THESIS APPROVAL

GRADUATE SCHOOL, KASETSART UNIVERSITY

Master of Engineering (Chemical Engineering)

DEGREE

Chemical Engineering — **FIELD**

Chemical Engineering — **DEPARTMENT**

TITLE: Mathematical Analysis of TAP Models for Unimodal- and Bimodal-Pore-Structure Catalyst Pellets

NAME: Mr. Wisuthchai Boonwatcharapunsakun

THIS THESIS HAS BEEN ACCEPTED BY

______________________________ **THESIS ADVISOR**

(Associate Professor Phungphai Phanawadee, D.Sc.)

______________________________ **THESIS CO-ADVISOR**

(Associate Professor Metta Chareonpanich, D.Eng.)

______________________________ **DEPARTMENT HEAD**

(Associate Professor Paisan Kongkachuichay, Ph.D.)

APPROVED BY THE GRADUATE SCHOOL ON ______________________________

______________________________ **DEAN**

(Associate Professor Gunjana Theeragool, D.Agr.)

THESIS

MATHEMATICAL ANALYSIS OF TAP MODELS FOR UNIMODAL- AND BIMODAL-PORE-STRUCTURE CATALYST PELLETS

WISUTHCHAI BOONWATCHARAPUNSAKUN

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
Master of Engineering (Chemical Engineering)
Graduate School, Kasetsart University
2008

Wisuthchai Boonwatcharapunsakun 2008: Mathematical Analysis of TAP Models for Unimodal- and Bimodal-Pore-Structure Catalyst Pellets. Master of Engineering (Chemical Engineering), Major Field: Chemical Engineering, Department of Chemical Engineering. Thesis Advisor: Associate Professor Phungphai Phanawadee, D.Sc. 146 pages.

The TAP transient pulse response experiment has been used for heterogeneous catalytic reaction studies. The observable quantity in the experiment is a time-dependent exit flow rate curve. The size and the shape of the exit flow curve contain information on gas transport and chemical kinetics. New moment expressions of the exit flow rate for the unimodal- and bimodal-pore-structure catalysts are presented. The fingerprints of the exit flow rate curves for irreversible adsorption/reaction and desorption for unimodal- and bimodal porous cases were found to be similar to non-porous cases. In addition, the characteristics of the distribution of surface concentration due to irreversible adsorption in the porous catalyst pellet were analyzed. The correlation between the effectiveness factor and the distribution of fractional surface coverage in the pellets developed in an irreversible adsorption process in a TAP experiment is similar to the correlation between the effectiveness factor and gas concentration distribution in steady-state conditions.

____________________ ____________________ ___ / ___ / ___

Student’s signature Thesis Advisor’s signature

ACKNOWLEDGEMENTS

I would like to express my sincere thank to my thesis advisor, Assoc. Prof. Dr. Phungphai Phanawadee, for his kindness, support, guidance, and revisions of this thesis, and to my thesis co-advisor, Assoc. Prof. Dr. Metta Chareonpanich, for her comments and suggestions.

Furthermore, I would like to thank all of my friends, especially, Mr. Watcharin Soikham for suggestions and Ms. Pichamat Tantake for support and encouragement.

The financial support from the Kasetsart University Research and Development Institute, the National Center of Excellence for Petroleum, Petrochemicals, and Advance materials, and the National Nanotechnology Center under the National Science and Technology Development Agency is also acknowledged.

Finally, I am deeply thankful to my family for their continuous support and encouragement.

Wisuthchai Boonwatcharapunsakun
October 2008

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

Page

TABLE OF CONTENTS (Continued)

Page

LIST OF TABLES

LIST OF FIGURES

Figure **Page**

LIST OF FIGURES (Continued)

LIST OF ABBREVIATIONS

A	=	cross-sectional area of the reactor, m^2
A'	=	quantity, defined by Eq. (164)
A''	=	quantity, defined by Eq. (199)
A_n	=	quantity, defined by Eq. (107)
B'	=	quantity, defined by Eq. (188)
B''	=	quantity, defined by Eq. (217)
C_b	=	gas concentration in the bed for non-porous case and gas concentration in the interparticle region, mol/m^3 for unimodal and bimodal porous cases
C_c	=	gas concentration in the macropore regions, mol/m^3
C_m	=	gas concentration in the mesopore region, mol/m^3
C_p	=	gas concentration in the intraparticle regions, mol/m^3
C_b^*	=	dimensionless gas concentration in the interparticle region
C_c^*	=	dimensionless gas concentration in the macropore region
C_m^*	=	dimensionless gas concentration in the mesopore region
C_p^*	=	dimensionless gas concentration in the intraparticle region
$\bar{C}_b^*$	=	C_b^* in Laplace domain
$\bar{C}_c^*$	=	C_c^* in Laplace domain
$\bar{C}_m^*$	=	C_m^* in Laplace domain
$\bar{C}_p^*$	=	C_p^* in Laplace domain
d_{particle}	=	average particle diameter, m
d_{pellet}	=	average pellet diameter, m
$d_{\text{macropore}}$	=	average macropore diameter, m
d_{mesopore}	=	average mesopore diameter, m

LIST OF ABBREVIATIONS (Continued)

$\bar{d}$	=	average diameter of the interstitial voids between the pellets in the reactor, m
D_b	=	effective Knudsen diffusivity of gas in the bed, m^2/s, for non-porous case and effective Knudsen diffusivity of gas in the interparticle region, m^2/s, for unimodal and bimodal porous cases
D_c	=	effective Knudsen diffusivity of gas in the macropore region, m^2/s
D_m	=	effective Knudsen diffusivity of gas in the mesopore region, m^2/s
D_p	=	effective Knudsen diffusivity of gas in the intraparticle regions, m^2/s
F	=	exit flow rate, mol/s
$F(s)$	=	exit flow rate in Laplace domain
F^*	=	dimensionless exit flow rate, defined by $F^* = F \times \frac{e_b L^2}{N_p D_b}$
$F^*(s)$	=	dimensionless exit flow rate in Laplace domain
k_a	=	adsorption or reaction rate constant, m^3 of gas/mol s
k_a'	=	apparent adsorption or reaction rate constant, (1/s), defined by $k_a' = k_a \times \frac{r_s(1-e_b)}{e_b}$ for non-porous case, $k_a' = k_a \times \frac{r_s}{e_p}$ for unimodal porous case and $k_a' = k_a \times \frac{r_s}{e_m}$ for bimodal porous case

LIST OF ABBREVIATIONS (Continued)

k_a^*	=	dimensionless adsorption or reaction rate constant, defined by $k_a^* = k_a' \times \frac{e_b L^2}{D_b}$
k_d	=	desorption rate constant, m^3 of gas/mol s
k_d^*	=	dimensionless desorption rate constant, defined by Eq. (29)
L	=	length of the reactor, m
L_{cat}	=	length of the catalyst zone, m
L_1	=	length of the first zone in a three-zone reactor, m
L_2	=	length of the second zone in a three-zone reactor, m
L_3	=	length of the third zone in a three-zone reactor, m
m_j	=	j^{th} moment expression of the PI-normalized exit flow rate
m_0	=	zeroth moment expression of the PI-normalized exit flow rate
m_1	=	first moment expression of the PI-normalized exit flow rate
m_2	=	second moment expression of the PI-normalized exit flow rate
m_3	=	third moment expression of the PI-normalized exit flow rate
m_j^*	=	j^{th} moment expression of the dimensionless exit flow rate
m_0^*	=	zeroth moment expression of the dimensionless exit flow rate
m_1^*	=	first moment expression of the dimensionless exit flow rate
m_2^*	=	second moment expression of the dimensionless exit flow rate
m_3^*	=	third moment expression of the dimensionless exit flow rate
M_T	=	Thiele modulus, defined by Eq. (100)
$M_{T,ma}$	=	macropore Thiele modulus, defined by Eq. (178)
$M_{T,me}$	=	mesopore Thiele modulus, defined by Eq. (179)
MW	=	molecular weight

LIST OF ABBREVIATIONS (Continued)

N_p	=	number of moles of gas in the inlet pulse, mol
p_n	=	parameter defined by Eq. (106)
r	=	radial coordinate of the catalyst pellet for unimdal porous case, m
$r_{\pm}$	=	collections of parameters (see Eq. 105)
r_c	=	radial coordinate of the catalyst pellet for bimdal porous case, m
r_m	=	radial coordinate of the particle with mesopores, m
r_{D1}	=	ratio of effective Knudsen diffusivity of gas in the interparticle region of the first zone to the second zone (see Eq. 44)
r_{D3}	=	ratio of effective Knudsen diffusivity of gas in the interparticle region of the third zone to the second zone (see Eq. 45)
r_{e1}	=	ratio of interparticle void fraction of the first zone to the second zone (see Eq. 46)
r_{e3}	=	ratio of interparticle void fraction of the third zone to the second zone (see Eq. 47)
R	=	radius of the catalyst pellet for unimdal porous case, m
R_c	=	radius of the catalyst pellet for bimdal porous case, m
R_m	=	radius of the particle with mesopores, m
s	=	Laplace variable, l/s
t	=	time, s
T	=	temperature, K
z	=	axial coordinate of the reactor, m
z_1	=	axial coordinate at the boundary between zone 1 and 2
z_2	=	axial coordinate at the boundary between zone 2 and 3

LIST OF ABBREVIATIONS (Continued)

Greek letters

a	=	catalyst number, the ratio of the number of active site of the catalyst to the number of the reactant gas molecules in the inlet pulse, defined by $a = \dfrac{r_s}{N_p/(1-e_b)AL}$ for non-porous and unimodal porous cases and $a = \dfrac{r_s}{N_p/(1-e_c)(1-e_b)AL}$ for bimodal porous case
b	=	ratio of intraparticle to interparticle void volumes in unimodal porous case defined by $b = \dfrac{e_p(1-e_b)}{e_b}$
b_c	=	ratio of macropore to interparticle void volumes in bimodal porous case defined by $b_c = \dfrac{e_c(1-e_b)}{e_b}$
b_m	=	ratio of mesopore to interparticle void volumes in bimodal porous case defined by $b_m = \dfrac{e_m(1-e_c)}{e_c}$
g	=	ratio of the interparticle to the intraparticle transport characteristic times, defined by $g = \dfrac{t_b}{t_p}$ for unimodal porous case
g_c	=	ratio of the interparticle to the macropore transport characteristic times, defined by $g_c = \dfrac{t_b}{t_c}$ for bimodal porous case

LIST OF ABBREVIATIONS (Continued)

g_m	=	ratio of the interparticle to the mesopore transport characteristic times, defined by $g_m = \frac{t_b}{t_m}$ for bimodal porous case
$d(t-0^+)$	=	Dirac delta function placed at $t = 0^+$
e_b	=	interparticle void fraction in the bed, m^3 of void in the interparticle region/ m^3 of bed
e_p	=	intraparticle void fraction, m^3 of void in intraparticle region/ m^3 of catalyst pellet, defined for bimodal porous case
e_c	=	macropore void fraction, m^3 of void in macropore region/ m^3 of catalyst pellet, in bimodal porous case
e_m	=	mesopore void fraction, m^3 of void in mesopore region/ m^3 of mesoporous particle, in bimodal porous case
z_1	=	ratio of the length of the first zone to the length of the reactor, defined by $z_1 = \frac{L_1}{L}$
z_2	=	ratio of the length of the second zone to the length of the reactor, defined by $z_2 = \frac{L_2}{L}$
z_3	=	ratio of the length of the third zone to the length of the reactor, defined by $z_3 = \frac{L_3}{L}$
h	=	effectiveness factor (see Eq.99)
h_{ma}	=	macropore effectiveness factor (see Eq.176)
h_{me}	=	mesopore effectiveness factor (see Eq.177)
$h_{overall}$	=	overall effectiveness factor (see Eq.175)
q	=	fractional surface coverage

LIST OF ABBREVIATIONS (Continued)

q_{∞}	=	q after one pulse
$q_{\infty,r=R}$	=	q_{∞} at the external surface of the catalyst pellet
$q_{\infty,r_c=R_c \text{ and } r_m=R_m}$	=	q_{∞} at the external surface of the mesoporous particle and at the external surface of the catalyst pellet in bimodal porous case
$q_{\infty,r_m=R_m}$	=	q_{∞} at the external surface of the mesoporous particle
q^{*}	=	pulse-intensity-normalized surface concentration
$\overline{q}^{*}$	=	q^{*} in Laplace domain
q_{∞}^{*}	=	q^{*} after one pulse
$q_{\infty,r=1}^{*}$	=	q_{∞}^{*} at the external surface of the catalyst pellet
$q_{\infty,r_c=1 \text{ and } r_m=1}^{*}$	=	q_{∞}^{*} at the external surface of the mesoporous particle and at the external surface of the catalyst pellet in bimodal porous case
$q_{\infty,r_m=1}^{*}$	=	q_{∞}^{*} at the external surface of the mesoporous particle in bimodal porous case
x	=	dimensionless axial coordinate of the reactor, defined by $x = \dfrac{z}{L}$
x_1	=	dimensionless axial coordinate of the first inert zone, defined by $x_1 = \dfrac{z_1}{L}$
x_2	=	dimensionless axial coordinate of the second inert zone, defined by $x_2 = \dfrac{z_2}{L}$
r	=	dimensionless radial coordinate of the catalyst pellet in unimodal porous case, defined by $r = \dfrac{r}{R}$

LIST OF ABBREVIATIONS (Continued)

r_p = dimensionless radial coordinate of the catalyst pellet in bimodal porous case, defined by $r_c = \frac{r_c}{R_c}$

r_m = dimensionless radial coordinate of the particle with mesopores, defined by $r_m = \frac{r_m}{R_m}$

r_s = concentration of active site, mol/m^3 of the catalyst pellets for unimodal porous case or concentration of active site, mol/m^3 of the mesoporous particles for bimodal porous case

t = dimensionless time, defined by $t = t \times \frac{D_b}{e_b L^2}$

t_b = interparticle transport characteristic time, defined by $t_b = \frac{e_b L^2}{D_b}$

t_c = macropore transport characteristic time, defined by $t_c = \frac{e_c R_c^2}{D_c}$ for bimodal porous case

t_m = mesopore transport characteristic time, defined by $t_m = \frac{e_m R_m^2}{D_m}$ for bimodal porous case

$t_{\max}$ = dimensionless time at which the dimensionless exit flow is maximum

t_p = intraparticle transport characteristic time, defined by $t_p = \frac{e_p R^2}{D_p}$ for unimodal porous case

t_{res} = dimensionless mean residence time

t' = tortuosity factor

t'_{inter} = interparticle tortuosity factor

LIST OF ABBREVIATIONS (Continued)

t'_{intra} = intraparticle tortuosity factor in unimodal porous case

t'_{macro} = macropore tortuosity factor in bimodal porous case

t'_{meso} = mesopore tortuosity factor in bimodal porous case

y = dimensionless kinetic parameter defined by $y = \dfrac{k_a r_s (1-e_b) L_{cat}^2}{D_b}$ for non-porous and unimodal porous cases, and $y = \dfrac{k_a r_s (1-e_b)(1-e_c) L_{cat}^2}{D_b}$ for bimodal porous case

Subscripts

1 = component 1 or zone 1

2 = component 2 or zone 2

3 = zone 3

MATHEMATICAL ANALYSIS OF TAP MODELS FOR UNIMODAL- AND BIMODAL-PORE-STRUCTURE CATALYST PELLETS

INTRODUCTION

Information of chemical reaction kinetics is required for design and optimization of chemical reactors. Two types of experiment including steady-state and transient experiments have been applied for kinetic studies. Most industrial catalysts are tested by steady-state experiments providing kinetic parameters at commercial operating conditions. The design of the reactor is accomplished using parameters from this type of experiment. On the other hand, the transient experiment is applied when detail mechanisms are required.

The temporal analysis of products or TAP is a transient experimental technique for heterogeneous catalytic reaction studies. In a TAP pulse response experiment, a narrow gas pulse is injected into an evacuated microreactor packed with catalyst particles. At the reactor exit the gas molecules of each species are detected by a mass spectrometer providing a time-dependent response curve. The intensity of the response is proportional to the gas exit flow rate. The size and shape of the transient response curve contain information of gas transport and chemical kinetics. The simplest reactor is the one-zone reactor which is uniformly packed with catalyst or inert particles. Another type of reactor is the three-zone reactor which contains a catalyst bed sandwiched between two inert beds. The advantage of the three-zone reactor is that the temperature distribution in the catalyst bed is more uniform than the one-zone reactor.

Usually, the size and shape of the experimental responses can be simply used for primary interpretation. Fingerprints of the exit flow rate curve for non-porous catalyst pellets for irreversible adsorption/reaction and reversible adsorption has been reported by Gleaves et al. (1997). Quantitative interpretation of TAP transient response data requires mathematical models that describe the processes in the TAP reactor. Estimation of either transport or kinetic parameters can be performed by curve fitting (regression analysis) between experimental and model responses. Another alternative is the use of moment analysis of the exit flow rate.

When the moment analysis is applied, analytical expressions of the moment of the exit flow rate are required. Moment expressions of the exit flow rate for a one-zone reactor packed with non-porous catalyst for simple processes, i.e., diffusion, diffusion with irreversible adsorption/reaction or with reversible adsorption have been determined (Gleaves et al., 1988, 1997; Huinink et al., 1996). For a three-zone reactor, moment expressions of the exit flow rate, i.e., first moment for diffusion-only (Phanawadee et. al., 1999), zeroth moment for diffusion with irreversible adsorption/reaction (Phanawadee 1997), first and second moments for diffusion with reversible adsorption/reaction (Constales et al., 2001) have been reported.

Those mentioned works are related to non-porous catalysts. In the case of unimodal-pore-structure catalyst, the reported moment expressions of the exit flow rate for a one-zone reactor includes the first, second, and third moment expressions for diffusion-only (Colaris et al., 2002), and the zeroth (Monrudee 2002; Phanawadee et al., 2005) and first moment expressions (Monrudee 2002) for diffusion with irreversible adsorption/reaction. For a three-zone reactor, the reported moment expression of the exit flow rate is the zeroth moment expressions for diffusion with irreversible adsorption/reaction (Monrudee 2002; Phanawadee et al., 2005)**.** Each of the reported zeroth moment expression for diffusion with irreversible adsorption/reaction for both one-zone and three-zone reactors includes the effectiveness factor, h , typically defined in steady-state conditions. It was shown that the rate constant in porous case decreases by a factor of h similarly to steady-state conditions. The quantity h is related to the unvaried gas concentration profile in steady-state conditions, while the gas concentration in TAP transient experiments changes with time. Accordingly it was suggested that h in the moment expressions is an average quantity of the whole pulse experiment. Applicibility of h in TAP transient experiments is not obvious. It is expected that analysis of the surface concentration profile due to irreversible adsorption process would provide more information on the characteristic of TAP porous system.

Many catalytic systems involve bimodal-pore-structure catalyst. A biporous system of Zeolite on silica-alumina support has been investigated using TAP technique (Schuurman et al., 2005). Kinetic parameters were determined by regression analysis. Since moment analysis has also been used for parameter estimation, it will be useful to develop moment expressions for bimodal porous case.

In this work, new moment expressions of the exit flow rate will be determined for the unimodal and bimodal-pore-structure catalysts. The characteristics of the distribution of surface concentration due to irreversible adsorption in the porous catalyst pellet will be analyzed. In addition, the fingerprints of the exit flow rate curves for irreversible adsorption/reaction and reversible adsorption for non-porous cases will be investigated for their validity for porous cases.

OBJECTIVES

The objectives of this work include

1. Determination of new moment expressions of the exit flow rate for unimodal and bimodal-pore-structure catalyst pellets.

2. Analysis of the characteristics of surface concentration distribution in the porous catalyst pellet for irreversible adsorption.

3. Investigation of the exit-flow-rate-curve fingerprints for irreversible adsorption/reaction and reversible adsorption in non-porous catalyst case to determine their validity for porous catalyst case

Scope

The moment expressions will be determined for different cases as follows:

1. The one-zone reactor packed with unimodal-pore-structure catalyst pellets for diffusion with reversible adsorption case.

2. The three-zone reactor packed with unimodal-pore-structure catalyst pellets for diffusion, diffusion with irreversible adsorption/reaction and with reversible adsorption.

3. The one-zone and three-zone reactors packed with bimodal-pore-structure catalyst pellets for diffusion, diffusion with irreversible adsorption/reaction, and with reversible adsorption cases.

The characteristics of surface concentration distribution in the porous catalyst pellet for irreversible adsorption will be analyzed for two cases as follows:

1. The one-zone reactor packed with unimodal-pore-structure catalyst pellets.

2. The one-zone reactor packed with bimodal-pore-structure catalyst pellets.

Fingerprints of the exit flow rate curve for irreversible adsorption/reaction and desorption are determined for two cases as follows:

1. The one-zone reactor packed with unimodal-pore-structure catalyst pellets.

2. The one-zone reactor packed with bimodal-pore-structure catalyst pellets.

LITERATURE REVIEW

In TAP pulse response experiments, the gas transport is governed by Knudsen diffusion. In this regime, the diffusivity of the individual component of a gas mixture is independent of pressure, concentration, or the composition of the gas mixture. The effective Knudsen diffusivity of a gas in a packed bed can be determined by (Huizenga and Smith 1986)

$$D_b = \frac{e_b}{t'} \frac{\bar{d}}{3} \sqrt{\frac{8RT}{p\,MW}} \tag{1}$$

where $\bar{d}$ is the average diameter of the interstitial voids between the pellets in the reactor (m), e_b is the void fraction in the bed, t' is the tortuosity factor and MW is the molecular weight.

For spherical pellets,

$$\bar{d} = \frac{2e_b}{3(1-e_b)} d_{\text{pellet}} \tag{2}$$

where d_{pellet} is the average pellet diameter (m).

The effective Knudsen diffusivity of a gas can be calculated from the effective Knudsen diffusion coefficient of another gas in the same system using the correlation

$$D_{e,1} \frac{\sqrt{MW_1}}{\sqrt{T_1}} = D_{e,2} \frac{\sqrt{MW_2}}{\sqrt{T_2}} \tag{3}$$

where D_e, MW, and T are the effective Knudsen diffusivity, molecular weight, and temperatures respectively, and subscripts 1 and 2 refer to gas 1 and gas 2 respectively.

Mathematical models

Quantitative interpretation of TAP transient responses requires the mathematical models that describe the chemical and transport phenomena in the TAP reactors. These mathematical models are based on time-dependent differential mass balances resulting in partial differential equations (PDEs). Most TAP models are based on the following assumptions:

1. The catalyst bed and inert particle bed are uniformly packed.

2. The temperature distribution in the reactor is uniform.

3. There is no radial concentration gradient in the bed and one-dimensional models are applied to describe the processes.

For simple models that are described by linear differential equations, analytical moment expressions of the exit flow rate can be determined. When moment expressions of the exit flow rate are known, the moment method can be performed. The moment or moment-related quantity is calculated from the experimental response and the corresponding expression is used for parameter estimation. The moment expressions of the exit flow rate for determining the diffusivities of gas and reaction rate constants has been applied by many researchers (Huinink 1995; Huinink et al., 1996; Phanawadee 1997; Yablonskii et al., 1998; Colaris et al., 2002; Shekhtman 2003).

One-zone reactor packed with non-porous catalyst pellets

The mathematical models of one-zone and three-zone reactors packed with non-porous catalyst pellets for simple cases, i.e., diffusion, diffusion with irreversible adsorption/reaction and with reversible adsorption have been reported by Gleaves et al. (1997).

- Diffusion case

In the Knudsen diffusion regime, the mass balance equation for a non-reacting gas in the reactor is given by

$$e_b \frac{\partial C_b}{\partial t} = D_b \frac{\partial^2 C_b}{\partial z^2} \quad (4)$$

where C_b is the gas concentration in the bed (mol/m^3), D_b is the effective Knudsen diffusivity in the bed (m/s^2), t is the time (s), z is the axial coordinate (m), and e_b is the void fraction in the bed.

Initial and boundary conditions are as follows:

Initial condition:

$$0 \le z \le L,\ t = 0,\ C_b = 0 \quad (5)$$

Boundary conditions:

$$z = 0,\ -D_b \frac{\partial C_b}{\partial z} = \frac{N_p}{A} d\left(t - 0^+\right) \quad (6)$$

$$z = L,\ C_b = 0 \quad (7)$$

where A is the cross-sectional area of the reactor (m^2), L is the length of the reactor (m), N_p is the number of moles of the gas in the inlet pulse (mol).

Eq. (5) specifies that there is no gas concentration at $t = 0$. Eq. (6) specifies that the flux at the reactor entrance is represented by the Dirac delta function. Eq. (7)

results from the fact that the outlet of the reactor is maintained at vacuum conditions, and the gas concentration at the reactor exit is very close to zero.

A system of different equations is usually analyzed using a generalized or dimensional form. Eqs. (4) - (7) can be expressed in a dimensionless form as follows:

$$\frac{\partial C_b^*}{\partial t} = \frac{\partial^2 C_b^*}{\partial x^2} \tag{8}$$

Initial condition:

$$0 \le x \le 1,\ t = 0,\ C_b^* = 0 \tag{9}$$

Boundary conditions:

$$x = 0,\ \frac{\partial C_b^*}{\partial x} = -1 \tag{10}$$

$$x = 1,\ C_b^* = 0 \tag{11}$$

C_b^* is the dimensionless gas concentration defined by

$$C_b^* = \frac{C_b}{N_p / e_b AL} \tag{12}$$

x is the dimensionless axial coordinate defined by

$$x = \frac{z}{L} \tag{13}$$

and t is the dimensionless time defined by

$$t = t \times \frac{D_b}{e_b L^2} \quad (14)$$

- Diffusion with irreversible adsorption/reaction case

If the adsorption or reaction rate is first order in gas concentration and in surface concentration, the mass balance equation for the reactant gas in the gas phase and on catalyst surface can be described by

$$e_b \frac{\partial C_b}{\partial t} = D_b \frac{\partial^2 C_b}{\partial z^2} - r_s \left(1 - e_b\right) k_a C_b \left(1 - q\right) \quad (15)$$

$$\frac{\partial q}{\partial t} = k_a C_b \left(1 - q\right) \quad (16)$$

where r_s is the concentration of active site (mol/m^3 of the catalyst pellet), k_a is the adsorption/reaction rate constant (m^3 of gas/mol s), and q is the fractional surface coverage of the occupied sites.

Eqs. (15) and (16) can be simplified by assuming that the pulse intensity is very small compared to the number of active sites in the reactor and consequently the term $\left(1 - q\right)$ is close to unity for fresh catalyst. Eqs. (15) and (16) can then be written as

$$e_b \frac{\partial C_b}{\partial t} = D_b \frac{\partial^2 C_b}{\partial z^2} - r_s \left(1 - e_b\right) k_a C_b \quad (17)$$

$$\frac{\partial q}{\partial t} = k_a C_b \quad (18)$$

The initial and boundary conditions for the mass balance equation in the reactor, Eq. (17) are the same as those for diffusion case given by Eqs. (5) - (7). The initial condition for adsorbed reactant gas on the catalyst surface, Eq. (18), is given by

$$0 \le L \le 1,\ t = 0,\ q = 0 \tag{19}$$

The apparent adsorption/reaction rate constant, k'_a (1/s), is defined as

$$k'_a = k_a \times \frac{r_s\left(1 - e_b\right)}{e_b} \tag{20}$$

The dimensionless apparent adsorption/reaction rate constant is defined as

$$k_a^* = k'_a \times \frac{e_b L^2}{D_b} \tag{21}$$

Eqs. (17) - (19) can be written in a dimensionless form respectively as

$$\frac{\partial C_b^*}{\partial t} = \frac{\partial^2 C_b^*}{\partial x^2} - k_a^* C_b^* \tag{22}$$

$$\frac{\partial q^*}{\partial t} = k_a^* C_b^* \tag{23}$$

$$0 \le x \le 1,\ t = 0,\ q^* = 0 \tag{24}$$

where

$$q^* = a \times q \tag{25}$$

and

$$a = \frac{r_s}{N_p / (1-e_b) AL} \tag{26}$$

The variable q^* in Eq. (23) is called pulse-intensity-normalized surface concentration which is the product of the fractional surface coverage and the catalyst number, a . The catalyst number is the ratio of the number of moles of active sites and the number of moles of reactant gas in the inlet pulse.

- Diffusion with reversible adsorption case

When reversible adsorption occurs, the mass balance equations for reactant gas in the reactor and on the catalyst surface are described as follows:

$$e_b \frac{\partial C_b}{\partial t} = D_b \frac{\partial^2 C_b}{\partial z^2} - r_s \left(k_a C_b - k_d q \right) \tag{27}$$

$$\frac{\partial q}{\partial t} = k_a C_b - k_d q \tag{28}$$

where k_d is the desorption rate constant (s^{-1}).

Defining the dimensionless desorption rate constant as

$$k_d^* = k_d \times \frac{e_b L^2}{D_b} \tag{29}$$

Eqs. (27) and (28) can be written in dimensionless form as

$$\frac{\partial C_b^*}{\partial t} = \frac{\partial^2 C_b^*}{\partial x^2} - \left(k_a^* C_b^* - k_d^* q^* \right) \tag{30}$$

$$\frac{\partial q^*}{\partial t} = k_a^* C_b^* - k_d^* q^* \tag{31}$$

The initial and boundary conditions for Eqs. (30) and (31) are the same as those for diffusion with irreversible adsorption/reaction case.

Three-zone reactor packed with non-porous catalyst pellets

- Diffusion, diffusion with irreversible adsorption/reaction, and with reversible adsorption cases

Figure 1 represents a schematic of a three-zone reactor**.** Catalyst pellets are packed in the middle zone of the reactor between two inert zones containing non-porous inert particles.

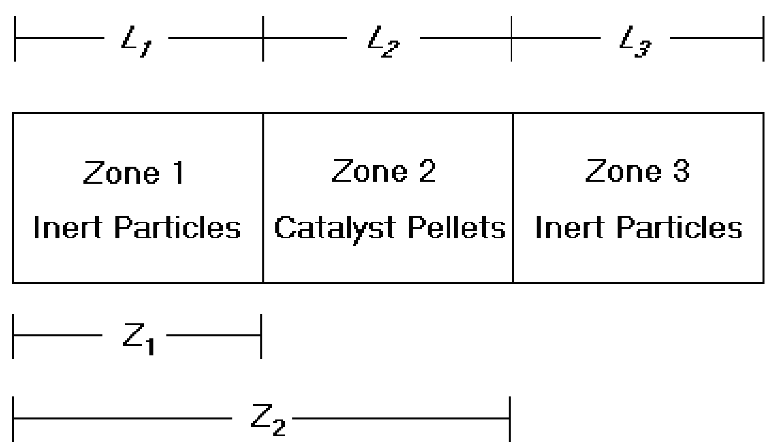

Figure 1 A schematic of a three-zone reactor.

The mass balance equations for the catalyst zone are the same as those describe the one-zone reactor. The mass balance equations for the two inert zones are described by

Zone 1:

$$e_{b,1}\frac{\partial C_{b,1}}{\partial t}=D_{b,1}\frac{\partial^2 C_{b,1}}{\partial z^2} \tag{32}$$

Zone 3:

$$e_{b,3}\frac{\partial C_{b,3}}{\partial t}=D_{b,3}\frac{\partial^2 C_{b,3}}{\partial z^2} \tag{33}$$

The initial conditions and the inlet and outlet boundary conditions are the same as those for the one-zone reactor given by Eqs. (5) – (7). Additional boundary conditions are required at the two boundaries between adjacent zones as follows:

$$z=z_1,\ C_{b,1}=C_{b,2} \tag{34}$$

$$z=z_1,\ -D_{e,1}\frac{\partial C_{b,1}}{\partial z}=-D_{e,2}\frac{\partial C_{b,2}}{\partial z} \tag{35}$$

$$z=z_2,\ C_{b,2}=C_{b,3} \tag{36}$$

$$z=z_2,\ -D_{e,2}\frac{\partial C_{b,2}}{\partial z}=-D_{e,3}\frac{\partial C_{b,3}}{\partial z} \tag{37}$$

where z_1 is the axial coordinate at the boundary between zones 1 and 2, z_2 is the axial coordinate at the boundary between zones 2 and 3. Eqs. (34) and (36) show that the concentrations at the zone boundaries are continuous. Eqs. (35) and (37) correspond to the fact that the inlet flux and outlet flux between two adjacent zones are equal.

Eqs. (32) – (37) can be written in the dimensionless form as

Zone 1:

$$r_{e1}\frac{\partial C_{b,1}^{*}}{\partial t} = r_{D1}\frac{\partial^2 C_{b,1}^{*}}{\partial x^2} \tag{38}$$

Zone 3:

$$r_{e3}\frac{\partial C_{b,3}^{*}}{\partial t} = r_{D3}\frac{\partial^2 C_{b,3}^{*}}{\partial x^2} \tag{39}$$

Boundary conditions:

$$x = x_1,\ C_{b,1}^{*} = C_{b,2}^{*}, \tag{40}$$

$$x = x_1,\ -r_{D1}\frac{\partial C_{b,1}^{*}}{\partial x} = -\frac{\partial C_{b,2}^{*}}{\partial x} \tag{41}$$

$$x = x_2,\ C_{b,2}^{*} = C_{b,3}^{*} \tag{42}$$

$$x = x_2,\ -\frac{\partial C_{b,2}^{*}}{\partial x} = -r_{D3}\frac{\partial C_{b,3}^{*}}{\partial x} \tag{43}$$

r_{D1} and r_{D3} are defined by

$$r_{D1} = D_{b,1} / D_{b,2} \tag{44}$$

$$r_{D3} = D_{b,3} / D_{b,2} \tag{45}$$

r_{e1} and r_{e3} are defined by

$$r_{e1} = e_{b,1} / e_{b,2} \tag{46}$$

$$r_{e3} = e_{b,3} / e_{b,2} \tag{47}$$

One-zone reactor packed with unimodal-pore-structure catalyst pellets

The mathematical models for spherical porous catalyst pellets packed in a one-zone reactor for diffusion and diffusion with irreversible adsorption/reaction have been analyzed by Phanawadee et al., (2005). For porous pellets, the gas transport involves interparticle and intraparticle regions.

- Diffusion case

The mass balance equation for the non-reacting gas in the interparticle region is described by

$$e_b \frac{\partial C_b}{\partial t} = D_b \frac{\partial^2 C_b}{\partial z^2} - \frac{3}{R}\left(1 - e_b\right) D_p \left.\frac{\partial C_p}{\partial r}\right|_{r=R} \tag{48}$$

where C_b and C_p are the gas concentration in the interparticle and interparticle regions (mol/m^3) respectively , D_b and D_p are the effective Knudsen diffusivity of the gas in the interparticle and intraparticle regions (m^2/s) respectively, e_b and e_p are the interparticle and intraparticle void fractions respectively, z is the axial coordinate of the reactor (m), R is the radius of the catalyst pellet (m), and r is the radial coordinate of the catalyst pellet.

The second term on the right hand side of Eq. (48) corresponds to the flow of the gas into the spherical catalyst pellets. The initial and boundary conditions are the same as those for non-porous catalysts given by Eqs. (9) – (11).

The mass balance equation for non-reacting gas in the intraparticle region is described by

$$e_p \frac{\partial C_p}{\partial t} = D_p \left[\frac{\partial^2 C_p}{\partial r^2} + \frac{2}{r} \frac{\partial C_p}{\partial r} \right] \quad (49)$$

The initial and boundary conditions are described as follows:

Initial condition:

$$0 \le r \le R,\ t = 0,\ C_p = 0 \quad (50)$$

Boundary conditions:

$$r = R,\ C_p = C_b \quad (51)$$

$$r = 0,\ \frac{\partial C_p}{\partial r} = 0 \quad (52)$$

Eq. (50) specifies that the initial gas concentration in the pores is zero. Eq. (51) specifies that at the outermost of the pellet the gas concentrations are continuous. Eq. (52) follows the symmetric geometry. Eqs. (50) - (52) can be expressed in a dimensionless form using the following dimensionless parameters:

Dimensionless gas concentration in interparticle region:

$$C_b^* = \frac{C_b}{N_p / e_b AL} \tag{53}$$

Dimensionless gas concentration in intraparticle region:

$$C_p^* = \frac{C_p}{N_p / e_p \left(1 - e_b\right) AL} \tag{54}$$

Dimensionless axial coordinate:

$$x = \frac{z}{L} \tag{55}$$

Dimensionless radial coordinate:

$$r = \frac{r}{R} \tag{56}$$

Ratio of interparticle to intraparticle void volumes:

$$b = \frac{e_p \left(1 - e_b\right)}{e_b} \tag{57}$$

Ratio of the interparticle to the intraparticle transport characteristic times:

$$g = \frac{t_b}{t_p} = \frac{\left(\dfrac{e_b L^2}{D_b}\right)}{\left(\dfrac{e_p R^2}{D_p}\right)} \tag{58}$$

Written in dimensionless form, Eqs. (50) - (52) become

Interparticle region:

$$\frac{\partial C_b^*}{\partial t} = \frac{\partial^2 C_b^*}{\partial x^2} - 3g \left. \frac{\partial C_p^*}{\partial r} \right|_{r=1} \tag{59}$$

Intraparticle region:

$$\frac{\partial C_p^*}{\partial t} = g \left[\frac{\partial^2 C_p^*}{\partial r^2} + \frac{2}{r} \frac{\partial C_p^*}{\partial r} \right] \tag{60}$$

Initial condition:

$$0 \le r \le 1,\ t = 0,\ C_p^* = 0 \tag{61}$$

Boundary conditions:

$$r = 1,\ C_p^* = b\, C_b^* \tag{62}$$

$$r = 0,\ \frac{\partial C_p^*}{\partial r} = 0 \tag{63}$$

- Diffusion with irreversible adsorption/reaction case

When assuming that the first-order reaction takes place in the catalyst pores, the mass balance equation in the interparticle region is the same as that used to describe for diffusion-only case (Eq. 59). The mass balance equations for reactant gas in the intraparticle region and on catalyst surface are given respectively in dimensional and dimensionless forms as follows:

Dimensional equation:

$$e_p \frac{\partial C_p}{\partial t} = D_p \left[\frac{\partial^2 C_p}{\partial r^2} + \frac{2}{r} \frac{\partial C_p}{\partial r} \right] - r_s k_a C_p \tag{64}$$

$$\frac{\partial q}{\partial t} = k_a C_p \tag{65}$$

Dimensionless equation:

$$\frac{\partial C_p^*}{\partial t} = g \left[\frac{\partial^2 C_p^*}{\partial r^2} + \frac{2}{r} \frac{\partial C_p^*}{\partial r} \right] - k_a^* C_p^* \tag{66}$$

$$\frac{\partial q^*}{\partial t} = k_a^* C_p^* \tag{67}$$

where k_a^* is the dimensionless apparent adsorption/reaction rate constant defined by

$$k_a^* = k_a' \times \frac{e_b L^2}{D_b} = \frac{r_s k_a}{e_p} \times \frac{e_b L^2}{D_b} \tag{68}$$

and q^* is the pulse-intensity-normalized surface concentration defined by

$$q^* = a \times q = \frac{r_s}{N_p / \left(1 - e_b\right) AL} \times q \tag{69}$$

The initial and boundary conditions for the reactant gas in the interparticle and intraparticle regions are the same as those for diffusion-only case. The initial condition for the reactant gas on the catalyst surface is given by

Dimensional form:

$$0 \le R \le 1,\ t = 0,\ q = 0 \tag{70}$$

Dimensionless form:

$$0 \le r \le 1,\ t = 0,\ q^* = 0 \tag{71}$$

Three-zone reactor packed with unimodal-pore-structure catalyst pellets

- Diffusion and diffusion with irreversible adsorption/reaction cases

The mathematical model for spherical porous catalyst pellets packed in a three-zone reactor for diffusion and diffusion with irreversible adsorption/reaction has been proposed by Monrudee (2002). The dimensionless mass balance equation in the two inert zones, zones 1 and 3, is described by Eqs. (38) and (39), respectively. The mass balance equations that describe the catalyst zone are the same as those used to describe the one-zone reactor. The initial conditions and the inlet and outlet boundary conditions are the same as those for the one-zone reactor given by Eqs. (9) – (11). The boundary conditions at the two boundaries between adjacent zones are given by Eqs. (40) – (43).

Moment analysis

In TAP experiments, the observed data detected by a mass spectrometer is the intensity which is a function of time. The intensity is proportional to the gas exit flow rate. The exit flow rate, F (mol/s), can be determined by

$$F = -A \cdot D_b \left. \frac{\partial C_b}{\partial z} \right|_{z=L} \tag{72}$$

Usually, the exit flow rate of the reactant gas is normalized by the number of moles of the reactant gas in the inlet pulse providing the pulse-intensity-normalized (PI-normalized) exit flow rate (Gleaves et al., 1997).

The j^{th} moment of the PI-normalized exit flow rate is defined by

$$m_j = \int_0^{\infty} \frac{F}{N_p} \cdot t^j dt \qquad (73)$$

The zeroth moment is equal to the ratio of the number of moles of the reactant gas leaving the reactor to the number of moles of the reactant gas in the inlet pulse. The ratio of the first and the zeroth moments is the mean residence time of the gas exiting the reactor.

For diffusion and diffusion with reversible adsorption cases, the zeroth moment of the PI-normalized exit flow rate is equal to unity due to the conservation of mass. The zeroth moment of the PI-normalized exit flow rate for diffusion with irreversible adsorption/reaction is related to the conversion of the reactant gas as follows

$$m_0 = 1 - X \qquad (74)$$

where X is the gas conversion. Practically, the conversion is determined by the use of an internal standard (inert gas).

The analytical expressions for the j^{th} moment of the PI-normalized exit flow rate can be determined by the method described in the literature (Andersen and White 1971; Constales et al., 2001). The set of mass balance equations are transformed into Laplace domain. The moment expressions can then be determined from the Laplace-domain solution for the PI-normalized exit flow rate using

$$m_j = (-1)^j \lim_{s \to 0} \frac{\partial^j}{\partial s^j} \left(\frac{F(s)}{N_p} \right) \tag{75}$$

Eqs. (72), (73) and (75) can be written in the dimensionless form as follows:

$$F^* = -\left.\frac{\partial C_b^*}{\partial x}\right|_{x=1} \tag{76}$$

$$m_j^* = \int_0^\infty F^* t^j dt \tag{77}$$

$$m_j^* = (-1)^j \lim_{s \to 0} \frac{\partial^j F^*(s)}{\partial s^j} \tag{78}$$

The relationship between the j^{th} moment expression of the PI-normalized exit flow rate and that of the dimensionless exit flow rate can be described as

$$m_j^* = \left(\frac{D_b}{e_b \cdot L^2} \right)^j m_j \tag{79}$$

Moment expressions

The reported moment expressions of the exit flow rate in the literature are listed in Table 1.

Table 1 The reported moment expressions of the exit flow rate for different TAP-reactor configurations in the literature.

Processes \ Configurations	Non-porous		Unimodal-pore-structure	
	One-zone reactor	Three-zone reactor	One-zone reactor	Three-zone reactor
Diffusion	m_0^*, m_1^* (Gleaves et al., 1997)	m_0^*, m_1^* (Phanawadee et al., 1999)	m_0^*, m_1^*, m_2^*, m_3^* (Colaris et al., 2002)	-
Diffusion with irreversible adsorption/reaction	m_0^*, m_1^* (Gleaves et al., 1997)	m_0^* (Phanawadee et al., 1997)	m_0^*, m_1^* (Monrudee 2002; Phanawadee et. al., 2005)	m_0^* (Monrudee 2002; Phanawadee et. al., 2005)
Diffusion with reversible adsorption	m_0^*, m_1^* (Gleaves et al., 1997)	m_0^*, m_1^*, m_2^* (Constales et al., 2001)	-	-

The moment expressions listed in table 1 are shown for different cases as follows:

Non-porous case

- One-zone reactor, diffusion :

$$m_0^* = 1 \tag{80}$$

$$m_1^* = \frac{1}{2} \tag{81}$$

- One-zone reactor, diffusion with irreversible adsorption/reaction :

$$m_0^* = \frac{1}{\cosh\sqrt{y}} = 1 - X \qquad (82)$$

$$m_1^* = \frac{1}{2}\frac{\operatorname{sech}\sqrt{y}\ \tanh\sqrt{y}}{\sqrt{y}} \qquad (83)$$

The parameter y is the dimensionless kinetic parameter defined by

$$y = \frac{k_a r_s (1-e_b) L_{cat}^2}{D_b} \qquad (84)$$

It is noted that for a one-zone reactor, $L_{cat} = L$.

- One-zone reactor, diffusion with reversible adsorption :

$$m_0^* = 1 \qquad (85)$$

$$m_1^* = \frac{1}{2}\left(1 + \frac{k_a'}{k_d}\right) \qquad (86)$$

- Three-zone reactor, diffusion :

$$m_0^* = 1 \qquad (87)$$

$$m_1^* = \frac{z_3}{r_{D3}}\left[\frac{1}{2} z_3 r_{e3} + z_2 + z_1 r_{e1}\right] + z_2\left[\frac{1}{2} z_2 + z_1 r_{e1}\right] + \frac{z_1}{r_{D1}}\left[\frac{1}{2} z_1 r_{e1}\right] \qquad (88)$$

z is the ratio of the length of i[th] zone to the reactor length, and subscripts 1, 2 and 3 refer to the first, second and third zones respectively.

- Three-zone reactor, diffusion with irreversible adsorption/reaction :

$$m_0^* = \frac{1}{\cosh\sqrt{y} + \frac{z_3}{r_{D3} z_2}\sqrt{y}\,\sinh\sqrt{y}} = 1 - X \qquad (89)$$

- Three-zone reactor, diffusion with reversible adsorption :

$$m_0^* = 1 \qquad (90)$$

$$m_1^* = \frac{z_3}{r_{D3}}\left[\frac{1}{2} z_3 r_{e3} + z_2\left(1 + \frac{k_a^*}{k_d^*}\right) + z_1 r_{e1}\right] + z_2\left[\frac{1}{2} z_2\left(1 + \frac{k_a^*}{k_d^*}\right) + z_1 r_{e1}\right] + \frac{z_1}{r_{D1}}\left[\frac{1}{2} z_1 r_{e1}\right] \qquad (91)$$

$$m_2^* = -\frac{1}{4}\left[\begin{array}{l} \frac{z_1 z_2}{r_{D1}}\left[z_1^2 r_{e1}^2 + 2 z_1 z_2 r_{e1}\left(1 + \frac{k_a^*}{k_d^*}\right)\right] \\ + \frac{z_1 z_3}{r_{D1} r_{D3}}\left[z_1^2 r_{e1}^2 + 2 z_1 z_3 r_{e1} r_{e3} + 4 z_1 z_2 r_{e1}\left(1 + \frac{k_a^*}{k_d^*}\right)\right] \\ + \frac{z_2 z_3}{r_{D3}}\left[\begin{array}{l} z_2^2\left(1 + \frac{k_a^*}{k_d^*}\right)^2 + 2 z_2 z_3 r_{e3}\left(1 + \frac{k_a^*}{k_d^*}\right) \\ + 4 z_1 z_2 r_{e1}\left(1 + \frac{k_a^*}{k_d^*}\right) + 4 z_1 z_3 r_{e1} r_{e3} - \frac{k_a^*}{k_d^{*2}} \end{array}\right] \\ + z_2^2\left[z_1 z_2 r_{e1}\left(1 + \frac{k_a^*}{k_d^*}\right) - \frac{k_a^*}{k_d^{*2}}\right] \\ + \frac{z_3^2}{r_{D3}^2}\left[z_1 z_3 r_{e1} r_{e3} + z_2 z_3 r_{e3}\left(1 + \frac{k_a^*}{k_d^*}\right)\right] \end{array}\right] + 2\left(m_1^*\right)^2 \qquad (92)$$

Unimodal porous case

- One-zone reactor, diffusion :

$$m_0^* = 1 \tag{93}$$

$$m_1^* = \frac{1}{2}[b+1] \tag{94}$$

$$m_2^* = \frac{1}{2}\left[\frac{5}{6}[b+1]^2 + \frac{2}{15}b\left[\frac{(b+1)^2}{g}\right]\right] \tag{95}$$

$$m_3^* = \frac{1}{2}\left[\frac{61}{60}[b+1]^3 + \frac{1}{3}b\,[b+1]\left[\frac{1}{g}\right] + \frac{4}{105}b\left[\frac{1}{g}\right]\right] \tag{96}$$

- One-zone reactor, diffusion with irreversible adsorption/reaction :

$$m_0^* = \frac{1}{\cosh\sqrt{y\,h}} = 1 - X \tag{97}$$

$$m_1^* = \frac{1}{2}\frac{\operatorname{sech}\sqrt{y\,h}\,\tanh\sqrt{y\,h}}{\sqrt{y\,h}}\left[\frac{3}{2}b\left(\frac{1}{\sqrt{\frac{k_a^*}{g}}\tanh\sqrt{\frac{k_a^*}{g}}} - \frac{1}{\sinh^2\sqrt{\frac{k_a^*}{g}}}\right) + 1\right] \tag{98}$$

The parameter h is the effectiveness factor defined as follows

$$h = \frac{3}{3M_T}\left(\frac{1}{\tanh 3M_T} - \frac{1}{3M_T}\right) \tag{99}$$

The parameter M_T is the Thiele modulus defined by

$$M_T = \frac{\sqrt{\frac{k_a^*}{g}}}{3} = \frac{R}{3}\sqrt{\frac{k_a r_s}{D_p}} \tag{100}$$

- Three-zone reactor, diffusion with irreversible adsorption/reaction :

$$m_0^* = \frac{1}{\cosh\sqrt{y\,h} + \frac{z_3}{r_{D3} z_2}\sqrt{y\,h}\,\sinh\sqrt{y\,h}} = 1 - X \tag{101}$$

The parameter y in the moment expressions for diffusion with irreversible adsorption/reaction for non-porous and unimodal porous cases is the dimensionless kinetic parameter. The difference of the two cases is that the active sites are on the external surface of the catalyst pellets for the non-porous case. The parameter h is the typical effectiveness factor defined similarly to that in steady-state conditions. Due to the change of concentration with time during the TAP experiments, h changes with time and position. Hence h is equivalent to the average of h over the whole pulse (Phanawadee, 2005).

To interpret by moment analysis, the number of required moment expressions for estimating transport and kinetic parameters is equal to the number of unknown parameters. The effective Knudsen diffusivities of a reactant gas can be calculated from the effective Knudsen diffusivity of an inert gas in the same system by using Eq. (3). The inert gas diffusivity is determined using moment expressions for diffusion-only case.

Solutions of the exit flow rate for simple cases and fingerprints of the exit flow rate for irreversible adsorption/reaction and reversible adsorption

The size and shape of the exit flow rate curve depends on the gas transport and kinetics. Gleaves et. al. (1997) have been reported fingerprints of the exit flow rate curve from one-zone and three-zone reactors packed with non-porous catalyst pellets for diffusion with irreversible adsorption/reaction, and with reversible adsorption.

One-zone reactor, diffusion

The analytical solution of the dimensionless exit flow rate for the one-zone reactor packed with non-porous pellets for diffusion-only case is described by

$$F_A^* = p\sum_{n=0}^{\infty}(-1)^n (2n+1)\exp\left(-(n+0.5)^2 p^2 t\right) \tag{102}$$

The curve described by Eq. (102) is called standard diffusion curve and is shown in Figure 2. The time at the maximum, $t_{\max}$, is equal to 0.17 and the maximum dimensionless exit flow is equal to 1.85. The mean residence time, t_{res}, determined by the dividing the first moment by zeroth moment, is equal to 0.5.

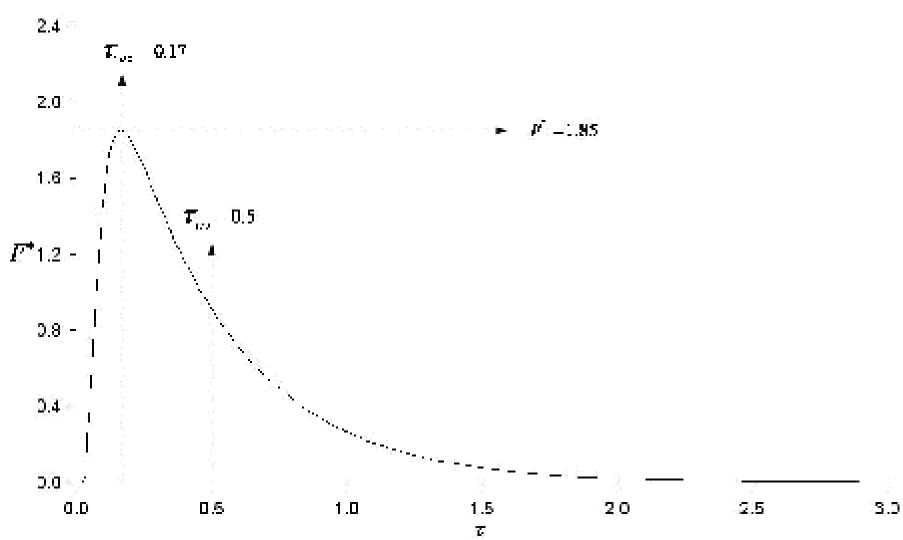

Figure 2 Standard diffusion curve showing key time characteristics.

One-zone reactor, diffusion with irreversible adsorption/reaction

For diffusion with irreversible adsorption/reaction the solution of the exit flow rate is described by

$$F_A^* = p\ \exp\left(-k_a^* t\right) \sum_{n=0}^{\infty} (-1)^n\ (2n+1) \exp\left(-(n+0.5)^2\ p^2 t\right) \qquad (103)$$

For diffusion-only case, k_a^* in Eq. (103) is equal to zero. Figure 3 shows the exit flow rate curves for diffusion and diffusion with irreversible adsorption/reaction cases.

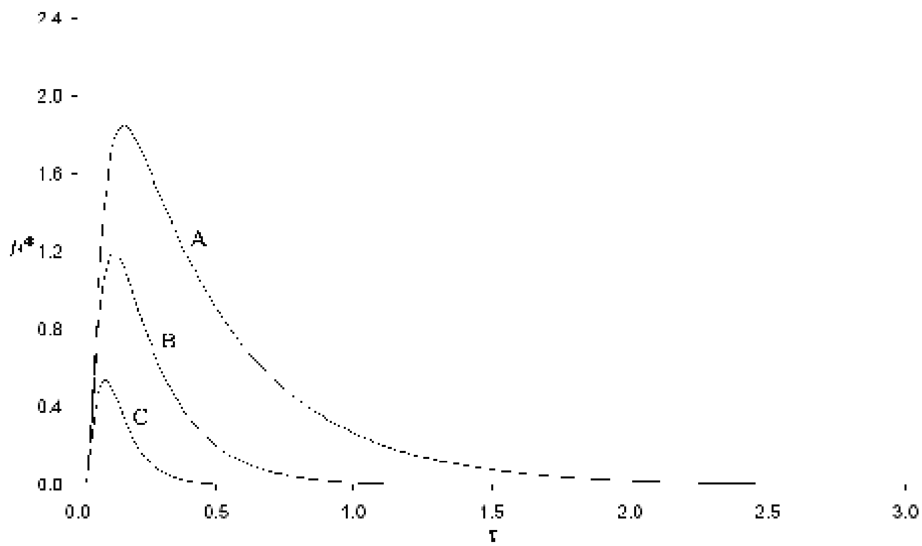

Figure 3 Dimensionless exit flow rate curves calculated for the one-zone reactor packed with non-porous catalyst pellets for diffusion with irreversible adsorption/reaction case: A) k_a^* = 0; B) k_a^* = 3; C) k_a^* = 10.

As shown in Figure 3, the fingerprint for irreversible adsorption/reaction is inside-flow. The curve of the exit flow rate for irreversible adsorption/reaction is always smaller than, and does not cross the curve for diffusion-only case.

One-zone reactor, diffusion with reversible adsorption

The analytical solution of the exit flow rate for the one-zone reactor packed with non-porous pellets for diffusion with reversible adsorption is described by

$$F_A^* = p\sum_{n=0}^{\infty}(-1)^n(2n+1)\left[A_n \exp(r_- t) + (1-A_n)\exp(r_+ t)\right] \tag{104}$$

where

$$r_\pm = \frac{-\left(p_n^2+k_a^*+k_d^*\right) \pm \sqrt{\left(p_n^2+k_a^*+k_d^*\right)^2 - 4p_n^2 k_d^*}}{2} \tag{105}$$

$$p_n = (n+0.5)p \tag{106}$$

$$A_n = \frac{\left(r_+ + p_n^2 + k_a^*\right)}{r_+ - r_-} \tag{107}$$

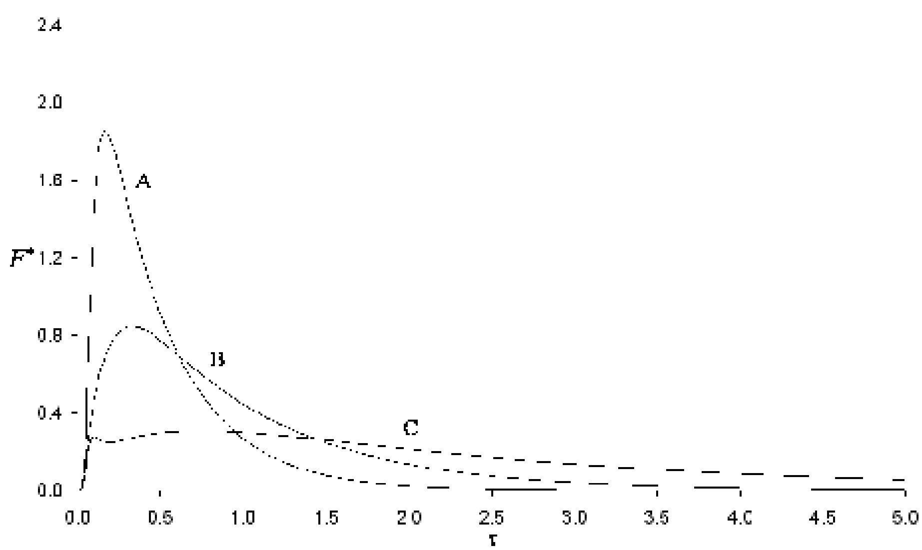

Figure 4 Dimensionless exit flow rate curves calculated for the one-zone reactor packed with non-porous catalyst pellets for diffusion with reversible adsorption case: (A) $k_a^*=0$; (B) $k_a^*=20$, $k_d^*=20$; (C) $k_a^*=20$, $k_d^*=5$.

Figure 4 shows the comparison between the dimensionless exit flow rate curves calculated from the one-zone reactor packed with non-porous catalyst pellets for diffusion and diffusion with irreversible adsorption/reaction cases**.** The flow curve for diffusion with reversible adsorption will cross the flow curve for diffusion case. The point at which the curves intersect depends on the dimensionless adsorption and desorption rate constants. This behavior results from the delay of the molecular transport throughout the reactor caused by the reversible interaction of gas with catalyst. The flow curve is characterized by two peaks (two-hump curve) when the adsorption rate constant is large and the desorption rate constant is small. The first of the two peaks resembles an irreversible adsorption curve. This peak is governed by the interaction between diffusion and adsorption, and is called the 'adsorption peak'. The second peak is caused by slow desorption, and is called the 'desorption peak'.

Three-zone reactor, diffusion with irreversible adsorption/reaction, and with reversible adsorption

For a three-zone reactor, the analytical solutions of the exit flow rate for diffusion, diffusion with irreversible adsorption/reaction, and with reversible adsorption have not been reported. The exit flow rate curves for these cases can be obtained by solving the three-zone models numerically. The fingerprints for diffusion with irreversible adsorption/reaction and reversible adsorption for the three-zone reactor are similar to those for the one-zone reactor.

CALCULATION METHODS

Determination of the moment expressions involves formulation of partial differential equations (PDEs) describing the processes in TAP reactor. The PDEs were transformed into a dimensionless form.

The equations were then transformed into Laplace domain. The analytical solutions of the exit flow rate were determined. The moment expressions were determined from the solution of the exit flow rate using Eq. (78).

To analyze the characteristic of the distribution of q for irreversible adsorption, the solution of q in Laplace domain was determined. The solution of q at the end of the experiment in time domain was obtained by using the final value theorem.

To investigate the fingerprints of the exit flow rate curves, the dimensionless exit flow rate curves were calculated from the obtained solutions of the dimensionless exit flow rate. Using the inverse discrete Fourier transform via the fast Fourier algorithm, the numerical solutions of the exit flow rate in time domain were obtained.

Mathematical models

The assumptions in the mathematical models include 1) the catalyst and inert particle bed are uniformly packed, 2) there is no radial concentration gradient in the bed, and 3) the temperature distribution in the reactor is uniform. Differential equations involved in this work are reported as follows:

One-zone reactor packed with unimodal-pore-structure catalyst pellets

- Diffusion with reversible adsorption case

The set of partial differential equations for diffusion with reversible adsorption case is similar to that for diffusion with irreversible adsorption/reaction except that the mass balance equation in the intraparticle region involves reversible adsorption. The dimensionless mass balance equations in the intraparticle region and on the catalyst surface for diffusion with reversible adsorption case are described by

Intraparticle region:

$$\frac{\partial C_p^*}{\partial t} = g\left[\frac{\partial^2 C_p^*}{\partial r^2} + \frac{2}{r}\frac{\partial C_p^*}{\partial r}\right] - k_a^* C_p^* + k_d^* q^* \tag{108}$$

$$\frac{\partial q^*}{\partial t} = k_a^* C_p^* - k_d^* q^* \tag{109}$$

where k_d^* is the dimensionless desorption rate constant defined by Eq. (29).

Three-zone reactor packed with unimodal-pore-structure catalyst pellets

- Diffusion, diffusion with irreversible adsorption/reaction, and diffusion with reversible adsorption cases

The dimensionless mass balance equations in the two inert zones, (zones 1 and 3) are described by Eqs. (38) and (39), respectively. The mass balance equations that describe the catalyst zone are the same as those used to describe the one-zone reactor. The initial conditions and the inlet and outlet boundary conditions are the same as those for the one-zone reactor given by Eqs. (9) – (11). The boundary conditions at the two boundaries between adjacent zones are given by Eqs. (40) – (43).

One-zone reactor packed with bimodal-pore-structure catalyst pellets

The catalyst pellet with bimodal-pore-structure involves macropore and mesopore regions (see Figure 5). Each region is in a spherical space. This corresponds to the case in which spherical particles with mesopores are compressed into spherical pellets. The void between the compressed particles is referred as the macropore region. The gas transport in the catalyst bed therefore takes place in three regions including interparticle, macropore, and mesopore regions. This study does not include the case involving micropore domain in order to focus only the case in which Knudsen diffusion is applied.

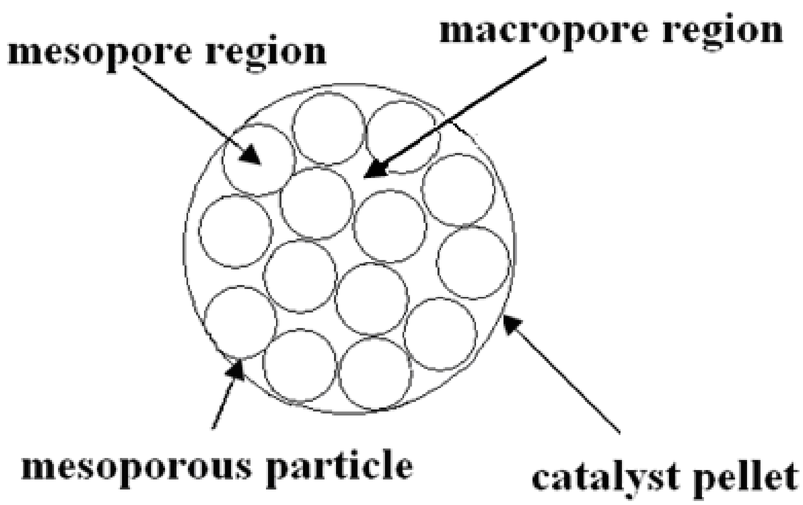

Figure 5 A schematic of bimodal-pore-structure catalyst pellet

- Diffusion case

The mass balance equations for non-reacting gas can be written in different regions as follows:

Interparticle region:

$$e_b \frac{\partial C_b}{\partial t} = D_b \frac{\partial^2 C_b}{\partial z^2} - \frac{3}{R_c}(1-e_b) D_c \left.\frac{\partial C_c}{\partial r_c}\right|_{r_c=R_c} \tag{110}$$

Macropore region:

$$e_c \frac{\partial C_c}{\partial t} = D_c \left[\frac{\partial^2 C_c}{\partial r_c^2} + \frac{2}{r_c}\frac{\partial C_c}{\partial r_c}\right] - \frac{3}{R_m}(1-e_c) D_m \left.\frac{\partial C_m}{\partial r_m}\right|_{r_m=R_m} \tag{111}$$

Mesopore region:

$$e_m \frac{\partial C_m}{\partial t} = D_m \left[\frac{\partial^2 C_m}{\partial r_m^2} + \frac{2}{r_m}\frac{\partial C_m}{\partial r_m}\right] \tag{112}$$

where C_b, C_c and C_m are the gas concentrations in the interparticle, macropore and mesopore regions respectively, z is the axial coordinate of the reactor, r_c is the radial coordinate of the catalyst pellet, R_c is the radius of the catalyst pellet, r_m is the radial coordinate of the mesoporous particle, R_m is the radius of the mesoporous particle, t is the time, and e_b, e_c, and e_m are the interparticle, macropore and mesopore void fractions respectively.

The second term on the right-hand side of Eqs. (111) and (112) corresponds to the flow of the gas into the pellets and mesoporous particles.

The initial and boundary conditions are described as follows:

Initial conditions:

$$0 \le z \le L,\ t = 0,\ C_b = 0 \tag{113}$$

$$0 \le r_c \le R_c,\ t = 0,\ C_c = 0 \tag{114}$$

$$0 \le r_m \le R_m,\ t = 0,\ C_m = 0 \tag{115}$$

Boundary conditions:

Interparticle region:

$$x = 0,\ -D_b \frac{\partial C_b}{\partial z} = d\left(t - 0^+\right)\frac{N_p}{A} \tag{116}$$

$$x = L,\ C_b = 0 \tag{117}$$

Macropore region:

$$r_c = R_c,\ C_c = C_b \tag{118}$$

$$r_c = 0,\ \frac{\partial C_c}{\partial r_c} = 0 \tag{119}$$

Mesopore region:

$$r_m = R_m,\ C_m = C_c \tag{120}$$

$$r_m = 0,\ \frac{\partial C_m}{\partial r_m} = 0 \tag{121}$$

Eqs. (116) and (117) are the same as those for non-porous case. Eqs. (118) – (121) follow the conditions assumed for spherical catalyst pellets with bimodal-pore-structure (Jayaraman 1993). Eqs. (116) – (121) can be expressed in the dimensionless form using the following dimensionless parameters:

Dimensionless gas concentration in interparticle:

$$C_b^* = \frac{C_b}{N_p / e_b AL} \tag{122}$$

Dimensionless gas concentration in macropore:

$$C_c^* = \frac{C_c}{N_p / e_c (1 - e_b) AL} \tag{123}$$

Dimensionless gas concentration in mesopore:

$$C_m^* = \frac{C_m}{N_p / e_m (1-e_c)(1-e_b) AL} \tag{124}$$

Dimensionless axial coordinate of the reactor:

$$x = \frac{z}{L} \tag{125}$$

Dimensionless radial coordinate of the catalyst pellet:

$$r_c = \frac{r_c}{R_c} \tag{126}$$

Dimensionless radial coordinate of the compressed particle with mesopores:

$$r_m = \frac{r_m}{R_m} \tag{127}$$

Dimensionless time:

$$t = t \times \frac{D_b}{L^2 e_b} \tag{128}$$

Ratio of the interparticle to the macropore transport characteristic times:

$$g_c = \frac{t_b}{t_c} = \frac{\left(\frac{e_b L^2}{D_b}\right)}{\left(\frac{e_c R_c^2}{D_c}\right)} \tag{129}$$

Ratio of the macropore to the mesopore transport characteristic times:

$$g_m = \frac{t_b}{t_m} = \frac{\left(\dfrac{e_b L^2}{D_b}\right)}{\left(\dfrac{e_m R_m^2}{D_m}\right)} \tag{130}$$

Ratio of macropore to interparticle void volumes:

$$b_c = \frac{e_c\left(1-e_b\right)}{e_b} \tag{131}$$

Ratio of mesopore to macropore void volumes:

$$b_m = \frac{e_m\left(1-e_c\right)}{e_c} \tag{132}$$

The definitions of dimensionless parameters and variables in the interparticle and macropore regions have been defined similarly to those for the unimodal porous case (Phanawadee et al., 2005). Written in the dimensionless form, Eqs. (110) – (121) are given by

Interparticle region:

$$\frac{\partial C_b^*}{\partial t} = \frac{\partial^2 C_b^*}{\partial x^2} - 3g_p \left.\frac{\partial C_p^*}{\partial r_p}\right|_{r_p=1} \tag{133}$$

Macropore region:

$$\frac{\partial C_c^*}{\partial t} = g_p\left[\frac{\partial^2 C_c^*}{\partial r_c^2} + \frac{2}{r_c}\frac{\partial C_c^*}{\partial r_c}\right] - 3g_c \left.\frac{\partial C_c^*}{\partial r_c}\right|_{r_c=1} \tag{134}$$

Mesopore region:

$$\frac{\partial C_m^*}{\partial t} = g_m \left[\frac{\partial^2 C_m^*}{\partial r_m^2} + \frac{2}{r_m} \frac{\partial C_m^*}{\partial r_m} \right] \tag{135}$$

Initial conditions:

$$0 \le x \le 1,\ t = 0,\ C_b^* = 0 \tag{136}$$

$$0 \le r_c \le 1,\ t = 0,\ C_c^* = 0 \tag{137}$$

$$0 \le r_m \le 1,\ t = 0,\ C_m^* = 0 \tag{138}$$

Boundary conditions:

Interparticle region:

$$x = 0,\ \frac{\partial C_b^*}{\partial x} = -1 \tag{139}$$

$$x = 1,\ C_b^* = 0 \tag{140}$$

Macropore region:

$$r_c = 1,\ C_c^* = b_c C_b^* \tag{141}$$

$$r_c = 0,\ \frac{\partial C_c^*}{\partial r_c} = 0 \tag{142}$$

Mesopore region:

$$r_m = 1,\ C_m^* = b_m C_c^* \tag{143}$$

$$r_m = 0,\ \frac{\partial C_m^*}{\partial r_m} = 0 \tag{144}$$

- Diffusion with irreversible adsorption/reaction case

The mathematical model for diffusion with irreversible adsorption/reaction is similar to that of diffusion case except that the mass balance equations for the reactant gas in the macropore region and on the catalyst surface involve the irreversible adsorption term and are described by

$$e_m \frac{\partial C_m}{\partial t} = D_m \left[\frac{\partial^2 C_m}{\partial r_m^2} + \frac{2}{r_m} \frac{\partial C_m}{\partial r_m} \right] - r_s k_a C_m \tag{145}$$

$$\frac{\partial q}{\partial t} = k_a C_m \tag{146}$$

Eqs. (145) and (146) can be written in a dimensionless form as

$$\frac{\partial C_m^*}{\partial t} = g_m \left[\frac{\partial^2 C_m^*}{\partial r_m^2} + \frac{2}{r_m} \frac{\partial C_m^*}{\partial r_m} \right] - k_a^* C_m^* \tag{147}$$

$$\frac{\partial q^*}{\partial t} = k_a^* C_m^* \tag{148}$$

where k_a^* is the dimensionless apparent adsorption/reaction rate constant defined by

$$k_a^* = k_a' \times \frac{e_b L^2}{D_b} = \frac{r_s k_a}{e_m} \times \frac{e_b L^2}{D_b} \tag{149}$$

and q^* is the pulse-intensity-normalized surface concentration defined by

$$q^* = a \times q = \frac{r_s}{N_p / (1-e_c)(1-e_b)AL} \times q \tag{150}$$

The parameters k_a' and a in Eqs. (149) and (150) are the apparent adsorption/reaction rate constant and the catalyst number, respectively. The initial and boundary conditions for Eq. (147) are the same as those presented for diffusion. The initial condition in the mesopore region is given in dimensional form as

$$0 \le r_m \le R_m,\ t = 0,\ q = 0 \tag{151}$$

and in dimensionless form as

$$0 \le r_m \le 1,\ t = 0,\ q^* = 0 \tag{152}$$

- Diffusion with reversible adsorption case

The mathematical model for diffusion with reversible adsorption case is similar to that for diffusion with irreversible adsorption/reaction except that the mass balance equation in the mesopore region involves reversible adsorption. The mass balance equations in the mesopore region and on the catalyst surface are described by

$$e_m \frac{\partial C_m}{\partial t} = D_m \left[\frac{\partial^2 C_m}{\partial r_m^2} + \frac{2}{r_m} \frac{\partial C_m}{\partial r_m} \right] - r_s \left(k_a C_m - k_d q \right) \tag{153}$$

$$\frac{\partial q}{\partial t} = k_a C_m - k_d q \tag{154}$$

Eqs. (153) and (154) can be written in a dimensionless form as

$$\frac{\partial C_m^*}{\partial t} = g_m \left[\frac{\partial^2 C_m^*}{\partial r_m^2} + \frac{2}{r_m} \frac{\partial C_m^*}{\partial r_m} \right] - \left(k_a^* C_m^* - k_d^* q^* \right) \tag{155}$$

$$\frac{\partial q^*}{\partial t} = k_a^* C_m^* - k_d^* q^* \tag{156}$$

where k_d^* is the dimensionless desorption rate constant defined by Eq. (29).

Three-zone reactor packed with bimodal-pore-structure catalyst pellets

- Diffusion, diffusion with irreversible adsorption/reaction, and diffusion with reversible adsorption cases

The dimensionless mass balance equations in the two inert zones, zones 1 and 3, are described by Eqs. (38) and (39), respectively. The mass balance equations that describe the catalyst zone are the same as those used to describe the one-zone reactor. The initial conditions and the inlet and outlet boundary conditions are the same as those for the one-zone reactor given by Eqs. (9) – (11). The boundary conditions at the two boundaries between adjacent zones are given by Eqs. (40) – (43).

RESULTS AND DISCUSSION

Results will be reported in 3 sections. Section 1 shows the moment expressions of the dimensionless exit flow rate determined for different TAP-reactor configurations. Application of these moment expressions for estimating transport and kinetic parameters will also be discussed. The characteristics of the distribution of surface coverage for irreversible adsorption case will be described in section 2. In section 3, fingerprints of the exit flow rate for irreversible adsorption/reaction and desorption for the one-zone reactor packed with unimodal and bimodal-pore-structure catalyst pellets will be reported.

1. Moment expressions

The moment expressions of the dimensionless exit flow rate determined for different TAP-reactor configurations are listed in table 2. Derivation of these moment expressions is provided in Appendices.

Table 2 Itemized moment expressions of the dimensionless exit flow rate determined for different cases and appendixes in which the derivation for the expressions are shown.

Configurations / Processes	Unimodal-pore-structure		Bimodal- pore-structure	
	One-zone reactor	Three-zone reactor	One-zone reactor	Three-zone reactor
Diffusion	-	m_0^*, m_1^*, m_2^* (Appendix B)	$m_0^*, m_1^*, m_2^*, m_3^*$ (Appendix E)	m_0^*, m_1^*, m_2^* (Appendix H)
Diffusion with irreversible adsorption/reaction	-	m_1^* (Appendix C)	m_0^*, m_1^* (Appendix F)	m_0^*, m_1^* (Appendix I)
Diffusion with reversible adsorption	m_0^*, m_1^*, m_2^* (Appendix A)	m_0^*, m_1^*, m_2^* (Appendix D)	m_0^*, m_1^*, m_2^* (Appendix G)	m_0^*, m_1^*, m_2^* (Appendix J)

The expressions listed in table 2 are reported as follows:

1.1 Unimodal porous case

1.1.1 One-zone reactor, diffusion with reversible adsorption :

$$m_0^* = 1 \tag{157}$$

$$m_1^* = \frac{1}{2}\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right] \tag{158}$$

$$m_2^* = \frac{1}{2}\left[\frac{5}{6}\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right]^2 + \frac{2b}{15}\left[\frac{\left(1+\frac{k_a^*}{k_d^*}\right)^2}{g}+15\frac{k_a^*}{k_d^{*2}}\right]\right] \tag{159}$$

1.1.2 Three-zone reactor, diffusion :

$$m_0^* = 1 \tag{160}$$

$$m_1^* = \frac{z_3}{r_{D3}}\left[\frac{1}{2}z_3 r_{e3} + z_2\left[b+1\right] + z_1 r_{e1}\right] + z_2\left[\frac{1}{2}z_2\left[b+1\right]+z_1 r_{e1}\right] + \frac{z_1}{r_{D1}}\left[\frac{1}{2}z_1 r_{e1}\right] \tag{161}$$

$$m_2^* = -\frac{1}{4}\left[\begin{array}{l} \frac{z_1 z_2}{r_{D1}}\left[z_1^2 r_{e1}^2 + 2z_1 z_2 r_{e1}\left[b+1\right]\right] \\ + \frac{z_1 z_3}{r_{D1} r_{D3}}\left[z_1^2 r_{e1}^2 + 2z_1 z_3 r_{e1} r_{e3} + 4z_1 z_2 r_{e1}\left[b+1\right]\right] \\ + \frac{z_2 z_3}{r_{D3}}\left[\begin{array}{l} z_2^2\left[b+1\right]^2 + 2z_2 z_3 r_{e3}\left[b+1\right] \\ +4z_1 z_2 r_{e1}\left[b+1\right] + 4z_1 z_3 r_{e1} r_{e3} - \left[\frac{8}{15} b\left[\frac{1}{g}\right]\right] \end{array}\right] \\ +z_2^2\left[z_1 z_2 r_{e1}\left[b+1\right] - \left[\frac{4}{15} b\left[\frac{1}{g}\right]\right]\right] \\ + \frac{z_3^2}{r_{D3}^2}\left[z_1 z_3 r_{e1} r_{e3} + z_2 z_3 r_{e3}\left[b+1\right]\right] \end{array}\right] + 2\left(m_1^*\right)^2$$

(162)

1.1.3 Three-zone reactor, diffusion with irreversible adsorption/reaction :

$$m_1^* = \left\{\begin{array}{l} \frac{z_3}{r_{D3}}\left[\frac{1}{2} z_3 r_{e3} + \frac{1}{2} z_2 A'\left(1 + \frac{\tanh\sqrt{y h}}{\sqrt{y h}}\right) + z_1 r_{e1}\right]\cosh\sqrt{y h} \\ +z_2\left[\frac{1}{2} z_2 A' + z_1 r_{e1}\right]\frac{\sinh\sqrt{y h}}{\sqrt{y h}} + \frac{z_1}{r_{D1}}\left[\frac{1}{2} z_1 r_{e1}\right]\cosh\sqrt{y h} \\ + \frac{z_1 z_3}{r_{D1} r_{D3}}\left[z_1 z_2 r_{e1}\sqrt{y h}\,\sinh\sqrt{y h}\right] \end{array}\right\} \qquad (163)$$

The quantity A' in Eq. (163) is defined by

$$A' = \left\{\frac{3b}{2}\left(\frac{1}{\sqrt{\frac{k_a^*}{g}}\tanh\sqrt{\frac{k_a^*}{g}}} - \operatorname{csch}^2\sqrt{\frac{k_a^*}{g}}\right) + 1\right\} \qquad (164)$$

1.1.4 Three-zone reactor, diffusion with reversible adsorption :

$$m_0^* = 1 \tag{165}$$

$$m_1^* = \left\{ \begin{array}{l} \frac{z_3}{r_{D3}}\left[\frac{1}{2}z_3 r_{e3} + z_2\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right]+z_1 r_{e1}\right] \\ +z_2\left[\frac{1}{2}z_2\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right]+z_1 r_{e1}\right]+\frac{z_1}{r_{D1}}\left[\frac{1}{2}z_1 r_{e1}\right] \end{array} \right\} \tag{166}$$

$$m_2^* = -\frac{1}{4}\left[\begin{array}{l} \frac{z_1 z_2}{r_{D1}}\left[z_1^2 r_{e1}^2 + 2z_1 z_2 r_{e1}\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right]\right] \\ +\frac{z_1 z_3}{r_{D1} r_{D3}}\left[z_1^2 r_{e1}^2 + 2z_1 z_3 r_{e1} r_{e3} + 4z_1 z_2 r_{e1}\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right]\right] \\ +\frac{z_2 z_3}{r_{D3}}\left[\begin{array}{l} z_2^2\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right]^2 + 2z_2 z_3 r_{e3}\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right] \\ +4z_1 z_2 r_{e1}\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right]+4z_1 z_3 r_{e1} r_{e3} \\ -\left[\frac{8}{15}b_c\left[\frac{\left(1+\frac{k_a^*}{k_d^*}\right)^2}{g_c}+15\frac{k_a^*}{k_d^{*2}}\right]\right] \end{array} \right] \\ +z_2^2\left[\begin{array}{l} z_1 z_2 r_{e1}\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right] \\ -\left[\frac{4}{15}b_c\left[\frac{\left(1+\frac{k_a^*}{k_d^*}\right)^2}{g_c}+15\frac{b_m}{g_m}\frac{k_a^*}{k_d^{*2}}\right]\right] \end{array} \right] \\ +\frac{z_3^2}{r_{D3}^2}\left[z_1 z_3 r_{e1} r_{e3} + z_2 z_3 r_{e3}\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right]\right] \end{array} \right] + 2\left(m_1^*\right)^2 \tag{167}$$

1.2 Bimodal porous case

1.2.1 One-zone reactor, diffusion :

$$m_0^* = 1 \tag{168}$$

$$m_1^* = \frac{1}{2}\left[\beta_c\left(\beta_m + 1\right) + 1\right] \tag{169}$$

$$m_2^* = \frac{1}{2}\left[\frac{5}{6}\left[\beta_c\left(\beta_m + 1\right) + 1\right]^2 + \frac{2}{15}\beta_c\left[\frac{\left(\beta_m + 1\right)^2}{\gamma_c} + \frac{\beta_m}{\gamma_m}\right]\right] \tag{170}$$

$$m_3^* = \frac{1}{2}\left[\begin{array}{l}\frac{61}{60}\left[\beta_c\left(\beta_m + 1\right) + 1\right]^3 + \frac{1}{3}\beta_c\left[\beta_c + 1\right]\left[\frac{\left(\beta_m + 1\right)^2}{\gamma_c} + \frac{\beta_m}{\gamma_m}\right] \\ + \frac{4}{105}\beta_c\left[\frac{\left(\beta_m + 1\right)^3}{\gamma_c^2} + \frac{\beta_m}{\gamma_m^2} + \frac{21}{15}\beta_m\gamma_c\gamma_m\right]\end{array}\right] \tag{171}$$

1.2.2 One-zone reactor, diffusion with irreversible adsorption/reaction :

$$m_0^* = \frac{1}{\cosh\sqrt{\psi\,\eta_{overall}}} = 1 - X \tag{172}$$

$$m_1^* = \frac{1}{2}\left[\frac{\operatorname{sech}\sqrt{y\, h_{overall}}\,\tanh\sqrt{y\, h_{overall}}}{\sqrt{y\, h_{overall}}} \times \left[\frac{3}{2} b_c \left(\frac{1}{\sqrt{\frac{k_a^* b_m h_{me}}{g_c}}\,\tanh\sqrt{\frac{k_a^* b_m h_{me}}{g_c}}} - \frac{1}{\sinh^2\sqrt{\frac{k_a^* b_m h_{me}}{g_c}}} \right) \times \left[\frac{3}{2} b_m \left(\frac{1}{\sqrt{\frac{k_a^*}{g_m}}\,\tanh\sqrt{\frac{k_a^*}{g_m}}} - \frac{1}{\sinh^2\sqrt{\frac{k_a^*}{g_m}}} \right) + 1 \right] + 1 \right] \right] \tag{173}$$

The parameter y is the dimensionless kinetic parameter for bimodal porous case defined by

$$y = \frac{k_a r_s (1-e_b)(1-e_c) L_{cat}^2}{D_b} \tag{174}$$

It is noted that for a one-zone reactor, $L_{cat} = L$.

The quantity $h_{overall}$ is the overall effectiveness factor which is the product of macropore and mesopore effectiveness factors.

$$h_{overall} = h_{ma} \times h_{me} \tag{175}$$

Macropore and mesopore effectiveness factors are calculated using

Macropore effectiveness factor:

$$h_{ma} = \frac{3}{3M_{T,ma}}\left(\frac{1}{\tanh 3M_{T,ma}} - \frac{1}{3M_{T,ma}} \right) \tag{176}$$

Mesopore effectiveness factor:

$$h_{me} = \frac{3}{3M_{T,me}}\left(\frac{1}{\tanh 3M_{T,me}} - \frac{1}{3M_{T,me}}\right) \tag{177}$$

The quantity $M_{T,ma}$ is the macropore Thiele modulus defined by

$$M_{T,ma} = \frac{1}{3}\sqrt{\frac{k_a^* b_m h_{me}}{g_c}} = \frac{R_c}{3}\sqrt{\frac{k_a r_s (1-e_c) h_{me}}{D_c}} \tag{178}$$

The quantity $M_{T,me}$ is the mesopore Thiele modulus defined by

$$M_{T,me} = \frac{1}{3}\sqrt{\frac{k_a^*}{g_m}} = \frac{R_m}{3}\sqrt{\frac{k_a r_s}{D_m}} \tag{179}$$

The definition of the effectiveness factors and Thiele moduli described by Eqs. (175) – (179), are the same as those in steady-state models (Jayaraman, 1993).

1.2.3 One-zone reactor, diffusion with reversible adsorption :

$$m_0^* = 1 \tag{180}$$

$$m_1^* = \frac{1}{2}\left[b_c\left(b_m\left(1+\frac{k_a^*}{k_d^*}\right)+1\right)+1\right] \tag{181}$$

$$m_2^* = \frac{1}{2}\left[\frac{5}{6}\left[b_c\left(b_m+1\right)+1\right]^2 + \frac{2}{15}b_c\left[\frac{\left(b_m\left(1+\frac{k_a^*}{k_d^*}\right)+1\right)^2}{g_c} + \frac{b_m\left(1+\frac{k_a^*}{k_d^*}\right)}{g_m} + 15\frac{b_m}{g_m}\frac{k_a^*}{k_d^{*2}}\right]\right] \quad (182)$$

1.2.4 Three-zone reactor, diffusion :

$$m_0^* = 1 \quad (183)$$

$$m_1^* = \left\{\begin{array}{l} \frac{z_3}{r_{D3}}\left[\frac{1}{2}z_3 r_{e3} + z_2\left[b_c\left(b_m+1\right)+1\right] + z_1 r_{e1}\right] \\ +z_2\left[\frac{1}{2}z_2\left[b_c\left(b_m+1\right)+1\right] + z_1 r_{e1}\right] + \frac{z_1}{r_{D1}}\left[\frac{1}{2}z_1 r_{e1}\right] \end{array}\right\} \quad (184)$$

$$m_2^* = -\frac{1}{4}\left[\begin{array}{l} \frac{z_1 z_2}{r_{D1}}\left[z_1^2 r_{e1}^2 + 2z_1 z_2 r_{e1}\left[b_c\left(b_m+1\right)+1\right]\right] \\ +\frac{z_1 z_3}{r_{D1} r_{D3}}\left[z_1^2 r_{e1}^2 + 2z_1 z_3 r_{e1} r_{e3} + 4z_1 z_2 r_{e1}\left[b_c\left(b_m+1\right)+1\right]\right] \\ +\frac{z_2 z_3}{r_{D3}}\left[\begin{array}{l} z_2^2\left[b_c\left(b_m+1\right)+1\right]^2 + 2z_2 z_3 r_{e3}\left[b_c\left(b_m+1\right)+1\right] \\ +4z_1 z_2 r_{e1}\left[b_c\left(b_m+1\right)+1\right] + 4z_1 z_3 r_{e1} r_{e3} \\ -\left[\frac{8}{15}b_c\left[\frac{\left(b_m+1\right)^2}{g_c} + \frac{b_m}{g_m}\right]\right] \end{array}\right] \\ +z_2^2\left[z_1 z_2 r_{e1}\left[b_c\left(b_m+1\right)+1\right] - \left[\frac{4}{15}b_c\left[\frac{\left(b_m+1\right)^2}{g_c} + \frac{b_m}{g_m}\right]\right]\right] \\ +\frac{z_3^2}{r_{D3}^2}\left[z_1 z_3 r_{e1} r_{e3} + z_2 z_3 r_{e3}\left[b_c\left(b_m+1\right)+1\right]\right] \end{array}\right] + 2\left(m_1^*\right)^2 \quad (185)$$

1.2.5 Three-zone reactor, diffusion with irreversible adsorption/reaction :

$$m_0^* = \frac{1}{\cosh\sqrt{y\,h_{overall}} + \dfrac{z_3}{r_{D3} z_2}\sqrt{y\,h_{overall}}\,\sinh\sqrt{y\,h_{overall}}} = 1 - X \tag{186}$$

$$m_1^* = \left\{ \begin{array}{l} \dfrac{z_3}{r_{D3}}\left[\dfrac{1}{2} z_3 r_{e3} + \dfrac{1}{2} z_2 B'\left(1 + \dfrac{\tanh\sqrt{y\,h_{overall}}}{\sqrt{y\,h_{overall}}}\right) + z_1 r_{e1}\right]\cosh\sqrt{y\,h_{overall}} \\ + z_2\left[\dfrac{1}{2} z_2 B' + z_1 r_{e1}\right]\dfrac{\sinh\sqrt{y\,h_{overall}}}{\sqrt{y\,h_{overall}}} + \dfrac{z_1}{r_{D1}}\left[\dfrac{1}{2} z_1 r_{e1}\right]\cosh\sqrt{y\,h_{overall}} \\ + \dfrac{z_1 z_3}{r_{D1} r_{D3}}\left[z_1 z_2 r_{e1}\sqrt{y\,h_{overall}}\,\sinh\sqrt{y\,h_{overall}}\right] \end{array} \right\} \tag{187}$$

The quantity B' in Eq. (187) is defined by

$$B' = \left\{ \begin{array}{l} \left[\left[\dfrac{3}{2} b_c\left(\dfrac{1}{\sqrt{\dfrac{k_a^* b_m h_{me}}{g_c}}\tanh\sqrt{\dfrac{k_a^* b_m h_{me}}{g_c}}} - \dfrac{1}{\sinh^2\sqrt{\dfrac{k_a^* b_m h_{me}}{g_c}}}\right)\right]\right] \\ \times\left[\dfrac{3}{2} b_m\left(\dfrac{1}{\sqrt{\dfrac{k_a^*}{g_m}}\tanh\sqrt{\dfrac{k_a^*}{g_m}}} - \dfrac{1}{\sinh^2\sqrt{\dfrac{k_a^*}{g_m}}}\right) + 1\right] + 1 \end{array} \right\} \tag{188}$$

1.2.6 Three-zone reactor, diffusion with reversible adsorption :

$$m_0^* = 1 \tag{189}$$

$$m_1^* = \left\{ \begin{array}{l} \dfrac{z_3}{r_{D3}}\left[\dfrac{1}{2} z_3 r_{e3} + z_2\left[b_c\left(b_m\left(1 + \dfrac{k_a^*}{k_d^*}\right) + 1\right) + 1\right] + z_1 r_{e1}\right] \\ + z_2\left[\dfrac{1}{2} z_2\left[b_c\left(b_m\left(1 + \dfrac{k_a^*}{k_d^*}\right) + 1\right) + 1\right] + z_1 r_{e1}\right] + \dfrac{z_1}{r_{D1}}\left[\dfrac{1}{2} z_1 r_{e1}\right] \end{array} \right\} \tag{190}$$

$$
\begin{aligned}
m_2^* = \frac{1}{4} \Bigg[& \frac{z_1 z_2}{r_{D1}} \left[z_1^2 r_{e1}^2 + 2 z_1 z_2 r_{e1} \left[b_c \left(b_m \left(1 + \frac{k_a^*}{k_d^*} \right) + 1 \right) + 1 \right] \right] \\
& + \frac{z_1 z_3}{r_{D1} r_{D3}} \left[z_1^2 r_{e1}^2 + 2 z_1 z_3 r_{e1} r_{e3} + 4 z_1 z_2 r_{e1} \left[b_c \left(b_m \left(1 + \frac{k_a^*}{k_d^*} \right) + 1 \right) + 1 \right] \right] \\
& + \frac{z_2 z_3}{r_{D3}} \Bigg[z_2^2 \left[b_c \left(b_m \left(1 + \frac{k_a^*}{k_d^*} \right) + 1 \right) + 1 \right]^2 \\
& \qquad + 2 z_2 z_3 r_{e3} \left[b_c \left(b_m \left(1 + \frac{k_a^*}{k_d^*} \right) + 1 \right) + 1 \right] \\
& \qquad + 4 z_1 z_2 r_{e1} \left[b_c \left(b_m \left(1 + \frac{k_a^*}{k_d^*} \right) + 1 \right) + 1 \right] + 4 z_1 z_3 r_{e1} r_{e3} \\
& \qquad - \left[\frac{8}{15} b_c \left[\frac{\left(b_m \left(1 + \frac{k_a^*}{k_d^*} \right) + 1 \right)^2}{g_c} + \frac{b_m \left(1 + \frac{k_a^*}{k_d^*} \right)}{g_m} + 15 \frac{b_m}{g_m} \frac{k_a^*}{k_d^{*2}} \right] \right] \Bigg] \\
& + z_2^2 \Bigg[z_1 z_2 r_{e1} \left[b_c \left(b_m \left(1 + \frac{k_a^*}{k_d^*} \right) + 1 \right) + 1 \right] \\
& \qquad - \left[\frac{4}{15} b_c \left[\frac{\left(b_m \left(1 + \frac{k_a^*}{k_d^*} \right) + 1 \right)^2}{g_c} + \frac{b_m \left(1 + \frac{k_a^*}{k_d^*} \right)}{g_m} + 15 \frac{b_m}{g_m} \frac{k_a^*}{k_d^{*2}} \right] \right] \Bigg] \\
& + \frac{z_3^2}{r_{D3}^2} \left[z_1 z_3 r_{e1} r_{e3} + z_2 z_3 r_{e3} \left[b_c \left(b_m \left(1 + \frac{k_a^*}{k_d^*} \right) + 1 \right) + 1 \right] \right] \Bigg] + 2 \left(m_1^* \right)^2
\end{aligned}
\tag{191}
$$

It is noted that for diffusion expressions, making $b = 0$ in the moment expressions for unimodal porous case, the corresponding expressions for the non-porous case can be obtained. Making $b_c = 0$ and $b_m = 0$ in the moment expressions for bimodal porous case, the corresponding expressions for the non-porous and unimodal porous cases can be obtained, respectively.

To estimate transport and kinetic parameters, the moment expressions of the dimensionless exit flow rate are transformed into the moment expressions of the PI-normalized exit flow rate using Eq. (79). The moment expressions of the PI-normalized exit flow rate are as follows:

1.3 Unimodal porous case

1.3.1 One-zone reactor, diffusion with reversible adsorption :

$$m_0 = 1 \qquad (192)$$

$$m_1 = \frac{1}{2} t_b \left[b \left(1 + \frac{k'_a}{k_d} \right) + 1 \right] \qquad (193)$$

$$m_2 = \frac{1}{2} t_b \left[\frac{5}{6} \left[b \left(1 + \frac{k'_a}{k_d} \right) + 1 \right]^2 t_b + \frac{2}{15} b \left[\left(1 + \frac{k'_a}{k_d} \right)^2 t_p + 15 \frac{k'_a}{k_d^2} t_b \right] \right] \qquad (194)$$

1.3.2 Three-zone reactor, diffusion :

$$m_0 = 1 \qquad (195)$$

$$m_1 = \left\{ \begin{array}{l} \dfrac{L_3}{D_{b,3}} \left[\dfrac{1}{2} L_3 e_3 + L_2 e_2 \left[b + 1 \right] + L_1 e_1 \right] \\ + \dfrac{L_2}{D_{b,2}} \left[\dfrac{1}{2} L_2 e_2 \left[b + 1 \right] + L_1 e_1 \right] + \dfrac{L_1}{D_{b,1}} \left[\dfrac{1}{2} L_1 e_1 \right] \end{array} \right\} \qquad (196)$$

$$m_2 = -\frac{1}{4}\left[\begin{array}{l} \frac{L_1 L_2}{D_{b,1} D_{b,2}}\left[L_1^2 e_1^2 + 2L_1 L_2 e_1 e_2 [b+1]\right] \\ +\frac{L_1 L_3}{D_{b,1} D_{b,3}}\left[L_1^2 e_1^2 + 2L_1 L_3 e_1 e_3 + 4L_1 L_2 e_1 e_2 [b+1]\right] \\ +\frac{L_2 L_3}{D_{b,2} D_{b,3}}\left[\begin{array}{l} L_2^2 e_2^2 [b+1]^2 + 2L_2 L_3 e_2 e_3 [b+1] \\ +4L_1 L_2 e_1 e_2 [b+1] + 4L_1 L_3 e_1 e_3 - \frac{8}{15} b t_p \end{array}\right] \\ +\frac{L_2^2}{D_{b,2}^2}\left[L_1 L_2 e_1 e_2 [b+1] - \frac{4}{15} b t_p\right] \\ +\frac{L_3^2}{D_{b,2} D_{b,3}}\left[L_1 L_3 e_1 e_3 + L_2 L_3 e_2 e_3 [b+1]\right] \end{array}\right] + 2(m_1)^2$$

(197)

1.3.3 Three-zone reactor, diffusion with irreversible adsorption/reaction :

$$m_1 = \left\{\begin{array}{l} \frac{L_3}{D_{b,3}}\left[\frac{1}{2} L_3 e_3 + \frac{1}{2} L_2 e_2 A''\left(1 + \frac{\tanh\sqrt{y h}}{\sqrt{y h}}\right) + L_1 e_1\right]\cosh\sqrt{y h} \\ +\frac{L_2}{D_{b,2}}\left[\frac{1}{2} L_2 e_2 A'' + L_1 e_1\right]\frac{\sinh\sqrt{y h}}{\sqrt{y h}} + \frac{L_1}{D_{b,1}}\left[\frac{1}{2} L_1 e_1\right]\cosh\sqrt{y h} \\ +\frac{L_1 L_3}{D_{b,1} D_{b,3}}\left[L_1 L_2 e_1 e_2 \sqrt{y h}\,\sinh\sqrt{y h}\right] \end{array}\right\}$$

(198)

The quantity A'' in Eq. (198) is defined by

$$A'' = \left\{\frac{3b}{2}\left(\frac{1}{R\sqrt{\frac{k_a r_s}{D_p}}\tanh R\sqrt{\frac{k_a r_s}{D_p}}} - \operatorname{csch}^2 R\sqrt{\frac{k_a r_s}{D_p}}\right) + 1\right\} \qquad (199)$$

1.3.4 Three-zone reactor, diffusion with reversible adsorption :

$$m_0 = 1 \tag{200}$$

$$m_1 = \left\{ \begin{aligned} & \frac{L_3}{D_{b,3}} \left[\frac{1}{2} L_3 e_3 + L_2 e_2 \left[b \left(1 + \frac{k'_a}{k_d} \right) + 1 \right] + L_1 e_1 \right] \\ & + \frac{L_2}{D_{b,2}} \left[\frac{1}{2} L_2 e_2 \left[b \left(1 + \frac{k'_a}{k_d} \right) + 1 \right] + L_1 e_1 \right] + \frac{L_1}{D_{b,1}} \left[\frac{1}{2} L_1 e_1 \right] \end{aligned} \right\} \tag{201}$$

$$m_2 = -\frac{1}{4} \left[\begin{aligned} & \frac{L_1 L_2}{D_{b,1} D_{b,2}} \left[L_1^2 e_1^2 + 2 L_1 L_2 e_1 e_2 \left[b \left(1 + \frac{k'_a}{k_d} \right) + 1 \right] \right] \\ & + \frac{L_1 L_3}{D_{b,1} D_{b,3}} \left[L_1^2 e_1^2 + 2 L_1 L_3 e_1 e_3 + 4 L_1 L_2 e_1 e_2 \left[b \left(1 + \frac{k'_a}{k_d} \right) + 1 \right] \right] \\ & + \frac{L_2 L_3}{D_{b,2} D_{b,3}} \left[\begin{aligned} & L_2^2 e_2^2 \left[b \left(1 + \frac{k'_a}{k_d} \right) + 1 \right]^2 + 2 L_2 L_3 e_2 e_3 \left[b \left(1 + \frac{k'_a}{k_d} \right) + 1 \right] \\ & + 4 L_1 L_2 e_1 e_2 \left[b \left(1 + \frac{k'_a}{k_d} \right) + 1 \right] + 4 L_1 L_3 e_1 e_3 \\ & - \left[\frac{8}{15} b \left[\left(1 + \frac{k'_a}{k_d} \right)^2 t_p + 15 \frac{k'_a}{k_d^2} \right] \right] \end{aligned} \right] \\ & + \frac{L_2^2}{D_{b,2}^2} \left[L_1 L_2 e_1 e_2 \left[b \left(1 + \frac{k'_a}{k_d} \right) + 1 \right] - \left[\frac{4}{15} b \left[\left(1 + \frac{k'_a}{k_d} \right)^2 t_p + 15 \frac{k'_a}{k_d^2} \right] \right] \right] \\ & + \frac{L_3^2}{D_{b,2} D_{b,3}} \left[L_1 L_3 e_1 e_3 + L_2 L_3 e_2 e_3 \left[b \left(1 + \frac{k'_a}{k_d} \right) + 1 \right] \right] \end{aligned} \right] + 2 \left(m_1 \right)^2 \tag{202}$$

1.4 Bimodal porous case

1.4.1 One-zone reactor, diffusion :

$$m_0 = 1 \tag{203}$$

$$m_1 = \frac{1}{2} t_b \left[b_c \left(b_m + 1 \right) + 1 \right] \tag{204}$$

$$m_2 = \frac{1}{2} t_b \left[\frac{5}{6} \left[b_c \left(b_m + 1 \right) + 1 \right]^2 t_b + \frac{2}{15} b_c \left[\left(b_m + 1 \right)^2 t_c + b_m t_m \right] \right] \tag{205}$$

$$m_3 = \frac{1}{2} t_b \left[\begin{array}{l} \frac{61}{60} \left[b_c \left(b_m + 1 \right) + 1 \right]^3 t_b^2 \\ + \frac{1}{3} b_c \left[b_c \left(b_m + 1 \right) + 1 \right] \left[\left(b_m + 1 \right)^2 t_c + b_m t_m \right] t_b \\ + \frac{4}{105} b_c \left[\left(b_m + 1 \right)^3 t_c^2 + \frac{21}{15} b_m \left(b_m + 1 \right) t_c t_m + b_m t_m^2 \right] \end{array} \right] \tag{206}$$

1.4.2 One-zone reactor, diffusion with irreversible adsorption/reaction :

$$m_0 = \frac{1}{\cosh \sqrt{y h_{overall}}} = 1 - X \tag{207}$$

$$m_1 = \frac{1}{2} t_b \left[\begin{array}{l} \dfrac{\operatorname{sech}\sqrt{y\,h_{overall}}\,\tanh\sqrt{y\,h_{overall}}}{\sqrt{y\,h_{overall}}} \\ \times \left[\begin{array}{l} \dfrac{3}{2} b_c \left(\begin{array}{l} \dfrac{1}{R_c\sqrt{\dfrac{k_a r_s (1-e_c) h_{me}}{D_c}}\,\tanh R_c\sqrt{\dfrac{k_a r_s (1-e_c) h_{me}}{D_c}}} \\ -\operatorname{csch}^2 R_c\sqrt{\dfrac{k_a r_s (1-e_c) h_{me}}{D_c}} \end{array} \right) \\ \times \left[\dfrac{3}{2} b_m \left(\dfrac{1}{R_m\sqrt{\dfrac{k_a r_s}{D_m}}\,\tanh R_m\sqrt{\dfrac{k_a r_s}{D_m}}} - \operatorname{csch}^2 R_m\sqrt{\dfrac{k_a r_s}{D_m}} \right) + 1 \right] + 1 \end{array} \right] \end{array} \right] \quad (208)$$

1.4.3 One-zone reactor, diffusion with reversible adsorption :

$$m_0 = 1 \quad (209)$$

$$m_1 = \frac{1}{2} t_b \left[b_c \left[b_m \left(1 + \frac{k_a'}{k_d} \right) + 1 \right] + 1 \right] \quad (210)$$

$$m_2 = \frac{1}{2} t_c \left[\begin{array}{l} \dfrac{5}{6} \left[b_c \left[b_m \left(1 + \dfrac{k_a'}{k_d} \right) + 1 \right] + 1 \right]^2 t_b \\ + \dfrac{2}{15} b_c \left[\left[b_m \left(1 + \dfrac{k_a'}{k_d} \right) + 1 \right]^2 t_c + b_m \left(1 + \dfrac{k_a'}{k_d} \right) t_m + 15 b_m t_m \dfrac{k_a'}{k_d^2} \right] \end{array} \right] \quad (211)$$

1.4.4 Three-zone reactor, diffusion :

$$m_0 = 1 \quad (212)$$

$$m_1 = \left\{ \begin{array}{l} \frac{L_3}{D_{b,3}}\left[\frac{1}{2}L_3 e_3 + L_2 e_2\left[b_c\left(b_m+1\right)+1\right]+L_1 e_1\right] \\ +\frac{L_2}{D_{b,2}}\left[\frac{1}{2}L_2 e_2\left[b_c\left(b_m+1\right)+1\right]+L_1 e_1\right]+\frac{L_1}{D_{b,1}}\left[\frac{1}{2}L_1 e_1\right] \end{array} \right\} \tag{213}$$

$$m_2 = -\frac{1}{4}\left[\begin{array}{l} \frac{L_1 L_2}{D_{b,1}D_{b,2}}\left[L_1^2 e_1^2 + 2L_1 L_2 e_1 e_2\left[b_c\left(b_m+1\right)+1\right]\right] \\ +\frac{L_1 L_3}{D_{b,1}D_{b,3}}\left[L_1^2 e_1^2 + 2L_1 L_3 e_1 e_3 + 4L_1 L_2 e_1 e_2\left[b_c\left(b_m+1\right)+1\right]\right] \\ +\frac{L_2 L_3}{D_{b,2}D_{b,3}}\left[\begin{array}{l} L_2^2 e_2^2\left[b_c\left(b_m+1\right)+1\right]^2 \\ +2L_2 L_3 e_2 e_3\left[b_c\left(b_m+1\right)+1\right] \\ +4L_1 L_2 e_1 e_2\left[b_c\left(b_m+1\right)+1\right]+4L_1 L_3 e_1 e_3 \\ -\left[\frac{8}{15}b_c\left[\left(b_m+1\right)^2 t_c + b_m t_m\right]\right] \end{array} \right] \\ +\frac{L_2^2}{D_{b,2}^2}\left[\begin{array}{l} L_1 L_2 e_1 e_2\left[b_c\left(b_m+1\right)+1\right] \\ -\left[\frac{4}{15}b_c\left[\left(b_m+1\right)^2 t_c + b_m t_m\right]\right] \end{array} \right] \\ +\frac{L_3^2}{D_{b,2}D_{b,3}}\left[L_1 L_3 e_1 e_3 + L_2 L_3 e_2 e_3\left[b_c\left(b_m+1\right)+1\right]\right] \end{array} \right] + 2\left(m_1\right)^2 \tag{214}$$

1.4.5 Three-zone reactor, diffusion with irreversible adsorption/reaction :

$$m_0 = \frac{1}{\cosh\sqrt{y\,h_{overall}} + \frac{D_{b,2}L_3}{D_{b,3}L_2}\sqrt{y\,h_{overall}}\,\sinh\sqrt{y\,h_{overall}}} = 1 - X \tag{215}$$

$$m_1 = \left\{ \begin{array}{l} \dfrac{L_3}{D_{b,3}} \left[\dfrac{1}{2} L_3 e_3 + \dfrac{1}{2} L_2 e_2 B'' \left(1 + \dfrac{\tanh \sqrt{y\, h_{overall}}}{\sqrt{y\, h_{overall}}} \right) + L_1 e_1 \right] \cosh \sqrt{y\, h_{overall}} \\ + \dfrac{L_2}{D_{b,2}} \left[\dfrac{1}{2} L_2 e_2 B'' + L_1 e_1 \right] \dfrac{\sinh \sqrt{y\, h_{overall}}}{\sqrt{y\, h_{overall}}} + \dfrac{L_1}{D_{b,1}} \left[\dfrac{1}{2} L_1 e_1 \right] \cosh \sqrt{y\, h_{overall}} \\ + \dfrac{L_1 L_3}{D_{b,1} D_{b,3}} \left[L_1 L_2 e_1 e_2 \sqrt{y\, h_{overall}} \sinh \sqrt{y\, h_{overall}} \right] \end{array} \right\} \tag{216}$$

The quantity B'' in Eq. (216) is defined by

$$B'' = \left\{ \begin{array}{l} \left[\dfrac{3}{2} b_c \left(\begin{array}{l} \dfrac{1}{R_c \sqrt{\dfrac{k_a r_s (1-e_c) h_{me}}{D_c}} \tanh R_c \sqrt{\dfrac{k_a r_s (1-e_c) h_{me}}{D_c}}} \\ - \dfrac{1}{\sinh^2 R_c \sqrt{\dfrac{k_a r_s (1-e_c) h_{me}}{D_c}}} \end{array} \right) \right] \\ \times \left[\dfrac{3}{2} b_m \left(\dfrac{1}{R_m \sqrt{\dfrac{k_a r_s}{D_m}} \tanh R_m \sqrt{\dfrac{k_a r_s}{D_m}}} - \dfrac{1}{\sinh^2 R_m \sqrt{\dfrac{k_a r_s}{D_m}}} \right) + 1 \right] + 1 \end{array} \right\} \tag{217}$$

1.4.6 Three-zone reactor, diffusion with reversible adsorption :

$$m_0 = 1 \tag{218}$$

$$m_1 = \left\{ \begin{array}{l} \dfrac{L_3}{D_{b,3}} \left[\dfrac{1}{2} L_3 e_3 + L_2 e_2 \left[b_c \left(b_m \left(1 + \dfrac{k_a'}{k_d} \right) + 1 \right) + 1 \right] + L_1 e_1 \right] \\ + \dfrac{L_2}{D_{b,2}} \left[\dfrac{1}{2} L_2 e_2 \left[b_c \left(b_m \left(1 + \dfrac{k_a'}{k_d} \right) + 1 \right) + 1 \right] + L_1 e_1 \right] + \dfrac{L_1}{D_{b,1}} \left[\dfrac{1}{2} L_1 e_1 \right] \end{array} \right\} \tag{219}$$

$$
m_2 = -\frac{1}{4}\left[\begin{aligned}
&\frac{L_1L_2}{D_{b,1}D_{b,2}}\left[L_1^2e_1^2+2L_1L_2e_1e_2\left[b_c\left(b_m\left(1+\frac{k_a'}{k_d}\right)+1\right)+1\right]\right]\\
&+\frac{L_1L_3}{D_{b,1}D_{b,3}}\left[L_1^2e_1^2+2L_1L_3e_1e_3+4L_1L_2e_1e_2\left[b_c\left(b_m\left(1+\frac{k_a'}{k_d}\right)+1\right)+1\right]\right]\\
&+\frac{L_2L_3}{D_{b,2}D_{b,3}}\left[\begin{aligned}
&L_2^2e_2^2\left[b_c\left(b_m\left(1+\frac{k_a'}{k_d}\right)+1\right)+1\right]^2\\
&+2L_2L_3e_2e_3\left[b_c\left(b_m\left(1+\frac{k_a'}{k_d}\right)+1\right)+1\right]\\
&+4L_1L_2e_1e_2\left[b_c\left(b_m\left(1+\frac{k_a'}{k_d}\right)+1\right)+1\right]+4L_1L_3e_1e_3\\
&-\left[\frac{8}{15}b_c\left[\left(b_m\left(1+\frac{k_a'}{k_d}\right)+1\right)^2t_c+b_m\left(1+\frac{k_a'}{k_d}\right)t_m+15\frac{b_m}{g_m}\frac{k_a'}{k_d^2}\right]\right]
\end{aligned}\right]\\
&+\frac{L_2^2}{D_{b,2}^2}\left[\begin{aligned}
&L_1L_2e_1e_2\left[b_c\left(b_m\left(1+\frac{k_a'}{k_d}\right)+1\right)+1\right]\\
&-\left[\frac{4}{15}b_c\left[\left(b_m\left(1+\frac{k_a'}{k_d}\right)+1\right)^2t_c+b_m\left(1+\frac{k_a'}{k_d}\right)t_m+15\frac{b_m}{g_m}\frac{k_a'}{k_d^2}\right]\right]
\end{aligned}\right]\\
&+\frac{L_3^2}{D_{b,2}D_{b,3}}\left[L_1L_3e_1e_3+L_2L_3e_2e_3\left[b_c\left(b_m\left(1+\frac{k_a'}{k_d}\right)+1\right)+1\right]\right]
\end{aligned}\right]+2(m_1)^2
\tag{220}
$$

To determine transport and kinetic parameters using these moment expressions, the parameters related to the configuration of the reactors and the catalyst pellets, i.e., the void fractions in different regions, length of reactor, length and position of the catalyst bed, and radius of catalyst pellet, are predetermined. Gas diffusivities are determined from the diffusion response curves by applying moment expressions for diffusion case. For a one-zone reactor packed with porous pellets, the number of required moment expressions is equal to the number of diffusivities in different regions. Diffusivity of a reactant gas can be calculated from diffusivity of the inert gas for the same bed using Eq. (3). Typically, a three-zone reactor is usually packed with the same non-porous inert particles in the first and third zones. The gas diffusivity in the inert particle zone is determined from diffusion experiment with a one-zone reactor packed the same inert particles. The diffusivities in different region in the catalyst zone are then determined. The kinetic parameter (s) is determined using moment expression (s) after all diffusivities are known.

Table 3 shows the calculated parameters from corresponding moment expressions. For a one-zone reactor in the case of diffusion, the first and second moment expressions in unimodal porous case provide the effective Knudsen diffusivities in the interparticle and intraparticle regions, D_b and D_p, respectively. In the case of diffusion with irreversible adsorption/reaction, irreversible adsorption/reaction rate constant, k_a , can be determined from two different expression, i.e., the conversion expression (the zeroth moment expression) and the mean residence time (the ratio of zeroth to first moment expression). In the case of diffusion with reversible adsorption case, adsorption and desorption rate constants, k_a and k_d , can be determined by solving the first and second moment expressions simultaneously. For a three-zone reactor provided that the diffusivity in the inert bed is known, the diffusivities in the catalyst bed and adsorption and desorption rate constants from corresponding moment expressions are obtained similarly to those for the one-zone reactor. In bimodal porous case for a one-zone reactor, the diffusivities and adsorption and desorption rate constants from corresponding moment expressions are determined similarly to those for unimodal porous case except that there is an additional porous region. For a three-zone reactor, the third moment expression has not been determined, and consequently only the diffusivity in the interparticle region can be calculated from the first moment expression. The kinetic parameters can be determined if all diffusivities are predetermined.

Table 3 The obtained parameters from corresponding moment expressions.

Configurations / Processes	Unimodal-pore-structure		Bimodal-pore-structure	
	One-zone reactor	Three-zone reactor	One-zone reactor	Three-zone reactor
Diffusion	Eq.(94)**; $m_1 \rightarrow D_b$ Eq.(95)**; $m_2 \rightarrow D_p$	Eq.(196); $m_1 \rightarrow D_{b,2}$ Eq.(197); $m_2 \rightarrow D_p$	Eq.(204); $m_1 \rightarrow D_b$ Eq.(205); m_2, Eq.(206); m_3 $\rightarrow \begin{cases} D_c \\ D_m \end{cases}$	Eq.(213); $m_1 \rightarrow D_{b,2}$ Eq.(214); m_2
Diffusion with irreversible adsorption/reaction	Eq.(97)**; $m_0 \rightarrow k_a$ Eq.(98)**; $m_0 \rightarrow k_a$	Eq.(101)**; $m_0 \rightarrow k_a$ $\frac{\text{Eq.}(198)}{\text{Eq.}(101)^{**}}; \frac{m_1}{m_0} \rightarrow k_a$	Eq.(207); $m_0 \rightarrow k_a$ $\frac{\text{Eq.}(208)}{\text{Eq.}(207)}; \frac{m_1}{m_0} \rightarrow k_a$	Eq.(215); m_0 $\frac{\text{Eq.}(216)}{\text{Eq.}(215)}; \frac{m_1}{m_0}$
Diffusion with reversible adsorption	Eq.(193); m_1, Eq.(194); m_2 $\rightarrow \begin{cases} k_a \\ k_d \end{cases}$	Eq.(201); m_1, Eq.(202); m_2 $\rightarrow \begin{cases} k_a \\ k_d \end{cases}$	Eq.(210); m_1, Eq.(211); m_2 $\rightarrow \begin{cases} k_a \\ k_d \end{cases}$	Eq.(219); m_1 Eq.(220); m_2

**Previous work

2. Characteristics of the distribution of surface coverage for irreversible adsorption case

The profiles of the surface coverage in the irreversible adsorption case are determined for unimodal and bimodal cases.

2.1 Unimodal porous case

The analytical solution of the pulse-intensity-normalized surface concentration after one pulse ($t = \infty$) for unimodal porous case is described by (derivation is provided in Appendix A)

$$q_{\infty}^{*} = \sqrt{\frac{b\,k_a^{*}}{h}} \times \frac{\sinh\left(\sqrt{\frac{k_a^{*}}{g}}\,r\right)}{r\,\sinh\sqrt{\frac{k_a^{*}}{g}}} \times \frac{\sinh\left(\sqrt{b\,k_a^{*}h}\,(1-x)\right)}{\cosh\sqrt{b\,k_a^{*}h}} \qquad (221)$$

Eq. (221) can be used to calculate q_{∞}^{*} in the catalyst pellet at different positions in the reactor. The analysis in this work involves q_{∞}^{*} at $r = 1$ (at the external surface of catalyst pellet) which is described by

$$q_{\infty,r=1}^{*} = \sqrt{\frac{b\,k_a^{*}}{h}} \times \frac{\sinh\left(\sqrt{b\,k_a^{*}h}\,(1-x)\right)}{\cosh\sqrt{b\,k_a^{*}h}} \qquad (222)$$

From Eqs. (221) and (222), we can write

$$\frac{q_{\infty}^{*}(r)}{q_{\infty,r=1}^{*}} = \frac{\sinh\left(\sqrt{\frac{k_a^{*}}{g}}\,r\right)}{r\,\sinh\sqrt{\frac{k_a^{*}}{g}}} \qquad (223)$$

Using Eq. (69), Eq. (223) can be written as

$$\frac{q_\infty(r)}{q_{\infty,r=R}} = \frac{\sinh\left(r\sqrt{\frac{k_a r_s}{D_p}}\right)}{(r/R)\sinh R\sqrt{\frac{k_a r_s}{D_p}}} \tag{224}$$

Eq. (224) describes the distribution of $q_\infty / q_{\infty,r=R}$ in the catalyst pellet. The distribution of $q_\infty / q_{\infty,r=R}$ depends on the parameters related to the catalyst pellet, i.e., radius of the catalyst pellet (r), irreversible adsorption rate constant (k_a) and effectiveness Knudsen diffusivity of the reactant gas in the catalyst pellet (D_p). Eq. (224) suggests that $q_\infty / q_{\infty,r=R}$ in catalyst pellets at different axial reactor coordinates is the same.

In steady-state experiments, the effectiveness factor, h, has been used for estimating the performance of catalyst particles. The parameter h is defined as the ratio of the rate of reaction in the catalyst pellet to the rate without diffusion resistance. Consequently, for a first-order reaction, the quantity h is the ratio of the averaged gas concentration in the pellet to the gas concentration at the external surface of the catalyst pellet. The magnitude of h therefore depends on the distribution of the gas concentration profile. In steady-state conditions, the distribution of gas concentration is described by (CN. Satterfield)

$$\frac{C}{C_s} = \frac{\sinh\left(r\sqrt{\frac{k_a r_s}{D_p}}\right)}{(r/R)\sinh R\sqrt{\frac{k_a r_s}{D_p}}} \tag{225}$$

where C_s is the gas concentration at the external surface of the catalyst pellet.

Eqs. (224) and (225) show that the distribution of $q_{\infty}/q_{\infty,r=R}$ in TAP experiment with irreversible adsorption process is the same as the distribution of C/C_s in steady-state experiment with irreversible reaction. In other words, the correlation between the effectiveness factor and fraction surface coverage developed in an irreversible adsorption process in a TAP experiment is similar to the correlation between the effectiveness factor and gas concentration for irreversible reaction case in steady-state conditions. Recall that in steady state conditions the average gas concentration divided by the gas concentration at the external surface of the spherical catalyst pellet (derived from Eq. 224) is described by

$$\frac{C_{avg}}{C_s} = h = \frac{3}{3M_T}\left(\frac{1}{\tanh 3M_T} - \frac{1}{3M_T}\right) \tag{226}$$

where M_T (Thiele modulus) is defined by Eq. (100).

For TAP experiments, we can wrtie

$$\frac{q_{\infty,avg}}{q_{\infty,r=R}} = h = \frac{3}{3M_T}\left(\frac{1}{\tanh 3M_T} - \frac{1}{3M_T}\right) \tag{227}$$

Since $q_{\infty}(r)$ is a result of the exposure of the catalyst surface to gas molecules, the difference in magnitude of q_{∞} at each r is due to the difference in time-average gas concentration. Eq. (227) shows that the averaged adsorption rate in the pellet differs from the rate at the external surface of the pellet by a factor of h. The conversion expression for porous case (Eq. 97) in TAP conditions therefore involve h like in steady-state conditions.

2.2 Bimodal porous case

The analytical solution of the pulse-intensity-normalized surface concentration after one pulse ($t=\infty$) for bimodal porous case is described by (derivation is provided in Appendix F)

$$q_\infty^* = \sqrt{\frac{b_c b_m k_a^*}{h_{ma} h_{me}}} \times \frac{\sinh\left(\sqrt{\frac{k_a^*}{g_m}} r_m\right)}{r_m \sinh\sqrt{\frac{k_a^*}{g_m}}} \times \frac{\sinh\left(\sqrt{\frac{b_m k_a^* h_{me}}{g_c}} r_c\right)}{r_c \sinh\sqrt{\frac{b_m k_a^* h_{me}}{g_c}}} \times \frac{\sinh\left(\sqrt{b_c b_m h_{ma} h_{me}}\,(1-x)\right)}{\cosh\sqrt{b_c b_m h_{ma} h_{me}}} \tag{228}$$

Eq. (228) can be used to calculate q_∞^* in the particle at different positions in the catalyst pellet placed at different positions in the reactor. From Eq. (228), the expression for $q_{\infty,r_m=1}^*$ (q_∞^* at the external surface of the particle) is given by

$$q_{\infty,r_m=1}^* = \sqrt{\frac{b_c b_m k_a^*}{h_{ma} h_{me}}} \times \frac{\sinh\left(\sqrt{\frac{b_m k_a^* h_{me}}{g_c}} r_c\right)}{r_c \sinh\sqrt{\frac{b_m k_a^* h_{me}}{g_c}}} \times \frac{\sinh\left(\sqrt{b_c b_m h_{ma} h_{me}}\,(1-x)\right)}{\cosh\sqrt{b_c b_m h_{ma} h_{me}}} \tag{229}$$

From Eqs. (150), (228) and (229), we can write

$$\frac{q_\infty^*(r_m)}{q_{\infty,r_m=1}^*} = \frac{q_\infty(r_m)}{q_{\infty,r_m=R_m}} = \frac{\sinh\left(\sqrt{\frac{k_a^*}{g_m}} r_m\right)}{r_m \sinh\sqrt{\frac{k_a^*}{g_m}}} = \frac{\sinh\left(r_m\sqrt{\frac{k_a r_s}{D_m}}\right)}{(r_m/R_m)\sinh R_m\sqrt{\frac{k_a r_s}{D_m}}} \tag{230}$$

Eq. (230) describes the distribution of $q_\infty / q_{\infty,r_m=R_m}$ in the spherical mesoporous particle. In this case, we can write

$$\frac{q_{\infty,avg}}{q_{\infty,r_m=R_m}} = h_{me} = \frac{3}{3M_{T,me}}\left(\frac{1}{\tanh 3M_{T,me}} - \frac{1}{3M_{T,me}}\right) \tag{231}$$

Eq. (231) shows a correlation for the mesoporous region in the bimodal case similarly to the unimodal case.

3. Fingerprints of the exit flow rate for irreversible adsorption/reaction and reversible adsorption

The domain of parameters used in the calculations is based on the typical conditions that can be found in TAP pulse experiments. The simulation is performed using a one-zone and three-zone reactors packed with porous catalyst pellets for diffusion with irreversible adsorption/reaction and with reversible adsorption. For the three-zone reactor, the length of zone, interparticle gas diffusivity and void fraction in all zones are assumed to be equal. The active substance for unimodal and bimodal porous cases is supposed to be uniformly distributed on the surface inside catalyst pellets and mesoporous silica particles, respectively. The Laplace-domain solutions of the dimensionless exit flow rate are provided in Appendix A for unimodal porous case and Appendices F and G for bimodal porous case.

3.1 Unimodal porous case

In the unimodal porous case, the parameter b and g are involved in the calculation. The magnitude of b is calculated using Eqs. (57). The magnitude of g is calculated using (Phanawadee et al., 2005)

$$g = 6\frac{(1-e_b)}{e_b}\frac{t'_{\text{inter}}}{t'_{\text{intra}}}\frac{d_{\text{pore}}L^2}{d^3_{\text{pellet}}} \tag{232}$$

Eq. (232) results from Eqs. (1), (2) and (58). The simulation result will be shown for g equal to 10 and b equal to 0.75. The magnitudes of these parameters correspond to the reactor length, L, of 2.54×10^{-2} m, the average pore diameter, d_{pore}, of 120 nm, the average pellet diameter, d_{pellet}, of 300 μm, the inter- and intraparticle void fractions (e_b and e_p) of 0.36 (spherical pellet) and 0.42, respectively, and the ratio of the interparticle to intraparticle tortuosity factors, $t'_{\text{inter}}/t'_{\text{intra}}$, of 1/3. The chosen value of the ratio of the tortuosity factor corresponds to t'_{inter} of 1.5 for spherical pellets (Huizenga and Smith 1986) and t'_{intra} of 4.5, an average of the typical values, which ranges from 2 to 7 (Satterfield 2001).

3.1.1 Diffusion with irreversible adsorption/reaction.

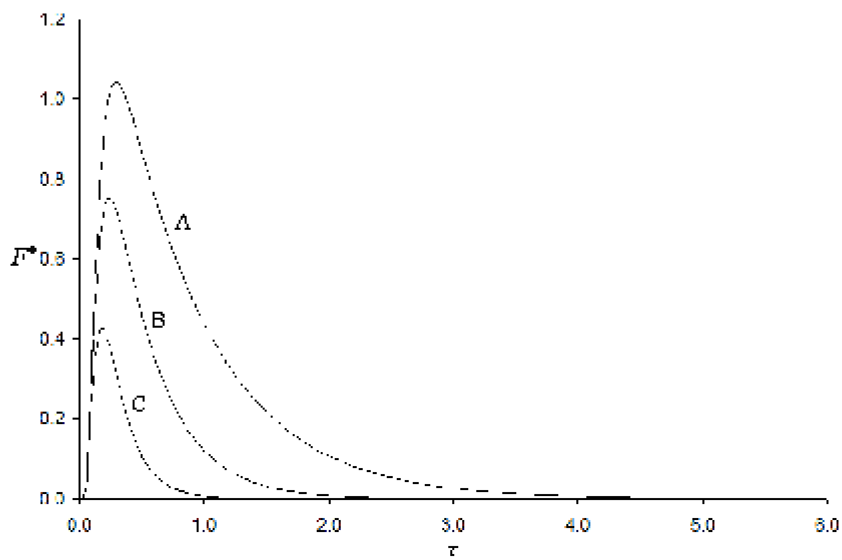

Figure 6 Dimensionless exit flow rate curves calculated for the one-zone reactor packed with unimodal-pore-structure catalyst pellets for diffusion with irreversible adsorption/reaction case: A) $k_a^* = 0$; B) $k_a^* = 3$; C) $k_a^* = 10$**.**

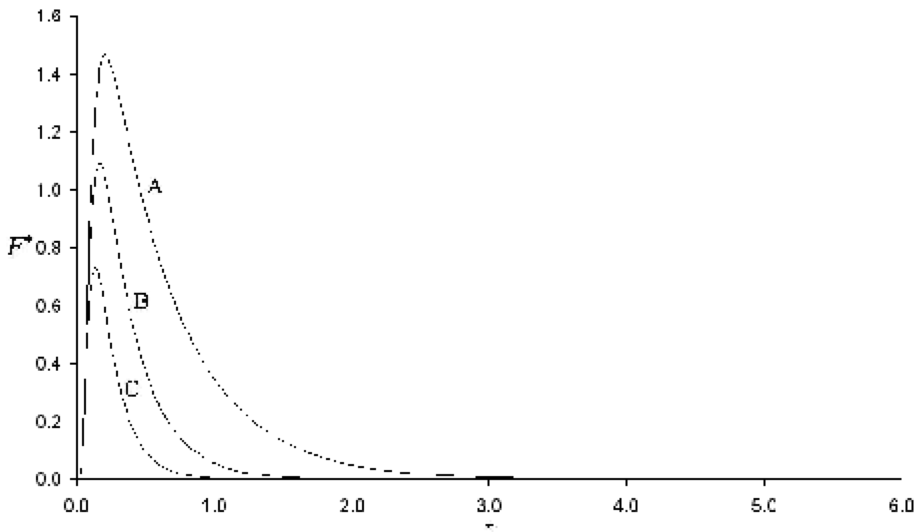

Figure 7 Dimensionless exit flow rate curves calculated for the three-equal-zone reactor packed with unimodal-pore-structure catalyst pellets for diffusion with irreversible adsorption/reaction case: A) k_a^* = 0; B) k_a^* = 10; C) k_a^* = 30**.**

Figures 6 and 7 show the comparison between the dimensionless exit flow rate curves calculated for the one-zone and three-zone reactors packed with unimodal-pore-structure catalyst pellets for diffusion and diffusion with irreversible adsorption/reaction cases**.** The peak height of the dimensionless exit flow rate curve and the mean dimensionless residence time decreases when the value of k_a^* increases. The curve for irreversible adsorption/reaction is inside and does not cross the curve for diffusion-only (k_a^* = 0). This fingerprint for irreversible adsorption/reaction is similar to that reported for non-porous case (Gleaves et al., 1997).

3.1.2 Diffusion with reversible adsorption/reaction

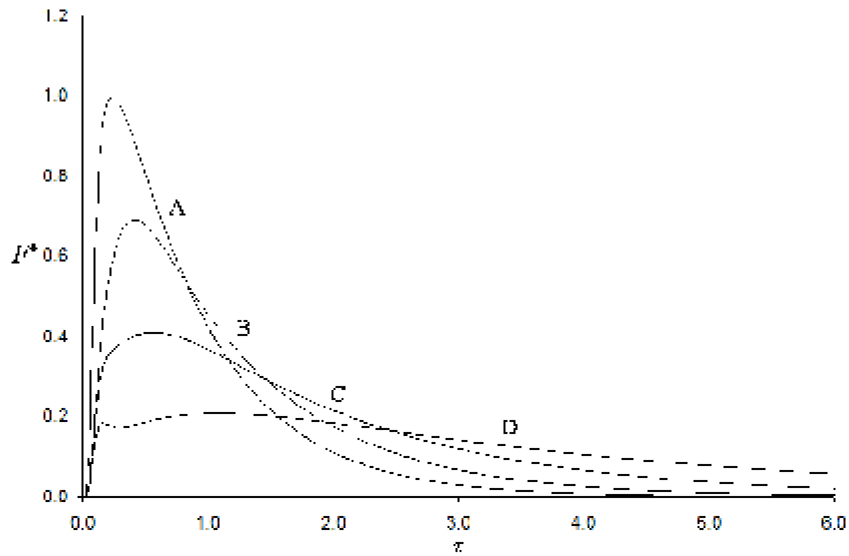

Figure 8 Dimensionless exit flow rate curves calculated for the one-zone reactor packed with unimodal-pore-structure catalyst pellets for diffusion with reversible adsorption case: A) $k_a^* = 0$; B) $k_a^* = 20$, $k_d^* = 20$; C) $k_a^* = 20$, $k_d^* = 7$; D) $k_a^* = 20$, $k_d^* = 4$.

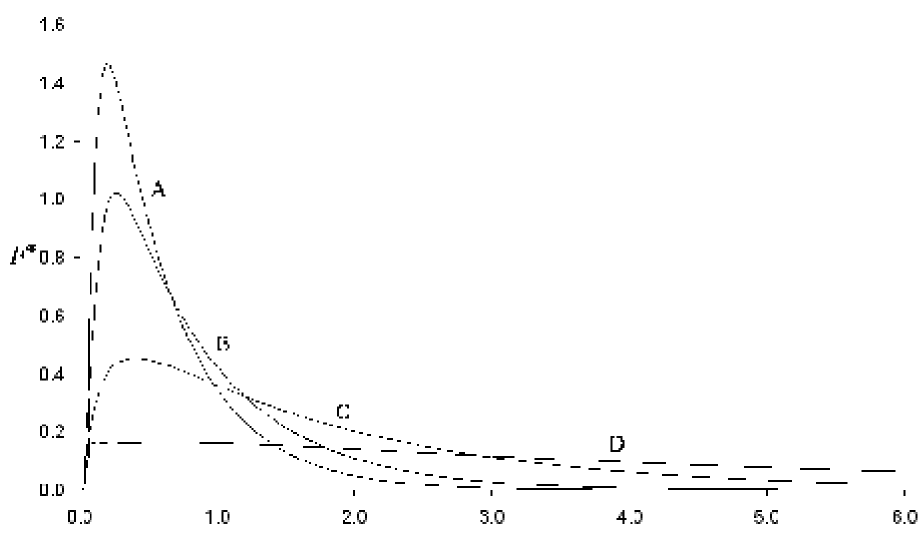

Figure 9 Dimensionless exit flow rate curves calculated for the three-equal-zone reactor packed with unimodal-pore-structure catalyst pellets for diffusion with reversible adsorption case: A) $k_a^* = 0$; B) $k_a^* = 300$, $k_d^* = 150$; C) $k_a^* = 300$, $k_d^* = 30$; D) $k_a^* = 300$, $k_d^* = 8.5$.

Figures 8 and 9 show the comparison between dimensionless exit flow rate curves calculated for the one-zone and three-zone reactors packed with unimodal-pore-structure catalyst pellets for diffusion and diffusion with reversible adsorption cases. In this case, the exit flow rate curve for diffusion with reversible adsorption cross the curve for diffusion-only case. When k_a^* is large and k_d^* is small, the exit flow rate curve is characterized by the two peaks ('two-hump curve'). These characteristics of the exit flow rate for reversible adsorption are also similar to those reported for non-porous case (Gleave et al., 1997).

3.2 Bimodal porous case

The simulation result will be shown for b_c, b_m, g_c and g_m equal to 0.36, 1.24, 191 and 11470, respectively. The magnitude of b_c, b_m is calculated using Eqs. (131) and (132). The magnitude of g_c and g_m is calculated using

$$g_c = 6\frac{(1-e_b)}{e_b}\frac{t'_{\text{inter}}}{t'_{\text{macro}}}\frac{d_{\text{macropore}}L^2}{d^3_{\text{pellet}}} \tag{233}$$

$$g_m = 6\frac{(1-e_b)}{e_b}\frac{t'_{\text{inter}}}{t'_{\text{meso}}}\frac{d_{\text{mesopore}}L^2}{d_{\text{pellet}}d^2_{\text{particle}}} \tag{234}$$

Eq. (233) results from Eqs. (1), (2) and (129). Eq. (234) results from Eqs. (1), (2) and (130). The magnitudes of L, d_{pellet}, e_b and t'_{inter} are the same as those in the unimodal porous case. The parameters involved in the calculation are as follows: $d_{\text{macropore}}$ = 0.75 μm, d_{mesopore} = 6nm, d_{particle} = 2 μm, e_c = 0.36, e_m = 0.70, t'_{macro} = 1.5, t'_{meso} = 4.5.

3.2.1 Diffusion with irreversible adsorption/reaction

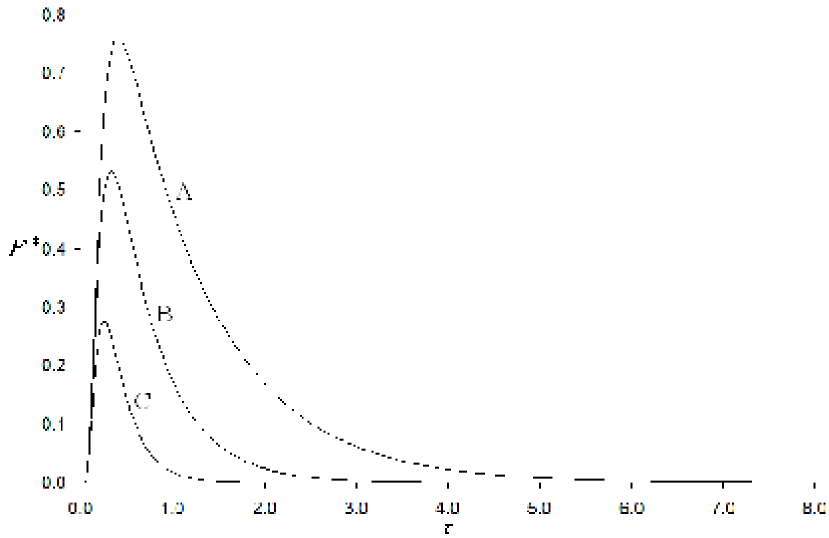

Figure 10 Dimensionless exit flow rate curves calculated for the one-zone reactor packed with bimodal-pore-structure catalyst pellets for diffusion with irreversible adsorption/reaction case: A) $k_a^* = 0$; B) $k_a^* = 3$; C) $k_a^* = 10$**.**

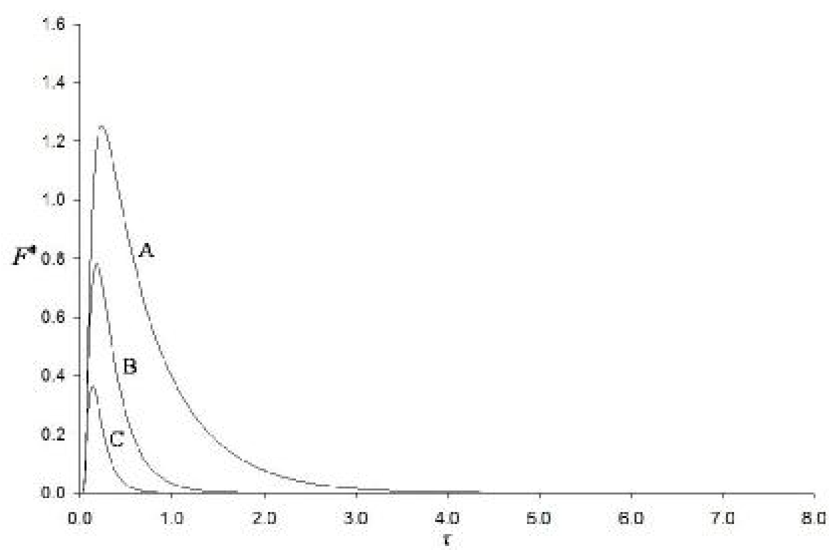

Figure 11 Dimensionless exit flow rate curves calculated for the three-equal-zone reactor packed with bimodal-pore-structure catalyst pellets for diffusion with irreversible adsorption/reaction case: A) $k_a^* = 0$; B) $k_a^* = 10$; C) $k_a^* = 15$**.**

Figures 10 and 11 show the comparison between the dimensionless exit flow rate curves calculated for the one-zone and three-zone reactors packed with bimodal-pore-structure catalyst pellets for diffusion and diffusion with irreversible adsorption/reaction cases**.** The curve of the exit flow rate for diffusion with irreversible adsorption/reaction does not cross the curve for diffusion-only case ($k_a^* = 0$). This result is similar to those for non-porous and unimodal porous cases.

3.2.2 Diffusion with reversible adsorption/reaction

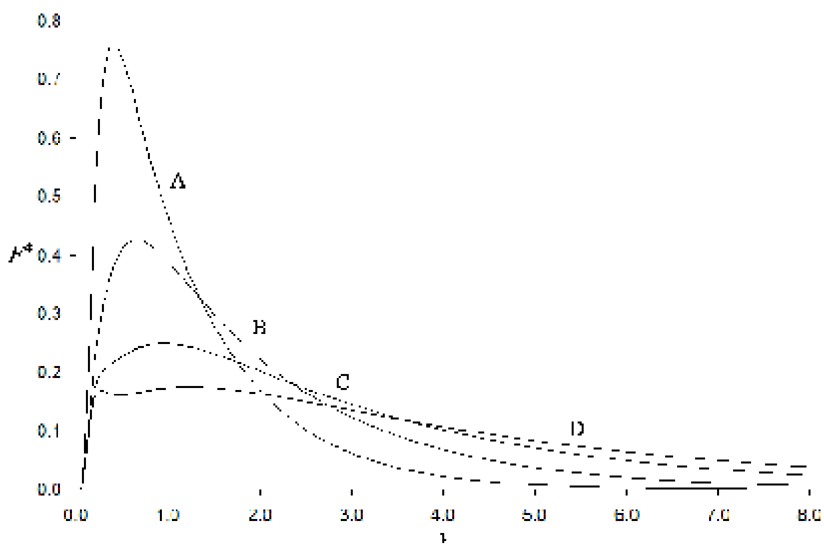

Figure 12 Dimensionless exit flow rate curves calculated for the one-zone reactor packed with bimodal-pore-structure catalyst pellets for diffusion with reversible adsorption case: A) $k_a^* = 0$; B) $k_a^* = 20$, $k_d^* = 10$; C) $k_a^* = 20$, $k_d^* = 4$; D) $k_a^* = 20$, $k_d^* = 2.5$.

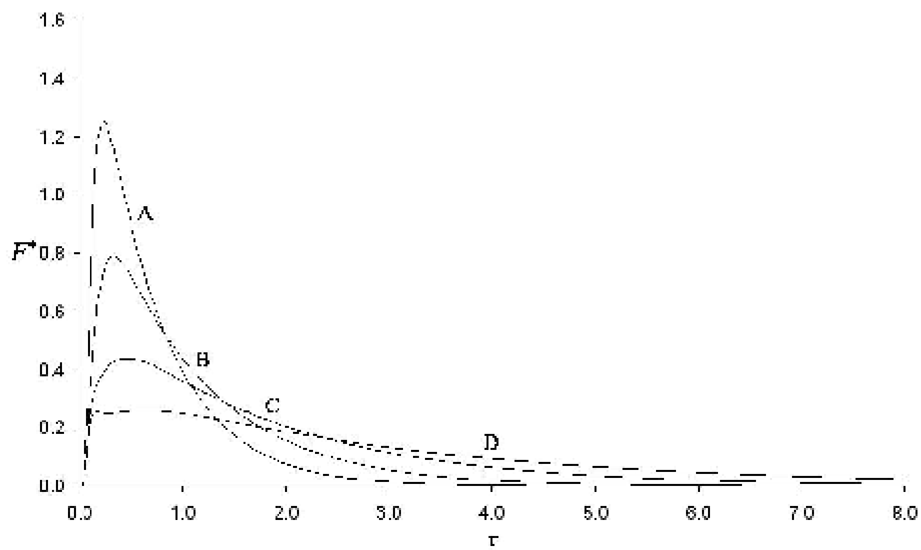

Figure 13 Dimensionless exit flow rate curves calculated for the three-equal-zone reactor packed with bimodal-pore-structure catalyst pellets for diffusion with reversible adsorption case: A) $k_a^* = 0$; B) $k_a^* = 90$, $k_d^* = 30$; C) $k_a^* = 90$, $k_d^* = 10$; D) $k_a^* = 90$, $k_d^* = 5$.

Figures 12 and 13 show the comparison between the dimensionless exit flow rate curves calculated for the one-zone and three-zone reactors packed with bimodal-pore-structure catalyst pellets for diffusion and diffusion with reversible adsorption cases. It was found that the fingerprints of the exit flow for reversible adsorption for bimodal porous case are also similar to that for non-porous and unimodal porous cases.

CONCLUSIONS

New moment expressions of the exit flow rate for the unimodal and bimodal-pore-structure catalysts have been determined. The moment expressions in unimodal and bimodal porous cases for irreversible adsorption/reaction are similar to those for non-porous cases. For unimodal porous case, the rate constant, y , is multiplied by an effectiveness factor, h , while for bimodal porous case y is multiplied by an overall effectiveness factor, $h_{overall}$. The overall effectiveness factor is the product of mesopore and macropore effectiveness factors, h_{ma} and h_{me} , of the two porous regions in the catalyst pellet. The effectiveness factors are defined similarly to those in steady-state conditions.

The characteristics of the distribution of surface concentration due to irreversible adsorption in the porous catalyst pellet packed in a one-zone reactor have been analyzed. The distribution of q / q_s in the catalyst pellet is the same as the distribution of C / C_s in steady-state conditions. In other words, the correlation between the effectiveness factors and fraction surface coverage developed in an irreversible adsorption process in a TAP experiment is similar to the correlation between the effectiveness factor and gas concentration in steady-state conditions.

In addition, the fingerprints of the exit flow rate curves that are good for non-porous cases have been investigated to determine their validity for porous cases. It was found that the fingerprints of the exit flow rate for irreversible adsorption/reaction and desorption for unimodal and bimodal porous cases are similar to those reported for non-porous case.

LITERATURE CITED

Anderssen, A.S. and E.T. White. 1971. Parameter estimation by the weighted moments method. **Chem. Eng. Sci.** 26 (8): 1203-1221.

Colaris, A.H.J., J.H.B.J. Hoebink, M.H.J.M. de Croon, and J.C. Schouten. 2002. Intrapellet diffusivities from TAP pulse responses via moment-based analysis. **AIChE Journal.** 48: 2587-2596.

Constales, D., G.S. Yablonsky, G.B. Marin and J.T. Gleave. 2001. Multi-zone TAP-reactors theory and application: I. The global transfer matrix equation. **Chem. Eng. Sci.** 56: 133-149.

Gleaves, J.T., J.R. Ebner and T.C. Kuechler. 1988. Temporal analysis of products (TAP) – a unique catalyst evaluation system with submillisecond time resolution. **Catal. Rev. Sci. Eng.** 30 (1): 49-116.

Gleaves, J.T., G.S. Yablonskii, P. Phanawadee and Y. Schuurman. 1997. TAP-2: an interrogative kinetics approach. **Appl. Catal. A: General.** 160: 55-88.

Huinink, J.P. 1995. **A Quantitative Analysis of Transient Kinetic Experiments: The Oxidation of *CO* by O_2/*NO* on *Pt*.** PhD Thesis, Eindoven Univ. of Technology, Eindhoven, The Netherlands.

Huinink, J.P., J.H.B.J. Hoebink and G.B. Marin. 1996. Pulse Experiments over Catalyst Beds: A Window of Measurable Reaction Rate Coefficients. **Can. J. Chem. Eng.** 74: 580-585.

Huizenga, D.G. and D.M. Smith. 1986. Knudsen diffusion in random assemblages of uniform spheres. **AICHE J.** 32: 1-6.

Hung, F. R. 2005. Ph. D. thesis, North Carolina State University.

Jayaraman, V. K. 1993. The effect of shape on the effectiveness of biporous pellets. **J. Catalysis.** 141 (2): 737-739.

Monrudee, P. 2002. **Simulation of Catalytic Processes in a TAP reactor packed with a porous catalyst sample**. M.S. Thesis, Kasetsart University.

Phanawadee, P. 1997. **Theory and methodology of TAP Knudsen pulse response experiments**. Ph.D. thesis, Washington University, St. Louis, MO.

Phanawadee, P., G.S. Yablosaky, P. Preechasanongkit and K. Somapa. 1999. A new correlation for determination of the effective Knudsen diffusivity of a gas in a TAP reactor. **Ind. Eng. Chem. Res.** 38: 2877-2878.

Phanawadee, P., M. Phongaksorn, N. Chaimongkol, A. Jaree and J. Limtrakul. 2005. Mathematical analysis of TAP models for porous catalyst. **J. Chem. Eng.** 115: 51-62.

Satterfield, C.N. 2001. **Hterogeneous Catalyst in Industrial Practice**. 2^{nd} ed. McGraw-Hill, New York.

Schuurman, Y., C. Delattre, I. Pitault, J.P. Reymond and M. Forissier. 2005. Effect of coke deposition on transport and sorption in FCC catalysts studied by temporal analysis of products. **J. Chem. Eng.** 60: 1007-1017.

Shekhtman, S.O. 2003, **Interrogative Kinetics: A New Methodology for Catalyst Characterization**. Ph.D. thesis, Washington University, St. Louis, MO.

Yablonskii, G.S., S.O. Shekhtman, S. Chen and J.T. Gleaves. 1998. Moment-Based Analysis of Transient Response Catalytic Studies (TAP Experiment). **Ind. Eng. Chem. Res. 1998.** 37: 2193-2202.

APPENDICES

Appendix A

Derivation of the Laplace-Domain Solution and Zeroth, First and Second Moment Expressions of the Dimensionless Exit Flow Rate for the One-Zone Reactor Packed with Unimodal-Pore-Structure Catalyst Pellets for Diffusion with Reversible Adsorption Case

A.1. Laplace-Domain Solution and Moment Expressions

The dimensionless mass balance equations in the interparticle and intraparticle regions, and boundary conditions are transformed to Laplace domain described as follows:

Interparticle region:

$$s\overline{C}_b^* - 0 = \frac{d^2\overline{C}_b^*}{dx^2} - 3g\left.\frac{d\overline{C}_p^*}{dr}\right|_{r=1} \qquad \text{A-1}$$

Intraparticle region:

$$s\overline{C}_p^* - 0 = g\left[\frac{d^2\overline{C}_p^*}{dr^2} + \frac{2}{r}\frac{d\overline{C}_p^*}{dr}\right] - \left(k_a^*\overline{C}_p^* - k_d^*\overline{q}^*\right) \qquad \text{A-2}$$

$$s\overline{q}^* - 0 = k_a^*\overline{C}_p^* - k_d^*\overline{q}^* \qquad \text{A-3}$$

Boundary conditions:

Interparticle region:

$$x = 0, \quad \frac{d\overline{C}_b^*}{dx} = -1 \qquad \text{A-4}$$

$$x = 1, \quad \overline{C}_b^* = 0 \qquad \text{A-5}$$

Intraparticle region:

$$r = 1, \quad \bar{C}_p^* = b\,\bar{C}_b^* \qquad \text{A-6}$$

$$r = 0, \quad \frac{d\bar{C}_p^*}{dr} = 0 \qquad \text{A-7}$$

where s = Laplace transform variable

$\bar{C}_b^*$ = C_b^* in Laplace domain

$\bar{C}_p^*$ = C_p^* in Laplace domain

$\bar{q}^*$ = q^* in Laplace domain

Rearranging equation A-3 gives

$$\bar{q}^* = \frac{k_a^*\bar{C}_p^*}{s + k_d^*} \qquad \text{A-8}$$

Substituting equation A-3 into A-2 and rearranging gives

$$\frac{d^2\bar{C}_p^*}{dr^2} + \frac{2}{r}\frac{d\bar{C}_p^*}{dr} - k_1^2\bar{C}_p^* = 0 \qquad \text{A-9}$$

where

$$k_1 = \sqrt{\frac{s + \left(1 - \frac{k_d^*}{s + k_d^*}\right)k_a^*}{g}} \qquad \text{A-10}$$

The solution for $\overline{C}_p^*$ in equation A-9 is

$$\overline{C}_p^* = \frac{1}{r}\left(G_1 e^{k_1 r} + G_2 e^{-k_1 r}\right) \qquad \text{A-11}$$

where G_1 and G_2 are integration constant. The integration constant, G_1 and G_2, are determined from the boundary conditions, equation A-6 and A-7.

$$G_1 = \frac{b\,\overline{C}_b^*}{2\sinh k_1} \qquad \text{A-12}$$

$$G_2 = -\frac{b\,\overline{C}_b^*}{2\sinh k_1} \qquad \text{A-13}$$

Substituting the expressions for G_1 (equation-A-12) and G_2 (equation A-13) into equation A-11 and rearranging, the solution for $\overline{C}_p^*$ can be written as

$$\overline{C}_p^* = b\,\overline{C}_b^* \frac{\sinh\left(k_1 r\right)}{r \sinh k_1} \qquad \text{A-14}$$

Differentiating equation A-14 with respect to r_p, rearranging, and replacing $r_p = 1$ give

$$\left.\frac{d\overline{C}_p^*}{d\,r}\right|_{r=1} = b\,\overline{C}_b^* \left[\frac{k_1}{\tanh k_1} - 1\right] \qquad \text{A-15}$$

Substituting equation A-15 into equation A-1, and rearranging give

$$\frac{d^2\overline{C}_b^*}{dx^2} - k_2^2 \overline{C}_b^* = 0 \qquad \text{A-16}$$

where

$$k_2 = \sqrt{3bg\left[\frac{k_1}{\tanh k_1} - 1\right] + s} \qquad \text{A-17}$$

The solution for $\bar{C}_b^*$ can be obtained similarly to $\bar{C}_p^*$ and is as follows:

$$\bar{C}_b^* = G_3 e^{k_2 x} + G_4 e^{-k_2 x} \qquad \text{A-18}$$

where G_3 and G_4 are integration constant, equation A-19 and A-20. Using boundary conditions, equations A-4 and A-5, give

$$G_3 = \frac{-e^{-k_2}}{2k_2 \cosh k_2} \qquad \text{A-19}$$

$$G_4 = \frac{e^{k_2}}{2k_2 \cosh k_2} \qquad \text{A-20}$$

Substituting the expressions for G_3 (equation-A-19) and G_4 (equation A-20) into equation A-18 and rearranging, the solution for $\bar{C}_b^*$ can be written as

$$\bar{C}_b^* = \frac{\sinh\left(k_2\left(1 - x\right)\right)}{k_2 \cosh k_2} \qquad \text{A-21}$$

The Laplace-domain solution of the dimensionless exit flow rate, $F^*(s)$, can be determined by

$$F^*(s) = -\left.\frac{\partial \bar{C}_b^*}{\partial x}\right|_{x=1} = \frac{1}{\cosh k_2} \qquad \text{A-22}$$

The zeroth, first and second moment expressions of the dimensionless exit flow rate can be determined from equation A-23.

$$m_j^* = (-1)^j \lim_{s\to 0} \frac{\partial^j F^*(s)}{\partial s^j} \quad \text{A-23}$$

When $j = 0$, the zeroth moment expressions of the dimensionless exit flow rate can be written as

$$m_0^* = \lim_{s\to 0} F^*(s) \quad \text{A-24}$$

Substituting equation A-22 into equation A-24 gives

$$m_0^* = 1 \quad \text{A-25}$$

where

$$\lim_{s\to 0} k_2 = 0 \quad \text{A-26}$$

When $j = 1$, the first moment expressions of the dimensionless exit flow rate can be written as

$$m_1^* = -\lim_{s\to 0} \frac{dF^*(s)}{ds} \quad \text{A-27}$$

where

$$\frac{dF^*(s)}{ds} = -\frac{\operatorname{sech} k_2 \tanh k_2}{2k_2}\left\{\left[\frac{3b}{2}\left(1+\frac{k_a^* k_d^*}{\left(s+k_d^*\right)^2}\right)\left(\frac{1}{k_1 \tanh k_1} - \operatorname{csch}^2 k_1\right)\right]+1\right\}$$

A-28

When taking the limit of $\frac{dF^*(s)}{ds}$ as s goes to zero, the solution of $\frac{dF^*(s)}{ds}$ is undetermined $\left(\frac{0}{0}\right)$. To determine this solution, Taylor series expressions are applied which minimum $(j+1)$ expansion terms are used without loss of accuracy. The Taylor series expressions of $\operatorname{csch} x$, $\tanh x$, and $\operatorname{sech} x$ can be described as

$$\operatorname{csch} x = \frac{1}{x} - \frac{x}{6} + \frac{7x^3}{360} - \frac{31x^5}{15120} + \ldots \qquad \text{A-29}$$

$$\tanh x = x - \frac{x^3}{3} + \frac{2x^5}{15} - \frac{17x^7}{315} + \ldots \qquad \text{A-30}$$

$$\operatorname{sech} x = 1 - \frac{x^2}{2} + \frac{5x^4}{24} - \frac{61x^6}{720} + \ldots \qquad \text{A-31}$$

Substituting equations A-29 to A-31 into equation A-28 and rearranging give

$$\frac{dF^*(s)}{ds} = -\left(1 - \frac{5k_3^2}{6} + \frac{k_3^4}{6}\right) \times \left(\left[\frac{b}{24}\left(1 + \frac{k_{a,p}^* k_d^*}{\left(s + k_d^*\right)^2}\right) \times \left(\frac{24 - 5k_1^2 + \left(\frac{k_1^4}{3}\right)}{1 + \left(\frac{k_1^2}{3}\right)} \right) + 1 \right] + 1 \right) \qquad \text{A-32}$$

Taking limit equation A-32 as s goes to zero, the first moment expression of the dimensionless exit flow rate is

$$m_1^* = \frac{1}{2}\left[b\left(1 + \frac{k_a^*}{k_d^*}\right) + 1 \right] \qquad \text{A-33}$$

When $j = 2$, the second moment expression of the dimensionless exit flow rate can be written as

$$m_2^* = \lim_{s\to 0} \frac{d^2F^*(s)}{ds^2} \qquad \text{A-34}$$

From equation A-28, the solution of $\frac{d^2F^*(s)}{ds^2}$ can be written as

$$\frac{d^2F^*(s)}{ds^2} = \frac{d}{ds}\left(\frac{dF^*(s)}{ds}\right) = \frac{z\left(\frac{du}{ds}\right) - u\left(\frac{dz}{du}\right)}{z^2} = A + B + C - D \qquad \text{A-35}$$

where

$$\frac{dF^*(s)}{ds} = \frac{u}{z} \qquad \text{A-36}$$

$$\text{u=sech}\, k_2 \tanh k_2 \left\{\left[\frac{3b}{2}\left(1 + \frac{k_a^* k_d^*}{\left(s+k_d^*\right)^2}\right)\left(\frac{1}{k_1 \tanh k_1} - \text{csch}^2\, k_1\right)\right] + 1\right\} \qquad \text{A-37}$$

$$z = 2k_2 \qquad \text{A-38}$$

$$A = \frac{\text{sech}\, k_2^2 \tanh^2 k_2^2}{4k_2^2}\left\{\left[\frac{3b}{2}\left(1 + \frac{k_a^* k_d^*}{\left(s+k_d^*\right)^2}\right) \times \left(\frac{1}{k_1 \tanh k_1} - \text{csch}^2\, k_1\right)\right] + 1\right\}^2 \qquad \text{A-39}$$

$$B=-\frac{\operatorname{sech} k_2^2\left(1-\tanh^2 k_2^2\right)}{4k_2^2}\left\{\left[\begin{array}{l}\dfrac{3b}{2}\left(1+\dfrac{k_a^* k_d^*}{\left(s+k_d^*\right)^2}\right)\times \\ \left(\dfrac{1}{k_1\tanh k_1}-\operatorname{csch}^2 k_1\right)\end{array}\right]+1\right\}^2 \qquad \text{A-40}$$

$$C=-\frac{3b}{2}\frac{\operatorname{sech} k_2^2\tanh k_2^2}{4k_2^2}\left\{\begin{array}{l}\dfrac{1}{g}\left(1+\dfrac{k_a^* k_d^*}{\left(s+k_d^*\right)^2}\right)^2\times \\ \left(-\dfrac{\coth k_1}{k_1^3}-\dfrac{\coth^2 k_1}{k_1^2}+\dfrac{2\operatorname{csch}^2 k_1\coth k_1}{k_1^3}\right) \\ -4\left(\dfrac{k_a^* k_d^*}{\left(s+k_d^*\right)^3}\right)\left(\dfrac{1}{k_1\tanh k_1}-\operatorname{csch}^2 k_1\right)\end{array}\right\} \qquad \text{A-41}$$

$$D=-\frac{\operatorname{sech} k_2^2\tanh k_2^2}{4k_2^3}\left\{\left[\begin{array}{l}\dfrac{3b}{2}\left(1+\dfrac{k_a^* k_d^*}{\left(s+k_d^*\right)^2}\right)\times \\ \left(\dfrac{1}{k_1\tanh k_1}-\operatorname{csch}^2 k_1\right)\end{array}\right]+1\right\}^2 \qquad \text{A-42}$$

Applying Taylor series expressions to equations A-39 to A-42 and taking limit as s goes to zero, the second moment expression of the dimensionless exit flow rate is given by

$$m_2^*=\frac{1}{2}\left[\frac{5}{6}\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right]^2+\frac{2b}{15}\left[\frac{\left(1+\dfrac{k_a^*}{k_d^*}\right)^2}{g}+15\frac{k_a^*}{k_d^{*2}}\right]\right] \qquad \text{A-43}$$

A.2. Laplace-Domain Solution of the Dimensionless Exit Flow Rate for Diffusion with Irreversible Adsorption/Reaction Case

When $k_d^* = 0$, the Laplace-domain solution of the dimensionless exit flow rate, Eq. (22), can be simplified to that for diffusion with irreversible adsorption/reaction as follows:

$$F^*(s) = -\left.\frac{\partial \overline{C}_b^*}{\partial x}\right|_{x=1} = \frac{1}{\cosh k_2} \qquad \text{A-44}$$

where

$$k_2 = \sqrt{3bg\left[\frac{k_1}{\tanh k_1} - 1\right] + s} \qquad \text{A-45}$$

$$k_1 = \sqrt{\frac{s + k_a^*}{g}} \qquad \text{A-46}$$

A.3. Derivation of q_∞^* for Irreversible Adsorption after One Pulse

The analytical solution of the pulse-intensity-normalized surface concentration after one pulse ($t = \infty$) for unimodal porous case, q_∞^*, can be derived as follows:

When $k_d^* = 0$, equation A-3 becomes

$$s\overline{q}^* = k_a^* \overline{C}_p^* \qquad \text{A-47}$$

Substituting equations A-14 and A-21 into equation A-47 gives

$$s\overline{q}^{*} = b\,k_a^{*} \times \frac{\sinh\left(k_1 r\right)}{r\sinh k_1} \times \frac{\sinh\left(k_2\left(1-x\right)\right)}{k_2\cosh k_2} \qquad \text{A-48}$$

The final value theorem is described by equation A-50.

$$\lim_{t\to\infty} f\left(t\right) = \lim_{s\to 0} sf\left(s\right) \qquad \text{A-49}$$

Therefore

$$\lim_{t\to\infty} q^{*}\left(t\right) = \lim_{s\to 0} s\overline{q}^{*}\left(s\right) \qquad \text{A-50}$$

Applying equation A-50 to equation A-48, the time-domain solution of the pulse-intensity-normalized surface concentration after one pulse ($t = \infty$) is as follows:

$$q_{\infty}^{*} = \sqrt{\frac{b\,k_a^{*}}{h}} \times \frac{\sinh\left(\sqrt{\frac{k_a^{*}}{g}}\,r\right)}{r\sinh\sqrt{\frac{k_a^{*}}{g}}} \times \frac{\sinh\left(\sqrt{b\,k_a^{*}h}\left(1-x\right)\right)}{\cosh\sqrt{b\,k_a^{*}h}} \qquad \text{A-51}$$

where

$$\sqrt{\frac{k_a^{*}}{g}} = \lim_{s\to 0} k_1 \qquad \text{A-52}$$

and

$$\sqrt{b\,k_a^{*}h} = \lim_{s\to 0} k_2 \qquad \text{A-53}$$

Appendix B

Derivation of the Laplace-Domain Solution and Zeroth, First and Second Moment Expressions of the Dimensionless Exit Flow Rate for the Three-Zone Reactor Packed with Unimodal-Pore-Structure Catalyst Pellets for Diffusion Case

The dimensionless mass balance equations of each zone for diffusion case and boundary conditions are transformed to Laplace domain as follows:

Zone 1:

$$r_{e1} s\overline{C}^{*}_{b,1} - 0 = r_{D1} \frac{\partial^2 \overline{C}^{*}_{b,1}}{\partial x^2} \quad \text{B-1}$$

Zone 2:

Interparticle region:

$$s\overline{C}^{*}_{b} - 0 = \frac{d^2 \overline{C}^{*}_{b}}{dx^2} - 3g \left. \frac{d\overline{C}^{*}_{p}}{dr} \right|_{r=1} \quad \text{B-2}$$

Intraparticle region:

$$s\overline{C}^{*}_{p} - 0 = g \left[\frac{d^2 \overline{C}^{*}_{p}}{dr^2} + \frac{2}{r} \frac{d\overline{C}^{*}_{p}}{dr} \right] \quad \text{B-3}$$

Zone 3:

$$r_{e3} s\overline{C}^{*}_{b,3} - 0 = r_{D3} \frac{\partial^2 \overline{C}^{*}_{b,3}}{\partial x^2} \quad \text{B-4}$$

Boundary conditions:

Interparticle region:

$$x = 0, \quad \frac{d\overline{C}^{*}_{b}}{dx} = -1 \quad \text{B-5}$$

$$x = 1, \quad \bar{C}_b^* = 0 \tag{B-6}$$

Intraparticle region:

$$r = 1, \quad \bar{C}_p^* = b\,\bar{C}_b^* \tag{B-7}$$

$$r = 0, \quad \frac{d\bar{C}_p^*}{d\,r} = 0 \tag{B-8}$$

At the adjacent zones in the reactor:

$$x = x_1\,, \; \bar{C}_{b,1}^* = \bar{C}_{b,2}^* \tag{B-9}$$

$$x = x_1\,, \; -r_{D1}\frac{\partial\bar{C}_{b,1}^*}{\partial x} = -\frac{\partial\bar{C}_{b,2}^*}{\partial x} \tag{B-10}$$

$$x = x_2\,, \; \bar{C}_{b,2}^* = \bar{C}_{b,3}^* \tag{B-11}$$

$$x = x_2\,, \; -\frac{\partial\bar{C}_{b,2}^*}{\partial x} = -r_{D3}\frac{\partial\bar{C}_{b,3}^*}{\partial x} \tag{B-12}$$

To determine Laplace-domain solution of the dimensionless exit flow rate, the solution of $\bar{C}_{b,1}^*$, $\bar{C}_{b,2}^*$ and $\bar{C}_{b,3}^*$ are required. These solutions can be determined by solving each solution independently as follows:

Zone 1:

Rearranging B-1, the solution for $\bar{C}^*_{b,1}$ can be written as

$$\bar{C}^*_{b,1} = G_1 e^{K_1 x} + G_2 e^{-K_1 x} \quad \text{B-13}$$

where

$$K_1 = \sqrt{\frac{r_{e1}}{r_{D1}} s} \quad \text{B-14}$$

Zone 2:

Derivation of solution for $\bar{C}^*_{b,2}$ is similar to the derivation for a one-zone reactor, Appendix A, when k^*_a and $k^*_d = 0$. The solution for $\bar{C}^*_{b,2}$ is as follows

$$\bar{C}^*_{b,2} = G_3 e^{K_2 x} + G_4 e^{-K_4 x} \quad \text{B-15}$$

where

$$K_2 = \sqrt{3bg\left[\frac{k_1}{\tanh k_1} - 1\right] + s} \quad \text{B-16}$$

$$k_1 = \sqrt{\frac{s}{g}} \quad \text{B-17}$$

Zone 3:

Rearranging B-4 and applying the method of separation of variables, the solution for $\bar{C}^*_{b,3}$ can be written as

$$\bar{C}^*_{b,3} = G_5 e^{K_3 x} + G_6 e^{-K_3 x} \qquad \text{B-18}$$

where

$$K_3 = \sqrt{\frac{r_{e3}}{r_{D3}} s} \qquad \text{B-19}$$

Using boundary conditions, equations B-5, B-6 and B-9 to B-12, the integration constants G_1, G_2, G_3, G_4, G_5 and G_6, are as follows:

$$G_1 = \frac{1}{K_1} - G_2 \qquad \text{B-20}$$

$$G_2 = \frac{Q_1 Q_4 - Q_6 Q_2}{Q_1 Q_3 + Q_2 Q_5} \qquad \text{B-21}$$

$$G_3 = \frac{-Q_2 \left(Q_3 Q_6 + Q_4 Q_5 \right)}{Q_1 Q_3 + Q_2 Q_5} \qquad \text{B-22}$$

$$G_4 = \frac{Q_1 \left(Q_3 Q_6 + Q_4 Q_5 \right)}{Q_1 Q_3 + Q_2 Q_5} = \frac{-Q_1}{Q_2} G_3 \qquad \text{B-23}$$

$$G_5 = \frac{e^{-K_3 x_2}}{2} \left[\left(G_3 e^{K_2 x_2} + G_4 e^{-K_2 x_2} \right) + \frac{1}{r_{D3}} \left(G_3 e^{K_2 x_2} - G_4 e^{-K_2 x_2} \right) \right] \qquad \text{B-24}$$

$$G_6 = \frac{e^{K_3 x_2}}{2}\left[\left(G_3 e^{K_2 x_2} + G_4 e^{-K_2 x_2}\right) - \frac{1}{r_{D3}}\left(G_3 e^{K_2 x_2} - G_4 e^{-K_2 x_2}\right)\right] \qquad \text{B-25}$$

The constants Q_1, Q_2, Q_3, Q_4, Q_5 and Q_6 are written as

$$Q_1 = \frac{e^{K_3(1-x_2)+K_2 x_2} + e^{-K_3(1-x_2)+K_2 x_2}}{2} + \frac{K_2}{r_{D3} K_3}\frac{e^{K_3(1-x_2)+K_2 x_2} - e^{-K_3(1-x_2)+K_2 x_2}}{2} \qquad \text{B-26}$$

$$Q_2 = \frac{e^{K_3(1-x_2)-K_2 x_2} + e^{-K_3(1-x_2)-K_2 x_2}}{2} - \frac{K_2}{r_{D3} K_3}\frac{e^{K_3(1-x_2)-K_2 x_2} - e^{-K_3(1-x_2)-K_2 x_2}}{2} \qquad \text{B-27}$$

$$Q_3 = \frac{e^{-K_2 x_1}}{2}\left[\left(e^{K_1 x_1} + e^{-K_1 x_1}\right) + \frac{r_{D1} K_1}{K_2}\left(e^{K_1 x_1} - e^{-K_1 x_1}\right)\right] \qquad \text{B-28}$$

$$Q_4 = \frac{e^{x_1(K_1 - K_2)}}{2}\left[\frac{1}{K_2} + \frac{1}{r_{D1} K_1}\right] \qquad \text{B-29}$$

$$Q_5 = \frac{e^{K_2 x_1}}{2}\left[\left(e^{K_1 x_1} + e^{-K_1 x_1}\right) - \frac{r_{D1} K_1}{K_2}\left(e^{K_1 x_1} - e^{-K_1 x_1}\right)\right] \qquad \text{B-30}$$

$$Q_6 = \frac{e^{x_1(K_1 + K_2)}}{2}\left[\frac{1}{K_2} - \frac{1}{r_{D1} K_1}\right] \qquad \text{B-31}$$

The Laplace-domain solution of the dimensionless exit flow rate can be described by

$$F^*(s) = -\left.\frac{\partial \bar{C}^*_{b,3}}{\partial x}\right|_{x=1} = K_3\left(G_5 e^{K_3} + G_6 e^{-K_3}\right) \qquad \text{B-32}$$

Substituting equation B-24 and E-25 into equation E-32 and rearranging give

$$F^*(s) = \frac{\exp(C)\begin{Bmatrix}\sinh^2(A)\sinh(C) - \cosh^2(A)\sinh(C) \\ -\sinh^2(A)\cosh(C) + \cosh^2(A)\cosh(C)\end{Bmatrix}}{\begin{Bmatrix}\cosh(A)\cosh(B)\cosh(C) + \dfrac{r_{D1}K_1}{K_2}\cosh(A)\sinh(B)\sinh(C) \\ + \dfrac{K_2}{r_{D3}K_3}\sinh(A)\sinh(B)\cosh(C) + \dfrac{r_{D1}K_1}{r_{D3}K_3}\sinh(A)\cosh(B)\sinh(C)\end{Bmatrix}}$$

B-33

where

$$C = K_1 z_1, \quad z_1 = x_1 \qquad \text{B-34}$$

$$B = K_2 z_2, \quad z_2 = (x_2 - x_1) \qquad \text{B-35}$$

$$A = K_3 z_3, \quad z_3 = (1 - x_2) \qquad \text{B-36}$$

Defining the solution of $F^*(s)$ as

$$F^*(s) = \frac{M}{N} \qquad \text{B-37}$$

where

$$M = \exp(C)\begin{Bmatrix}\sinh^2(A)\sinh(C) - \cosh^2(A)\sinh(C) \\ -\sinh^2(A)\cosh(C) + \cosh^2(A)\cosh(C)\end{Bmatrix} \qquad \text{B-38}$$

$$N = \begin{Bmatrix}\cosh(A)\cosh(B)\cosh(C) + \dfrac{r_{D1}K_1}{K_2}\cosh(A)\sinh(B)\sinh(C) \\ + \dfrac{K_2}{r_{D3}K_3}\sinh(A)\sinh(B)\cosh(C) + \dfrac{r_{D1}K_1}{r_{D3}K_3}\sinh(A)\cosh(B)\sinh(C)\end{Bmatrix} \qquad \text{B-39}$$

The zeroth moment expression of the dimensionless exit flow rate is

$$m_0^* = 1 \qquad \text{B-40}$$

where

$$\lim_{s \to 0} M = 1 \qquad \text{B-41}$$

and

$$\lim_{s \to 0} N = 1 \qquad \text{B-42}$$

The first moment expression of the dimensionless exit flow rate can be determined by

$$m_1^* = -\lim_{s \to 0} \frac{dF^*(s)}{ds} \qquad \text{B-43}$$

Denoting

$$\frac{dF^*(s)}{ds} = \frac{N\dfrac{dM}{ds} - M\dfrac{dN}{ds}}{N^2} \qquad \text{B-44}$$

The solution of $\frac{dM}{ds}$ is

$$\frac{dM}{ds} = M_1 - M_2 - M_3 + M_4 = 0 \qquad \text{B-45}$$

where

$$M_1 = \frac{d}{ds}\left(\exp(C)\sinh^2(A)\sinh(C)\right) = \left[\begin{array}{l} \frac{z_1}{2K_1}\frac{r_{e1}}{r_{D1}}\exp(C)\sinh^2(A)\sinh(C) \\ +\frac{z_3}{K_3}\frac{r_{e3}}{r_{D3}}\exp(C)\sinh(A)\cosh(A)\sinh(C) \\ +\frac{z_1}{2K_1}\frac{r_{e1}}{r_{D1}}\exp(C)\sinh^2(A)\cosh(C) \end{array}\right]$$

B-46

$$M_2 = \frac{d}{ds}\left(\exp(C)\cosh^2(A)\sinh(C)\right) = \left[\begin{array}{l} \frac{z_1}{2K_1}\frac{r_{e1}}{r_{D1}}\exp(C)\cosh^2(A)\sinh(C) \\ +\frac{z_3}{K_3}\frac{r_{e3}}{r_{D3}}\exp(C)\sinh(A)\cosh(A)\sinh(C) \\ +\frac{z_1}{2K_1}\frac{r_{e1}}{r_{D1}}\exp(C)\cosh^2(A)\cosh(C) \end{array}\right]$$

B-47

$$M_3 = \frac{d}{ds}\left(\exp(C)\sinh^2(A)\sinh(C)\right) = \left[\begin{array}{l} \frac{z_1}{2K_1}\frac{r_{e1}}{r_{D1}}\exp(C)\sinh^2(A)\cosh(C) \\ +\frac{z_3}{K_3}\frac{r_{e3}}{r_{D3}}\exp(C)\sinh(A)\cosh(A)\sinh(C) \\ +\frac{z_1}{2K_1}\frac{r_{e1}}{r_{D1}}\exp(C)\sinh^2(A)\sinh(C) \end{array}\right]$$

B-48

$$M_4 = \frac{d}{ds}\left(\exp(C)\cosh^2(A)\sinh(C)\right) = \left[\begin{array}{l} \frac{z_1}{2K_1}\frac{r_{e1}}{r_{D1}}\exp(C)\cosh^2(A)\cosh(C) \\ +\frac{z_3}{K_3}\frac{r_{e3}}{r_{D3}}\exp(C)\sinh(A)\cosh(A)\sinh(C) \\ +\frac{z_1}{2K_1}\frac{r_{e1}}{r_{D1}}\exp(C)\cosh^2(A)\sinh(C) \end{array}\right]$$

B-49

The solution of $\frac{dN}{ds}$ is

$$\frac{dN}{ds} = N_1 + N_2 + N_3 + N_4 \tag{B-50}$$

where

$$N_1 = \frac{d}{ds}\left(\cosh(A)\cosh(B)\cosh(C)\right) = \frac{1}{2} \times \begin{bmatrix} \frac{z_3}{K_3}\frac{r_{e3}}{r_{D3}}\sinh(A)\cosh(B)\cosh(C) \\ \frac{z_2[1]}{K_2}\cosh(A)\sinh(B)\cosh(C) \\ \frac{z_1}{K_1}\frac{r_{e1}}{r_{D1}}\cosh(A)\cosh(B)\sinh(C) \end{bmatrix} \tag{B-51}$$

$$N_2 = \frac{d}{ds}\left(\frac{r_{D1}K_1}{K_2}\cosh(A)\sinh(B)\sinh(C)\right) = \frac{1}{2} \times \begin{bmatrix} \frac{r_{e1}}{K_1K_2}\cosh(A)\sinh(B)\sinh(C) \\ -\frac{r_{D1}K_1[1]}{K_2^3}\cosh(A)\sinh(B)\sinh(C) \\ +\frac{z_3K_1}{K_2K_3}\frac{r_{D1}r_{e3}}{r_{D3}}\sinh(A)\sinh(B)\sinh(C) \\ +\frac{z_2r_{D1}K_1[1]}{K_2^2}\cosh(A)\cosh(B)\sinh(C) \\ +\frac{z_1r_{e1}}{K_2}\cosh(A)\sinh(B)\cosh(C) \end{bmatrix} \tag{B-52}$$

$$N_3 = \frac{d}{ds}\left(\frac{K_2}{r_{D3}K_3}\sinh(A)\sinh(B)\cosh(C)\right) = \frac{1}{2}\times\begin{bmatrix} \frac{[1]}{r_{D3}K_2K_3}\sinh(A)\sinh(B)\cosh(C) \\ -\frac{K_2}{K_3^3}\frac{r_{e3}}{r_{D3}^2}\sinh(A)\sinh(B)\cosh(C) \\ +\frac{z_3K_2}{r_{D3}s}\cosh(A)\sinh(B)\cosh(C) \\ +\frac{z_2[1]}{r_{D3}K_3}\sinh(A)\cosh(B)\cosh(C) \\ +\frac{z_1K_2}{K_1K_3}\frac{r_{e1}}{r_{D1}r_{D3}}\sinh(A)\sinh(B)\cosh(A) \end{bmatrix}$$

B-53

$$N_4 = \frac{d}{ds}\left(\frac{r_{D1}K_1}{r_{D3}K_3}\sinh(A)\cosh(B)\sinh(C)\right) = \frac{1}{2}\times\begin{bmatrix} \frac{z_3}{rK_3}\frac{r_{e1}}{r_{D3}}\cosh(A)\cosh(B)\sinh(C) \\ -\frac{K_2}{K_3^3}\frac{r_{e3}}{r_{D3}^2}\sinh(A)\sinh(B)\cosh(C) \\ +\frac{z_1K_2}{2K_3}\frac{r_{e1}}{r_{D3}}\sinh(A)\cosh(B)\cosh(C) \end{bmatrix}$$

B-54

The quantity [1] in Eq. (184) is defined by

$$[1] = \frac{3b}{2}\left(\frac{1}{k_1\tanh k_1} - \operatorname{csch}^2 k_1\right) + 1 \qquad \text{B-55}$$

Taking limit of equations E-51 to E-55 as s goes to zero, gives

$$\lim_{s\to 0} N_1 = \frac{1}{2}\left[z_3^{\,2}\frac{r_{e3}}{r_{D3}} + z_2^{\,2}[b+1] + z_1^{\,2}\frac{r_{e1}}{r_{D1}}\right] \qquad \text{B-56}$$

$$\lim_{s\to 0} N_2 = z_2 z_1 r_{e1} \qquad \text{B-57}$$

$$\lim_{s\to 0} N_3 = \frac{z_3 z_2}{r_{D3}}\left[b+1\right] \qquad \text{B-58}$$

$$\lim_{s\to 0} N_4 = z_3 z_1 \frac{r_{e1}}{r_{D3}} \qquad \text{B-59}$$

Substituting equations B-56 to B-59 into equation B-43 and rearranging, the first moment expression of the dimensionless exit flow rate is

$$m_1^* = \left\{ \begin{array}{l} \dfrac{z_3}{r_{D3}}\left[\dfrac{1}{2} z_3 r_{e3} + z_2\left[b+1\right] + z_1 r_{e1}\right] \\ + z_2\left[\dfrac{1}{2} z_2\left[b+1\right] + z_1 r_{e1}\right] + \dfrac{z_1}{r_{D1}}\left[\dfrac{1}{2} z_1 r_{e1}\right] \end{array} \right\} \qquad \text{B-60}$$

From equation B-44, the solution of $\dfrac{d^2 F^*(s)}{ds^2}$ can be written as

$$\frac{d^2 F^*(s)}{ds^2} = -\frac{M}{N}\frac{d^2 N}{ds^2} + 2\frac{M}{N^3}\left(\frac{dN}{ds}\right)^2 \qquad \text{B-61}$$

The second moment expression of the dimensionless exit flow rate is

$$m_2^* = -\frac{1}{4}\left[\begin{array}{l} \dfrac{z_1 z_2}{r_{D1}}\left[z_1^2 r_{e1}^2 + 2 z_1 z_2 r_{e1}\left[b+1\right]\right] \\ + \dfrac{z_1 z_3}{r_{D1} r_{D3}}\left[z_1^2 r_{e1}^2 + 2 z_1 z_3 r_{e1} r_{e3} + 4 z_1 z_2 r_{e1}\left[b+1\right]\right] \\ + \dfrac{z_2 z_3}{r_{D3}}\left[\begin{array}{l} z_2^2\left[b+1\right]^2 + 2 z_2 z_3 r_{e3}\left[b+1\right] \\ + 4 z_1 z_2 r_{e1}\left[b+1\right] + 4 z_1 z_3 r_{e1} r_{e3} - \left[\dfrac{8}{15} b\left[\dfrac{1}{g}\right]\right] \end{array} \right] \\ + z_2^2\left[z_1 z_2 r_{e1}\left[b+1\right] - \left[\dfrac{4}{15} b\left[\dfrac{1}{g}\right]\right]\right] \\ + \dfrac{z_3^2}{r_{D3}^2}\left[z_1 z_3 r_{e1} r_{e3} + z_2 z_3 r_{e3}\left[b+1\right]\right] \end{array} \right] + 2\left(m_1^*\right)^2 \qquad \text{B-62}$$

Appendix C

Derivation of the Laplace-Domain Solution and First Moment Expressions of the Dimensionless Exit Flow Rate for the Three-Zone Reactor Packed with Unimodal-Pore-Structure Catalyst Pellets for Diffusion with Irreversible Adsorption/Reaction Case

Derivation of the Laplace-domain solution for a three-zone reactor packed with unimodal-pore-structure catalyst pellets for diffusion with irreversible adsorption/reaction case is similar to that for diffusion case, Appendix B, except that the derivation in catalyst zone is the same as that in Appendix A. The Laplace-domain solution of the dimensionless exit flow rate for this case is as follows

$$F^*(s)=\frac{\exp(C)\begin{Bmatrix}\sinh^2(A)\sinh(C)-\cosh^2(A)\sinh(C)\\-\sinh^2(A)\cosh(C)+\cosh^2(A)\cosh(C)\end{Bmatrix}}{\begin{Bmatrix}\cosh(A)\cosh(B)\cosh(C)+\dfrac{r_{D1}K_1}{K_2}\cosh(A)\sinh(B)\sinh(C)\\+\dfrac{K_2}{r_{D3}K_3}\sinh(A)\sinh(B)\cosh(C)+\dfrac{r_{D1}K_1}{r_{D3}K_3}\sinh(A)\cosh(B)\sinh(C)\end{Bmatrix}} \qquad \text{C-1}$$

where

$$C=K_1 z_1, \quad z_1=x_1 \qquad \text{C-2}$$

$$B=K_2 z_2, \quad z_2=(x_2-x_1) \qquad \text{C-3}$$

$$A=K_3 z_3, \quad z_3=(1-x_2) \qquad \text{C-4}$$

and

$$K_1=\sqrt{\frac{r_{e1}}{r_{D1}}s} \qquad \text{C-5}$$

$$K_2=\sqrt{3bg\left[\frac{k_1}{\tanh k_1}-1\right]+s} \qquad \text{C-6}$$

$$k_1 = \sqrt{\frac{k_a^* + s}{g}} \qquad \text{C-7}$$

$$K_3 = \sqrt{\frac{r_{e3}}{r_{D3}} s} \qquad \text{C-8}$$

Derivation of the moment expressions of the dimensionless exit flow rate for this case is also similar to that for diffusion-only case, Appendix B. The first moment expressions of the dimensionless exit flow rate are as follows

$$m_1^* = \left\{ \begin{array}{l} \frac{z_3}{r_{D3}} \left[\frac{1}{2} z_3 r_{e3} + \frac{1}{2} z_2 A' \left(1 + \frac{\tanh \sqrt{y\,h}}{\sqrt{y\,h}} \right) + z_1 r_{e1} \right] \cosh \sqrt{y\,h} \\ + z_2 \left[\frac{1}{2} z_2 A' + z_1 r_{e1} \right] \frac{\sinh \sqrt{y\,h}}{\sqrt{y\,h}} + \frac{z_1}{r_{D1}} \left[\frac{1}{2} z_1 r_{e1} \right] \cosh \sqrt{y\,h} \\ + \frac{z_3 z_1}{r_{D3} r_{D1}} \left[z_2 z_1 r_{e1} \sqrt{y\,h} \sinh \sqrt{y\,h} \right] \end{array} \right\} \qquad \text{C-9}$$

The quantity A' in equation C-10 is defined by

$$A' = \frac{3b}{2} \left(\frac{1}{\sqrt{\frac{k_a^*}{g}} \tanh \sqrt{\frac{k_a^*}{g}}} - \operatorname{csch}^2 \sqrt{\frac{k_a^*}{g}} \right) + 1 \qquad \text{C-10}$$

Appendix D

Derivation of the Laplace-Domain Solution and Zeroth, First and Second Moment Expressions of the Dimensionless Exit Flow Rate for the Three-Zone Reactor Packed with Unimodal-Pore-Structure Catalyst Pellets for Diffusion with Reversible Adsorption Case

Derivation of the Laplace-domain solution for a three-zone reactor packed with unimodal-pore-structure catalyst pellets for diffusion with reversible adsorption case is similar to that for diffusion case, Appendix B, except that the derivation in catalyst zone is the same as that in Appendix A. The Laplace-domain solution of the dimensionless exit flow rate for this case is as follows

$$F^*(s)=\frac{\exp(C)\begin{Bmatrix}\sinh^2(A)\sinh(C)-\cosh^2(A)\sinh(C)\\-\sinh^2(A)\cosh(C)+\cosh^2(A)\cosh(C)\end{Bmatrix}}{\begin{Bmatrix}\cosh(A)\cosh(B)\cosh(C)+\dfrac{r_{D1}K_1}{K_2}\cosh(A)\sinh(B)\sinh(C)\\+\dfrac{K_2}{r_{D3}K_3}\sinh(A)\sinh(B)\cosh(C)+\dfrac{r_{D1}K_1}{r_{D3}K_3}\sinh(A)\cosh(B)\sinh(C)\end{Bmatrix}}$$

D-1

where

$$A=K_3z_3,\quad z_3=(1-x_2)$$ D-2

$$B=K_2z_2,\quad z_2=(x_2-x_1)$$ D-3

$$C=K_1z_1,\quad z_1=x_1$$ D-4

The quantity K_1, K_2 and K_3 are given by

$$K_1=\sqrt{\frac{r_{e1}}{r_{D1}}s}$$ D-5

$$K_2=\sqrt{3bg\left[\frac{k_1}{\tanh k_1}-1\right]+s}$$ D-6

where

$$k_1 = \sqrt{\frac{s}{g}} \qquad \text{D-7}$$

$$K_3 = \sqrt{\frac{r_{e3}}{r_{D3}} s} \qquad \text{D-8}$$

Derivation of the moment expressions of the dimensionless exit flow rate for this case is also similar to that for diffusion-only case, Appendix B. The zeroth, first and second moment expressions of the dimensionless exit flow rate are as follows

$$m_0^* = 1 \qquad \text{D-9}$$

$$m_1^* = \left\{ \begin{array}{l} \frac{z_3}{r_{D3}} \left[\frac{1}{2} z_3 r_{e3} + z_2 \left[b \left(1 + \frac{k_a^*}{k_d^*} \right) + 1 \right] + z_1 r_{e1} \right] \\ + z_2 \left[\frac{1}{2} z_2 \left[b \left(1 + \frac{k_a^*}{k_d^*} \right) + 1 \right] + z_1 r_{e1} \right] + \frac{z_1}{r_{D1}} \left[\frac{1}{2} z_1 r_{e1} \right] \end{array} \right\} \qquad \text{D-10}$$

$$m_2^* = -\frac{1}{4}\left[\begin{array}{l} \frac{z_1 z_2}{r_{D1}}\left[z_1^2 r_{e1}^2 + 2z_1 z_2 r_{e1}\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right]\right] \\ +\frac{z_1 z_3}{r_{D1} r_{D3}}\left[z_1^2 r_{e1}^2 + 2z_1 z_3 r_{e1} r_{e3} + 4z_1 z_2 r_{e1}\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right]\right] \\ +\frac{z_2 z_3}{r_{D3}}\left[\begin{array}{l} z_2^2\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right]^2 + 2z_2 z_3 r_{e3}\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right] \\ +4z_1 z_2 r_{e1}\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right] + 4z_1 z_3 r_{e1} r_{e3} \\ -\left[\frac{8}{15} b_c\left[\frac{\left(1+\frac{k_a^*}{k_d^*}\right)^2}{g_c} + 15\frac{k_a^*}{k_d^{*2}}\right]\right] \end{array}\right] \\ +z_2^2\left[\begin{array}{l} z_1 z_2 r_{e1}\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right] \\ -\left[\frac{4}{15} b_c\left[\frac{\left(1+\frac{k_a^*}{k_d^*}\right)^2}{g_c} + 15\frac{b_m}{g_m}\frac{k_a^*}{k_d^{*2}}\right]\right] \end{array}\right] \\ +\frac{z_3^2}{r_{D3}^2}\left[z_1 z_3 r_{e1} r_{e3} + z_2 z_3 r_{e3}\left[b\left(1+\frac{k_a^*}{k_d^*}\right)+1\right]\right] \end{array}\right] + 2\left(m_1^*\right)^2$$

D-11

Appendix E

Derivation of the Laplace-Domain Solution and Zeroth, First, Second, and Third Moment Expressions of the Dimensionless Exit Flow Rate for the One-Zone Reactor Packed with Bimodal-Pore-Structure Catalyst Pellets for Diffusion Case

The dimensionless mass balance equations, equations (99) – (101), and boundary conditions, equations (107) – (110), are transformed to Laplace domain described as follows:

Interparticle region:

$$s\bar{C}_b^* - 0 = \frac{d^2\bar{C}_b^*}{dx^2} - 3g_c \left.\frac{d\bar{C}_c^*}{dr_c}\right|_{r_c=1} \tag{E-1}$$

Macropore region:

$$s\bar{C}_c^* - 0 = g_c\left[\frac{d^2\bar{C}_c^*}{dr_c^2} + \frac{2}{r_c}\frac{d\bar{C}_c^*}{dr_c}\right] - 3g_m \left.\frac{d\bar{C}_m^*}{dr_m}\right|_{r_m=1} \tag{E-2}$$

Mesopore region:

$$s\bar{C}_m^* - 0 = g_m\left[\frac{d^2\bar{C}_m^*}{dr_m^2} + \frac{2}{r_m}\frac{d\bar{C}_m^*}{dr_m}\right] \tag{E-3}$$

Boundary conditions:

Interparticle region:

$$x = 0, \quad \frac{d\bar{C}_b^*}{dx} = -1 \tag{E-4}$$

$$x = 1, \quad \bar{C}_b^* = 0 \tag{E-5}$$

Macropore region:

$$r_c = 1, \quad \bar{C}_c^* = b_c\bar{C}_b^* \tag{E-6}$$

$$r_c = 0, \quad \frac{d\overline{C}_c^*}{d\,r_c} = 0 \tag{E-7}$$

Mesopore region:

$$r_m = 1, \quad \overline{C}_m^* = b_m \overline{C}_c^* \tag{E-8}$$

$$r_m = 0, \quad \frac{d\overline{C}_m^*}{d\,r_m} = 0 \tag{E-9}$$

where s = Laplace transform variable

$\overline{C}_b^*$ = C_b^* in Laplace domain

$\overline{C}_c^*$ = C_c^* in Laplace domain

$\overline{C}_m^*$ = C_m^* in Laplace domain

Rearranging equation E-3 gives

$$\frac{d^2\overline{C}_m^*}{d\,r_m^2} + \frac{2}{r_m}\frac{d\overline{C}_m^*}{d\,r_m} - k_1^2\overline{C}_m^* = 0 \tag{E-10}$$

where

$$k_1 = \sqrt{\frac{s}{g_m}} \tag{E-11}$$

The solution for $\bar{C}_m^*$ in equation E-10 is given by

$$\bar{C}_m^* = \frac{1}{r_m}\left(G_1 e^{k_1 r_m} + G_2 e^{-k_1 r_m}\right) \qquad \text{E-12}$$

where G_1 and G_2 are integration constant. The integration constant, G_1 and G_2, are determined from the boundary conditions, equation E-8 and E-9.

$$G_1 = \frac{b_m \bar{C}_c^*}{2\sinh k_1} \qquad \text{E-13}$$

$$G_2 = -\frac{b_m \bar{C}_c^*}{2\sinh k_1} \qquad \text{E-14}$$

Substituting the expressions for G_1 (equation E-13) and G_2 (equation E-14) into equation D-12 and rearranging, the solution for $\bar{C}_m^*$ is

$$\bar{C}_m^* = b_m \bar{C}_c^* \frac{\sinh\left(k_1 r_m\right)}{r_m \sinh k_1} \qquad \text{E-15}$$

Differentiating equation E-15 with respect to r_m, rearranging, and replacing $r_m = 1$ give

$$\left.\frac{d\bar{C}_m^*}{d r_m}\right|_{r_m=1} = b_m \bar{C}_c^* \left[\frac{k_1}{\tanh k_1} - 1\right] \qquad \text{E-16}$$

Substituting equation E-16 into equation E-2, and rearranging give

$$\frac{d^2\bar{C}_c^*}{d r_c^2} + \frac{2}{r_c}\frac{d\bar{C}_c^*}{d r_c} - k_2^2 \bar{C}_c^* = 0 \qquad \text{E-17}$$

where

$$k_2 = \sqrt{\frac{3b_m g_m \left[\frac{k_1}{\tanh k_1} - 1\right] + s}{g_c}} \qquad \text{E-18}$$

The solution for $\bar{C}_c^*$ in equation E-17 is

$$\bar{C}_c^* = \frac{1}{r_c}\left(G_3 e^{k_2 r_c} + G_4 e^{-k_2 r_c}\right) \qquad \text{E-19}$$

where G_3 and G_4 are integration constant. The integration constant, G_3 and G_4, are determined from the boundary conditions, equation E-6 and E-7.

$$G_1 = \frac{b_c \bar{C}_b^*}{2\sinh k_2} \qquad \text{E-20}$$

$$G_2 = -\frac{b_c \bar{C}_b^*}{2\sinh k_2} \qquad \text{E-21}$$

Substituting equations E-20 and E-21 into equation E-19 and rearranging, the solution for $\bar{C}_c^*$ can be written as

$$\bar{C}_c^* = b_c \bar{C}_b^* \frac{\sinh\left(k_2 r_c\right)}{r_c \sinh k_2} \qquad \text{E-22}$$

Differentiating equation E-22 with respect to r_c, rearranging, and replacing $r_c = 1$ give

$$\left.\frac{d\bar{C}_c^*}{d r_c}\right|_{r_c=1} = b_c \bar{C}_b^* \left[\frac{k_2}{\tanh k_2} - 1\right] \qquad \text{E-23}$$

Substituting equation E-23 into equation E-2, and rearranging give

$$\frac{d^2\bar{C}_b^*}{dx^2} - k_3^2\bar{C}_b^* = 0 \qquad \text{E-24}$$

where

$$k_3 = \sqrt{3bg_c\left[\frac{k_2}{\tanh k_2} - 1\right] + s} \qquad \text{E-25}$$

Similarly to $\bar{C}_m^*$ and $\bar{C}_c^*$, the solution for $\bar{C}_b^*$ is

$$\bar{C}_b^* = G_5 e^{k_3 x} + G_6 e^{-k_3 x} \qquad \text{E-26}$$

where G_5 and G_6 are integration constant, equations E-27 and E-28. Using boundary conditions, equations E-4 and E-5, give

$$G_5 = \frac{-e^{-k_3}}{2k_3 \cosh k_3} \qquad \text{E-27}$$

$$G_6 = \frac{e^{k_3}}{2k_3 \cosh k_3} \qquad \text{E-28}$$

Substituting equations E-27 and E-28 into equation E-12 and rearranging, the solution for $\bar{C}_b^*$ can be written as

$$\bar{C}_b^* = \frac{\sinh\left(k_3\left(1-x\right)\right)}{k_3 \cosh k_3} \qquad \text{E-29}$$

The Laplace-domain solution of the dimensionless exit flow rate, $F^*(s)$, can be determined by

$$F^*(s) = -\left.\frac{\partial \bar{C}_b^*}{\partial x}\right|_{x=1} = \frac{1}{\cosh k_3} \qquad \text{E-30}$$

The zeroth, first, second, and third moment expressions of the dimensionless exit flow rate in Laplace domain can be determined from equation E-31.

$$m_j^* = (-1)^j \lim_{s \to 0} \frac{\partial^j F^*(s)}{\partial s^j} \qquad \text{E-31}$$

When $j = 0$, the zeroth moment expressions of the dimensionless exit flow rate can be written as

$$m_0^* = \lim_{s \to 0} F^*(s) \qquad \text{E-32}$$

Substituting equations E-30 into equation E-32, the zeroth moment expressions of the dimensionless exit flow rate is given by

$$m_0^* = 1 \qquad \text{E-33}$$

where

$$\lim_{s \to 0} k_3 = 0 \qquad \text{E-34}$$

When $j = 1$, the first moment expressions of the dimensionless exit flow rate can be written as

$$m_1^* = -\lim_{s\to 0}\frac{dF^*(s)}{ds} \quad \text{E-35}$$

Differentiating equation E-30 respects to s give

$$\frac{dF^*(s)}{ds} = -\frac{\operatorname{sech} k_3 \tanh k_3}{2k_3}\left\{\begin{matrix}\left[\left[\frac{3b_c}{2}\left(\frac{1}{k_2\tanh k_2} - \operatorname{csch}^2 k_2\right)\right]\times\right. \\ \left.\left[\frac{3b_m}{2}\left(\frac{1}{k_1\tanh k_1} - \operatorname{csch}^2 k_1\right)+1\right]+1\right]\end{matrix}\right\} \quad \text{E-36}$$

Applying Taylor series expressions to equation E-36 and substituting into equation E-35, the first moment expressions of the dimensionless exit flow rate is

$$m_1^* = \frac{1}{2}\left[b_c\left(b_m+1\right)+1\right] \quad \text{E-37}$$

When $j = 2$, the second moment expressions of the dimensionless exit flow rate can be written as

$$m_2^* = \lim_{s\to 0}\frac{d^2F^*(s)}{ds^2} \quad \text{E-38}$$

From equation E-36, the solution for $\frac{d^2F^*(s)}{ds^2}$ can be written as

$$\frac{d}{ds}\left(\frac{d\bar{F}^*}{ds}\right) = \frac{z\left(\frac{du}{ds}\right) - u\left(\frac{dz}{du}\right)}{z^2} = A+B+C-D \quad \text{E-39}$$

where

$$u=\operatorname{sech} k_3 \tanh k_3 \left\{ \begin{aligned} &\left[\frac{3b_c}{2}\left(\frac{1}{k_2 \tanh k_2} - \operatorname{csch}^2 k_2\right)\right] \times \\ &\left[\frac{3b_m}{2}\left(\frac{1}{k_1 \tanh k_1} - \operatorname{csch}^2 k_1\right) + 1\right] + 1 \end{aligned} \right\} \quad \text{E-40}$$

$$z = 2k_3 \quad \text{E-41}$$

$$A = \frac{\operatorname{sech} k_3 \tanh^2 k_3}{4k_3^2} \left\{ \begin{aligned} &\left[\frac{3b_c}{2}\left(\frac{1}{k_2 \tanh k_2} - \operatorname{csch}^2 k_2\right)\right] \times \\ &\left[\frac{3b_m}{2}\left(\frac{1}{k_1 \tanh k_1} - \operatorname{csch}^2 k_1\right) + 1\right] + 1 \end{aligned} \right\}^2 \quad \text{E-42}$$

$$B = -\frac{\operatorname{sech} k_3 \left(1 - \tanh^2 k_3\right)}{4k_3^2} \left\{ \begin{aligned} &\left[\frac{3b_c}{2}\left(\frac{1}{k_2 \tanh k_2} - \operatorname{csch}^2 k_2\right)\right] \times \\ &\left[\frac{3b_m}{2}\left(\frac{1}{k_1 \tanh k_1} - \operatorname{csch}^2 k_1\right) + 1\right] + 1 \end{aligned} \right\}^2 \quad \text{E-43}$$

$$C = -\frac{3b_c}{2}\frac{\operatorname{sech} k_3 \tanh k_3}{4k_3} \left\{ \begin{aligned} &\frac{1}{g_c}\left[\frac{3b_m}{2}\left(\frac{1}{k_1 \tanh k_1} - \operatorname{csch}^2 k_1\right) + 1\right]^2 \times \\ &\left[-\frac{\coth k_2}{k_2^3} - \frac{\operatorname{csch}^2 k_2}{k_2^2} + \frac{2\operatorname{csch}^2 k_2 \coth k_2}{k_2}\right] \\ &+ \frac{3b_m}{2g_m}\left[\frac{1}{k_2 \tanh k_2} - \operatorname{csch}^2 k_2\right] \times \\ &\left[-\frac{\coth k_1}{k_1^3} - \frac{\coth^2 k_1}{k_1^2} + \frac{2\operatorname{csch}^2 k_1 \coth k_1}{k_1^3}\right] \end{aligned} \right\}^2$$

E-44

$$D = -\frac{\operatorname{sech} k_3 \tanh k_3}{4k_3^3}\left\{\begin{array}{l}\left[\frac{3b_c}{2}\left(\frac{1}{k_2 \tanh k_2} - \operatorname{csch}^2 k_2\right)\right]\times \\ \left[\frac{3b_m}{2}\left(\frac{1}{k_1 \tanh k_1} - \operatorname{csch}^2 k_1\right)+1\right]+1\end{array}\right\}^2 \qquad \text{E-45}$$

Applying Taylor series expressions to equations E-42 to E-45 and taking limit as s goes to zero, the second moment expression of the dimensionless exit flow rate is

$$m_2^* = \frac{1}{2}\left[\frac{5}{6}\left[b_c\left(b_m+1\right)+1\right]^2 - \frac{2}{15}b_c\left[\frac{b_m}{g_m}+\frac{\left(b_m+1\right)^2}{g_c}\right]\right] \qquad \text{E-46}$$

When $j=3$, the third moment expressions of the dimensionless exit flow rate can be written as

$$m_3^* = -\lim_{s\to 0}\frac{d^3F^*(s)}{ds^3} \qquad \text{E-47}$$

From equation E-39, the solution for $\frac{d^2F^*(s)}{ds^2}$ can be written as

$$\frac{d^2F^*(s)}{ds^2} = X + Y + Z \qquad \text{E-48}$$

where

$$X = -\frac{\operatorname{sech} k_3[1]^3}{8}\left[\begin{array}{l}3\frac{\tanh k_3}{k_3^5} - 3\frac{\left(1-\tanh^2 k_3\right)}{k_3^4} \\ +3\frac{\tanh^2 k_3}{k_3^4} + \frac{\tanh^3 k_3}{k_3^3} - 5\frac{\tanh k_3\left(1-\tanh^2 k_3\right)}{k_3^3}\end{array}\right] \qquad \text{E-49}$$

$$Y = \frac{9b_c \operatorname{sech} k_3 [1][2]}{4k_3^2}\left[\tanh^2 k_3 \text{-} \left(1-\tanh^2 k_3\right) + \frac{\tanh k_3}{k_3}\right] \qquad \text{E-50}$$

$$Z = -\frac{3b_c \operatorname{sech} k_3 \tanh k_3}{2k_3}\left[\begin{array}{l} \dfrac{[3]^3}{g_c}\left[\begin{array}{l} \dfrac{3}{8k_2^5 \tanh k_2} + \dfrac{3\left(1-\tanh^2 k_2\right)}{8k_2^4 \tanh^2 k_2} \\ -\dfrac{3\left(1-\tanh^2 k_2\right)^3}{4k_2^2 \tanh^4 k_2} - \dfrac{5\left(1-\tanh^2 k_2\right)^2}{4k_2^2 \tanh^2 k_2} \\ -\dfrac{\left(1-\tanh^2 k_2\right)}{2k_2^2} \end{array}\right] \\ +\dfrac{9b_m [3]}{g_m g_c}\left[-\dfrac{\coth k_2}{k_2^3} - \dfrac{\operatorname{csch}^2 k_2}{k_2^2} + \dfrac{2\operatorname{csch}^2 k_2 \coth k_2}{k_2}\right] \\ +\dfrac{3b_m}{2g_m^2}\left(\dfrac{1}{k_2 \tanh k_2} - \operatorname{csch}^2 k_2\right) \\ \times\left[\begin{array}{l} \dfrac{3}{8k_1^5 \tanh k_1} + \dfrac{3\left(1-\tanh^2 k_1\right)}{8k_1^4 \tanh^2 k_1} \\ -\dfrac{3\left(1-\tanh^2 k_1\right)^3}{4k_1^2 \tanh^4 k_1} - \dfrac{5\left(1-\tanh^2 k_1\right)^2}{4k_1^2 \tanh^2 k_1} \\ -\dfrac{\left(1-\tanh^2 k_1\right)}{2k_1^2} \end{array}\right] \end{array}\right]$$

E-51

The quantity [1], [2], and [3[are given by

$$[1] = \left\{\frac{3b_c}{2}\left[\frac{1}{k_2 \tanh k_2} - \operatorname{csch}^2 k_2\right][3] + 1\right\} \qquad \text{E-52}$$

$$[2] = \left\{\begin{array}{l} \dfrac{[3]^2}{g_c}\left[-\dfrac{\coth k_2}{k_2^3} - \dfrac{\operatorname{csch}^2 k_2}{k_2^2} + \dfrac{2\operatorname{csch}^2 k_2 \coth k_2}{k_2}\right] \\ +\dfrac{3b_m}{2g_m}\left[\dfrac{1}{k_2 \tanh k_2} - \operatorname{csch}^2 k_2\right]\left[-\dfrac{\coth k_1}{k_1^3} - \dfrac{\coth^2 k_1}{k_1^2} + \dfrac{2\operatorname{csch}^2 k_1 \coth k_1}{k_1^3}\right] \end{array}\right\}$$

E-53

$$[3]=\left[\frac{3b_m}{2}\left(\frac{1}{k_1\tanh k_1}-\operatorname{csch}^2 k_1\right)+1\right] \qquad \text{E-54}$$

Applying Taylor series expressions to equations E-49 to E-51 and taking limit as s goes to zero, the third moment expressions of the dimensionless exit flow rate is

$$m_3^*=\frac{1}{2}\left[\begin{array}{l}\frac{61}{60}\left[b_c\left(b_m+1\right)+1\right]^3+\frac{1}{3}b_c\left[b_c+1\right]\left[\frac{b_m}{g_m}+\frac{\left(b_m+1\right)^2}{g_c}\right]\\+\frac{4}{105}b_c\left[\frac{b_m}{g_m^2}+\frac{\left(b_m+1\right)^3}{g_c^2}+\frac{21}{15}b_m g_c g_m\right]\end{array}\right] \qquad \text{E-55}$$

Appendix F

Derivation of the Laplace-Domain Solution and Zeroth and First Moment Expressions of the Dimensionless Exit Flow Rate for the One-Zone Reactor Packed with Bimodal-Pore-Structure Catalyst Pellets for Diffusion with Irreversible Adsorption/Reaction Case

F.1. Laplace-Domain Solution and Moment Expressions

Derivation of the Laplace-domain solution of the dimensionless exit flow rate for the one-zone reactor packed with bimodal-pore-structure catalyst pellets for diffusion with irreversible adsorption/reaction is similar to that for diffusion case in Appendix E except that derivation in mesopore region is different.

The mass balance equations in mesopore region and on catalyst surface in mesopore region for diffusion with irreversible adsorption/reaction are described by

$$\frac{\partial C_m^*}{\partial t} = g_m \left[\frac{d^2 C_m^*}{d r_m^2} + \frac{2}{r_m} \frac{d C_m^*}{d r_m} \right] - k_a^* C_m^* \qquad \text{F-1}$$

$$\frac{\partial q^*}{\partial t} = k_a^* C_m^* \qquad \text{F-2}$$

Transforming equations F-1 and F-2 into Laplace domain give

$$s\overline{C}_m^* - 0 = g_m \left[\frac{d^2 \overline{C}_m^*}{d r_m^2} + \frac{2}{r_m} \frac{d \overline{C}_m^*}{d r_m} \right] - k_a^* \overline{C}_m^* \qquad \text{F-3}$$

$$s\overline{q}^* - 0 = k_a^* \overline{C}_m^* \qquad \text{F-4}$$

Rearranging equation F-3 gives

$$\frac{d^2 \overline{C}_m^*}{d r_m^2} + \frac{2}{r_m} \frac{d \overline{C}_m^*}{d r_m} - k_1 \overline{C}_m^* = 0 \qquad \text{F-5}$$

where

$$k_1 = \sqrt{\frac{k_a^* + s}{g_m}} \tag{F-6}$$

The Constants of k_2 and k_3 and solutions of $\bar{C}_m^*$, $\bar{C}_p^*$, $\bar{C}_b^*$ and $F^*(s)$ are the same as those for diffusion-only in Appendix D and are as follows:

$$k_2 = \sqrt{\frac{3b_m g_m \left[\frac{k_1}{\tanh k_1} - 1\right] + s}{g_p}} \tag{F-7}$$

$$k_3 = \sqrt{3b_c g_c \left[\frac{k_2}{\tanh k_2} - 1\right] + s} \tag{F-8}$$

$$\bar{C}_m^* = b_m \bar{C}_c^* \frac{\sinh(k_1 r_m)}{r_m \sinh k_1} \tag{F-9}$$

$$\bar{C}_c^* = b_c \bar{C}_b^* \frac{\sinh(k_2 r_c)}{r_c \sinh k_2} \tag{F-10}$$

$$\bar{C}_b^* = \frac{\sinh(k_3(1-x))}{k_3 \cosh k_3} \tag{F-11}$$

$$F^*(s) = -\left.\frac{\partial \bar{C}_b^*}{\partial x}\right|_{x=1} = \frac{1}{\cosh k_3} \tag{F-12}$$

Taking limit equation F-12 as s goes to zero, the zeroth moment expression of the dimensionless exit flow rate is

$$m_0^* = \frac{1}{\cosh\sqrt{y\, h_{overall}}} \qquad \text{F-13}$$

where

$$\lim_{s \to 0} k_3 = \sqrt{y\, h_{overall}} \qquad \text{F-14}$$

$h_{overall}$ in equation F-13 is the overall effectiveness factor defined by

$$h_{overall} = h_{ma} \times h_{me} \qquad \text{F-15}$$

where

h_{ma} is macropore effectiveness factor,

$$h_{ma} = \frac{3}{3M_{T,ma}}\left(\frac{1}{\tanh 3M_{T,ma}} - \frac{1}{3M_{T,ma}}\right) \qquad \text{F-16}$$

h_{me} is mesopore effectiveness factor,

$$h_{me} = \frac{3}{3M_{T,me}}\left(\frac{1}{\tanh 3M_{T,me}} - \frac{1}{3M_{T,me}}\right) \qquad \text{F-17}$$

The parameters $M_{T,ma}$ and $M_{T,me}$ are Macropore Thiele modulus and Mesopore Thiele modulus and are defined respectively by

$$M_{T,ma} = \frac{1}{3}\sqrt{\frac{b_m k_a^* h_{me}}{g_c}} \qquad \text{F-18}$$

$$M_{T,me} = \frac{1}{3}\sqrt{\frac{k_a^*}{g_m}} \qquad \text{F-19}$$

Differentiating equation F-12 respects to s, the solution for $\frac{dF^*(s)}{ds}$ is

$$\frac{dF^*(s)}{ds} = \frac{\operatorname{sech} k_3 \tanh k_3}{2k_3}\left[\left[\frac{3}{2}b_p\left(\frac{1}{k_2\tanh k_2} - \frac{1}{\sinh^2 k_2}\right)\right] \times \left[\frac{3}{2}b_m\left(\frac{1}{k_1\tanh k_1} - \frac{1}{\sinh^2 k_1}\right) + 1\right] + 1\right] \qquad \text{F-20}$$

Taking limit equation F-20 as s goes to zero, the first moment expression of the dimensionless exit flow rate is

$$m_1^* = \frac{1}{2}\frac{\operatorname{sech}\sqrt{y\,h_{overall}}\tanh\sqrt{y\,h_{overall}}}{\sqrt{y\,h_{overall}}}\left[\left[\frac{3}{2}b_c\left(\frac{1}{\sqrt{\frac{b_m k_a^* h_{me}}{g_c}}\tanh\sqrt{\frac{b_m k_a^* h_{me}}{g_c}}} - \frac{1}{\sinh^2\sqrt{\frac{b_m k_a^* h_{me}}{g_c}}}\right)\right] \times \left[\frac{3}{2}b_m\left(\frac{1}{\sqrt{\frac{k_a^*}{g_m}}\tanh\sqrt{\frac{k_a^*}{g_m}}} - \frac{1}{\sinh^2\sqrt{\frac{k_a^*}{g_m}}}\right) + 1\right] + 1\right] \qquad \text{F-21}$$

$$\lim_{s\to 0} k_2 = \sqrt{\frac{b_m k_a^* h_{me}}{g_c}} \qquad \text{F-22}$$

$$\lim_{s\to 0} k_1 = \sqrt{\frac{k_a^*}{g_m}} \qquad \text{F-23}$$

F.2. Derivation of q_∞^* for Irreversible Adsorption after One Pulse

The analytical solution for the pulse-intensity-normalized surface concentration after one pulse ($t = \infty$), q_∞^*, for bimodal porous case can be derived as follows:

Substituting equations F-9 into equation F-4 gives

$$s\overline{q}^* = b_m b_c k_a^* \times \frac{\sinh(k_1 r_m)}{r_m \sinh k_1} \times \frac{\sinh(k_2 r_c)}{r_c \sinh k_2} \times \frac{\sinh(k_3(1-x))}{k_3 \cosh k_3} \qquad \text{F-24}$$

Applying equation A-50, the final value theorem, to equation F-24, the time-domain solution of the pulse-intensity-normalized surface concentration after one pulse ($t = \infty$) is as follows:

$$q_\infty^* = \sqrt{\frac{b_c b_m k_a^*}{h_{ma} h_{me}}} \times \frac{\sinh\left(\sqrt{\frac{k_a^*}{g_m}}\, r_m\right)}{r_m \sinh\sqrt{\frac{k_a^*}{g_m}}} \times \frac{\sinh\left(\sqrt{\frac{b_m k_a^* h_{me}}{g_c}}\, r_c\right)}{r_c \sinh\sqrt{\frac{b_m k_a^* h_{me}}{g_c}}} \times \frac{\sinh\left(\sqrt{b_c b_m h_{ma} h_{me}}\,(1-x)\right)}{\cosh\sqrt{b_c b_m h_{ma} h_{me}}}$$

F-25

where

$$\sqrt{\frac{k_a^*}{g_m}} = \lim_{s\to 0} k_1 \qquad \text{F-26}$$

$$\sqrt{\frac{b_m k_a^* h_{me}}{g_c}} = \lim_{s\to 0} k_2 \qquad \text{F-27}$$

$$\sqrt{b_c b_m h_{ma} h_{me}} = \lim_{s\to 0} k_3 \qquad \text{F-28}$$

Appendix G

Derivation of the Laplace-Domain Solution and Zeroth, First and Second Moment Expressions of the Dimensionless Exit Flow Rate for the One-Zone Reactor Packed with Bimodal-Pore-Structure Catalyst Pellets for Diffusion with Reversible Adsorption Case

Derivation of the Laplace-domain solution of the dimensionless exit flow rate for one-zone reactor packed with bimodal-pore-structure catalyst pellets for diffusion with reversible adsorption is also similar to that for diffusion with irreversible adsorption/reaction in Appendix E.

The mass balance equation in mesopore region for diffusion with reversible adsorption is described by

$$\frac{\partial C_m^*}{\partial t} = g_m \left[\frac{d^2 C_m^*}{d r_m^2} + \frac{2}{r_m} \frac{d C_m^*}{d r_m} \right] - \left(k_a^* C_m^* - k_d^* q^* \right) \qquad \text{G-1}$$

$$\frac{\partial q^*}{\partial t} = k_a^* C_m^* - k_d^* q^* \qquad \text{G-2}$$

Transforming equation G-1 into Laplace domain gives

$$s\overline{C}_m^* - 0 = g_m \left[\frac{d^2 \overline{C}_m^*}{d r_m^2} + \frac{2}{r_m} \frac{d \overline{C}_m^*}{d r_m} \right] - \left(k_a^* \overline{C}_m^* - k_d^* \overline{q}^* \right) \qquad \text{G-3}$$

$$s\overline{q}^* - 0 = k_a^* \overline{C}_m^* - k_d^* \overline{q}^* \qquad \text{G-4}$$

Rearranging equation G-4 gives

$$\overline{q}^* = \frac{k_a^* \overline{C}_m^*}{s + k_d^*} \qquad \text{G-5}$$

Substituting equation G-5 into equation G-3 and rearranging give

$$\frac{d^2 \overline{C}_m^*}{d r_m^2} + \frac{2}{r_m} \frac{d \overline{C}_m^*}{d r_m} - k_1^2 \overline{C}_m^* = 0 \qquad \text{G-6}$$

where

$$k_1 = \sqrt{\frac{s + \left(1 - \frac{k_d^*}{s + k_d^*}\right) k_a^*}{g_m}} \qquad \text{G-7}$$

The constants of k_2 and k_3 and the solutions of $\bar{C}_m^*$, $\bar{C}_c^*$, $\bar{C}_b^*$ and $F^*(s)$ are also the same as those for diffusion case.

Taking limit $F^*(s)$ as s goes to zero, the zeroth moment expression of the dimensionless exit flow rate is

$$m_0^* = 1 \qquad \text{G-8}$$

Differentiating $F^*(s)$ respects to s, the solution for $\frac{dF^*(s)}{ds}$ is

$$\frac{dF^*(s)}{ds} = -\frac{\operatorname{sech} k_3 \tanh k_3}{2k_3} \left[\left[\frac{3}{2} b_c \left(\frac{1}{k_2 \tanh k_2} - \frac{1}{\sinh^2 k_2} \right) \right] \times \left[\frac{3}{2} b_m \left(1 + \frac{k_a^* k_d^*}{\left(s + k_d^*\right)^2} \right) \left(\frac{1}{k_1 \tanh k_1} - \frac{1}{\sinh^2 k_1} \right) + 1 \right] + 1 \right]$$

G-9

Applying Taylor series expressions and taking limit equation G-9 as s goes to zero, the first moment expression of the dimensionless exit flow rate is

$$m_1^* = \frac{1}{2} \left[b_c \left(b_m \left(1 + \frac{k_a^*}{k_d^*} \right) + 1 \right) + 1 \right] \qquad \text{G-10}$$

From equation G-9, the solution for $\frac{d^2F^*(s)}{ds^2}$ can be written as

$$\frac{d}{ds}\left(\frac{dF^*(s)}{ds}\right)=\frac{z\left(\frac{du}{ds}\right)-u\left(\frac{dz}{du}\right)}{z^2}=A+B+C-D \qquad \text{G-11}$$

where

$$\frac{dF^*(s)}{ds}=\frac{u}{z} \qquad \text{G-12}$$

$$\text{u=sech } k_3 \tanh k_3\left[\begin{array}{l}\left[\frac{3}{2}b_c\left(\frac{1}{k_2\tanh k_2}-\frac{1}{\sinh^2 k_2}\right)\right]\times \\ \left[\frac{3}{2}b_m\left(1+\frac{k_a^*k_d^*}{\left(s+k_d^*\right)^2}\right)\left(\frac{1}{k_1\tanh k_1}-\frac{1}{\sinh^2 k_1}\right)+1\right]+1\end{array}\right] \qquad \text{G-13}$$

$$z=2k_3 \qquad \text{G-14}$$

$$A=\frac{\text{sech } k_3 \tanh^2 k_3}{4k_3^2}\left\{\begin{array}{l}\left[\frac{3b_c}{2}\left(\frac{1}{k_2\tanh k_2}-\text{csch}^2 k_2\right)\right]\times \\ \left[\frac{3b_m}{2}\left(1+\frac{k_a^*k_d^*}{\left(s+k_d^*\right)^2}\right)\left(\frac{1}{k_1\tanh k_1}-\text{csch}^2 k_1\right)+1\right]+1\end{array}\right\}^2$$

G-15

$$B=-\frac{\text{sech } k_3\left(1-\tanh^2 k_3\right)}{4k_3^2}\left\{\begin{array}{l}\left[\frac{3b_c}{2}\left(\frac{1}{k_2\tanh k_2}-\text{csch}^2 k_2\right)\right]\times \\ \left[\frac{3b_m}{2}\left(1+\frac{k_a^*k_d^*}{\left(s+k_d^*\right)^2}\right)\left(\frac{1}{k_1\tanh k_1}-\text{csch}^2 k_1\right)+1\right]+1\end{array}\right\}^2$$

G-16

$$C=-\frac{3b_c}{2}\frac{\operatorname{sech}k_3\tanh k_3}{4k_3}\left\{\begin{array}{l}\frac{1}{g_c}\left[\frac{3b_m}{2}\left(1+\frac{k_a^*k_d^*}{\left(s+k_d^*\right)^2}\right)\left(\frac{1}{k_1\tanh k_1}-\operatorname{csch}^2 k_1\right)+1\right]^2\times\\ \left[-\frac{\coth k_2}{k_2^3}-\frac{\operatorname{csch}^2 k_2}{k_2^2}+\frac{2\operatorname{csch}^2 k_2\coth k_2}{k_2}\right]\\ +\frac{3b_m}{2g_m}\left(1+\frac{k_a^*k_d^*}{\left(s+k_d^*\right)^2}\right)\left[\frac{1}{k_2\tanh k_2}-\operatorname{csch}^2 k_2\right]\times\\ \left[-\frac{\coth k_1}{k_1^3}-\frac{\coth^2 k_1}{k_1^2}+\frac{2\operatorname{csch}^2 k_1\coth k_1}{k_1^3}\right]\\ -4\frac{k_a^*k_d^*}{\left(s+k_d^*\right)^3}\left(\frac{1}{k_1\tanh k_{11}}-\operatorname{csch}^2 k_{11}\right)\end{array}\right]^2$$

G-17

$$D=-\frac{\operatorname{sech}k_3\tanh k_3}{4k_3^3}\left\{\begin{array}{l}\left[\frac{3b_c}{2}\left(\frac{1}{k_2\tanh k_2}-\operatorname{csch}^2 k_2\right)\right]\times\\ \left[\frac{3b_m}{2}\left(1+\frac{k_a^*k_d^*}{\left(s+k_d^*\right)^2}\right)\left(\frac{1}{k_1\tanh k_1}-\operatorname{csch}^2 k_1\right)+1\right]+1\end{array}\right\}^2$$

G-18

Applying Taylor series expressions to equation G-15 to G-18 and taking limit as s goes to zero, the second moment expression of the dimensionless exit flow rate is

$$m_2^*=\frac{5}{12}\left[b_c\left(b_m+1\right)+1\right]^2-\frac{b_c}{15}\left[\frac{\left(b_m\left(1+\frac{k_a^*}{k_d^*}\right)+1\right)^2}{g_c}+\frac{b_m\left(1+\frac{k_a^*}{k_d^*}\right)}{g_m}+15\frac{b_m}{g_m}\frac{k_a^*}{k_d^{*2}}\right]$$

G-19

Appendix H

Derivation of the Laplace-Domain Solution and Zeroth, First and Second Moment Expressions of the Dimensionless Exit Flow Rate for the Three-Zone Reactor Packed with Bimodal-Pore-Structure Catalyst Pellets for the Diffusion Case

Derivation of the Laplace-domain solution of the dimensionless exit flow rate for the three-zone reactor packed with bimodal-pore-structure catalyst pellets for diffusion case is similar to that for unimodal case. The mass balance equations in inert zone 1 and 3 are solve similarly to that for unimodal case while the mass balance equations in the catalyst zone are solve similarly to that for one-zone reactor.

The Laplace-domain solution of the dimensionless exit flow rate is as follows

$$F^*(s)=\frac{\exp(C)\begin{Bmatrix}\sinh^2(A)\sinh(C)-\cosh^2(A)\sinh(C)\\ -\sinh^2(A)\cosh(C)+\cosh^2(A)\cosh(C)\end{Bmatrix}}{\begin{Bmatrix}\cosh(A)\cosh(B)\cosh(C)+\frac{r_{D1}K_1}{K_2}\cosh(A)\sinh(B)\sinh(C)\\ +\frac{K_2}{r_{D3}K_3}\sinh(A)\sinh(B)\cosh(C)+\frac{r_{D1}K_1}{r_{D3}K_3}\sinh(A)\cosh(B)\sinh(C)\end{Bmatrix}} \quad \text{H-1}$$

where

$$C=K_1 z_1, \quad z_1=x_1 \quad \text{H-2}$$

$$B=K_2 z_2, \quad z_2=(x_2-x_1) \quad \text{H-3}$$

$$A=K_3 z_3, \quad z_3=(1-x_2) \quad \text{H-4}$$

The quantity K_1, K_2 and K_3 are as follows:

$$K_1=\sqrt{\frac{r_{e1}}{r_{D1}}s} \quad \text{H-5}$$

$$K_2=\sqrt{3b_c g_c\left[\frac{k_2}{\tanh k_2}-1\right]+s} \quad \text{H-6}$$

$$k_2 = \sqrt{\frac{3b_m g_m \left[\frac{k_1}{\tanh k_1} - 1 \right] + s}{g_c}} \qquad \text{H-7}$$

$$k_1 = \sqrt{\frac{s}{g_m}} \qquad \text{H-8}$$

$$K_3 = \sqrt{\frac{r_{e3}}{r_{D3}} s} \qquad \text{H-9}$$

Derivation of the zeroth, first and second moment expressions of the dimensionless exit flow rate for this case is similar to that for unimodal case, Appendix B. The zeroth, first and second moment expressions of the dimensionless exit flow rate are as follows

$$m_0^* = 1 \qquad \text{H-10}$$

$$m_1^* = \left\{ \begin{aligned} &\frac{z_3}{r_{D3}} \left[\frac{1}{2} z_3 r_{e3} + z_2 \left[b_c \left(b_m + 1 \right) + 1 \right] + z_1 r_{e1} \right] \\ &+ z_2 \left[\frac{1}{2} z_2 \left[b_c \left(b_m + 1 \right) + 1 \right] + z_1 r_{e1} \right] + \frac{z_1}{r_{D1}} \left[\frac{1}{2} z_1 r_{e1} \right] \end{aligned} \right\} \qquad \text{H-11}$$

$$m_2^* = -\frac{1}{4}\left[\begin{array}{l} \frac{z_1 z_2}{r_{D1}}\left[z_1^{\,2} r_{e1}^2 + 2 z_1 z_2 r_{e1}\left[b_c\left(b_m+1\right)+1\right]\right] \\ + \frac{z_1 z_3}{r_{D1} r_{D3}}\left[z_1^{\,2} r_{e1}^2 + 2 z_1 z_3 r_{e1} r_{e3} + 4 z_1 z_2 r_{e1}\left[b_c\left(b_m+1\right)+1\right]\right] \\ + \frac{z_2 z_3}{r_{D3}}\left[\begin{array}{l} z_2^{\,2}\left[b_c\left(b_m+1\right)+1\right]^2 + 2 z_2 z_3 r_{e3}\left[b_c\left(b_m+1\right)+1\right] \\ +4 z_1 z_2 r_{e1}\left[b_c\left(b_m+1\right)+1\right] + 4 z_1 z_3 r_{e1} r_{e3} \\ -\left[\frac{8}{15} b_c\left[\frac{\left(b_m+1\right)^2}{g_c} + \frac{b_m}{g_m}\right]\right] \end{array}\right] \\ + z_2^{\,2}\left[z_1 z_2 r_{e1}\left[b_c\left(b_m+1\right)+1\right] - \left[\frac{4}{15} b_c\left[\frac{\left(b_m+1\right)^2}{g_c} + \frac{b_m}{g_m}\right]\right]\right] \\ + \frac{z_3^{\,2}}{r_{D3}^2}\left[z_1 z_3 r_{e1} r_{e3} + z_2 z_3 r_{e3}\left[b_c\left(b_m+1\right)+1\right]\right] \end{array}\right] + 2\left(m_1^*\right)^2$$

H-12

Appendix I

Derivation of the Laplace-Domain Solution and Zeroth and First Moment Expressions of the Dimensionless Exit Flow Rate for the Three-Zone Reactor Packed with Bimodal-Pore-Structure Catalyst Pellets for the Diffusion with Irreversible Adsorption/Reaction Case

Derivation of the Laplace-domain solution and zeroth and first moment expression of the dimensionless exit flow rate for the three-zone reactor packed with bimodal-pore-structure catalyst pellets for diffusion with irreversible adsorption/reaction is similar to those for diffusion case in Appendix H.

The Laplace-domain solution of the dimensionless exit flow rate is as follows

$$F^*(s) = \frac{\exp(C)\begin{Bmatrix}\sinh^2(A)\sinh(C) - \cosh^2(A)\sinh(C) \\ -\sinh^2(A)\cosh(C) + \cosh^2(A)\cosh(C)\end{Bmatrix}}{\begin{Bmatrix}\cosh(A)\cosh(B)\cosh(C) + \frac{r_{D1}K_1}{K_2}\cosh(A)\sinh(B)\sinh(C) \\ + \frac{K_2}{r_{D3}K_3}\sinh(A)\sinh(B)\cosh(C) + \frac{r_{D1}K_1}{r_{D3}K_3}\sinh(A)\cosh(B)\sinh(C)\end{Bmatrix}}$$

I-1

where

$$C = K_1 z_1, \quad z_1 = x_1 \qquad \text{I-2}$$

$$B = K_2 z_2, \quad z_2 = (x_2 - x_1) \qquad \text{I-3}$$

$$A = K_3 z_3, \quad z_3 = (1 - x_2) \qquad \text{I-4}$$

The quantity K_1, K_2 and K_3 are as follows

$$K_1 = \sqrt{\frac{r_{e1}}{r_{D1}} s} \qquad \text{I-5}$$

$$K_2 = \sqrt{3 b_c g_c \left[\frac{k_2}{\tanh k_2} - 1\right] + s} \qquad \text{I-6}$$

where

$$k_2 = \sqrt{\frac{3 b_m g_m \left[\frac{k_1}{\tanh k_1} - 1 \right] + s}{g_c}} \qquad \text{I-7}$$

$$k_1 = \sqrt{\frac{k_a^* + s}{g_m}} \qquad \text{I-8}$$

$$K_3 = \sqrt{\frac{r_{e3}}{r_{D3}} s} \qquad \text{I-9}$$

The zeroth and first moment expressions of the dimensionless exit flow rate are as follows

$$m_0^* = \frac{1}{\cosh \sqrt{y\, h_{overall}} + \frac{z_3}{r_{D3} z_2} \sqrt{y\, h_{overall}} \sinh \sqrt{y\, h_{overall}}} \qquad \text{I-10}$$

$$m_1^* = \left\{ \begin{array}{l} \frac{z_3}{r_{D3}} \left[\frac{1}{2} z_3 r_{e3} + \frac{1}{2} z_2 B' \left(1 + \frac{\tanh \sqrt{y\, h_{overall}}}{\sqrt{y\, h_{overall}}} \right) + z_1 r_{e1} \right] \cosh \sqrt{y\, h_{overall}} \\ + z_2 \left[\frac{1}{2} z_2 B' + z_1 r_{e1} \right] \frac{\sinh \sqrt{y\, h_{overall}}}{\sqrt{y\, h_{overall}}} + \frac{z_1}{r_{D1}} \left[\frac{1}{2} z_1 r_{e1} \right] \cosh \sqrt{y\, h_{overall}} \\ + \frac{z_3 z_1}{r_{D3} r_{D1}} \left[z_2 z_1 r_{e1} \sqrt{y\, h_{overall}} \sinh \sqrt{y\, h_{overall}} \right] \end{array} \right\} \qquad \text{I-11}$$

The quantity B' in equation I-11 is defined by

$$B' = \left\{ \begin{array}{l} \left[\dfrac{3b_c}{2} \left(\dfrac{1}{\sqrt{\dfrac{b_m k_a^* h_{me}}{g_c}} \tanh \sqrt{\dfrac{b_m k_a^* h_{me}}{g_c}}} - \operatorname{csch}^2 \sqrt{\dfrac{b_m k_a^* h_{me}}{g_c}} \right) \right] \\ \times \left[\dfrac{3b_m}{2} \left(\dfrac{1}{\sqrt{\dfrac{k_a^*}{g_m}} \tanh \sqrt{\dfrac{k_a^*}{g_m}}} - \operatorname{csch}^2 \sqrt{\dfrac{k_a^*}{g_m}} \right) + 1 \right] + 1 \end{array} \right\} \qquad \text{I-12}$$

Appendix J

Derivation of the Laplace-Domain Solution and Zeroth, First and Second Moment Expressions of the Dimensionless Exit Flow Rate for the Three-Zone Reactor Packed with Bimodal-Pore-Structure Catalyst Pellets for Diffusion with Reversible Adsorption

Derivation of the Laplace-domain solution and zeroth and first moment expression of the dimensionless exit flow rate for the three-zone reactor packed with bimodal-pore-structure catalyst pellets for diffusion with reversible adsorption is similar to those for diffusion case, Appendix H.

The Laplace-domain solution of the dimensionless exit flow rate is as follows

$$F^*(s)=\frac{\exp(C)\begin{Bmatrix}\sinh^2(A)\sinh(C)-\cosh^2(A)\sinh(C)\\-\sinh^2(A)\cosh(C)+\cosh^2(A)\cosh(C)\end{Bmatrix}}{\begin{Bmatrix}\cosh(A)\cosh(B)\cosh(C)+\frac{r_{D1}K_1}{K_2}\cosh(A)\sinh(B)\sinh(C)\\+\frac{K_2}{r_{D3}K_3}\sinh(A)\sinh(B)\cosh(C)+\frac{r_{D1}K_1}{r_{D3}K_3}\sinh(A)\cosh(B)\sinh(C)\end{Bmatrix}} \tag{J-1}$$

where

$$C=K_1z_1,\quad z_1=x_1 \tag{J-2}$$

$$B=K_2z_2,\quad z_2=(x_2-x_1) \tag{J-3}$$

$$A=K_3z_3,\quad z_3=(1-x_2) \tag{J-4}$$

The parameters K_1, K_2 and K_3 are as follows

$$K_1=\sqrt{\frac{r_{e1}}{r_{D1}}s} \tag{J-5}$$

$$K_2=\sqrt{3b_c g_c\left[\frac{k_2}{\tanh k_2}-1\right]+s} \tag{J-6}$$

$$k_2 = \sqrt{\frac{3b_m g_m \left[\frac{k_1}{\tanh k_1} - 1 \right] + s}{g_c}} \qquad \text{J-7}$$

$$k_1 = \sqrt{\frac{s + \left(\frac{k_d^*}{s + k_d^*} \right) k_a^*}{g_m}} \qquad \text{J-8}$$

$$K_3 = \sqrt{\frac{r_{e3}}{r_{D3}} s} \qquad \text{J-9}$$

The zeroth, first and second moment expressions of the dimensionless exit flow rate are as follows

$$m_0^* = 1 \qquad \text{J-10}$$

$$m_1^* = \left\{ \begin{array}{l} \frac{z_3}{r_{D3}} \left[\frac{1}{2} z_3 r_{e3} + z_2 \left[b_c \left(b_m \left(1 + \frac{k_a^*}{k_d^*} \right) + 1 \right) + 1 \right] + z_1 r_{e1} \right] \\ + z_2 \left[\frac{1}{2} z_2 \left[b_c \left(b_m \left(1 + \frac{k_a^*}{k_d^*} \right) + 1 \right) + 1 \right] + z_1 r_{e1} \right] + \frac{z_1}{r_{D1}} \left[\frac{1}{2} z_1 r_{e1} \right] \end{array} \right\} \qquad \text{J-11}$$

$$
m_2^* = \frac{1}{4}\left[\begin{aligned}
&\frac{z_1 z_2}{r_{D1}}\left[z_1^{\,2} r_{e1}^2 + 2 z_1 z_2 r_{e1}\left[b_c\left(b_m\left(1+\frac{k_a^*}{k_d^*}\right)+1\right)+1\right]\right] \\
&+\frac{z_1 z_3}{r_{D1} r_{D3}}\left[z_1^{\,2} r_{e1}^2 + 2 z_1 z_3 r_{e1} r_{e3} + 4 z_1 z_2 r_{e1}\left[b_c\left(b_m\left(1+\frac{k_a^*}{k_d^*}\right)+1\right)+1\right]\right] \\
&+\frac{z_2 z_3}{r_{D3}}\left[\begin{aligned}
&z_2^{\,2}\left[b_c\left(b_m\left(1+\frac{k_a^*}{k_d^*}\right)+1\right)+1\right]^2 \\
&+2 z_2 z_3 r_{e3}\left[b_c\left(b_m\left(1+\frac{k_a^*}{k_d^*}\right)+1\right)+1\right] \\
&+4 z_1 z_2 r_{e1}\left[b_c\left(b_m\left(1+\frac{k_a^*}{k_d^*}\right)+1\right)+1\right] + 4 z_1 z_3 r_{e1} r_{e3} \\
&-\left[\frac{8}{15} b_c\left[\frac{\left(b_m\left(1+\frac{k_a^*}{k_d^*}\right)+1\right)^2}{g_c} + \frac{b_m\left(1+\frac{k_a^*}{k_d^*}\right)}{g_m} + 15\frac{b_m}{g_m}\frac{k_a^*}{k_d^{*2}}\right]\right]
\end{aligned}\right] \\
&+z_2^{\,2}\left[\begin{aligned}
&z_1 z_2 r_{e1}\left[b_c\left(b_m\left(1+\frac{k_a^*}{k_d^*}\right)+1\right)+1\right] \\
&-\left[\frac{4}{15} b_c\left[\frac{\left(b_m\left(1+\frac{k_a^*}{k_d^*}\right)+1\right)^2}{g_c} + \frac{b_m\left(1+\frac{k_a^*}{k_d^*}\right)}{g_m} + 15\frac{b_m}{g_m}\frac{k_a^*}{k_d^{*2}}\right]\right]
\end{aligned}\right] \\
&+\frac{z_3^{\,2}}{r_{D3}^2}\left[z_1 z_3 r_{e1} r_{e3} + z_2 z_3 r_{e3}\left[b_c\left(b_m\left(1+\frac{k_a^*}{k_d^*}\right)+1\right)+1\right]\right]
\end{aligned}\right] + 2\left(m_1^*\right)^2
$$

J-12

CURRICULUM VITAE

NAME	: Mr. Wisuthchai BOONWATCHARAPUNSAKUN		
BIRTH DATE	: May 30, 1981		
BIRTH PLACE	: Bangkok, Thailand		
EDUCATION	: **YEAR**	**INSTITUTE**	**DEGREE/DIPLOMA**
	2004	Rajamangala Univ. Thanyaburi	B.Eng. (Chemical)