ELSEVIER

Chemical Engineering Journal 118 (2006) 17–22

Chemical Engineering Journal

www.elsevier.com/locate/cej

Derivation of a simple equation for the determination of kinetics coefficients in packed-bed reactors

Ahmet R. Özdural[a,*], Asli Alkan[a], Colin Webb[b]

[a] Chemical Engineering Department, Hacettepe University, Beytepe, 06532 Ankara, Turkey
[b] School of Chemical Engineering and Analytical Science, The University of Manchester, Sackville Street, Manchester M60 1QD, UK

Received 18 November 2005; received in revised form 7 January 2006; accepted 10 January 2006

Abstract

In this study we focus our attention on a strategy to deal with packed-bed catalytic reactors in order to present an alternative methodology for the derivation of a new explicit equation for the determination of apparent kinetics coefficients for first order reactions. The Özdural–Alkan methodology, originally used in membrane separations, was followed during the analytical solution of the governing PDE of the system whose solution have resulted the explicit equation sought. The apparent kinetics coefficients obtained through the above-mentioned explicit equation were compared and verified with the numerical solution results of the same system where two different numerical techniques were employed independently. It was concluded that the proposed equation successfully predicts the apparent first order kinetics coefficient in recycling packed-bed catalytic reactors with the use of a single reservoir concentration measurement and the corresponding time data.

Keywords: Reaction kinetics; Mathematical modeling; Packed-bed; Catalytic reactors; Computational techniques

1. Introduction

The successful design of a catalytic industrial reactor lies primarily on the reliability of the experimentally determined parameters used in the scale-up. As a consequence, it is very important to collect accurate and meaningful laboratory data, with proper experimental set-ups, and to interpret the data using sound mathematical techniques. In order to determine the apparent kinetic coefficients in continuous mode operating packed-bed catalytic reactors, via established techniques, simultaneous measurement of the concentration differences between the bed inlet and outlet flows are required [1]. However, when the reaction rate is low and/or the packed-bed reactor residence time is small, this imposes a significant limitation on the determination of apparent kinetic coefficients. In these circumstances, it is likely to come across with very small concentration differences between the bed inlet and outlet flows. Thus, the measurement of the concentration differences between the inlet and outlet streams, so as to find apparent kinetic coefficients, can be very difficult and inaccurate.

The aim of this study was the derivation of an explicit equation for the determination of apparent kinetics coefficients for first order reactions at recycling flow packed-bed catalytic reactors using the Özdural–Alkan technique described elsewhere [2]. This technique is free from the probable limitations of the above-mentioned once through flow systems and, benefiting the advantages of recycling flow systems, a new and simple explicit equation is proposed for the determination of apparent first order kinetic coefficients in packed-bed catalytic reactors. The proposed equation brings into a considerable advantage over currently employed procedures. It allows the determination of packed-bed catalytic reactor kinetics parameters, for first order reactions, by mathematical interpretation of the experimental data gathered from a bench scale recycling flow packed-bed catalytic reactor where cumulated time change of reservoir concentration is monitored. The experimentation can be continued as long as noticeable changes are observed in the reservoir concentration and thus makes it possible the use of the proposed equation for a wide range of experimental conditions.

Subsequent to the explicit equation derivation, to be used for the determination of apparent kinetics coefficients, validity of the predictions of the explicit equation was sought. For this purpose explicit equation predictions were compared and verified with the numerical solution results of the same system where two

---

[*] Corresponding author. Tel.: +90 312 2977475; fax: +90 312 2992124.
E-mail address: ozdural@hacettepe.edu.tr (A.R. Özdural).

1385-8947/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2006.01.004

Nomenclature

A, B	reactant and product, described in Eq. (1)
B_1, B_2	integration constants
C_A	reactant concentration in the void fraction of packed-bed catalytic reactor, mmol cm^{-3}
C_{A0}	reservoir initial concentration, mmol cm^{-3}
h	increment in distance used in numerical solution, cm
i	x panel index used in numerical solution
j	t panel index used in numerical solution
k	increment in time used in numerical solution, s
k_1	first order kinetics constant, cm^3 $\mathrm{g}_{\mathrm{catalyst}}^{-1}$ s^{-1}
L	packed-bed height, cm
m	mass of catalyst, g
N_A	reacted amount of A, mmol
Q	recycle rate, cm^3 s^{-1}
r_A	reaction rate based on mass of catalyst particles, $\mathrm{mmol}_{\mathrm{reacted}}$ $\mathrm{g}_{\mathrm{catalyst}}^{-1}$ s^{-1}
S	packed-bed cross-sectional area, cm^2
t	time, s
T	function described in Eq. (5)
V	reservoir solution volume, cm^3
x	cartesian coordinate, cm
X	function described in Eq. (5)

Greek letters

α	coefficient described in Eq. (4)
β	coefficient described in Eq. (33)
ε	void fraction of the packed-bed
λ^2	constant described in Eq. (8).
ν	interstitial velocity, cm s^{-1}
θ	corresponding time, when designated “thin slice of solution” is at packed-bed catalytic reactor inlet ($x = 0$), s
ρ_p	catalyst particle density, g cm^{-3}
τ_{bed}	residence time of packed-bed catalytic reactor ($\tau_{\mathrm{bed}} = L/\nu$), s
τ_{res}	residence time of reservoir ($\tau_{\mathrm{res}} = V/Q$), s

different numerical techniques were employed independently. Since the determination of apparent kinetics coefficients for first order irreversible reactions is envisaged the appropriate reaction kinetics based on the weight of catalyst beads can be expressed as follows [1]:

$$A \xrightarrow{k_1} B \tag{1}$$

$$-r_A = -\frac{1}{m}\frac{\mathrm{d}N_A}{\mathrm{d}t} = k_1 C_A \tag{2}$$

where A and B are the reactant and the product, respectively, k_1 the first order kinetics constant, cm^3 $\mathrm{g}_{\mathrm{catalyst}}^{-1}$ s^{-1}; C_A the reactant concentration in the void fraction of packed-bed catalytic reactor, mmol cm^{-3}; m the mass of catalyst, g; N_A the reacted amount of A, mmol; r_A the reaction rate based on mass of catalyst particles, $\mathrm{mmol}_{\mathrm{reacted}}$ $\mathrm{g}_{\mathrm{catalyst}}^{-1}$ s^{-1} and t is the time, s.

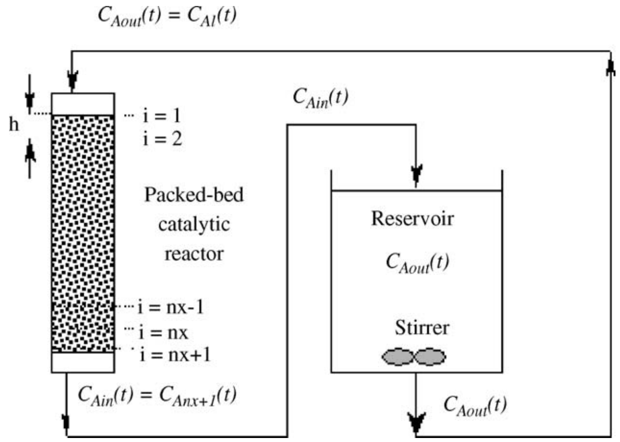

Fig. 1. Schematic drawing of the recycled packed-bed catalytic reactor.

2. Derivation of a simple explicit equation for the determination of apparent kinetics coefficients for first order irreversible reactions

Referring to Fig. 1, let’s take a control volume ($S\Delta x$) in the packed-bed reactor, where S is the column cross-sectional area, cm^2 and Δx is the height of elemental volume, cm. Neglecting axial dispersion, the material balance for A gives the following governing equation.

$$\nu\frac{\partial C_A}{\partial x} + \frac{\partial C_A}{\partial t} + \alpha k_1 C_A = 0 \tag{3}$$

where ε is the void fraction of the bed; ν the interstitial velocity, cm s^{-1} and ρ_p is the catalyst particle density, g cm^{-3} and

$$\alpha = \frac{(1-\varepsilon)}{\varepsilon}\rho_\mathrm{p} \tag{4}$$

For the present recycle system, the reactant concentration in the packed-bed catalytic reactor, C_A is a function of time and distance. By assuming a product solution for the partial differential Eq. (3) and applying the separation of variables technique,

$$C_A = X(x)T(t) \tag{5}$$

$$\frac{\partial C_A}{\partial x} = T\left(\frac{\partial X}{\partial x}\right) \tag{6}$$

$$\frac{\partial C_A}{\partial t} = X\left(\frac{\partial T}{\partial t}\right) \tag{7}$$

Substituting Eqs. (5)–(7) into Eq. (3) and after rearrangement:

$$\frac{1}{X}\frac{\mathrm{d}X}{\mathrm{d}x} = -\frac{1}{\nu T}\frac{\mathrm{d}T}{\mathrm{d}t} - \frac{\alpha k_1}{\nu} = -\lambda^2 \tag{8}$$

In Eq. (8) the first term and the second term can only become equal to each other if they are both equal to a same constant such as $-\lambda^2$ (positive or zero values of constant have no significance in relation to the solution of problem we are considering). From Eq. (8) the solutions of X and T are

$$X = B_1 \exp(-\lambda^2 x) \tag{9}$$

$$T = B_2 \exp\left\lfloor(\lambda^2\nu - \alpha k_1)t\right\rfloor \tag{10}$$

B_1 and B_2 are the integration constants. Substituting Eqs. (9) and (10) into Eq. (5) gives

$$C_A = B_1B_2\ \exp(-\lambda^2 x)\exp\left\lfloor(\lambda^2\nu - \alpha k_1)t\right\rfloor \tag{11}$$

Using the initial condition (at $t=0$; for all x, $C_A=0$ except $x=0$, $C_A=C_{A0}$), B_1B_2 becomes equal to C_{A0}. Hence,

$$C_A = C_{A0}\ \exp(-\lambda^2 x)\exp\left\lfloor(\lambda^2\nu - \alpha k_1)t\right\rfloor \tag{12}$$

Referring to Fig. 1, let us consider a “thin slice of solution” at the packed-bed catalytic reactor inlet ($x=0$), which is moving with a velocity of ν, under plug flow conditions. Furthermore, when this designated “thin slice of solution” is at packed-bed catalytic reactor inlet ($x=0$), let us show the corresponding time, as $t=\theta$. Since this designated “thin slice of solution” is moving with a velocity of ν, it will reach to the packed-bed catalytic reactor outlet ($x=L$), at a time, $t=\theta+\tau_{\text{bed}}$, where τ_{bed} is residence time in the packed-bed catalytic reactor ($\tau_{\text{bed}}=L/\nu$). Consequently, the boundary conditions ($t>0$) for the designated “thin slice of solution” moving with packed-bed interstitial fluid velocity become:

B.C. 1 for $t=\theta$ $(x=0)$ $C_A = C_{A\text{out}}|_{t=\theta}$
B.C. 2 for $t=\theta+t_{\text{bed}}$ $(x=L)$ $C_A = C_{A\text{in}}|_{t=\theta+\tau_{\text{bed}}}$

Employing B.C. 1 in Eq. (12) and solving for λ^2 gives

$$\lambda^2 = \frac{1}{\nu\theta}\ln\left\{\frac{C_{A\text{out}}|_{t=\theta}}{C_{A0}}\right\} + \frac{\alpha k_1}{\nu} \tag{13}$$

An interesting point arises for the present problem, where λ^2, as given in Eq. (13) contains the time term. Özdural and Alkan [2] observed this kind of behavior through the derivation of an explicit equation to be used for the determination of overall mass transfer coefficients in membrane separation operations. In order to elucidate the behavior of λ^2, associated with the present problem, the relationship between $C_{A\text{in}}|_{t=\vartheta+\tau_{\text{bed}}}$ and $C_{A\text{out}}|_{t=\theta}$ is required. For this purpose let us combine Eqs. (12) and (13).

$$C_A = C_{A\text{out}}|_{t=\theta}\left\{\frac{C_{A\text{out}}|_{t=\theta}}{C_{A0}}\right\}^{-x/\nu\theta}\exp\left[-\frac{\alpha k_1 x}{\nu}\right] \tag{14}$$

Employing B.C. 2 in Eq. (14) gives

$$C_{A\text{in}}|_{t=\vartheta+\tau_{\text{bed}}} = C_{A\text{out}}|_{t=\theta}\left\{\frac{C_{A\text{out}}|_{t=\theta}}{C_{A0}}\right\}^{-\tau_{\text{bed}}/\theta}\exp[-\alpha k_1\tau_{\text{bed}}] \tag{15}$$

where $\tau_{\text{bed}}=L/\nu$. Let us re-arrange Eq. (15)

$$\frac{1}{\theta}\ln\left\{\frac{C_{A\text{out}}|_{t=\theta}}{C_{A0}}\right\} = \frac{1}{\tau_{\text{bed}}}\ln\left[\frac{C_{A\text{out}}|_{t=\theta}}{C_{A\text{in}}|_{t=\vartheta+\tau_{\text{bed}}}}\right] - \alpha k_1 \tag{16}$$

If the R.H.S. of Eq. (16) is constant, so is λ^2 as given by Eq. (13). The second term of the R.H.S. of Eq. (16) is constant. Furthermore, it is not difficult to show that if the control volume moves with the velocity of ν (i.e. the above given B.C. 1 and B.C. 2 are pertinent) then $\partial C_A/\partial x$ term in Eq. (3) becomes zero, and final equation reduces to:

$$\frac{\mathrm{d}C_A}{\mathrm{d}t} + \alpha k_1 C_A = 0 \tag{17}$$

For the present recycling system, Eq. (17) is only valid for the case where “outside observer” is moving with the packed-bed interstitial fluid velocity. Thus, for a stationary observer, it is incorrect to use Eq. (17) for gaining an insight on C_A values. During the integration Eq. (17) the integral limits should be so chosen that the moving outside observer criterion be met such as given below.

$t=\theta,\ C_A = C_{A\text{out}}|_{t=\theta}$ and

$t=\theta+\tau_{\text{bed}},\ C_A = C_{A\text{in}}|_{t=\theta+\tau_{\text{bed}}}$

Integration of Eq. (17) gives

$$\ln\left[\frac{C_{A\text{out}}|_{t=\theta}}{C_{A\text{in}}|_{t=\vartheta+\tau_{\text{bed}}}}\right] = \alpha k_1\tau_{\text{bed}} \tag{18}$$

Substituting of Eq. (18) into Eq. (16) provides

$$\frac{1}{\theta}\ln\left\{\frac{C_{A\text{out}}|_{t=\theta}}{C_{A0}}\right\} = 0 \tag{19}$$

This proves that the first term of the R.H.S. of Eq. (16) is also a constant and so is λ^2.

It is obvious that if the packed-bed column is treated as a once through column (single pass, where there is no reservoir) both $C_{A\text{out}}|_{t=\theta}$ and C_{A0} might be regarded as the column inlet concentrations and have the same value. This explains why the term is found as zero in Eq. (19), since when $C_{A\text{out}}|_{t=\theta} = C_{A0}$ the logarithmic term in Eq. (19) becomes $\ln(1)=0$.

Since λ^2 value that is given in Eq. (13) is now proved to be a constant, then $\mathrm{d}\lambda/\mathrm{d}t=0$. The derivative of Eq. (13) gives

$$\frac{\mathrm{d}\lambda}{\mathrm{d}t} = \frac{1}{2\lambda}\left[-\frac{1}{\nu t^2}\ln\frac{C_{A\text{out}}|_{t=\theta}}{C_{A0}} + \frac{1}{\nu t}\frac{\mathrm{d}}{\mathrm{d}t}\left(\ln\frac{C_{A\text{out}}|_{t=\theta}}{C_{A0}}\right)\right] = 0 \tag{20}$$

where $\lambda\to\infty$ is a trivial solution. Therefore one should use the following relationship in order to satisfy $\mathrm{d}\lambda/\mathrm{d}t=0$ condition:

$$-\frac{1}{\nu t^2}\ln\frac{C_{A\text{out}}|_{t=\theta}}{C_{A0}} + \frac{1}{\nu t}\frac{\mathrm{d}}{\mathrm{d}t}\left(\ln\frac{C_{A\text{out}}|_{t=\theta}}{C_{A0}}\right) = 0 \tag{21}$$

From the properties of the derivatives of logarithmic functions [3]:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\ln\frac{C_{A\text{out}}|_{t=\theta}}{C_{A0}}\right) = \frac{1}{C_{A\text{out}}|_{t=\theta}}\frac{\mathrm{d}}{\mathrm{d}t}C_{A\text{out}}|_{t=\theta} \tag{22}$$

If Eq. (22) is substituted into Eq. (21) and rearranged

$$\frac{\mathrm{d}C_{A\text{out}}|_{t=\theta}}{\mathrm{d}t} = \frac{C_{A\text{out}}|_{t=\theta}}{t}\ln\frac{C_{A\text{out}}|_{t=\theta}}{C_{A0}} \tag{23}$$

With reference to Fig. 1, let us make a material balance around the reservoir where the reservoir inlet and outlet concentrations are evaluated for the same time, $t=\theta$.

(Input rate of reactant into the reservoir)

= (Output rate of reactant from the reservoir)

+ (Accumulation rate of reactant in the reservoir)

$$QC_{A\text{in}}|_{t=\theta} = QC_{A\text{out}}|_{t=\theta} + V\frac{\mathrm{d}C_{A\text{out}}}{\mathrm{d}t} \tag{24}$$

$$\frac{\mathrm{d}C_{A\text{out}}}{\mathrm{d}t} = \frac{1}{\tau_{\text{res}}}(C_{A\text{in}}|_{t=\theta} - C_{A\text{out}}|_{t=\theta}) \tag{25}$$

where Q is the recycle rate, $\text{cm}^3\,\text{s}^{-1}$; V the reservoir solution volume, cm^3 and τ_{res} is the residence time of reservoir, s.

$$\tau_{\text{res}} = \frac{V}{Q} \tag{26}$$

If τ_{bed} is small and/or the reaction rate is not very fast, then for a good approximation, $C_{A\text{in}}|_{t=\theta+\tau_{\text{bed}}} \cong C_{A\text{in}}|_{t=\theta}$. From Eqs. (15) and (25) one gets

$$\frac{\mathrm{d}C_{A\text{out}}}{\mathrm{d}t} = \frac{C_{A\text{out}}|_{t=\theta}}{\tau_{\text{res}}} \times \left\{ \left\{ \frac{C_{A\text{out}}|_{t=\theta}}{C_{A0}} \right\}^{-\tau_{\text{bed}}/\theta} \exp[-\alpha k_1 \tau_{\text{bed}}] - 1 \right\} \tag{27}$$

From Eq. (23) and (27) it is not difficult to obtain Eq. (28), which is the new explicit equation for the determination of apparent kinetics coefficients for first order reactions

$$k_1 = \frac{\varepsilon}{(1-\varepsilon)\rho_{\text{p}}} \frac{1}{\tau_{\text{bed}}} \ln \left[\frac{\left(\frac{C_{A\text{out}}|_t}{C_{A0}}\right)^{-\tau_{\text{bed}}/t}}{\ln\left(\frac{C_{A\text{out}}|_t}{C_{A0}}\right)^{\tau_{\text{res}}/t} + 1} \right] \tag{28}$$

Eq. (28) shows that, using only a single reservoir concentration measurement and the corresponding time data, the explicit determination of apparent kinetic coefficient, k_1 for the first order reaction is possible.

3. Numerical solution strategies for the determination of the change of reservoir concentration with time in recycling packed-bed catalytic reactor systems

The purpose of this section is to predict and compare $C_{A\text{out}}$ versus t profiles of the reservoir, by using two independent numerical solution strategies. The first numerical technique makes no reference to the λ^2 term that is given by Eq. (13), whereas the second numerical technique employs λ^2. For the same parameter values, if the $C_{A\text{out}}$ versus t profiles of the two independent numerical solution strategies were the same then this can be taken, as a further validation of λ^2 is indeed constant, besides the analysis given in Section 2.

3.1. Numerical generation of $C_{A\text{out}}$ versus t profiles with implicit scheme finite differences technique

The finite differences technique has been employed to provide a numerical solution to the re-circulating packed-bed catalytic reactor with an irreversible first order reaction where no reference is made to the λ^2 expression given in Eq. (13). Reservoir concentration $C_{A\text{out}}$ versus time t profiles, for a predetermined set of system parameters, was calculated with the employment of a certain value of k_1.

For the numerical solution of Eq. (3) in addition to the packed-bed reactor initial condition given in Section 2, the following reservoir initial condition is used so as to represent the recycling process that is composed of a packed-bed catalytic reactor and a reservoir:

$$\text{I.C. for reservoir}: \ t = 0; \quad C_A = C_{A0}$$

Furthermore, the boundary conditions in Section 2 are given for an outside observer moving with the interstitial velocity of ν. The corresponding boundary conditions for a stationary observer are:

$$\text{B.C. I} \quad \text{for } t > 0,\ x = 0, \quad C_A = C_{A\text{out}}(t) = C_{A1}(t)$$
$$\text{B.C. II} \quad \text{for } t > 0,\ x = L, \quad C_A = C_{A\text{in}}(t) = C_{Anx+1}(t)$$

$\partial C_A(x,t)/\partial x$ is evaluated by the central difference approximation and $\partial C_A(x,t)/\partial t$ is evaluated by the backward difference approximation. Fig. 1 shows that the column is divided into n hypothetical slices of thickness $\Delta x = h$ where time increment is $\Delta t = k$. For distance, x and time, t step indices i and j are used, respectively.

$i = 1$ (represents column inlet and well mixed reservoir):

$$C_{A1,j+1} = \left(1 - \frac{k}{\tau_{\text{res}}}\right) C_{A1,j} + \frac{k}{\tau_{\text{res}}} C_{Anx+1,j} \tag{29}$$

$1 < i < nx + 1$

The central difference approximation for $\partial C_A/\partial x$ gives

$$\frac{\partial C_A}{\partial x} = \frac{-\partial C_{Ai-1,j+1} + \partial C_{Ai+1,j+1}}{2h} \tag{30}$$

The backward (referring to the evaluation of $\partial C_A/\partial x$) difference approximation for $\partial C_A/\partial t$ gives

$$\frac{\partial C_A}{\partial t} = \frac{-\partial C_{Ai,j} + \partial C_{Ai,j+1}}{2h} \tag{31}$$

Substituting Eqs. (30) and (31) into Eq. (3)

$$-\beta C_{Ai-1,j+1} + C_{Ai,j+1} + \beta C_{Ai+1,j+1} = (1 - kk_1\alpha)C_{Ai,j} \tag{32}$$

$$\beta = \frac{k\nu}{2h} \tag{33}$$

$i = nx + 1$ (packed-bed outlet)

It is assumed that the reactant concentration at $i = nx + 1$ can be calculated by extrapolating $i = nx - 1$ and $i = nx$ data.

$$C_{Anx-1,j+1} - 2C_{Anx,j+1} + C_{Anx+1,j+1} = 0 \tag{34}$$

By solving the equation system presented in Fig. 2, we can determine $C_{A1}, C_{A2}, \ldots, C_{An+1}$ at time step $j+1$ from $C_{A1}, C_{A2}, \ldots, C_{An+1}$ at time step j.

$$\begin{bmatrix} 1 & 0 & 0 & 0 & \ldots & & & & 0 \\ -\beta & 1 & \beta & 0 & \ldots & & & & 0 \\ 0 & -\beta & 1 & \beta & \ldots & & & & 0 \\ . & . & . & . & & & & & . \\ . & . & . & & & & & & . \\ . & . & & & & & & & . \\ 0 & 0 & 0 & 0 & \ldots & -\beta & 1 & \beta & 0 \\ 0 & 0 & 0 & 0 & \ldots & 0 & -\beta & 1 & \beta \\ 0 & 0 & 0 & 0 & \ldots & 0 & 1 & -2 & 1 \end{bmatrix} \mathbf{x} \begin{bmatrix} C_{A1,j+1} \\ C_{A2,j+1} \\ C_{A3,j+1} \\ . \\ . \\ . \\ C_{Anx-1,j+1} \\ C_{Anx,j+1} \\ C_{Anx+1,j+1} \end{bmatrix} = \begin{bmatrix} (1-\frac{k}{\tau_{Res}})C_{A1,j} + \frac{k}{\tau_{Res}}C_{Anx+1,j} \\ (1-kk_1\alpha)C_{A2,j} \\ (1-kk_1\alpha)C_{A3,j} \\ . \\ . \\ . \\ (1-kk_1\alpha)C_{Anx-1,j} \\ (1-kk_1\alpha)C_{Anx,j} \\ 0 \end{bmatrix}$$

Fig. 2. Assembly of the set of $n+1$ equations for numerical solution.

3.2. *Alternative numerical generation of C_{Aout} versus t profiles associated with λ^2*

Eq. (27) is a first order ordinary differential equation where the dependent and the independent variables are reservoir concentration, C_{Aout} and time, *t*, respectively. Its solution gives C_{Aout} versus *t* profiles. On the other hand, the derivation of Eq. (27) is directly connected with λ^2 and thus the solution of Eq. (27) will obviously reflect the properties associated with λ^2. Eq. (27) is solved by numerical integration (fourth order Runge–Kutta method) using the same parameters of the above given λ^2 free implicit scheme finite differences techniques. The C_{Aout} versus *t* profiles, generated by the solution of Eq. (27), were compared with those obtained through the use of λ^2 free implicit scheme finite differences techniques.

4. Results and discussion

Table 1 gives the parameters used during the model solutions that were taken from the literature [4] where acetic acid and camphane reacted in a recycled packed-bed (Amberlist 15 catalyst particles) system, to give the pine-fragrance isobornyl acetate. The authors concluded that reaction rate was a pseudo first order, and the unavailable reservoir volume was estimated using the information given in the article. During the numerical generation of C_{Aout} versus *t* profiles, k_1 value of 2.1×10^{-2} cm^3 g$^{-1}_{\text{catalyst}}$ s^{-1} was employed in this study. The prediction of the reservoir concentration, C_{Aout} versus time, *t* profiles were carried out by two independent numerical solution methodologies as explained in the above given Sections 3.1 and 3.2, i.e. λ^2 free implicit scheme finite differences technique and the numerical integration by fourth order Runge–Kutta method that is related with λ^2. Time change of C_{Aout} predictions of both methods were compared with each other for every 20 min for the first 2 h and additionally for $t = 200$ and 400 min. Fig. 3 shows the comparison of C_{Aout} versus time predictions of the two independent numerical solution methods, where C_{Aout} values, obtained by the λ^2 free implicit scheme finite differences technique, were plotted against to those obtained by the numerical integration, using fourth order Runge–Kutta method, that is related with λ^2. Fig. 3 clearly illustrates that the predictions of both methods were in an excellent agreement. In addition to the theoretical analysis presented in Section 2, the consistency of the C_{Aout} values shown at Fig. 3 can be considered as a further justification of λ^2 that is given in Eq. (13), is a constant and thus its time derivative becomes zero.

Table 1
The parameters used

Parameter (units)	Value
Re-circulation rate, Q (cm^3 min^{-1})	4.0
Packed-bed reactor i.d. (cm)	1.0
Packed-bed height, h (cm)	3.9
Packed-bed porosity, ε	0.49
Reservoir volume, V (cm^3)	156.3
Reservoir initial concentration, C_{A0} (mmol cm^{-3})	4.48
Catalyst weight, m (g)	1.86

It is expected that, for a given recycled packed-bed catalytic reactor set-up, one should obtain the same k_1 values regardless of the reservoir C_{Aout} versus *t* data couple employed in Eq. (28) as long as the other parameters were the same. Furthermore, if t and the corresponding C_{Aout} data couple are gathered from a numerical solution by using either technique explained in Section 3, then the k_1 value obtained from Eq. (28) should be consistent with the k_1 value that was assumed during the numerical generation of C_{Aout} versus *t* profiles. Table 2 clearly demonstrates that the above-mentioned requirements were met precisely.

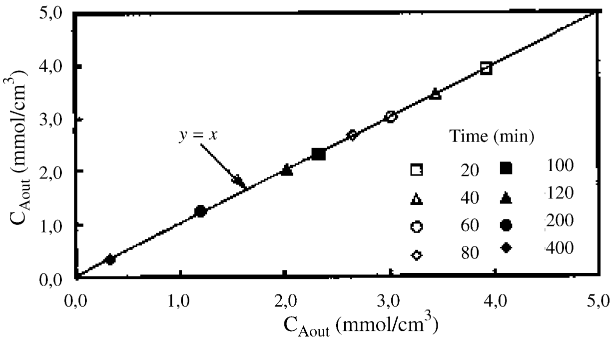

Fig. 3. Predictions of reservoir concentrations with two different numerical solution methods. *x*-axis = C_{Aout} values calculated by numerical integration that is related with λ^2, using fourth order Runge–Kutta equations. *y*-axis = C_{Aout} values calculated by λ^2 free implicit scheme finite differences technique.

Table 2
Apparent first order kinetics coefficient, k_1 values calculated from Eq. (28) for various times

t (min)	C_{Aout}[a] (mmol cm^{-3})	$k_1 \times 10^2$ (cm^3 g$^{-1}_{catalyst}$ s^{-1})	C_{Aout}[b] (mmol cm^{-3})	$k_1 \times 10^2$ (cm^3 g$^{-1}_{catalyst}$ s^{-1})
20	3.9343	2.1	3.9279	2.1
40	3.4497	2.1	3.4442	2.1
60	3.0247	2.1	3.0200	2.1
80	2.6521	2.1	2.6481	2.1
100	2.3254	2.1	2.3220	2.1
120	2.0390	2.1	2.0361	2.1
200	1.2052	2.1	1.2037	2.1
400	0.3237	2.1	0.3234	2.1

[a] After method in Section 3.1.

[b] After method in Section 3.2.

5. Conclusion

The present work proposes an equation for estimation of apparent first order irreversible kinetics coefficient in packed-bed catalytic reactors. Instead of the current practices that require simultaneous measurement of inlet and outlet concentrations of a packed-bed catalytic reactor, the first order irreversible reaction rate constant, k_1 value can be determined by Eq. (28) of this study. During the employment of the established techniques, one might frequently encounter the measurement of a small concentration difference between the inlet and outlet streams, and such small concentration differences might lead to inaccurate estimation of the kinetics coefficients. The proposed equation Eq. (28) allows the determination of packed-bed catalytic reactor apparent kinetics parameters, for first order reactions, by mathematical interpretation of the experimental data gathered from a bench scale recycling flow packed-bed catalytic reactor where cumulated time change of reservoir concentration is monitored. The experimentation can be continued as long as noticeable changes are observed in the reservoir concentration and thus makes it possible the use of the proposed equation for a wide range of experimental conditions. It was concluded that the proposed Eq. (28) successfully predicts the apparent first order kinetics coefficient in recycling packed-bed catalytic reactors with the use of a single reservoir concentration measurement and the corresponding time data.

References

[1] O. Levenspiel, Chemical Reaction Engineering, third ed., Wiley, New York, 1999.

[2] A.R. Özdural, A. Alkan, Derivation of a new explicit equation for the determination of overall mass transfer coefficients in continuous dialyzers, J. Membr. Sci. 223 (2003) 49–57.

[3] M.R. Spiegel, Mathematical Handbook of Formulas and Tables, McGraw Hill, New York, 1968.

[4] I.J. Dijs, H.L.F. Ochten, A.J.M. van der Heijden, J.W. Geus, L.W. Jenneskens, The catalytic performance of sulphonated cross-linked polystyrene beads in the formation of isobornyl acetate, Appl. Catal. A: Gen. 241 (2003) 185–203.