C_1 = $C_G/\bar{C}_G^o$, normalized concentration in the gas phase
C_2 = $m_1 C_L/\bar{C}_G^o$, normalized concentration in the liquid phase
C_3 = $m_1 C_S/\bar{C}_G^o$, normalized concentration on the surface of the particles
$\bar{C}_G^o$ = concentration of the diffusing component in the entering gas phase, gmol·cm^{-3}
D = axial dispersion coefficient, cm^2·s^{-1}
d_p = diameter of the particles, cm
d_T = reactor diameter, cm
E_i = defined in the Appendix
Fr = $v_G/(gd_T)^{1/2}$, Froude number
f = $w/(W\tau)$, normalized concentration of the particles
g = acceleration due to gravity, cm^2·s^{-1}
H = Henry's law constant, cm^3·atm·gmol^{-1}
J = column vector defined in the Appendix
k = mass transfer coefficient, cm·s^{-1}
k_1 = surface reaction rate constant, cm·s^{-1}
L = length of the reactor, cm
M_1 = $k_c a_w W L \tau/U_G$
m_1 = H/RT
N_1 = $k_a a L/U_G$
Pe_G = $U_G L/D_G$, Peclet number of the gas phase
Pe_{GL} = $U_G L/D_P$
Pe_P = $U_S L/D_P$, Peclet number of the particles
Q = $k_1 a_w W L \tau/U_G$
R = gas constant, cm^3·atm·gmol^{-1}·deg^{-1}
Re = $d_P U_t \rho_L/\mu_L$, particle Reynolds number
S = defined by Eq. 14
T = temperature, K
U_G = bubble rise velocity, cm·s^{-1}
U_S = mean settling velocity of the particles, cm·s^{-1}
U_t = particle terminal velocity, cm·s^{-1}
V_i = defined in the Appendix
v_G = superficial velocity of the gas, cm·s^{-1}
W = catalyst loading, g·cm^{-3}
W_L = catalyst loading, g/L of the reactor
w = concentration of the particles, g·cm^{-3}
X = gas phase conversion
X_i = defined by Eq. 10
y = vector $[y_1 y_2 y_3 y_4]^T$
y_i = ith element of the vector y
Z = z/L, normalized height from the bottom of the column
z = height from the bottom of the column, cm

Greek Letters

α = variable of the indicial equation
α_1, α_2, α_3 and α_4 = indicial roots defined by Eq. 8
ϵ = fractional gas holdup
μ_L = viscosity of the liquid, cP
ρ = density, g·cm^{-3}
τ = $(U_S L/D_P)[1 - \exp(-U_S L/D_P)]^{-1}$
ϕ = $\epsilon/(1 - \epsilon)$

Subscripts

0 = at Z = 0
a = gas-liquid
c = fluid-particle
G = gas-phase
L = liquid phase
P = particle
S = particle surface

LITERATURE CITED

Chaudhari, R. V., and P. A. Ramachandran, "Three Phase Slurry Reactors," *AIChE J.*, **26**, 177 (1980).

Deckwer, W. D., Y. Serpeman, M. Ralek, and B. Schmidt, "Modelling the Fischer-Tropsch Synthesis in the Slurry Phase," *Ind. Eng. Chem. Process Des. Dev.*, **21**, 231 (1982).

Govindararo, V. M. H., "On Dynamics of Bubble Column Slurry Reactors," *Chem. Eng. J.*, **9**, 229 (1975a).

———, "Analog Simulation of an Isothermal Semibatch Bubble Column Slurry Reactor," *Ann. Asso. Int. Calc. Analogique.*, **2**, 69 (1975b).

Hammer, H., "Bubble Column Reactors with Suspended Solids: Fundamentals, Design and Uses," *Int. Chem. Eng.*, **21**, 173 (1981).

Imafuku, K., T. Wang, K. Koide, and H. Kuboda, "The Behaviour of Suspended Solid Particles in the Bubble Column," *J. Chem. Eng. Japan*, **1**, 153 (1968).

Kaplan, W., *Operational Methods for Linear Systems*, Addison-Wesley Pub. Co., 456 (1962).

Kato, Y., A. Nishiwaki, T. Fukuda, and S. Tanaka, "The Behaviour of Suspended Solid Particles and Liquid in Bubble Columns," *J. Chem. Eng. Japan.*, **5**, 112 (1972).

Østergaard, K., "Gas-Liquid-Particle Operations in Chemical Reaction Engineering," *Adv. Chem. Eng.*, **7**, 71 (1968).

Shah, Y. T., *Gas-Liquid-Solid Reactor Design*, McGraw-Hill, ABP (1979).

Manuscript received October 5, 1982; revision received February 8, and accepted February 28, 1983.

Use of Packed Rectification Columns in Extractive Distillation

LLOYD BERG,
P. RATANAPUPECH, and
A. I. YEH

Department of Chemical Engineering
Montana State University
Bozeman, MT

Can extractive distillation be carried out in a packed rectification column or must it always be done in plate columns. To answer this question, four different packings were evaluated with ten different extractive distillation agents in the separation of ethyl acetate from the ethyl acetate-ethanol-water mixture and compared with a perforated plate column. The results showed that the packed columns were not quite as efficient as the plate column and that they ranked in the order: glass helices, Berl saddles, Intalox saddles, and glass Raschig rings.

TABLE 1. AZEOTROPIC PROPERTIES OF THE ETHYL ACETATE–ETHANOL–WATER SYSTEM

Compound	Compound B.P., °C	Azeo. B.P. °C	Azeotrope Composition
Ethyl Acetate	77.15		
Ethanol	78.3		
Water	100		
Ethyl Acetate–Water		70.38	8.5% water
Ethanol-Water		78.17	4% water
Ethyl Acetate–Ethanol		77.05	69% EtAc
Ethyl Acetate–Ethanol–Water		70.23	82.6% EtAc, 8.4% EtOH, 9% H_2O

TABLE 2. RELATIVE VOLATILITIES WITH SEVERAL COLUMN PACKINGS

Extractive Distillation Agent(s)	Column Packing Perforated Plates	Berl Saddles	Glass Helices	Rashig Rings	Intalox Saddles
1,5-Pentanediol	3.19	2.08	2.32	2.08	2.02
Propylene glycol	2.82	2.50	2.17	2.03	2.12
Dimethylsulfoxide	2.71	2.67	2.58	2.35	2.24
Triethylene Glycol	2.74	2.01	1.87	1.66	1.84
25% Tetraethylene glycol 25% Dimethylsulfoxide 25% 1,5-Pentanediol 25% Diethylene Glycol	2.40	1.92	—	—	1.94
50% Tetraethylene Glycol 50% Dimethylsulfoxide	2.36	2.32	2.55	1.87	2.09
Tetraethylene Glycol	2.30	1.87	1.97	1.69	1.84
50% Polyethylene Glycol 300 50% Triethylene Glycol	2.27	1.79	—	—	1.65
33.3% Polyethylene Glycol 300 33.3% Dimethylsulfoxide 33.3% Propylene Glycol	2.15	2.12	2.27	1.79	2.07
Hexylene Glycol	2.14	2.02	1.82	1.54	1.65
Calibrated Number of Plates	4.5	3.1	2.5	3.2	3.9

INTRODUCTION

Although extractive distillation has been employed for more than 60 years, still there is much to be learned. In 1923, Schneible described the use of glycerol as the extractive agent in the dehydration of ethanol. Three decades later, Drout (1952) described the use of glycols, and Smith (1951) patented glycol ethers for this purpose. The discovery of suitable extractive distillation agents is usually done in vapor-liquid equilibrium stills and commercial adaptation into bubble cap columns follows if the separation is attractive. It became a state of the art that extractive distillation did not work in packed columns and it is limited to plate columns. As recently as 1980, a patent examiner insisted that this limitation be included in the claims (Berg, 1981).

The purpose of this investigation was to determine whether extractive distillation could effectively be carried out in packed columns as well as in plate columns and to obtain some comparative data on several different types of packing.

EXPERIMENTAL

The separation of ethyl acetate from the ethyl acetate–ethanol–water azeotrope by extractive distillation was selected. This is a complex system with three binary and one ternary azeotrope, Table 1, but its separation is of some commercial importance. The composition of this azeotrope is 82.6 wt. % ethyl acetate, 8.4 wt. % ethanol and 9 wt. % water. With no extractive distillation agent, rectification will not separate these three and the relative volatility of the vapor to the liquid is one. A series of runs were made with ten different extrctive distillation agents in a perforated plate column and with four different column packing materials.

The plate column comprised six 3.8 cm diameter perforated Pyrex glass plates in a vacuum jacket. The column for the 1.27 cm porcelain Berl saddles and the 1.27 cm porcelain Intalox saddles was 61 cm long and 2.9 cm I.D. The column for the 0.7 cm Pyrex glass helices and the 6 × 6 mm flint glass Raschig rings was 22.9 cm long and 1.9 cm I.D. The actual plates in each column were determined with ethyl benzene–m-xylene as a test mixture. A run consisted of charging the ethyl acetate–ethanol–water mixture to the stillpot and boiling at total reflux for about an hour. The feed pump was then started and the extractive distillation agent at about 80–

TABLE 3. EXPERIMENTAL DATA FOR COLUMN PACKINGS

Perforated Plate Column

Extractive Agent		Time h	Bottoms wt. % EtOH	wt. % EtAc	Overhead wt. % EtOH	wt. % EtAc	Rel. Vol.
25% Tetraethylene Glycol 25% DMSO 25% 1,5-Pentanediol 25% Diethylene Glycol		1	82.50	17.50	9.35	90.65	2.34
		1.5	82.19	17.87	7.69	92.31	2.44
		2	81.82	18.18	7.89	92.11	2.41
50% Polyethylene Glycol 300 50% Triethylene Glycol		1	84.62	15.38	13.04	86.96	2.23
		1.5	86.30	13.70	13.10	86.90	2.29
		2	86.21	13.79	13.04	86.96	2.29
1,5-Pentanediol	Run #1	1	65.00	35.00	1.71	98.29	2.82
		1.5	64.72	35.28	99.16	3.30	
	Run #2	1	64.00	36.00	0.96	99.04	3.18
		1.5	67.05	32.95	0.89	99.1	3.33
	Run #3	1	70.65	29.35	1.07	98.93	3.32
		1.5	69.59	30.41	0.83	99.17	3.48
	Run #4	1	73.64	26.36	2.31	97.69	2.89
		1.5	74.88	25.12	1.66	98.34	3.16
Dimethylsulfoxide	Run #1	1	13.48	86.52	0.18	99.82	2.69
		11.5	14.24	85.76	0.17	99.83	2.77
	Run #2	1	57.61	42.39	1.39	98.61	2.76
		1.5	58.97	41.03	1.83	98.17	2.63
Tetraethylene Glycol	Run #1	1	77.01	22.99	8.65	91.35	2.21
		1.5	79.17	20.83	7.62	92.38	2.34
	Run #2	1	78.87	21.13	6.94	93.06	2.39
		1.5	79.12	20.88	8.65	91.35	2.27
Propylene Glycol	Run #1	1	54.48	45.52	1.22	98.78	2.76
		1.5	50.00	50.00	0.72	99.28	2.99

TABLE 3. *(Continued)*

Perforated Plate Column

			Bottoms		Overhead		
Extractive Agent		Time h	wt. % EtOH	wt. % EtAc	wt. % EtOH	wt. % EtAc	Rel. Vol.
	Run #2	1	54.00	46.00	1.75	98.25	2.54
		1.5	61.98	38.02	1.19	98.81	2.98
50% Tetraethylene Glycol		1	80.65	19.35	8.14	91.86	2.35
50% Dimethylsulfoxide		1.5	82.93	17.07	9.64	90.36	2.34
		2	80.65	19.35	7.80	92.20	2.38
33% Polyethylene Glycol 300		1	80.43	19.57	12.86	87.14	2.09
33% Dimethylsulfoxide		1.5	83.45	16.55	12.50	87.50	2.21
33% Propylene Glycol		2	85.06	14.94	15.15	84.85	2.16
Triethylene Glycol	Run #1	1	75.91	24.09	2.86	97.14	2.83
		1.5	75.40	24.60	2.97	97.03	2.78
	Run #2	1	77.26	22.74	3.84	96.16	2.68
		1.5	75.84	24.16	3.61	96.39	2.67
Hexylene Glycol	Run #1	1	73.53	26.47	7.65	92.35	2.18
		1.5	74.75	25.25	8.25	91.75	2.17
	Run #2	1	75.34	24.66	8.72	91.28	2.16
		1.5	75.00	25.00	10.66	89.34	2.05
Column Packed with Berl Saddles							
25% Tetraethylene Glycol		1	79.58	20.42	36.08	63.92	1.86
25% Dimethylsulfoxide		1.5	80.00	20.00	33.92	66.08	1.94
25% 1,5-Pentanediol		2	80.00	20.00	32.89	67.11	1.97
25% Diethylene Glycol							
50% Polyethylene Glycol 300		1	81.69	18.31	42.31	57.69	1.79
50% Triethylene Glycol		1.5	80.26	19.74	40.82	59.18	1.77
		2	83.02	16.98	43.31	56.69	1.82
1,5-Pentanediol		1	80.71	19.29	33.88	66.12	1.97
		1.5	81.97	18.03	30.38	69.62	2.13
		2	83.89	16.11	33.33	66.67	2.13
Dimethylsulfoxide		1	77.65	22.35	16.39	83.61	2.53
		1.5	83.05	16.95	17.39	82.61	2.76
		2	79.67	20.33	15.00	85.00	2.72
Tetraethylene Glycol		1	80.51	19.49	38.83	61.17	1.83
		1.5	83.19	16.81	40.77	59.23	1.89
		2	81.91	18.09	39.09	60.91	1.88
Propylene Glycol		1	77.06	22.94	17.02	82.98	2.46
		1.5	76.09	23.91	15.02	84.98	2.54
		2	76.84	23.16	16.42	83.58	2.49
50% Tetraethylene Glycol		1	80.00	20.00	24.00	76.00	2.27
50% Dimethylsulfoxide		1.5	80.85	19.15	23.08	76.92	2.35
		2	81.48	18.52	24.14	75.85	2.33
33% Polyethylene Glycol 300		1	79.31	20.69	28.26	71.74	2.08
33% Dimethylsulfoxide		1.5	80.00	20.00	25.93	74.07	2.19
33% Propylene Glycol		2	80.37	19.63	30.16	69.84	2.08
Triethylene Glycol		1	80.77	19.23	30.56	69.44	2.07
		12.5	80.28	19.72	33.93	66.07	1.95
		2	81.01	18.99	32.61	67.39	2.02
Hexylene Glycol		1	79.78	20.22	32.10	67.90	1.98
		1.5	80.00	20.00	30.00	70.00	2.06
		2	80.95	19.05	32.08	67.92	2.03
Column Packed with Helices							
33% Polyethylene Glycol 300		0.8	81.67	18.33	40.30	59.70	2.13
33% Dimethylsulfoxide		1.3	86.15	13.85	40.91	59.09	2.41
33% Propylene Glycol		1.8	83.15	16.85	39.13	60.87	2.26
1,5-Pentanediol		0.8	84.75	15.25	39.76	60.24	2.34
		1.3	84.07	15.93	40.51	59.49	2.27
		1.8	85.71	14.29	41.18	58.82	2.36
Dimethylsulfoxide		0.8	80.56	19.44	28.28	71.72	2.56
		1.3	85.19	14.81	35.16	64.84	2.57
		1.8	84.29	15.71	33.75	66.25	2.56
Tetraethylene Glycol		0.8	82.95	17.05	50.00	50.00	1.88
		1.3	85.71	14.29	49.03	50.97	2.08
		1.8	84.31	15.69	50.00	50.00	1.96
Propylene Glycol		0.8	82.35	17.65	41.54	58.46	2.12
		1.3	83.33	16.67	40.00	60.00	2.24
		1.8	80.77	19.23	37.97	62.03	2.16
50% Dimethylsulfoxide		0.8	81.65	18.35	34.42	65.58	2.35
50% Tetraethylene Glycol		1.3	83.56	16.44	30.38	69.62	2.67
		1.8	85.51	14.49	34.55	65.45	2.63
Triethylene Glycol		0.8	83.84	16.16	50.00	50.00	1.93
		1.3	80.72	19.28	49.67	50.33	1.78
		1.8	83.58	16.42	50.77	49.23	1.89
Hexylene Glycol		0.8	81.61	18.39	50.00	50.00	1.81
		1.3	80.95	19.05	49.30	50.70	1.80
		1.8	83.33	16.67	51.85	48.15	1.85

TABLE 3. (*Continued*)

Extractive Agent	Time h	Bottoms wt. % EtOH	Bottoms wt. % EtAc	Overhead wt. % EtOH	Overhead wt. % EtAc	Rel. Vol.
		Column Packed with Raschig Rings				
1,5-Pentanediol	1	80.39	19.61	27.50	72.50	2.10
	1.5	85.15	14.85	35.59	64.41	2.08
	2	85.11	14.89	36.17	63.83	2.06
Dimethylsulfoxide	1	83.33	16.67	23.26	76.74	2.40
	1.5	84.88	15.12	27.59	72.41	2.32
	2	84.21	15.79	28.13	71.88	2.33
Tetraethylene Glycol	1	81.48	18.52	47.89	52.11	1.63
	1.5	81.01	18.99	43.29	56.71	1.71
	2	84.88	15.12	48.78	51.22	1.74
Propylene Glycol	1	84.81	15.19	36.44	63.56	2.04
	1.5	85.36	13.64	40.00	60.00	2.02
	2	87.72	12.28	42.86	57.14	2.02
50% Dimethylsulfoxide	1	80.77	19.23	37.18	62.82	1.84
50% Tetraethylene Glycol	1.5	81.82	18.18	36.89	63.11	1.89
	2	85.48	14.52	43.24	56.76	1.89
Triethylene Glycol	1	81.10	18.90	45.45	54.55	1.67
	1.5	80.39	19.61	45.88	54.12	1.64
	2	82.81	17.19	48.54	51.46	1.66
Hexylene Glycol	1	79.35	20.65	51.47	48.53	1.50
	1.5	80.51	19.49	53.13	46.87	1.50
	2	83.87	16.13	53.04	46.96	1.61
33% Polyethylene Glycol 300	1	83.93	16.07	44.63	55.37	1.79
33% Dimethylsulfoxide	1.5	83.93	16.07	45.52	54.48	1.77
33% Propylene Glycol	2	84.85	15.15	45.61	54.39	1.81
		Column Packed with Intalox Saddles				
33% Polyethylene Glycol 300	1	81.03	18.97	19.15	80.85	2.10
33% Dimethylsulfoxide	1.5	81.71	18.29	22.83	77.17	2.01
33% Propylene Glycol	2	83.87	16.13	22.33	77.67	2.10
1,5-Pentanediol	1	81.75	18.25	23.00	77.00	2.00
	1.5	82.88	17.12	24.19	75.81	2.01
	2	83.13	16.87	23.20	76.80	2.05
Dimethylsulfoxide	1	80.51	19.49	17.07	82.93	2.16
	1.5	80.95	19.05	15.61	84.39	2.23
	2	82.76	17.24	15.23	84.77	2.32
Tetraethylene Glycol	1	82.35	17.65	30.62	69.38	1.83
	1.5	82.57	17.43	28.96	71.04	1.88
	2	81.57	18.43	30.08	69.92	1.82
Propylene Glycol	1	83.93	16.07	18.18	81.82	2.25
	1.5	83.33	16.67	22.41	77.59	2.08
	2	82.61	17.39	22.60	77.40	2.04
50% Dimethylsulfoxide	1	79.59	20.41	20.48	79.52	2.01
50% Tetraethylene Glycol	1.5	80.00	20.00	18.18	81.82	2.10
	2	79.90	20.10	16.54	83.46	2.16
Triethylene Glycol	1	81.40	18.60	28.04	71.96	1.86
	1.5	81.36	18.64	27.70	72.30	1.87
	2	81.71	18.29	31.33	68.67	1.80
Hexylene Glycol	1	81.17	18.83	35.42	64.58	1.70
	1.5	80.61	19.39	37.82	62.18	1.64
	2	80.95	19.05	39.24	60.76	1.62
25% Tetraethylene Glycol	1	83.52	16.48	26.44	73.56	1.97
25% Dimethylsulfoxide	1.5	80.88	19.12	25.66	74.34	1.90
25% 1,5-Pentanediol	2	82.46	17.54	26.24	73.76	1.94
25% Diethylene Glycol						
50% Polyethylene Glycol 300	1	79.85	20.15	35.29	64.71	1.66
50% Triethylene Glycol	1.5	80.00	20.00	38.00	62.00	1.62
	2	81.58	18.42	36.84	63.16	1.68

90°C. was fed into the top of the column at a rate of about twice the boilup rate. Samples from the overhead and the stillpot were taken every half hour and the operation continued until analysis showed a constant relative volatility. This was always two hours or less.

RESULTS AND CONCLUSIONS

The results are presented in Table 2 and 3 in which the relative volatilities are reported as ethyl acetate vs. ethanol. Table 3 lists the results of analyses for each extractive distillation system investigated with the several columns. The "time" column shows the length of time taken for each run. In each case investigated, the water remained in the stillpot. The bottoms analyses are on a water-extractive agent-free basis and the relative volatilities were calculated by the Fenske equation. Sampling was done after 1, 1.5 and 2 hours of operation.

When the runs are numbered for the same extractive agent, the extractive agent was reclaimed and reused to demonstrate its ability to be recycled. The perforated plate column is consistently the best. Helices and Berl saddles are not quite as effective as the perforated plates. Intalox saddles and Raschig rings were the poorest of the packings tested. However, since no attempt was made to find the optimum column diameter to packing diameter for the several packings tested, it is probably unfair to make a precise comparison with perforated plates. Further research probably will show certain packings in the proper column diameter: packing diameter ratio to be as good or better than perforated or bubble cap plates.

When 1,5-pentanediol is the extractive distillation agent, the perforated plate column gives a separation of an apparent relative volatility of ethyl acetate to ethanol of 3.19. With helices it is 2.32; with Berl saddles, 2.08; with Intalox saddles, 2.02; and with Raschig rings, 2.08. These data show that, although packed columns may not be quite as efficient as perforated plate columns, they can indeed be used in extractive distillation.

LITERATURE CITED

Berg, L., "Separation of Ethylbenzene from p- and m-Xylene by Extractive Distillation," U.S. Patent 4,292,142 (Sept. 29, 1981).

Drout, Jr., W. M., and J. W. Dowling, "Process to Dehydrate Alcohols Using Glycols," Fr. Patent 1,020,351 (Nov. 19, 1952).

Schneible, J., "Dehydration of Ethanol Using Glycerol," U.S. Patent 1,469,447 (Oct. 2, 1923).

Smith, P. V., and C. S. Carlson, "Dehydration of Ethanol with Ethoxyethanol or Butoxyethanol," U.S. Patent 2,559,519 (July 3, 1951).

Manuscript received November 8, 1982; revision received February 8, and accepted March 16, 1983.

Catalytic Conversion of Large Molecules: Effect of Pore Size and Concentration

D. D. DO

Department of Chemical Engineering
University of Queensland
St. Lucia, Qld. 4067, Australia

INTRODUCTION

Catalytic conversion of large molecules, such as heavy petroleum residue and coal-derived liquids, involves the restricted pore-diffusion transport of such molecules into the catalyst pellets. The sizes of molecules in these feedstocks range between 25×10^{-10} m and 150×10^{-10} m. The largest fraction is around 50×10^{-10} m (Ruckenstein and Tsai, 1981).

The degree of restriction of these molecules by the pore wall has been the subject of many investigations (Colton et al., 1975; Prasher and Ma, 1977; Prasher et al., 1978).

The catalytic conversion of large molecules, optimal pore size of catalyst pellets, has been reported for heavy petroleum residue (Eigenson et al., 1977; Ohtsuka, 1977) and for coal-derived liquids (Brooks et al., 1976; and Yet et al., 1976). In this paper we shall investigate the optimal pore size for these feedstocks with the assumption of first-order chemical kinetics (Sapre et al., 1980; Schuit and Gates, 1973). The interaction between diffusing molecules and the surface may play an important role in catalytic conversion of large molecules. In fact, Glandt (1981) has shown that the concentration is higher in the periphery of the pore than at the center. This interaction, however, is ignored in this work because the emphasis of this paper is on the interplay among diffusion, reaction and the nonlinear partition coefficient. Such interaction could be incorporated, but the mathematical analysis would then be very difficult.

SINGLE CATALYST PELLET

The mass balance equation for the reactant in the catalyst pellet is

$$D_e \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial C}{\partial r}\right) - \rho_p S_g k'' C = 0, \tag{1}$$

where

$$D_e = \frac{\epsilon_p D_b}{\tau} K_r. \tag{2}$$

The drag coefficient K_r, proposed by Renkin (1954) in his study of porous cellulose membrane, is used here in our analysis

$$K_r = 1 - 2.104\lambda + 2.09\lambda^3 - 0.95\lambda^5, \tag{3}$$

where

$$\lambda = a/r_p \tag{4}$$

The surface area is related to the pore radius and the pore volume as follows

$$r_p = 2V_g/S_g \tag{5}$$

We shall assume that the pore volume does not change with the pore radius. Thus, the surface area is proportional to the inverse of the pore radius.

Substituting Eq. 2 into Eq. 1, we obtain:

$$\frac{\epsilon_p D_b}{\tau} K_r(\lambda) \frac{1}{r^2} \frac{d}{d^r}\left(r^2 \frac{dC}{dr}\right) - \rho_p k'' \frac{S_{go} r_{po}}{r_p} \cdot C = 0. \tag{6}$$

At the pellet center, the usual symmetry condition

$$r = 0; \quad dC/dr = 0. \tag{7}$$

At the surface of the catalyst pellet, due to the comparable dimension between the rectangular molecular size and the pore size, partition coefficient was often used in many works. However, in the recent work of Glandt (1981), the pore surface concentration is nonlinearly related to the bulk concentration as follows:

$$C(R) = C_b \left[K_o + K_1^* \left(\frac{C_b}{C_m}\right) + K_2^* \left(\frac{C_b}{C_m}\right)^2\right], \tag{8}$$

where C_b is the bulk concentration, K_o is defined as for cylindrical pore

$$K_o = (1 - \lambda)^2, \tag{9}$$

and K_1^*, K_2^* are defined numerically in Glandt (1981) as functions of λ. C_m is defined as $C_m = 1/N_A d^3$. For our subsequent analysis, we have fitted a sixth-order polynomials to the curves of K_1^* and K_2^* vs. λ and have found

$$\frac{K_1^*}{K_o} = a\lambda + b\lambda^2 + c\lambda^3 + d\lambda^4 + e\lambda^5 + f\lambda^6, \tag{10}$$

where