A LABORATORY EXPERIMENT FOR UNDERGRADUATE INSTRUCTION: NON-IDEAL FLOW IN TUBULAR VESSELS

C. E. GIGOLA[*] , M. L. NARDINI[†] , A. C. OLIVERA[‡] and N. B. BRIGNOLE[*‡]

[*]*Planta Piloto de Ingeniería Química (PLAPIQUI), UNS– CONICET - Camino La Carrindanga km. 7, CC 717, Argentina - cgigola@plapiqui.edu.ar*

[†]*3M, Olga Cossettini 1031, Ciudad Autónoma de Buenos Aires, Argentina*

[‡]*Universidad Nacional del Sur, Av. Alem 1253, B8000CPB, Buenos Aires, Argentina*

Laboratorio de Investigación y Desarrollo en Computación Científica (LIDeCC-UNS), Departamento de Ciencias e Ingeniería de la Computación

***Abstract*— A laboratory experiment to reinforce the basic concepts of non-ideal flow is described. It consists of simple pulse-response measurements for gas that is flowing through an empty and a packed bed. It can provide information on the residence-time distribution function and other vessel parameters. Experimental results are compared with those predicted by the axial dispersed plug-flow model in order to obtain the Peclet number and the dispersion coefficient that characterize the flow behavior.**

***Keywords*— Non-ideal Flow - Axial Dispersion - Residence Time.**

I. INTRODUCTION

Undergraduate students at PLAPIQUI receive a formal course on kinetics and reactor design in the fourth year of their chemical engineering studies. Following well-known reactor-design textbooks (Smith, 1981; Levenspiel, 1972; Froment and Bischoff, 1979; Butt, 1980; Fogler, 2006), the basic design equations are introduced under the assumption of ideal flow behavior. The more realistic non-ideal situation, mainly arising from changes in the expected residence-time distribution, is then presented. The inherent difficulty of this subject may in part be overcome by experimentation. Consequently a laboratory experiment has been set up in our advanced Chemical Engineering Laboratory course. It consists of a simple stimulus-response experiment followed by qualitative and quantitative analysis of the elution curves by using the theory detailed in reactor textbooks. The necessary apparatus can be set up using common pieces of equipment that are no longer used for research work due to their technical obsolescence. The measurements and subsequent data analysis allows the students to reach the following objectives:

1- to observe deviations from plug-flow behavior in an empty and packed bed tube.

2- to estimate the dead volume of the connecting lines and the void volume of a packed bed.

3- to determine the residence-time distribution function for an empty and a packed bed tube.

4- to compare the concentration-versus-time curves with the prediction of the axial-dispersion model

5- to determine the Peclet number and the diffusion parameter, and to compare the resulting values with those derived from existing correlations.

II. BACKGROUND

Although the relevant theory is available in several textbooks, the main concepts and equations are reviewed here in order to facilitate the analysis of experimental data. As an introduction to the subject, the concept of distribution function is reviewed, and then the Residence-Time Distribution Function (RTDF) of a vessel with constant flow is presented. This dimensionless function, called F(t) by Levenspiel (1972) and Fogler (2006), is defined as the fraction of the exit stream with an age minor or equal to t. Consequently dF(t), which is the fraction of the exit stream with a residence time between t and t + dt , is the following:

$$dF(t) = E(t)dt \, . \qquad (1)$$

The E(t) function is also used as a RTDF. It is the time derivative of F(t) and gives the fraction of the exit stream that has a residence time equal to t. Consequently the relation between F(t) and E(t) functions is emphasized. For a vessel of unknown mixing behavior, the RTDF could be obtained by stimulus-response experiments; a pulse-response experiment leads directly to E(t), while a step-response experiment provides enough information to evaluate the F(t) function. In the former case, a fixed amount of tracer (M) may be injected in a short period of time into the carrier flow. Dispersion effects in the vessel volume will lead to a concentration-versus-time curve, which allows the calculation of the fraction of fluid with an age t as follows:

$$E(t) = (C(t)Q)/M, \qquad (2)$$

where C(t) is the tracer concentration at time t, in mole/cm^3, and Q is the volumetric flow-rate in cm^3/min.

The mean residence time, defined as the ratio between the reactor volume and the flow-rate ($V/Q = t_m$), is often introduced in Eq. (2) to obtain a dimensionless residence time, $\theta = t/t_m$. If E(t) dt is the fraction of fluid with a residence time between t and t + dt, it follows

that $E(\theta)\,d\theta$ is the fraction of fluid with a residence time between θ and $d\theta$. Consequently,

$$\begin{aligned} &E(t)\,dt = E(\theta)\,d\theta \text{ and} \\ &E(\theta) = E(t)\,dt/d\theta = E(t)t_m = E(t)\,V/Q \end{aligned} \quad (3)$$

Using Eq. (2) we obtain,

$$\begin{aligned} E(\theta) &= \left[(C(t)Q)/M\,t_m\right] \\ &= C(t)/(M/V) = C(t)/C_0' \end{aligned}, \quad (4)$$

where C_o' , which is the amount of tracer divided by the reactor volume, is not a true concentration. For a vessel of unknown volume, the mean residence time t_m could be obtained from experimental data taking into account that t_m is the mean value of the E(t) function defined as,

$$t_m = \int_0^\infty t\,E(t)\,dt\,. \quad (5)$$

Replacing E(t) by Eq. (2) and taking into account that:

$$M = Q\int_0^\infty C^*dt\,, \quad (6)$$

the mean residence time is given by:

$$t_m = \left[\int_0^\infty t\,C\,dt\right] \Big/ \left[\int_0^\infty C\,dt\right]. \quad (7)$$

In order to use discrete C(t) versus t values, Eq. (7) can be written as:

$$t_m = \left\{\sum t_i\,C_i\,\Delta t_i\right\}\Big/\left\{\sum C_i\Delta t_i\right\}. \quad (8)$$

In the reactor design course the students learn that the residence-time distribution function is the only information needed to calculate the conversion in a real reactor in the case of first-order reactions. For nonlinear kinetics the conversion will depend on the extent of mixing. Consequently a model that describes the flow of fluid in the vessel is required.

The dispersion model is commonly used to account for deviations from plug-flow behavior in tubular reactors. In this model the spreading of a tracer is ascribed to diffusion and convection in the axial direction. However, it has been shown (Butt, 1980) that the model can be applied to more complex situations that include radial diffusion, which is important in laminar flow, and the flow of fluids through packed beds.

A basic mass balance in the axial direction for an empty tube leads to

$$\delta C/\delta t = D_a\left[\delta^2 C/\delta z^2\right] - v\,\delta C/\delta z\,. \quad (9)$$

If we are dealing with a packed-bed reactor, equation (9) corresponds to a pseudo-homogeneous model. In dimensionless form the equation can be written as:

$$\delta(C/C_o')/\delta\theta = (D_a/vL)\left[\delta^2(C/C_o')/(\delta z^*)^2\right] - \delta(C/C_o')/\delta z^*\,. \quad (10)$$

For a pulse of tracer on a fluid with small dispersion effects, the solution to Eq. (10) is:

$$E(\theta) = C(\theta)/C_0' = \tfrac{1}{2}(Pe_L/\pi)^{1/2}\left\{\exp\left[-Pe_L(1-\theta)^2/4\right]\right\} \quad (11)$$

For large extents of dispersion, where the response to a pulse input leads to an unsymmetrical $E(\theta)$ function, the solution of Eq. (10) depends on the imposed boundary conditions. Our experimental set-up can be described as a "closed vessel" because mixing or dispersion effects are practically absent at the boundaries. In this case, it is impossible to obtain an analytical solution. However, an approximate equation (see Eqs. (12) and (13)) has been given by Froment and Bischoff (1979), that allows the prediction of the $E(\theta)$ function for different values of the Pe_L number.

$$E(\theta) = e^{Pe_L/2}\sum_1^\infty \left(\frac{(-1)^{i+1}\,8\alpha_i^2}{4\alpha_i^2 + 4Pe_L + Pe_L^2} * \exp\left[\frac{-\theta\left(Pe_L^2 + 4\alpha_i^2\right)}{4Pe_L}\right]\right), \quad (12)$$

$$\tan\alpha_i = \frac{4\,Pe_L\,\alpha_i}{4\,\alpha_i - Pe_L^2}\,. \quad (13)$$

Despite the complexity of these equations, the evaluation of function $E(\theta)$ is simple because the roots of Eq. (13) as function of the Pe_L number are available in the literature (Carslaw and Jaeguer, 1959). To compute the $E(\theta)$ function for different Pe_L numbers, a simple program was written using an Excel work sheet. Satisfactory results for $Pe_L < 40$ were obtained by including only four terms in Eq. (12). Consequently this equation can be fitted to experimental data in order to obtain the Pe_L number for vessels that exhibit a large deviation from plug-flow behavior. The values obtained from this procedure can be compared with those estimated from literature correlations that summarize theoretical and experimental data on the Peclet number for different flow situations. For laminar flow of fluids in empty tubes the Peclet number is given by the Taylor-Aris correlation, in terms of Reynolds ($Re > 1$) and Schmidt ($Sc > 0.23$) numbers (Butt, 1980);

$$1/Pe_d = 1/(Re_d Sc) + (Re_d Sc)/192\,, \quad (14)$$

where Peclet and Reynolds numbers are based on the tube diameter (d);

$$Pe_d = v\,d/D_a\,, \quad (15)$$

$$Re_d = (dv\rho)/\mu\,, \quad (16)$$

$$Sc = \mu/\rho D_m\,. \quad (17)$$

The other variables are the carrier-gas density (ρ), the carrier-gas viscosity (μ) and the molecular diffusivity of the tracer (D_m).

The Taylor-Aris correlation adequately represents experimental information from long empty tubes, where axial dispersion predominates (Wen and Fan, 1975). On the other hand, for gases flowing through packed beds the appropriate correlation of the Peclet number with the system properties is:

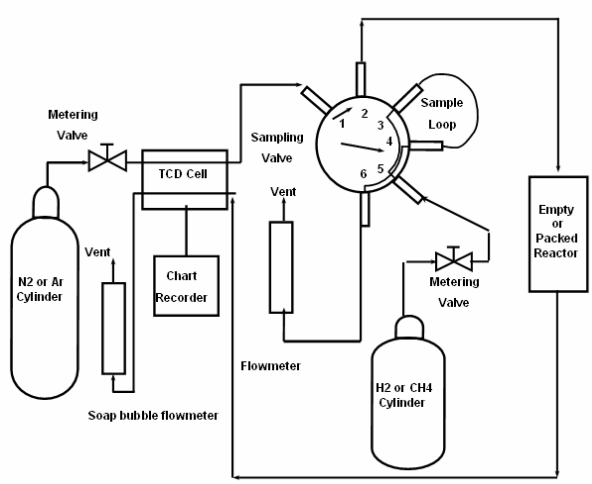

Figure 1. Schematic diagram of the apparatus for tracer experiments.

$$1/Pe_{d_p} = \left[0.3/\left(Re_{d_p} Sc\right)\right] + 0.5/\left[1+3.8\,(Re_{d_p} Sc)^{-1}\right], \quad (18)$$

where Peclet and Reynolds numbers are now based on the particle dimension (d_p):

$$Pe_{d_p} = u d_p / D_a , \quad (19)$$

$$Re_{d_p} = \left(v\, d_p\, \rho\right)/\mu . \quad (20)$$

To calculate the intersticial velocity u ($u = v/\varepsilon$), the interparticle porosity is required.

III. EXPERIMENTAL APPARATUS

The apparatus used for pulse- or step-response experiments is schematically shown in Fig. 1. It consists of a N_2 or Ar supply line, with a Brooks regulating valve to adjust the flow of the carrier gas. The flow first passes through the reference side of a GOW-MAC thermal conductivity detector (TCD) model 10-285, held at room temperature, and then enters a 6-port Valco sampling valve. Subsequently, the carrier gas is sent to the empty- or packed-bed reactor. A stainless steel tube (L = 112 cm; d = 1.13 cm; V = 112 cm^3) simulates the empty tubular reactor to be studied. An acrylic cylinder (L = 25 cm; d = 2.5 cm; V = 120.3 cm^3) is used as a packed-bed reactor. The cylinder ends have threaded aluminum caps to load or unload different packing materials. The reactor outlet is connected to the sample side of the TCD, where the output pulse shape is recorded. The flow-rate is measured with a soap bubble flow-meter.

Methane or hydrogen, and argon or nitrogen could be used as tracer and carrier, respectively. The tracer is injected into the proper carrier by means of a 1/8" SS loop (0.4 cm^3). For the empty-tube experiments methane is selected as tracer because it has low molecular diffusivity in Ar. In addition, the difference in thermal conductivity of these gases is adequate for TCD detection. On the other hand, the H_2-N_2 pair is more appropriate to study the flow behavior on the packed bed. The high molecular diffusivity of H_2 in N_2 avoids the presence of diffusion resistance in the porous solid. All connecting lines are constructed with 1/16" SS tubing to minimize the dead volume. The TCD power supply has an amp-meter to adjust the filament current (150 milliamps).

The TCD signal is sent to X-Y Houston Instruments 2000 Series chart recorder, which allows a large selection of millivolt (Y) and time (X) scales.

Porous and non-porous solids like alumina pellets, glass beads, etc. of different particle sizes are offered to the students as optional packing to perform the experiments.

IV. EXPERIMENTAL PROCEDURE

In the laboratory the students are briefly introduced to the use of the TCD (how to select the gas pair, the loop size, and the current value) and the X-Y chart recorder. The main instructions and recommendations given to the students are:

- the carrier flow rate should be set in the 50-200 cm^3/min. range.
- the system should be thoroughly purged before the TCD is turned on.
- the X-Y recorder should be zeroed and the pen speed and range settings should be selected to obtain an output profile that makes full use of the paper chart.
- the tracer pulse should be introduced by turning the sample valve and starting the recorder at the same time, i.e. as simultaneous operations.
- the experimental conditions should be observed by taking into account the assumptions and limitations of the theoretical model to be used for the analysis of data.
- the elution profiles for an input pulse at a constant flow-rate without a vessel should be obtained with the empty tube and with a bed packed with a selected solid.

The measurements may be carried out by a team of two or three students in a three-hour session.

V. RESULTS AND DISCUSSION

Figure 2 shows the typical peak height (h in mv) versus time-elution (t in sec) profiles due to a pulse of H_2 injected into an N_2 flow-rate of 97.3 cm^3/min. These curves were drawn by selecting h values at constant Δt intervals from the raw data. The curves clearly differ in the position and intensity of the peak maximum and also in the amount of dispersion. In the absence of a vessel (Fig. 2-a) there is a fast and intense response. When the experiment is performed with an empty vessel, the spreading of the tracer gives a less intense and nearly symmetrical peak. This fact take place even when the residence time increases by a factor of 60, as shown in Fig. 2-b. When using the acrylic vessel loaded with porous α-Al_2O_3 pellets, the deviation from plug-flow behavior is greater. Consequently, the response curve in Fig. 2-c becomes broader and the peak asymmetry increases.

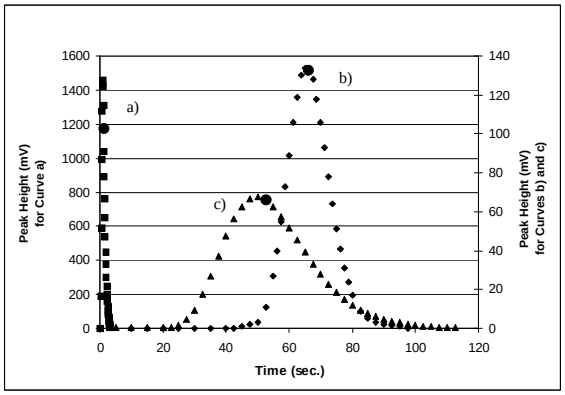

Figure 2. Output signal of a H_2 pulse injected into a N_2 flow. a) dispersion due to connecting lines; b) empty vessel; c) packed vessel. ● mean residence time. Q= 97.3 cm^3/min

As a preliminary assignment, the students are required to perform a mass balance taking into account that the area under each curve should be the same because it only depends on the injected amount of tracer. In other words,

$$M = Q \int_0^\infty C\, dt = \alpha \sum h(mv)\Delta t\,(sec)\,, \qquad (21)$$

where α is a constant.

In addition, the students can calculate the mean residence time using Eq. (8); from this quantity and the flow-rate, the void volume of the connecting lines, the empty vessel and the packed bed is estimated. The TCD signal h (mv) may easily be converted to concentration values by using the following equation:

$$C(t)\left(\mu mol/cm^3\right) = \left[M(\mu mol)\; h(mv)\right]/\left[Q(cm^3/min)A\;\left(mv\;sec\right)\right], \qquad (22)$$

The RTDF E(θ) is then;

$$E(\theta) = C(t)/C_o{}' = \left[M\,h/Q\,A\right]/\left(M/V\right) = \left(h\,V\right)/\left(Q\,A\right) = \left(h/A\right)t_m \,. \qquad (23)$$

Typical results for experiments carried out with an N_2 flow-rate of 97.3 cm^3/min are shown in Table 1. The reason for a large deficit in the mass balance in the absence of a vessel is the non-linear behavior of the TCD due to the high H_2 concentration. For the empty vessel and the packed vessel the mass balance gives close results. Table 1 also shows that the mean residence time for the H_2 pulse in the connecting lines can be neglected in comparison with the values obtained for an empty or packed vessel. Taking into account the flow-rate and the mean residence time, the volume of the connecting lines is indeed very small; about 2 cm^3. On the other hand, the volume of the empty tube is approximately 107 cm^3, which is in good agreement with the value derived from the physical dimensions: 112 cm^3. In the packed vessel the estimated void volume due to interparticle and intraparticle porosity is 86.5 cm^3. Using this value and the vessel volume, the total porosity is 86.5/120.3 = 0.72.

Table 1. Preliminary calculations based on the pulse-response experiments presented in Fig. 2.

Calculations	Without a vessel	Empty vessel	Packed vessel*	Using equation
Mass balance (mv x s)	1589	2205	2281	(20)
Mean residence time t_m (s)	1.2	65.9	53.3	(7)
Volume of connecting lines and vessel (cm^3)	2	107	86.5	Q x t_m
Maximum concentration of output pulse C_{max}(μmol/cm^3)	9.96	0.66	0.321	(21)

* Cylindrical pellets of α-Al_2O_3 pellets (d_p = 3.5 mm; l = 3.5 mm)

According to the supplier, the α-Al_2O_3 pellets have a packing density of 1.12 g/cm^3, an apparent density of 1.85 g/cm^3 and a pore volume of 0.27 cm^3/g. Therefore, the void fractions between pellets and due to pores are 0.39 and 0.30, respectively. Consequently, the expected total porosity is in very good agreement with the measured value.

The maximum concentration of the output pulse is reported in the last row of Table 1. In the absence of a vessel and due to the lack of dispersion, the highest value is obtained, although it may not be the true value due to the non-linear response of the TCD. For both the empty and packed vessel, the maximum H_2 concentration is strongly attenuated due to diffusion and dispersion effects.

These results demonstrate that the assumption of a "closed vessel" for our experimental set-up is reasonable because the dispersion of the tracer takes place mainly in the vessels. Consequently, experimental results could be compared with those predicted by equation (11) or (12) in order to estimate the model parameter. To obtain the experimental RTDF, $E(\theta) = C(\theta)/C_o'$ Eq. (22) is applied to selected h values at constant Δt intervals. The experimental E(θ) curves were fitted with Eqs. (11) and (8), using the Peclet number as the adjusting parameter. The results obtained using CH_4 as tracer for the empty and packed vessel are plotted in Figs. 3 and 4. It is observed that the deviations from plug-flow behavior are well represented by the dispersion model using a Peclet number of 500 for the empty vessel, and a value of 28 for the packed vessel. These model predictions could be compared with the values derived from Eqs. (14) and (18) mentioned above. Taking into account the Ar properties at normal pressure and temperature, the average gas velocity and the tube diameter, the Sc and Re for the experiments reported in Fig. 3 are Sc = 0.68 and Re_d = 14.

The molecular diffusivity of the tracer, Dm, was taken as 0.205 cm^2 /s (Reid *et al.*, 1987). The Taylor-Aris correlation (Eq. (14)) predicts that the Peclet number for the empty vessel is $Pe_d = (v \times d) / D_a = 6.5$.

Using the reactor length L and the reactor diameter d, the Peclet number Pe_L as defined in the dispersion model is $Pe_L = (v \times L) / D_a = (6.5 \times 112) / 1.13 = 644$.

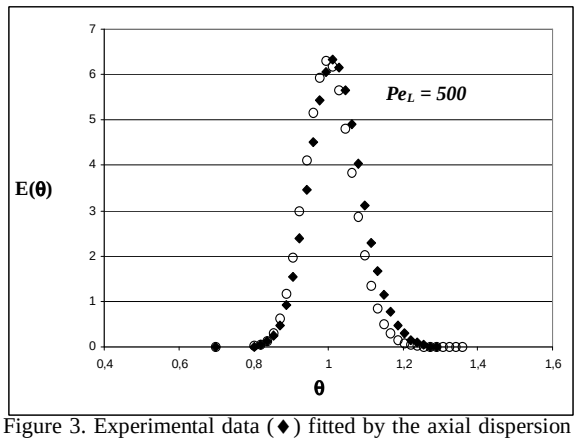

Figure 3. Experimental data (♦) fitted by the axial dispersion model (o) for a CH_4 input pulse into an empty vessel. Q (Ar) = 104 cm^3/min.

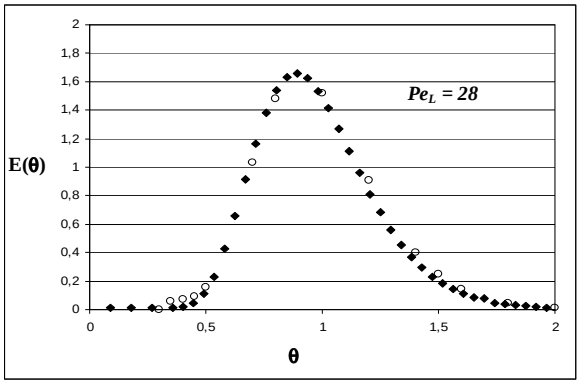

Figure 4. Experimental data (♦) fitted by the axial dispersion model (o) for an H_2 input pulse into a vessel packed with α-Al_2O_3 pellets. Q (N_2) = 97.3 cm^3/min.

Consequently, there is a reasonable approximation with the value obtained by comparing the experimental results with the dispersion model. Equation (18) was used to predict the Pe_{dp} number for the packed vessel taking into account that in this case the Reynolds number is based on the particle diameter ;

Sc = 0.68; Re_{dp} = 0.7

In this case, the molecular diffusivity of H_2 in N_2 was 0.77 cm^2/s (Reid *et al*., 1987). The Pe_{dp} number was found to be;

$Pe_{dp} = u \times d_p / D_a = (v / \varepsilon)\, d_p / D_a = 0.46$

When the reactor length L and the particle diameter d_p are introduced, the Pe_L is;

$Pe_L = 0.46 \times 25.4 / 0.35 = 34$

It is interesting to note that it is very close to the value determined by fitting the dispersion model to the experimental results.

Using the Peclet numbers derived from the pulse-response experiments, the dispersion coefficient is easily calculated. The results are presented in Table 2. It is observed that the dispersion coefficient for the empty tube is higher than the molecular diffusivity, indicating that pulse broadening is in part due to mixing effects.

Table 2. Peclet number and dispersion coefficient derived from the dispersion model. Values between parentheses are the Pe_L numbers estimated from Eqs. (14) and (18)

Vessel type	Pe_L	Dispersion Coefficient D_a (cm^2/s)
Empty	500 (644)	0.38
Packed	28 (34)	0.73

On the other hand, the flow in the packed vessel is characterized by a dispersion coefficient, which is similar to the tracer diffusivity. Consequently, the tracer dispersion occurs mainly by a molecular-diffusion mechanism in the intraparticle and interparticle void volume.

A limitation of these experiments is the need to use a flow-rate that should be compatible with the TCD operation. Consequently, higher values of the dispersion coefficient due to mixing in the axial direction, which are expected at much higher flow-rates, are not observed.

VI. CONCLUSIONS

Common and inexpensive laboratory apparatus were used to set up an experiment that provides information on the RTDF of empty or packed vessels. Experimental results could be treated in different ways to obtain information on flow behavior and on the system's properties, such as volumes, concentrations, bed porosity, etc. The experimental RTDF was used with an approximate analytical solution of the axial-dispersion model to obtain the Peclet number that characterizes the extent of dispersion for gas flow on an empty and a packed vessel. Good agreement was found between these values and those obtained from well-known correlations.

NOTATION

A: h Δt recorded area (mv s)
C(t) or C(θ) : tracer concentration (μmol/cm^3)
C_o': M/V tracer concentration (μmol/cm^3)
d: tube diameter (cm)
d_p: particle diameter (cm)
D_a: dispersion coefficient (cm^2/s)
D_m: molecular diffusivity (cm^2/s)
E(t) or E(θ): residence time distribution function from a pulse input
F(t) or F(θ): residence time distribution function from a step input
h: recorded signal (mv)
L: tube length (cm)
M: amount of tracer (μmol)
Q: volumetric flow rate (cm^3/min)
Pe_d : (v d/D_a) Peclet number based on the tube diameter
Pe_{dp}: (u d_p/D_a) Peclet number based on the particle diameter
Pe_L: (v L/D_a) or (u L/D_a) Peclet number based on the tube length
Re_d: (d v ρ/μ) Reynolds number based on the tube diameter
Re_{dp}: (v d_p ρ/μ) Reynolds number based on the particle diameter

S_c: (μ /ρ D_m) Schmidt number
t: time (min or s)
t_m: V/Q mean residence time
u: v/ε interstitial velocity (cm/s)
v: average gas velocity (cm/s)
V: vessel volume (cm^3)
z: axial coordinate (cm)
z^*: z/L dimensionless length

Greek Symbols

α: constant
α_i: root in Eq. (12)
ε: bed porosity
μ: gas viscosity (g cm/s)
θ: t/t_m dimensionless time
ρ: gas density (g/cm^3)

REFERENCES

Butt, J.B., *Reaction Kinetics and Reactor Design*, Prentice Hall, New Jersey (1980).

Carslaw, H.S. and J.C. Jaeger, *Conduction of Heat in Solids*, Oxford Universities Press, London (1959).

Froment, G.F. and K.B. Bischoff, *Chemical Reactor Analysis and Design*, Wiley, New York (1979).

Fogler, S., *Elements of Chemical Reactor Engineering*, 4th ed., Prentice Hall International Series in the Physical and Chemical Engineering Sciences, Upper Saddle River, New Jersey (2006).

Levenspiel, O., Chemical Reaction Engineering, 2nd ed., Wiley, New York (1972).

Reid, R., J.M. Prausnitz and B.E. Poling, *The Properties of Gases and Liquids*, Mc Graw Hill, New York (1987).

Smith, J.M., *Chemical Engineering Kinetics*, 3rd ed., McGraw -Hill, New York (1981).

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

Received: May 12, 2009.
Accepted: October 22, 2009.
Recommended by Subject Editor: Orlando Afano.