benzaldehyde results in an increase of the gas holdup at a fixed gas flow velocity. For a glass sintered disperser employed with 1.0M benzaldehyde in acetone solution, from the experimental data for the covered range of gas velocity, 10.50 to 110.04 cm/min, the gas holdup could be described by the term $0.100 \times U_g^{1.24}$.

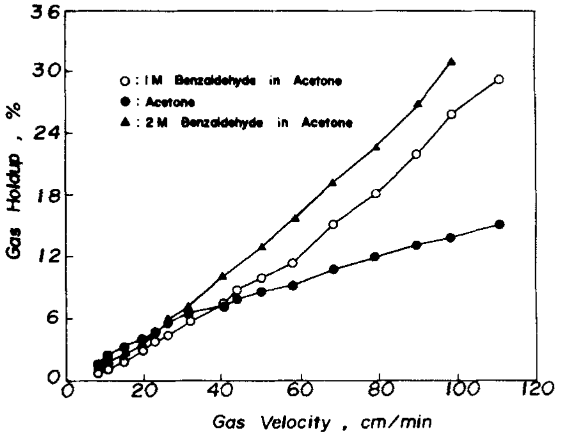


Figure 2. Gas holdup v. superficial gas velocity.

Figure 3 presents the results concerning the axial dispersion coefficient De in the bubble column, which is calculated by the method reported by Levenspeil and Smith (1957). Increasing the gas flow velocity from 7.86 to 55.89 cm/min causes the axial dispersion coefficient to increase from 21.93 to 41.07 cm²/min. It was also found that the effect of the liquid flow velocity in the range from 1.013 to 1.345 cm/min on the dispersion coefficient was insignificant.

To calculate the concentration profile of free radical $C_6H_5\dot{C}O_3$, some of the data and parameters for the calculation are evaluated based on the reports of Maslov and Blyumberg (1976) and Eissa et al. (1971). Figure 4 shows a typical calculation resulting from the concentration profile of the free radical in the radial direction. It is a parabolic profile and reveals a sharply increasing concentration of free radical $C_6H_5\dot{C}O_3$ from nearly zero to 2.64×10^{-6}M when the distance increases from the center of the tube to the surface of the tubular wall. This is reasonable since the free radical initiated on the surface of the tubular wall and is mainly terminated by the bimolecular termination in the bulk solution.

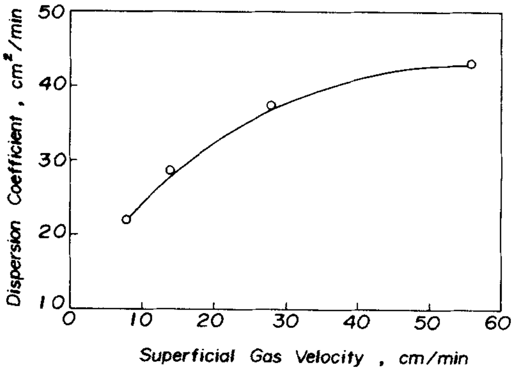


Figure 3. Axial dispersion coefficient v. superficial gas velocity.

Trace benzaldehyde in acetone solution; temp. 15°C

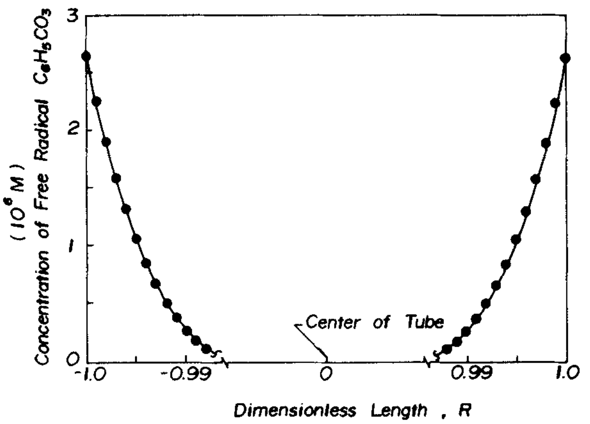


Figure 4. Radial concentration profile of free radical $C_6H_5\dot{C}O_3$ with $k_tR_o^2/Dr = 2.96 \times 10^{10}$; temp. 15°C.

As shown in Figure 5, increasing the concentration of benzaldehyde from 1.0 to 2.0M increased the concentration of perbenzoic acid from 0.401 to 0.850M at a fixed space-time point $z/L = 1.0$. The concentration of perbenzoic acid increases along the axis of reactor. The calculated concentration profile of perbenzoic acid along the axial direction correlates well with the experimental results for 1.0M benzaldehyde solution as shown in Figure 5. The curves also show that experimental results are higher than the theoretical results for a 2.0M benzaldehyde feed stream. This is possibly due to the rapid reaction and the inefficient removal of the heat of reaction, since the experimental result reveals that the highest temperature occurs at the middle of the reactor. At the top of the reactor, the reactions slow down and the heat generated becomes less, and a better correlation is obtained.

A liquid flow velocity increasing from 1.01 to 1.35 cm/min resulted in a decrease of the concentration of perbenzoic acid from 0.51 to 0.43M at the outlet of the reactor, as shown in Figure 6. The comparison of the experimental results with the theoretical aspects indicate that a good match was found. However, a deviation occurs when the liquid flow velocity is 1.35 cm/min.

The concentration profiles of perbenzoic acid along the axis of the reactor at gas flow rates of 13.97, 27.94, and 55.89 cm/min are as shown in Figure 7. Both the theoretical calculations and the experimental results show that the effect of gas flow velocity on the concentration distribution of perbenzoic acid along the reactor axis is insignificant. This indicates that the reaction is in the regime of kinetic control.

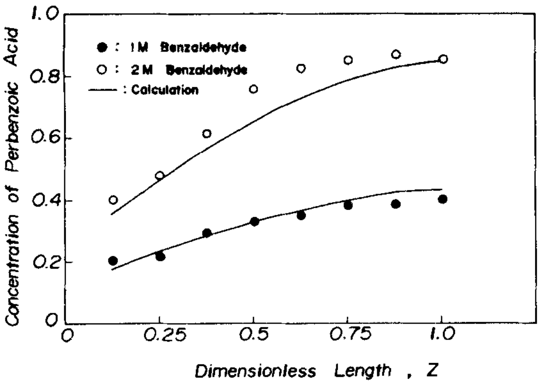


Figure 5. Concentration profiles of perbenzoic acid along axis at various concentrations of benzaldehyde.

Liquid velocity, 1.35 cm/min; oxygen velocity, 55.89 cm/min

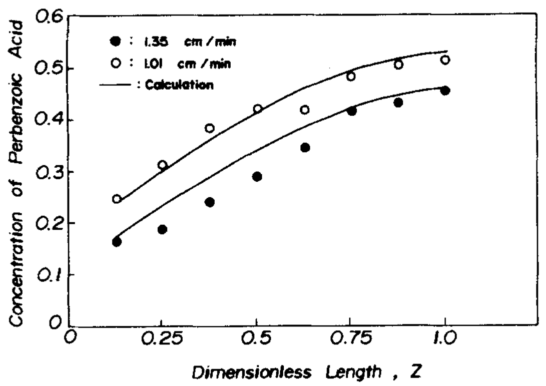


Figure 6. Concentration profiles of perbenzoic acid along axis at various liquid flow velocities.

Benzaldehyde, 1.0M; oxygen velocity, 27.94 cm/min

The summary in Table 1 compares experimental results with theoretical calculations at various space-time points. These results indicate that the experimental results correlate well with the theoretical calculations. There are still some deviations pres-

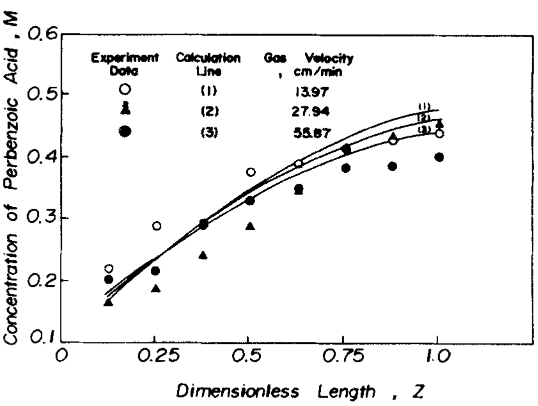


Figure 7. Concentration profiles of perbenzoic acid along axis at various gas flow velocities.

Benzaldehyde, 1.0M; liquid velocity, 1.35 cm/min

Table 1. Comparison of Experimental Data with Calculated Theoretical Results

Parameters			Concentration Distribution of Perbenzoic Acid Along Axial Direction, M					
			Exp.			Theory		
c_b M	U_l cm/min	U_g cm/min	0.25*	0.5	0.75	0.25	0.5	0.75
2	1.35	55.89	0.481	0.756	0.849	0.468	0.652	0.790
1	1.35	55.89	0.215	0.329	0.382	0.233	0.330	0.403
1	1.35	27.94	0.186	0.288	0.431	0.235	0.340	0.421
1	1.01	27.94	0.310	0.418	0.482	0.303	0.414	0.494
1	1.35	13.97	0.288	0.376	0.413	0.233	0.345	0.432

*0.25, 0.5, 0.75 = dimensionless length of reactor in axial direction ent between the theoretical and experimental results for the concentration profiles of perbenzoic acid. These deviations are possibly due to the hydrodynamic data, which were obtained in the system without reaction and which could have been a little different from those in the system with reaction.

Acknowledgment

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Notation

C = dimensionless concentration of component
c = concentration of component, M
Dc = column diameter, cm
De = axial dispersion coefficient, cm^2/min
Dr = radial dispersion coefficient, cm^2/min
K,k = reaction rate constants, $M^{-1} \cdot min^{-1}$
L = reactor length, cm
Lo = dispersion length, cm
Pe = Peclet number
r = rate of reaction, $M^{-1} \cdot min^{-1}$
R = dimensionless length of radial direction, r/Ro
Ro = radius of reactor, cm
$S{-}Co^{3+}$ = heterogenized Co^{3+} of active surface area, cm^2
$S{-}Co^{2+}$ = heterogenized Co^{2+} of active surface area, cm^2
t = reaction time, min
T = temperature, K
U = superficial velocity of fluid, cm/min
z = position of axial direction, cm
Z = dimensionless length of axial direction
ϵ = holdup of fluid, %

Subscripts

a = benzoic acid
b = bulk solution; benzaldehyde
f = free radical, $C_6H_5C\dot{O}_3$
fs = free radical $C_6H_5C\dot{O}_3$ on the surface of tubular wall
g = gas phase
i = component
l = liquid phase
L = length of reactor, cm
o = starting point of column
p = propagation; perbenzoic acid
s = solid phase

Literature Cited

Charpentier, J. C., "General Characteristics of Multiphase Gas-Liquid Reactors: Hydrodynamics and Mass Transfer," *Proc. NATO Advanced Study Inst.*, Sijthoff and Noordhoff, Netherlands, 157 (1981).

Chou, T. C., and C. C. Lee, "Heterogenizing Homogeneous Catalyst. 1: Oxidation of Acetaldehyde," *Ind. Eng. Chem. Fundam.*, **24**, 32 (1985).

Danckwerts, P. V., *Gas-Liquid Reactions*, McGraw-Hill, New York (1970).

Dang, V. D., "Steady-state Mass Transfer with Homogeneous and Heterogeneous Reactions," *Chem. Eng. Sci.*, **29**, 19 (1983).

Darde, T., N. Midoux, and J. S. Charpentier, "Complex Gas-Liquid Reactions: A Contribution to the Search for a Modeling Tool and for the Prediction of Selectivity," *Int. Chem. Eng.*, **25**, 67 (1985).

Eissa, S. H., M. M. El-Haiwagi, and M. A. Saleh, "Axial and Radial Mixing in a Cocurrent Bubble Column," *Ind. Eng. Chem. Process Des. Dev.*, **10** (1), 31 (1971).

Godbole, S. P., S. Joseph, Y. T. Shah, and N. L. Carr., "Hydrodynamics and Mass Transfer in a Bubble Column with an Organic Liquid," *Canad. J. Chem. Eng.*, **62**, 440 (1984).

Hagberg, C. G., and F. X. Krupa, "A Mathematical Model for Bubble Column Reactors and Application of It to Improve a Cumene Oxidation Process," *Int. Chem. Eng. Symp. XI*, 408 (1975).

Hwang, B. J., and T. C. Chou, "Heterogenizing Homogeneous Catalyst. 2: Effect of Particle Size and Two-phase Mixed Kinetic Model," *Ind. Eng. Chem. Res.*, **27**, 1132 (1987).

Kuo, M. C., and T. C. Chou, "Heterogenized homogeneous Catalyst. 3: Oxidation of Benzaldehyde in a Semibatch Tubular Wall Reactor," *Ind. Eng. Chem. Res.*, **26**, 1140 (1987).

Laurent, A., and J. C. Charpentier, "The Use of Experimental Laboratory-Scale Models in Predicting the Performance of Gas-Liquid Reactors," *Int. Chem. Eng.*, **23**, 265 (1983).

Levenspeil, O., and W. K. Smith, "Notes on the Diffusion-type Model for the Longitudinal Mixing of Fluids of Flow," *Chem. Eng. Sci.*, **6**, 227 (1957).

Lawrence, R. S., and J. A. Shaeiwitz, "Mass Transfer with Heterogeneous and First-order Homogeneous Reaction Using the Film Theory," *Chem. Eng. Sci.*, **38**, 635 (1983).

Maslov, S. A., and E. A. Blyumberg, "Liquid-phase Oxidation of Aldehyde," *Russ. Chem. Rev.*, **45**(2), 303 (1976).

Nigam, K. M., "Homogeneous-Heterogeneous Reactions in a Tubular Reactor: An Analytical Solution," *Chem. Eng. J.*, **25**, 147 (1982).

Parulekar, S. J., and D. Ramkrishna, "Analysis of Axially Dispersed System with General Boundary Conditions. I: Formulation," *Chem. Eng. Sci.*, **39** (11), 1571 (1984).

Saunby, J. B., and B. W. Kiff, "Liquid-phase Oxidation—Hydrocarbons to Petrochemical," *Hydro. Proc.*, 247 (Nov., 1976).

Schumpe, A., Y. Serpemen, and W. D. Decker, "Effective Use of Bubble Column Reactors," *Ger. Chem. Eng.*, **2**, 234 (1979).

Shah, Y. T., S. Joseph, D. N. Smith, and J. A. Ruether, "On the Behavior of the Gas Phase in a Bubble Column with Ethanol-Water Mixtures," *Ind. Eng. Chem. Process Des. Dev.*, **24**, 1140 (1985).

Shah, Y. T., B. G. Kelkar, S. P. Godbole, and W. D. Decker, "Design Parameters Estimations for Bubble Column Reactors," *AIChE J.*, **28**, 353 (1982).

Sharma, M. M., "Perspectives in Gas-Liquid Reactions," *Chem. Eng. Sci.*, **38**, 21 (1983).

Shioya, S., N. D. P. Dang, and I. J. Dunn, "Bubble Column Fermenter Modeling: A Comparison for Pressure Effects," *Chem. Eng. Sci.*, **33**, 1025 (1978).

Solomon, R. L., and J. L. Hudson, "Heterogeneous and Homogeneous Reactions in a Tubular Reactor," *AIChE J.*, **13**, 545 (1967).

Wen, C. Y., and L. T. Fan, *Models for Flow Systems and Chemical Reactors*, Marcel Dekker, New York (1975).

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