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Comparison between regression analysis and moment analysis for transport and kinetic parameter estimation in TAP experiments under a non-ideal inlet condition

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Abstract

Regression analysis and moment analysis for estimation of transport and kinetic parameters in TAP experiments were compared using different types of responses, including exit flow rate curves and normalized responses. The experimental responses were obtained from simulation under a non-ideal inlet flow condition. The parameter estimation was performed using the ideal model. The quantities used in the comparison are the percentage differences between the estimated and the real parameters including the gas diffusivity and the first order irreversible reaction rate constant. These quantities also indicate the validity/invalidity of the ideal inlet condition. For typical domains in TAP experiments, the diffusivity percentage difference obtained from the regression and the moment analyses was found to be small. However, the percentage difference of the reaction rate constant can be large and depends on the estimation methods, the types of the response, and the gas conversion. Small percentage differences of the reaction rate constant are obtained from the estimation method that uses the conversion as a measured quantity. Besides, the percentage difference from this method does not depend on the conversion due to the same conversion expression in the ideal and the non-ideal cases.

Keywords: Temporal analysis of products; TAP; Parameter estimation methods; Dirac delta function; Non-ideal condition

1. Introduction

A TAP pulse response experiment [1,2] is performed by injecting a narrow gas pulse into an evacuated microreactor. The gas exiting the reactor is monitored as a function of time with a quadrupole mass spectrometer producing a transient response at the spectrometer detector. The intensity of the transient response is proportional to the exit flow rate of the corresponding gas. Quantitative information of the phenomena in the reactor can be extracted from the size and the shape of the responses by the use of mathematical models that describe the processes in the reactor. The required mathematical solution therefore describes the gas exit flow rate. The experimental gas exit flow rate can be determined only when the absolute calibration factor has been obtained. Matching of the experimental and the model exit flow rates provides the estimated parameters. However, the use of the exit flow rate needs the information of the absolute calibration factor and the inlet pulse intensity that appears in the mathematical model [3]. Due to this disadvantage, many researchers used the experimental response curve without converting into the exit flow rate curve [4–7]. In this case, only the shape of the response is concerned.

In addition to the different types of response curves, i.e., the primary response and the exit flow rate, different calculation methods including regression analysis and moment analysis have been used for parameter estimation. The regression analysis involves comparing the experimental response to the model response based on the least square fit. When only the shape is concerned, the two area-equated responses, or usually unit-area normalized responses, are compared. Normalization with respect to the maximum value of the experimental response has also been used [8]. It should be noted that the application of the normalized

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Nomenclature

A	cross-sectional area of the reactor (cm^2)
C	gas concentration (mol/cm^3)
C^*	dimensionless gas concentration, defined by $C^* \equiv C/(N_p/\varepsilon_b AL)$
D_e	effective Knudsen diffusivity of gas (cm^2/s)
$D_{e,real}$	real diffusivity of gas (cm^2/s)
$D_{e,est}$	estimated diffusivity of gas (cm^2/s)
F^*	dimensionless exit flow rate, defined by $F^* \equiv F\varepsilon_b L^2/N_p D_e$
k	reaction rate constant (1/s)
k_{est}	estimated reaction rate constant (1/s)
k_{real}	real reaction rate constant (1/s)
L	length of the reactor (cm)
M_0^*	zeroth moment of the dimensionless exit flow rate
M_1^*	first moment of the dimensionless exit flow rate
M_i^*	ith moment of the dimensionless exit flow rate
N_P	number of moles of the gas in the inlet pulse (mol)
r_D	ratio of the gas diffusivity defined by Eq. (19)
t	time (s)
t_{res}	mean residence time (s)
$t_{res,nd}$	mean residence time in the non-ideal case (s)
t_{open}	opening duration time of the pulse valve (s)
X	conversion of the reactant gas
z	axial coordinate of the reactor (cm)

Greek symbols

ΔD_e	fractional difference of the diffusivity defined by Eq. (16)
Δk	fractional difference of the reaction rate constant defined by Eq. (17)
$\delta(\tau - 0+)$	Dirac delta function at $\tau = 0^+$
ε_b	fractional voidage of the bed
κ	dimensionless reaction rate constant,defined by $\kappa \equiv k(\varepsilon_b L^2/D_e)$
κ_{est}	estimated dimensionless reaction rate constant, defined by $\kappa_{est} \equiv k_{est}(\varepsilon_b L^2/D_{e,real})$
κ_{real}	real dimensionless reaction rate constant, defined by $\kappa_{real} \equiv k_{real}(\varepsilon_b L^2/D_{e,real})$
τ	dimensionless time, defined by $\tau \equiv tD_e/\varepsilon_b L^2$
τ_{open}	dimensionless opening duration time of the pulse valve, defined by $\tau_{open} \equiv t_{open}D_e/\varepsilon_b L^2$
τ_{res}	dimensionless mean residence time, defined by $\tau_{res} \equiv t_{res}D_e/\varepsilon_b L^2$
$\tau_{res,nd}$	dimensionless mean residence time, defined by $\tau_{res,nd} \equiv t_{res,nd}D_{e,real}/\varepsilon_b L^2$
ξ	dimensionless axial coordinate, defined by $\xi \equiv z/L$

Subscripts

est	estimated parameters
ideal	ideal inlet condition
nd	non-ideal inlet condition
real	real parameter

responses is limited to linear mathematical models in which the shape of the response is independent of the pulse intensity [5,9]

The moment method can be performed when moment or moment-related expressions for the exit flow rate are known. Simple expressions for several cases, e.g., the zeroth moment, which is unity minus conversion, for the diffusion combined with the first order irreversible reaction case in one- and three-zone reactors [10], and the mean residence time, which is the ratio of the first moment to the zeroth moment, for the diffusion-only case in one- [1,2] and three-zone reactors [11], have been reported. To use this method, the experimental moment or moment-related quantity is calculated from the response and the corresponding expression provides the estimated parameter. For an irreversible reaction case, the conversion can be obtained by the use of the internal standard (inert gas). In this case, the estimated rate constant is based on only the size of the experimental response. In the contrary, if the mean residence time is the applied quantity, due to its definition, only the shape of the experimental response is taken into account. The mean residence time of the gas exiting the reactor can be determined directly from the experimental response.

For the diffusion-only case, either the mean residence time used in the moment analysis or the unit-area normalized response used in the regression analysis seems to carry only the information of the response shape. However, due to the mass balance of a gas with no conversion, the size is already implicitly taken into account. In fact, the unit-area normalized response of a non-reactive gas is the pulse intensity (PI) normalized exit flow rate, which is the gas exit flow rate divided by the number of moles of the corresponding gas in the inlet pulse, whose area is unity due to the mass conservation. It has been proposed that the PI normalized exit flow rate can be applied for reactive gases, and the information of the absolute calibration factor and the pulse intensity is not needed [9]. However, this type of response has not been applied in practice yet.

The TAP experiment provides a possibility to monitor a small catalyst change observed by the change in the consecutive response during a multipulse experiment. The kinetic parameter extracted from this type of experiment is therefore expected to be as accurate as possible. It is of great interest to investigate how the different estimation procedures, i.e., different estimation methods and types of responses, affect the accuracy. If all the assumptions or the ideal conditions applied in the mathematical model are exactly true, the estimated parameter from different types of responses and methods would be identical, since the experimental and the model responses would coincide. A way to compare those methods should be based on a well-defined condition, which can be accomplished by simulation. We can assume a non-ideal condition in the model and calculate the responses, which are assumed to be the experimental responses. Parameters are then estimated by assuming the corresponding ideal condition and using different methods, and the deviations from the real parameters can be compared.

Generally, ideal conditions, e.g., uniform temperature distribution in the reactor, zero concentration at the reactor outlet, and the Dirac delta function to describe the inlet flow, are assumed to simplify the models [1,2]. Discussion on the non-uniform temperature distribution that might affect the parameter estimation has been given by Delgado et al. [12]. Different inlet and outlet conditions have been firstly discussed by Zou et al. [13]. Recently, Constales et al. [14] analyzed the non-ideal inlet and outlet conditions for the diffusion-only case in which a premixing zone was introduced at the reactor inlet and the molecular velocity was applied at the outlet. Based on the solution in the Laplace domain and the first and second order of approximation, it was shown that the ideal outlet condition is valid. It was also reported that the ideal inlet condition is valid for the TAP-2 system but not valid for the first version of the TAP system. This conclusion is based on a particular mathematical method and on the diffusion case. Although it was stated that the result for the diffusion case could be applied for other processes, the investigation for the case with reactions would provide more complete results.

For a practical purpose, the validity/invalidity of the assumption should be indicated by the deviation of the estimated parameter from the real one. Besides, the analysis should be made using different calculation methods. In this article, different parameter estimation methods, in which the ideal inlet condition is assumed, are used to estimate the parameters from the experimental responses simulated from a non-ideal inlet condition. An appropriate type of the non-ideal inlet flow rate will be applied. Parameter deviations from real values when using different methods will be compared. How well each method can handle the non-ideal condition as well as the validity of the ideal inlet condition will be clearly shown. The parameter estimation methods include both the regression and the moment analyses applied to different types of responses. For the diffusion-only case, the moment analysis applies the mean residence time as a measured quantity, and the regression analysis applies the unit-area normalized response. For the first order irreversible reaction case, the moment analysis includes the use of the gas conversion (size concerning) and the mean residence time (shape concerning). The regression analysis includes the fitting of the unit-area normalized responses (shape concerning) and the exit flow rates (size and shape concerning). The analysis is focused on a one-zone reactor, which is uniformly packed with catalyst pellets, due to its simplicity.

2. Mathematical models

The mathematical model for gas diffusion in the TAP reactor uniformly packed with non-porous catalyst pellets is described in a generalized dimensionless form [2] by

$$\frac{\partial C^*}{\partial \tau} = \frac{\partial^2 C^*}{\partial \xi^2} \tag{1}$$

The definition of the variables and parameters is given in the nomenclature. For diffusion combined with a first order irreversible reaction, we can write

$$\frac{\partial C^*}{\partial \tau} = \frac{\partial^2 C^*}{\partial \xi^2} - \kappa C^* \tag{2}$$

The ideal initial and boundary conditions are given by initial conditions:

$$\tau = 0; \qquad C^* = 0 \tag{3}$$

Ideal inlet boundary condition:

$$\xi = 0; \qquad -\frac{\partial C^*}{\partial \xi} = \delta(\tau - 0^+) \tag{4}$$

Outlet boundary condition:

$$\xi = 1; \qquad C^* = 0 \tag{5}$$

The dimensionless exit flow rate (F^*) can be calculated using

$$F^* = -\left.\frac{\partial C^*}{\partial \xi}\right|_{\xi=1} \tag{6}$$

For the diffusion-only case, the set of Eqs. (1), (3)–(5) can be solved for $C^*$and by the use of Eq. (6), the solution can be determined and is described [2] by

$$F^* = \pi \sum_{n=0}^{\infty} (-1)^n (2n+1) \exp(-(n+0.5)^2 \pi^2 \tau) \tag{7}$$

Similarly, the solution for the irreversible reaction case is given by

$$F^* = \pi \exp(-\kappa\tau) \sum_{n=0}^{\infty} (-1)^n (2n+1) \exp(-(n+0.5)^2 \pi^2 \tau) \tag{8}$$

The ith moment of the dimensionless exit flow rate is defined by

$$M_i^* = \int_0^{\infty} F^* \tau^i \, d\tau \tag{9}$$

The zeroth moment is described by

$$M_0^* = \int_0^{\infty} F^* \, d\tau \tag{10}$$

For the diffusion-only case, M_0^* is unity. When an irreversible reaction occurs, the conversion is described [2] by

$$X = 1 - M_0^* = 1 - \frac{1}{\cosh\sqrt{\kappa}} = 1 - \frac{1}{\cosh\sqrt{k\varepsilon_b L^2/D_e}} \tag{11}$$

The mean residence time is defined by

$$\tau_{res} = \frac{M_1^*}{M_0^*} = \frac{\int_0^{\infty} F^* \tau \, d\tau}{\int_0^{\infty} F^* \, d\tau} \tag{12}$$

The expressions for the mean residence time for the diffusion-only case is as follows:

$$\tau_{res} = \frac{t_{res} D_e}{\varepsilon_b L^2} = 0.5 \tag{13}$$

For the irreversible reaction case, we have [9]

$$\tau_{res} = \frac{\tanh\sqrt{\kappa}}{2\sqrt{\kappa}} = \frac{\tanh\sqrt{k\varepsilon_b L^2/D_e}}{2\sqrt{k\varepsilon_b L^2/D_e}}. \tag{14}$$

For the case in which the inlet flow rate is non-ideal, we write

$$\text{Non-ideal inlet boundary condition}: \xi = 0; \quad -\frac{\partial C^*}{\partial \xi} = f(\tau) \tag{15}$$

The type of the non-ideal condition was appropriately chosen in our study. The types of the non-ideal inlet condition include the premixing zone [13,14], a lagging delta function (delta function applied at time larger than 0^+) [15], the triangular shape [16,17] (see Fig. 1a), and the inlet flow determined from the experiment [4,18] (see Fig. 1b). The experimental inlet flow rate was determined in the first version of the TAP system by detecting the gas response when the reactor was not in place (reactor length was zero). The triangular shape has been used according to the specification of the pulse valve given by the manufacturer. The shape of the experimental inlet flow rate looks similar to the triangular shape except at the beginning period showing a lag time and at the tail. This is due to the overall lag in the first version of the TAP system. Discussion on the difference between the first and the second versions of the TAP system has been given in [14]. In our simulation study, we used the triangular inlet condition according to the valve function and we neglect the overall system lag.

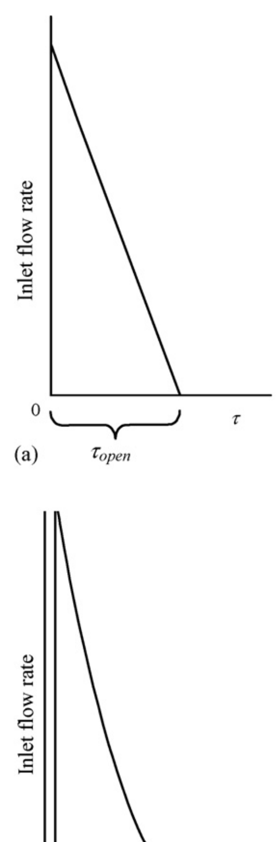

Fig. 1. Non-ideal inlet flow conditions: (a) triangular, (b) experimental.

3. Calculation methods

To compare the parameter estimation methods, there must be a simple quantity to indicate the difference. For the diffusion-only case, the estimated and the real diffusivities were compared using an indicating quantity defined by

$$\Delta D_e = \frac{D_{e,est} - D_{e,real}}{D_{e,real}} \tag{16}$$

To determine ΔD_e in our mathematical analysis, the response calculated from a given D_e or $D_{e,real}$ under the non-ideal inlet condition was assumed to be the experimental response. The estimated diffusivity was then determined from the response by assuming an ideal inlet condition. If $|\Delta D_e|$ obtained from a particular method is small, the method is not sensitive to the non-ideal condition. A sufficiently small magnitude of $|\Delta D_e|$ also indicates the validity of the ideal inlet condition. In the case of the irreversible reaction, we define a similar indicating quantity as

$$\Delta k = \frac{k_{est} - k_{real}}{k_{real}} = \frac{\kappa_{est} - \kappa_{real}}{\kappa_{real}}. \tag{17}$$

Practically, the estimation of the rate constant is performed after the diffusivity is predetermined from a diffusion experiment. Our simulation followed the practical procedure. Both κ_{real} and κ_{est} are the dimensionless rate constants that are normalized using the real gas diffusivity (see 'nomenclature' section). Using these definitions, we can easily analyze the problem.

4. Regression analysis

The analysis was performed using a generalized dimensionless form. When the regression analysis was applied, the non-ideal diffusion curve was calculated from the set of Eqs. (1), (3), (5), and (15). The area of the triangular dimensionless inlet flow rate curve is unity according to the mass conservation. The model exit flow rate under the ideal inlet condition was calculated using the equation:

$$F^* = r_D \pi \sum_{n=0}^{\infty} (-1)^n (2n+1) \exp(-(n+0.5)^2 \pi^2 r_D \tau) \tag{18}$$

where

$$r_D = \frac{D_{e,est}}{D_{e,real}} \tag{19}$$

The quantity ΔD_e can be determined from the estimated r_D using

$$\Delta D_e = r_D - 1 \tag{20}$$

One can see that the magnitudes of r_D and consequently ΔD_e depend only on the non-ideal dimensionless inlet flow rate, $f(\tau)$. When the shape of the inlet flow rate is triangular, ΔD_e depends only on τ_{open}, the dimensionless opening duration time of the pulse valve (see Fig. 1a).

The exit flow rate curve for the non-ideal condition was numerically calculated by the method of lines (MOL). The software used in our calculation is called Livermore Solver for Ordinary Differential equations with Automatic method switching for stiff and non-stiff problems (LSODA) [19]. The calculation used 1000 grids to span the axial coordinate, and a time step of 0.001. Accuracy of the numerical calculation was investigated by comparing the mean residence times determined from the calculated exit flow rate with those from the analytical expressions. Throughout the domain of the system parameters in this study, the difference was not larger than 0.1% for both diffusion-only and irreversible reaction cases. Besides, when determining r_D, the ideal model response was calculated by MOL in addition to the analytical solution, Eq. (18). The difference between the two r_D's obtained from the two ideal model responses did not exceed 0.02%.

For the irreversible reaction case, we calculated the exit flow rate curve using the set of Eqs. (2), (3), (5), and (15). In this case, the model response was estimated by the equation:

$$F^* = r_D \pi \exp(-\kappa_{est}\tau) \sum_{n=0}^{\infty} (-1)^n (2n + 1) \exp(-(n+0.5)^2 \pi^2 r_D \tau) \tag{21}$$

The parameter r_D was predetermined from Eq. (18). The estimated reaction rate constant, κ_{est}, was compared with the real rate constant in Eq. (2) providing Δk, which depends on the inlet flow rate, $f(\tau)$, and the reaction rate constant or conversion.

For the irreversible reaction case, the regression analysis involves two types of responses including the exit flow rate curve and the unit-area-normalized response. In the latter case, both the non-ideal exit flow rate curve and the curve calculated from Eq. (19) were unit-area-normalized before matching.

5. Moment analysis

For the diffusion-only case, when applying the mean residence time as the measured quantity, Eq. (13) is used to estimate the gas diffusivity from the mean residence time of the experimental response. In this case, the quantity 0.5 is equal to $t_{res,nd} D_{e,est}/\varepsilon_b L^2$. Defining the dimensionless mean residence time, $\tau_{res,nd}$, by $\tau_{res,nd} \equiv t_{res,nd} D_{e,real}/\varepsilon_b L^2$, we can write

$$r_D = \frac{D_{e,est}}{D_{e,real}} = \frac{0.5}{\tau_{res,nd}} \tag{22}$$

Using the method described in the literature [4,18], the analytical expressions for the ith moments of the exit flow rate and $\tau_{res,nd}$ can be determined. The method involves determination of the solution for the exit flow rate in Laplace domain. The solution can be used to determine moment expressions by simple mathematical procedures.

For the irreversible reaction case, our study involves the conversion and the mean residence time as the measured quantities. The analytical expressions for both quantities can be determined and used individually to estimate the reaction rate constant. The calculation used the predetermined r_D obtained from Eq. (22).

6. Results and discussion

The results from the regression analysis will be reported graphically and compared to those from the moment analysis. Moment and moment-related expressions involved in this study can be determined. For the diffusion-only case, we obtained

Non-ideal diffusion case:

$$\tau_{res,nd} = 0.5 + \frac{\tau_{open}}{3} \tag{23}$$

From Eqs. (20), (22), and (23), we can write

$$\Delta D_e = -\frac{1}{3}\left(\frac{\tau_{open}}{\tau_{res,nd}}\right) = -\frac{1}{3}\left(\frac{t_{open}}{t_{res,nd}}\right) \tag{24}$$

Eq. (24) clearly shows that ΔD_e is proportional to the ratio of the opening duration time and the mean residence time of the experimental response. It is noted that the proportional constant is −1 if the inlet flow rate is described by the lagging delta function.

Fig. 2 compares ΔD_e obtained from the regression analysis (circles) and the moment analysis (squares). At high $t_{open}/t_{res,nd}$, $|\Delta D_e|$ from the regression method is about two times larger. The solid circle and the solid square represent the case in which $t_{open}/t_{res,nd}$ is equal to 0.029 (or τ_{open} = 0.0147) corresponding to the experiment with t_{open} = 500 μs (typical condition in TAP-2 system) and t_{res} = 0.0172 s. This magnitude of t_{res} is obtained when the reactor length is 2.54 cm [2], the bed fractional voidage is 0.36 (spherical pellets) and the gas diffusivity is 68.4 cm^2/s. This diffusivity represents the case in which the gas

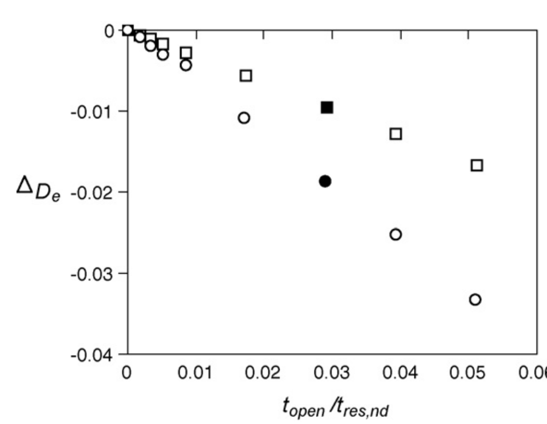

Fig. 2. Plots of ΔD_e vs. $t_{open}/t_{res,nd}$ for different estimation methods: regression analysis (circles) and moment analysis (squares); solid points refer to the representative case.

is methane, the lightest hydrocarbon, operated at 1000 °C in a packed bed of spherical pellets whose diameter is 325 μm. The calculation for the gas diffusivity in a packed bed of spherical pellets can be found in the literature [4,20]. For this representative case, $|\Delta D_e|$ does not exceed 2% for the regression analysis. This case was chosen to represent the experiment with a low mean residence time. So, the experiment with a heavier gas, a lower operating temperature, a longer reactor, smaller pellets, or smaller opening duration time of the pulse valve, would have smaller $|\Delta D_e|$.

It is also noted that typically the estimated diffusivity of the reactant gas is obtained from the diffusivity of the inert gas introduced into the reactor with the reactant gas. Since the ratio of the two diffusivities is proportional to the square root of the ratio of their molecular weights, ΔD_e of the two gases is the same.

For the irreversible reaction case, the expression for the zeroth moment of the exit flow rate was found to be the same as that in the ideal case. As a result, the conversion of the ideal and the non-ideal cases is identical. So, Eq. (11) becomes

$$X_{nd} = X_{ideal} = 1 - \frac{1}{\cosh\sqrt{\kappa_{real}}} = 1 - \frac{1}{\cosh\sqrt{k_{real}\varepsilon_b L^2/D_{e,real}}} \quad (25)$$

The identical conversion statement is true for multi-zone TAP reactors and for all non-ideal inlet conditions. The reason is that the time delay before the gas enters the catalyst bed does not affect the probability to react as long as the catalyst does not change during one pulse experiment. The same explanation was given for the conversion independence of the length of the first inert zone in a three-zone reactor [9].

When Eq. (25) is used to determine the rate constant with the predetermined estimated gas diffusivity, k_{real} is replaced by k_{est} and $D_{e,real}$ is replaced by $D_{e,est}$. The equation can then be written to include only dimensionless parameters as follows:

$$X = 1 - \frac{1}{\cosh\sqrt{\kappa_{est}/r_D}} \quad (26)$$

Accordingly, we obtain

$$\frac{\kappa_{est}}{\kappa_{real}} = r_D \quad (27)$$

Therefore

$$\Delta k = \Delta D_e \quad (28)$$

Eq. (28) shows that, when using the conversion as the measured quantity, Δk is equal to ΔD_e in the corresponding diffusion experiment (same τ_{open}). So, for the representative case, $|\Delta k|$ is equal to 0.96% as shown in Fig. 2 for the moment analysis. The situation is different when using the mean residence time as the measured quantity. The expression for the mean residence time is given by

Non-ideal inlet condition:

$$\tau_{res,nd} = \tau_{res,ideal} + \frac{\tau_{open}}{3} = \frac{\tanh\sqrt{\kappa_{real}}}{2\sqrt{\kappa_{real}}} + \frac{\tau_{open}}{3} \quad (29)$$

Similarly to Eq. (26) for the conversion using method, when we use the mean residence time of the simulated exit flow curve to determine the reaction rate constant with the predetermined estimated gas diffusivity, the rate constant, κ_{est}, appears in Eq. (14) as follows:

$$\tau_{res,nd} = \frac{\tanh\sqrt{\kappa_{est}/r_D}}{2\sqrt{\kappa_{est}/r_D}} \quad (30)$$

In this case there is no analytical expression for Δk. According to the mathematical model, Δk depends on τ_{open} and κ. However, it would be better to show Δk dependence on $t_{open}/t_{res,nd}$ and X, which are primary characteristics of the reactive response.

Fig. 3 shows Δk versus $t_{open}/t_{res,nd}$ for all different estimation methods at conversion equal to 1, 50, and 99%. At fixed reaction rate constant or conversion, when t_{open} is increased, $|\Delta k|$ increases as expected. Besides, the relationship between Δk and $t_{open}/t_{res,nd}$ is close to linear for all methods. The solid points show $t_{open}/t_{res,nd}$ for the representative case previously described. In these reactive conditions (fixed τ_{open}), the methane gas disappears with different rate constants and consequently different conversions. When the conversion is

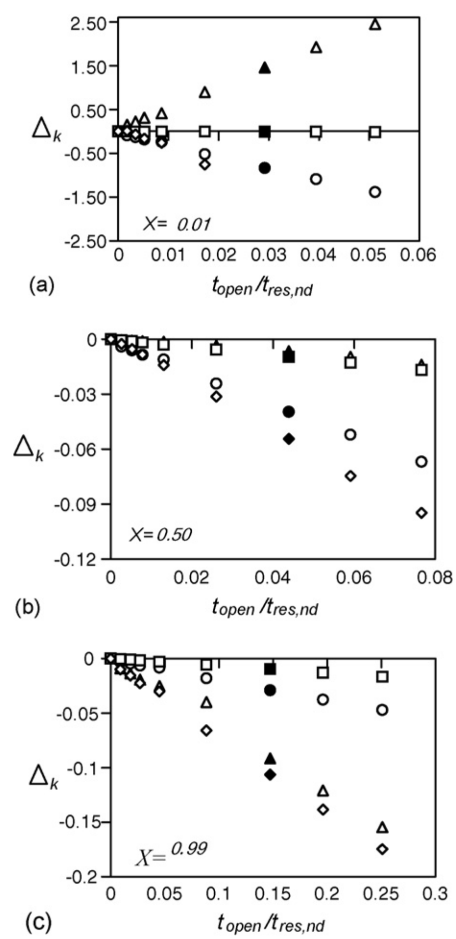

Fig. 3. Plots of Δk vs. $t_{open}/t_{res,nd}$ at conversion equal to 1% (a), 50% (b), and 99% (c) for different estimation methods: shape fitting (triangles), exit flow curve fitting (circles), conversion (squares), mean residence time (diamonds); solid points refer to the representative case.

increased from 1 to 99%, $t_{open}/t_{res,nd}$ increases due to the decrease of the mean residence time.

For the representative case when using the regression analysis with the unit-area normalized responses or shape-fitting method (solid triangle), Δk is approximately 150% at conversion equal to 1%. The very large Δk at this low conversion is due to the small κ_{real} of 0.02. When the conversions is increased to 50 and 99%, Δk is −0.7, and −9%, respectively. The minus sign corresponds to an underestimation of the reaction rate constant. Another method that involves only the response shape, i.e., the use of the mean residence time (diamonds), gives higher $|\Delta k|$ at $X = 50$ and 99% compared to the shape-fitting method. In Fig. 3a for conversion equal to 1%, there is no representative case shown for the mean residence time using method. For the representative case at this conversion, $t_{res,nd}$ is larger than 0.5, which is the magnitude of $t_{res,nd}$ for zero conversion (diffusion-only case). Therefore, the reaction rate constant cannot be determined using Eq. (30). This is a limitation of this method at very low conversion. The exit flow curve fitting method (circles) gives lower $|\Delta k|$ compared to the two methods that concern only the shape. All methods except for the conversion using method generally give much higher $|\Delta k|$ than $|\Delta D_e|$.

The information of Δk at other conversions between 1 and 99% for the representative case is shown in Fig. 4. All methods except the shape fitting method underestimate the reaction rate constant throughout the range of the conversion. For the shape fitting method, $|\Delta k|$ at 5% conversion is much smaller than that at 1% conversion but is still considerably large. For this method, small $|\Delta k|$ can be found in the range of the conversion between 25 and 75% within which $|\Delta k|$ does not exceed 3%. In the same conversion range, $|\Delta k|$ from the mean residence time using method is between 5 and 8%. For the exit flow curve fitting method, $|\Delta k|$ decreases from 6 to 3% when the conversion is increased from 25 to 99%.

Fig. 5 shows the comparison between the simulated non-ideal curve (solid line) and the ideal model curves corresponding to the estimated parameters at conversion equal to 99%. This figure clearly shows that using only the response shape

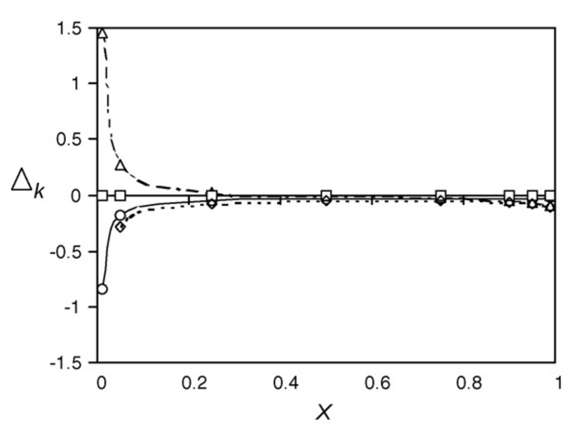

Fig. 4. Plots of Δk vs. X for the representative case for different estimation methods: shape fitting (triangles), exit flow curve fitting (circles), conversion (squares), mean residence time (diamonds).

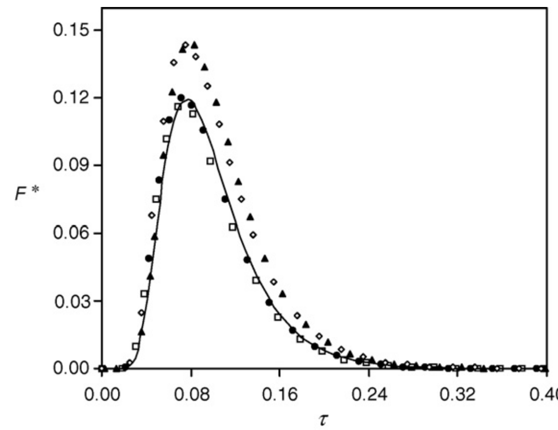

Fig. 5. Comparison of the exit flow rate curves: simulated non-ideal curve (solid line), shape fitting (triangles), exit flow curve fitting (circles), conversion (squares), mean residence time (diamonds).

does not provide the same conversion as that of the experimental response. When using only the shape, the conversion is calculated after the kinetic parameter is determined. An advantage of the conversion using method is that it gives the information of the conversion, which is the primary information related to the mass balance, prior to the reaction rate constant. Besides, this method gives small $|\Delta k|$ that does not depend on the conversion.

Although the results reported above are related to a one-zone reactor, small magnitudes of $|\Delta k|$ are also obtained for a three-zone reactor when the conversion using method is applied. Following the same mathematical procedure for the one-zone reactor and using the conversion expression for the three-zone reactor reported in [9,10], it can be easily proved that if all the three zones have the same gas diffusivity and the same fractional voidage, Δk is the same as that reported in this paper for each corresponding case (same τ_{open}) and for any catalyst zone lengths. The results from this study suggest that the size of the experimental response is an important characteristic that should be concerned in the quantitative interpretation procedure. However, in a real practice, size-concerning methods need calibration by the use of an inert gas. The error caused by this procedure is beyond the scope of this paper.

It is also noted that the 95% confidence interval for the estimated parameter from the curve fitting of each calculation is narrow. For example, the shape fitting in Fig. 5 gives the 95% confidence interval of ±0.2% of the estimated rate constant. The narrow range of the estimated parameter therefore does not affect the comparison among the estimation methods.

7. Conclusions

Parameter estimation methods, including regression analysis and moment analysis, have been compared using different types of responses, i.e., exit flow rate curve and normalized response, which were simulated under the triangular inlet flow condition. The quantities ΔD_e and Δk were used to indicate the accuracy of the estimated parameters for the diffusion-only and the irreversible reaction cases, respectively. The same quantities also indicate the validity of the ideal inlet condition. For the diffusion-only case, when applying the mean residence time, ΔD_e is proportional to $t_{open}/t_{res,nd}$ with a proportional constant of –1/3. For the representative case, $|\Delta D_e|$ is less than 1% when using the mean residence time, and is less than 2% when using the regression method.

For the irreversible reaction case, the relationship between Δk and $t_{open}/t_{res,nd}$ at fixed conversion is close to linear for all parameter estimation methods. All the methods in this study except for the conversion using method generally give higher $|\Delta k|$ than $|\Delta D_e|$ especially at low conversions. The conversion using method gives Δk that is equal to ΔD_e for the corresponding diffusion experiment (same τ_{open}). The Δk independence of the conversion is due to the identical conversion in the ideal and the non-ideal cases. It is suggested that the size of the experimental response should be involved in the quantitative interpretation procedure.

Our results also show that the validity of the delta function indicated by Δk depends on the calculation method and also the conversion. For the representative case in which the valve opening duration time is 500 μs (typical condition in the TAP-2 system), the delta function is valid throughout the domain of conversion only when the conversion is used as a measured quantity.

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