Analysis of Plug Flow Reactors with Variable Mass Density

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The design of plug flow reactors with variable mass density is examined. Equations which include a two-term constitutive equation for the reaction rate are derived for the flow of liquids and for the flow of ideal gases in steady plug flow reactors. It is shown that the addition of the second term in the constitutive equation can have a significant effect on the calculation of the reactor volume needed to carry out a specific conversion of the reactant. Published experimental plug flow reactor data support the observation that a reaction rate constitutive equation with two terms can provide a good representation of the experimental data for variable mass density reactors. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 4185–4189, 2014
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Introduction

One of the simplest flow reactors is the steady-state plug flow tubular reactor, which has a uniform velocity profile and no mixing or diffusion along the flow path. The analysis of such a reactor is straightforward under isothermal conditions when there is a constant tube diameter, a single reaction, and a constant mass density ρ.[1] However, the analysis is somewhat more complicated for a variable density ρ in the reactor. Here, an analysis of a variable density plug flow reactor for a homogeneous first-order irreversible reaction

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

with the usual rate constant k_1 is presented. The input to the reactor is pure component A, and thus a mixture of components A and B is present downstream in the reactor.

The constitutive equation for the reaction rate for the above reaction is usually written as

$$\frac{R_A}{M_A} = -k_1 c_A \tag{2}$$

where R_A is the rate of production of mass of species A per unit volume by a homogeneous chemical reaction, M_A is the molecular weight of component A, and c_A is the molar density of component A. A more general version of the constitutive equation for Eq. 1 can be derived using the continuum mechanics principle of equipresence.[2] This principle states that all of the dependent constitutive variables must depend on the same list of independent constitutive variables. Hence, for the reaction rate R_A, for isothermal conditions

$$R_A(\mathbf{x},t) = g[p(\mathbf{z},t), \mathbf{v}(\mathbf{z},t), \omega_A(\mathbf{z},t), \mathbf{x}, t] \tag{3}$$

where p is the pressure, $\mathbf{v}$ is the mass average velocity, ω_A is the mass fraction of component A, $\mathbf{z}$ is any point in the material, $\mathbf{x}$ is the point of interest, and t is time. It can be shown[2] that Eq. 3 can be rewritten as

$$R_A(\mathbf{x},t) = g[p(\mathbf{x},t), \nabla p(\mathbf{x},t), \mathbf{D}(\mathbf{x},t), \mathbf{W}(\mathbf{x},t), \omega_A(\mathbf{x},t), \nabla \omega_A(\mathbf{x},t)] \tag{4}$$

where $\mathbf{D}$ is the rate of strain tensor and $\mathbf{W}$ is the vorticity tensor. For a first-order theory for R_A (which is different than a first-order reaction rate), any term in the constitutive equation for R_A can have at most a total degree in $\nabla p, \nabla \omega_A, \mathbf{D}$, and $\mathbf{W}$ equal to 1. Hence, the expression for the linear or first-order theory for R_A can be written as

$$R_A = \varsigma(p, \omega_A) + \tau(p, \omega_A)\,\mathrm{tr}\,\mathbf{D} \tag{5}$$

This equation is based on the utilization of representation theorems of continuum mechanics.[3] Since

$$\mathrm{tr}\,\mathbf{D} = \nabla \cdot \mathbf{v} \tag{6}$$

it follows that Eq. 5 takes the following form which can be used in the species continuity equation for the plug flow reactor

$$\frac{R_A}{M_A} = -k_1 c_A (1 + k_2\,\mathrm{tr}\,\mathbf{D}) = -k_1 c_A (1 + k_2 \nabla \cdot \mathbf{v}) \tag{7}$$

This is the desired form for the reaction rate constitutive equation. The parameters k_1 and k_2 are assumed to be constant under isothermal conditions. The significance of the second term in the rate expression in Eq. 7 is that it allows for a possible dependence of any dependent constitutive variable on some of the independent constitutive variables.

Although a plug flow reactor may appear to be an oversimplified model of a flow reactor for liquid or gas streams flowing in tubes, Schmidt[1] has shown that the error introduced by the plug flow approximation is relatively small. It should be noted that the type of procedure used to derive Eq. 7 has been used to show that the mass diffusion flux is caused by a mass fraction gradient and also by a pressure

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gradient.[2] Also, Schmidt[1] has indicated that fractional conversion rather than concentration should be used when the mass density is a function of composition. Mass fraction as a measure of conversion is used here.

Although the reaction rate is almost always described by Eq. 2 for the reaction given by Eq. 1 (and therefore depends only on the molar density of the reactant and temperature), there exists the possibility that a more general result such as Eq. 7 may be applicable. As noted above, the continuum mechanics principle of equipresence suggests that all of the independent variables could possibly affect the dependent variables which are present in the equations of change. To illustrate this, consider examples from heat transfer and fluid mechanics. It can be shown[2] that the heat flux can depend on $\boldsymbol{D}$ and $\boldsymbol{W}$ as well as on the temperature gradient and that the extra stress can depend on both pressure and temperature gradients as well as on $\boldsymbol{D}$ and $\boldsymbol{W}$. Support for these results is provided by higher order results from the kinetic theory of gases[4] which show that $\boldsymbol{D}$ and $\boldsymbol{W}$ are also independent variables for the heat flux and that pressure and temperature gradients are also independent variables for the extra stress tensor. While utilization of the two-term constitutive equation for the reaction rate perhaps suggests that the reaction rate directly depends on the velocity field in the reactor, for a plug flow reactor the principal effect of the second term in the constitutive equation is the introduction of an additional mass fraction dependence as will be evident from Eq. 19. Effectively, the dependence of ω_A on the velocity derivative dv_x/dx disappears.

Examples of direct effects of velocity fields on the reaction rate include the influence of fluid shear on the kinetics of blood coagulation reactions,[5] on the inactivation of enzymes,[6] on the degradation of plasma fibrinogen,[7] on gelation kinetics,[8] and on the deactivation kinetics of proteins.[9] The shear described in the above references is generated experimentally from the velocity gradients which are present in laminar flows in cylindrical tubes or in circular flows in rotational viscometers. Such velocity gradients are not present in a plug flow reactor, nor are they described by the first-order theory for R_A (which was used to obtain Eq. 7). However, they are included when considering a second-order theory for which any term in the constitutive equation for R_A can have at most a total degree in $\nabla p, \nabla\omega_A, \boldsymbol{D}$,and $\boldsymbol{W}$ equal to 2. The equation for the second-order theory contains terms such as $\mathrm{tr}(\boldsymbol{D}\cdot\boldsymbol{D})$which include the velocity gradients present in the fluid flow experiments.

Solution of Transport Equations for Plug Flow Reactors

The transport equations which describe the plug flow reactor are the species continuity equation

$$\rho v_x \frac{d\omega_A}{dx} = R_A \tag{8}$$

the overall continuity equation

$$\frac{d(\rho v_x)}{dx} = 0 \tag{9}$$

the x component of the equation of motion

$$\rho v_x \frac{dv_x}{dx} = -\frac{dp}{dx} + \frac{dS_{xx}}{dx} \tag{10}$$

and the following form of the thermal equation of state

$$\frac{1}{\rho} = \omega_A \hat{V}_A + \omega_B \hat{V}_B \tag{11}$$

Here, x is the space coordinate variable in the flow direction, v_x is the x component of the mass average velocity, S_{xx} is the appropriate component of the extra stress tensor, and $\hat{V}_A$ and $\hat{V}_B$ are the partial specific volumes for components A and B. It is assumed here that the total stress tensor and thus the extra stress tensor are symmetric. Also, the tube is assumed to be horizontal so that the gravity term is zero.

Since the tube starts at $x=0$, the initial conditions for Eqs. 8–10 are simply

$$\omega_A(0) = 1 \tag{12}$$

$$v_x(0) = v_0 \tag{13}$$

$$p(0) = p_0 \tag{14}$$

and the initial mass density ρ_0 can be computed using

$$\frac{1}{\rho_0} = \hat{V}_A(0) \tag{15}$$

The reaction term in Eq. 8 is given by Eq. 7 with $c_A = \rho\omega_A/M_A$. Equations 8–11 represent a system of four equations which can be used to solve for ω_A, v_x, p, and ρ subject to Eqs. 12–15.

For liquid systems, it is reasonable to assume that $\hat{V}_A$ and $\hat{V}_B$ are independent of both composition and pressure so that the effect of pressure on the liquid density ρ is negligible. For ideal gas mixtures

$$\hat{V}_A = \frac{RT}{M_A p} \qquad \hat{V}_B = \frac{RT}{M_B p} \tag{16}$$

and thus

$$\frac{1}{\rho} = \frac{\omega_A RT}{M_A p} + \frac{\omega_B RT}{M_B p} \tag{17}$$

For gases flowing through pipes which either have no packing or are short packed pipes, it is reasonable to expect that the pressure drop will be small. Thus, $\hat{V}_A$, $\hat{V}_B$, and therefore the gas density ρ can be evaluated at a single pressure since the pressure is effectively constant in the pipe. Consequently, there is no need to consider Eq. 10, and Eqs. 8, 9, and 11 can be used to solve for ω_A, v_x, and ρ for both liquid mixtures and ideal gas mixtures.

The solution to Eqs. 8, 9, and 11 subject to Eqs. 12, 13, and 15 can be shown to be[2]

$$\left[(\omega_A - 1)\left(\frac{\hat{V}_A}{\hat{V}_B} - 1\right)(1 + k_1 k_2) + \ln\omega_A\right] = -\frac{k_1 x}{\rho_0 v_0 \hat{V}_B} \tag{18}$$

where the following expression was used for R_A

$$R_A = -\rho\omega_A k_1\left[1 + k_2\rho_0 v_0\left(\hat{V}_A - \hat{V}_B\right)\frac{d\omega_A}{dx}\right] \tag{19}$$

The numerator and denominator of the term $k_1 x/(\rho_0 v_0 \hat{V}_B)$ in Eq. 18 can be multiplied by the cross-sectional area of the tube to give $k_1 V_R/(Q\hat{V}_B/\hat{V}_A)$, where V_R is the volume of the reactor and Q is the volumetric flow rate of the incoming stream in the reactor. Consequently, Eq. 18 can be rewritten for liquid flow in the plug flow reactor as

$$\frac{\hat{V}_B}{\hat{V}_A}\left[(\omega_A-1)\left(\frac{\hat{V}_A}{\hat{V}_B}-1\right)(1+k_1k_2)+\ln\omega_A\right]=-\frac{k_1V_R}{Q}=-V_R^* \tag{20}$$

Since $\hat{V}_A/\hat{V}_B=M_B/M_A$ for ideal gases, for the flow of ideal gases in the plug flow reactor Eq. 20 gives

$$\frac{M_A}{M_B}\left[(\omega_A-1)\left(\frac{M_B}{M_A}-1\right)(1+k_1k_2)+\ln\omega_A\right]=-\frac{k_1V_R}{Q}=-V_R^* \tag{21}$$

Here, V_R^* is the dimensionless reactor volume. Equations 20 and 21 can be used to predict dimensionless reactor volumes for both liquid and ideal gas systems. Values of V_R^* for prescribed exit mass fractions ω_A can be calculated for particular values of $\hat{V}_A/\hat{V}_B$ or M_A/M_B if the two rate constants k_1 and k_2 are available. Note that the product k_1k_2 is dimensionless.

Rate constants such as k_1 and k_2 are often found experimentally using batch reactors. Constant pressure batch reactors can be used for liquid systems, and constant volume batch reactors can be used for gas systems. For a constant pressure batch reactor, the following equation can be derived for the time dependence of the mass fraction ω_A for a liquid system (as well for gases)

$$\ln\omega_A+k_1k_2\ln\left[\omega_A+(1-\omega_A)\frac{\hat{V}_B}{\hat{V}_A}\right]=-k_1t \tag{22}$$

The derivation of Eq. 22 is carried out on pages 70 and 71 of Ref. [2]. A nonlinear regression analysis based on Eq. 22 and ω_A vs. time data from a batch reactor can be used to determine k_1 and k_1k_2 (and hence k_2) for fixed $\hat{V}_A/\hat{V}_B$. For a constant volume batch reactor, it can be shown that the time dependence of ω_A is given by

$$\omega_A=\mathrm{e}^{-k_1t} \tag{23}$$

Although it is a simple matter to use this equation to determine k_1 using ω_A vs. t data, for an ideal gas mixture the constant volume batch reactor is a constant mass density system and no information on k_2 can be deduced from this experiment. However, both k_1 and k_2 can be determined for an ideal gas mixture using a plug flow reactor with a fixed length L and different volumetric flow rates Q. Data for the dependence of the exit mass fraction ω_A on Q can be used to carry out a nonlinear regression analysis based on Eq. 21 to determine $k_1$and k_2 for fixed M_A/M_B and fixed V_R. An alternative to a nonlinear regression analysis for a plug flow reactor is presented in the fourth section of this article.

In the above equations, the mass fraction ω_A was used as the concentration-type variable. This choice can sometimes lead to simpler results for the dependence of the concentration-type variable on time or reactor position. To illustrate, consider the ideal gas reaction

$$A\xrightarrow{k_1}3B \tag{24}$$

in a constant pressure batch reactor (probably not experimentally feasible). For this reaction and for this type of reactor, Schmidt[1] has shown, using the usual one-term constitutive equation, that the dependence of the molar density c_A on time can be described by

$$c_A=c_{A0}\frac{\mathrm{e}^{-k_1t}}{3-2\mathrm{e}^{-k_1t}} \tag{25}$$

where c_{A0} is the initial molar density of component A. However, for the special case where $k_2=0$, Eq. 22 gives

$$\omega_A=\mathrm{e}^{-k_1t} \tag{26}$$

which is a somewhat simpler form than Eq. 25. It can be easily shown that Eq. 25 can be converted to Eq. 26.

Prediction of Plug Flow Reactor Volumes

For steady plug flow reactors, the reactor design consists of finding the dimensionless reactor volume V_R^* needed to attain a desired outlet mass fraction ω_A. For the flow of liquid in a plug flow reactor, the required dimensionless reactor volume is found using Eq. 20 with given values of $\hat{V}_A/\hat{V}_B$ and k_1k_2. For the flow of an ideal gas in a plug flow reactor, Eq. 21 can be used to determine V_R^* for given values of M_A/M_B and k_1k_2. The dimensional reactor volume can then be calculated using the relationship $V_R=V_R^*Q/k_1$ and known values of k_1 and Q. Predicted values of V_R^* are presented in Table 1 for eight cases for liquid systems and for six cases for ideal gas systems. The $\hat{V}_A/\hat{V}_B$ values for liquid systems cover a reasonable density range for pure liquid components, and the M_A/M_B values for ideal gas systems are based on the reaction

$$A\rightarrow nB \tag{27}$$

with $n=2$, 3, and 4. As the importance of the second term in Eq. 7 has not been generally established at this time, two values of k_1k_2 are selected for use in the calculations: $k_1k_2=0$ (to illustrate no effect of the second term) and $k_1k_2=1$ (to illustrate a significant effect of the second term). The value of $k_1k_2=1$ was suggested by the experimental results presented in Table 2. Note that the calculations assume that the one-term reaction rate constitutive equation and the two-term reaction rate constitutive equation have the same value of k_1.

The target exit mass fraction for the cases in Table 1 is $\omega_A=0.1$, and the reactor volumes for variable density results presented in Table 1 are compared to the reactor volume for the constant density result, $V_R^*=2.303$, using the ratio r defined as

$$r=\frac{\text{Variable Density }V_R^*}{2.303} \tag{28}$$

For the flow of liquids in plug flow reactors, Table 1 shows that there can be as much as a 30% difference (Case 3) between the predicted variable density reactor volume and the reactor volume from a constant density calculation. However, this case has a large difference between $\hat{V}_A$ and $\hat{V}_B$. The difference between the specific volumes of the liquid components is usually closer to the 10% difference present in Cases 5–8. For such cases, the effect of density variation is quite small for liquids, as noted by Schmidt.[1] It is evident from Cases 1–8 that, when $k_2>0$, the predicted reactor volume is significantly closer to the reactor volume calculated using a constant density approximation.

For the flow of ideal gases in a plug flow reactor, Table 1 shows that there can be large values of r, that is, much greater reactor volumes are calculated for the variable density cases. This of course is an expected result.[1] However, it is also evident from Cases 9–14 that the introduction of a k_2 value greater than zero leads to very significant decreases in the dimensionless reactor volume. Hence, if k_2 is indeed

Table 1. Variable Density Predictions for V_R^*

Case	Fluid Type	$\hat{V}_A/\hat{V}_B$	M_A/M_B	k_1k_2	V_R^*	r
1	Liquid	1.50	–	0	1.835	0.797
2	Liquid	1.50	–	1	2.135	0.927
3	Liquid	0.67	–	0	3.004	1.304
4	Liquid	0.67	–	1	2.554	1.109
5	Liquid	1.11	–	0	2.163	0.939
6	Liquid	1.11	–	1	2.253	0.978
7	Liquid	0.9	–	0	2.459	1.068
8	Liquid	0.9	–	1	2.359	1.024
9	Ideal gas	–	2	0	3.705	1.609
10	Ideal gas	–	2	1	2.805	1.218
11	Ideal gas	–	3	0	5.108	2.218
12	Ideal gas	–	3	1	3.308	1.436
13	Ideal gas	–	4	0	6.510	2.827
14	Ideal gas	–	4	1	3.810	1.654

greater than zero, the predicted variable density reactor volumes are significantly closer to the reactor volumes calculated using a constant density approximation.

It appears that it would be useful to determine if k_2 is positive and to see if k_2 is significantly different from zero so that the appropriate reactor volume that is required can be determined. In the next section, experimental data are utilized to show that there can be a significant effect of the second term in Eq. 7.

Analysis of Plug Flow Reactor Data

In the previous section, it was shown that it is possible for a two-term reaction rate constitutive equation to have a significant effect on the design of a plug flow tubular reactor with variable mass density. To test the applicability of this two-term constitutive equation, plug flow reactor data collected by Walter[10] on the catalytic, gas-phase pyrolysis of ethylene chloride

$$A \rightarrow B+C \tag{29}$$

are examined. Here, component A is ethylene chloride, component B is vinyl chloride, and component C is hydrogen chloride. The above reaction was taken to be first order, and the feed was pure ethylene chloride for all experiments. Ethylene chloride and the two products are gases at the conditions of the experiments, and ideal gas behavior can be assumed. The reactor volume was the same for all experiments, and the exit ethylene chloride mass fraction was determined using data from the reactor exit stream. Since a single reactor volume was utilized, the exit mass fraction of ethylene chloride, ω_A, can be measured as a function of the incoming volumetric flow rate Q.

Note that the reactor utilizes pumice as a heterogeneous catalyst, and reaction occurs on the external surface of the pumice stone. However, the reaction analysis is carried out in terms of a homogeneous gas-phase reaction system, which requires that a homogeneous reaction rate be substituted into the species continuity equation for the system. This can be done by the utilization of a pseudo-homogeneous reaction rate formulated using the molar density of the reactant in the gas phase. Such a formulation is possible if the surface reaction is the rate-determining step and there is adsorption equilibrium in the system.

Table 2. Kinetic Reaction Parameters for Plug Flow Reactor Data of Walter[10]

Temperature (°C)	k_1, (s^{-1})	k_2, (s)	k_1k_2	R^2 Value
650	2.82	0.196	0.553	0.961
600	1.21	1.11	1.34	0.897

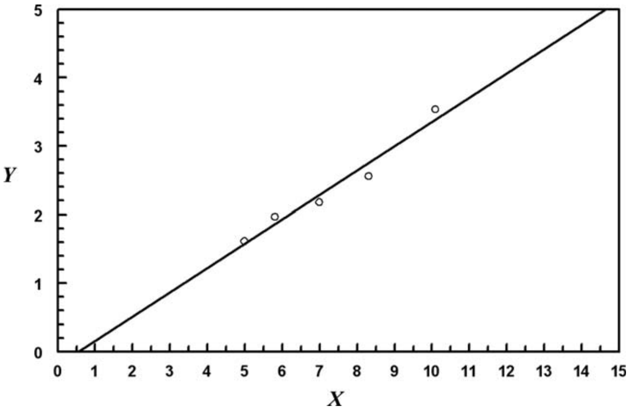

Figure 1. Least-squares fit of 650°C data from Walter.[10] X and Y are defined by Eqs. 33 and 32, respectively.

For the reaction given by Eq. 29, it is possible to utilize a variation of the analysis presented in the second section to derive the equation

$$-\frac{V_R}{Q}=\frac{1}{k_1}[(1-\omega_A)(1+k_1k_2)+2\ln\omega_A] \tag{30}$$

Effectively, V_R/Q is the contact time in the reactor. Note that for this reaction $A \rightarrow B+C$, the derivation of Eq. 30 uses a form of Eq. 21 with the two ratios of molecular weights including M_A, M_B, and M_C. However, the molecular weights do not appear explicitly in Eq. 30 because the molecular weight ratios yield values of 2 and 1/2. Also, the calculated ratios are valid for any values of M_B and M_C such that $M_B+M_C=M_A$. The expression for $A \rightarrow B+C$ does reduce to the expression for $A \rightarrow B$ when C is not present. In the derivation of Eq. 30, the partial specific volumes of the three gases in the reactor were assumed to be constant because it was shown, using the Ergun equation for a packed porous bed,[11] that the pressure drop in the reactor was negligible. Effectively, the results in this section are valid at constant pressure. As indicated in the second section, for a fixed reactor volume V_R, k_1 and k_2 can be determined from Eq. 30 using a nonlinear regression analysis based on the

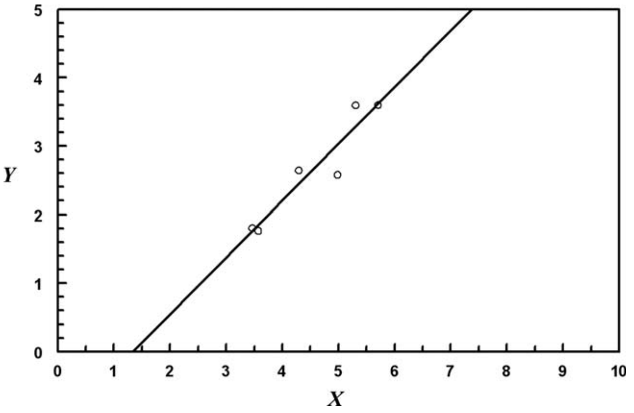

Figure 2. Least-squares fit of 600°C data from Walter.[10] X and Y are defined by Eqs. 33 and 32, respectively.

Table 3. Effect of k_2 on Dimensionless Reactor Volumes for Exit Mass Fraction = 0.1

Temperature (°C)	$V_R^*(k_2=0)$	$V_R^*(k_2 \neq 0)$	$V_R^*(k_2=0)/V_R^*(k_2 \neq 0)$
650	3.70	3.21	1.15
600	3.70	2.50	1.48

dependence of the exit mass fraction ω_A on the incoming volumetric flow rate Q. Alternatively, rearrangement of Eq. 30 produces

$$\frac{V_R}{Q(1-\omega_A)}=-k_2-\frac{1}{k_1}\left(1+\frac{2\ln\omega_A}{1-\omega_A}\right) \tag{31}$$

For this equation, the dependent variable Y is defined as

$$Y=\frac{V_R}{Q(1-\omega_A)} \tag{32}$$

and the independent variable X is defined as

$$X=-\left(1+\frac{2\ln\omega_A}{1-\omega_A}\right) \tag{33}$$

The linear form of Eq. 31 can be used in a least-squares analysis by fitting a straight line using the X and Y data. The slope $(1/k_1)$ and the intercept $(-k_2)$ will of course yield the required values of k_1 and k_2, and the value of k_2 will determine whether a one-term or two-term constitutive equation is needed.

Walter[10] obtained plug flow reactor data for the pyrolysis of ethylene chloride at four temperatures (500, 550, 600, and 650°C). Only the experimental data at 600 and 650°C are analyzed in this article because it appears that the data at these two temperatures have less scatter than the data at 500 and 550°C. The least-squares fit of the 650°C data is presented in Figure 1, and the least-squares fit of the 600°C data is presented in Figure 2. Values of k_1 and k_2 and the R^2 results for the least-squares fits for both temperatures are presented in Table 2. It can be shown that the error variances in the slopes and in the intercepts calculated for the above analysis are less than 5%.[12]

It is evident from Table 2 that Eq. 31 gives good representations (based on R^2 values) of the reactor data both at 650 and at 600°C. It is now of interest to calculate the reactor volumes needed to obtain a desired exit mass fraction ω_A of the reactant for a given volumetric flow rate. From Eq. 30, the dimensionless reactor volume V_R^* is given by

$$V_R^*=\frac{V_R k_1}{Q}=-[(1-\omega_A)(1+k_1k_2)+2\ln\omega_A] \tag{34}$$

An exit mass fraction of $\omega_A = 0.1$ is chosen for the calculations as the mass fractions for 600 and 650°C range from 0.004 to 0.15. It is thus possible to compare the values of V_R^* calculated using Eq. 34 for $k_2=0$ and for $k_2 \neq 0$ at 600°C and at 650°C. The calculated values of the dimensionless reactor volume V_R^* are presented in Table 3. It is evident from Table 2 that k_1k_2 for 600°C is greater than k_1k_2 for 650°C and, hence, there is a greater difference between V_R^* $(k_2=0)$ and $V_R^*(k_2 \neq 0)$ at the lower temperature. From Table 3, there is a significant difference between $V_R^*(k_2=0)$ and $V_R^*(k_2 \neq 0)$ at 600°C (48%) and a somewhat smaller difference at 650°C (15%). The analysis of the experimental data shows that the introduction of $k_2 \neq 0$ can have a significant influence on plug flow reactor design. Hence, a two-term constitutive equation should be considered in the analysis and design of gas-phase plug flow reactors.

Concluding Remarks

In this article, it is shown that the design of plug flow reactors for the first-order irreversible reaction described by Eq. 29 can be carried out using Eq. 34, and values of k_1 and k_2 can be determined using a linear least-squares analysis based on Eq. 31. The usual reaction rate quantity k_1 can be determined from the slope of Eq. 31, and the second reaction rate quantity k_2 can be determined from the intercept. A similar analysis using the methods described in the first two sections of this article can be applied to other first-order irreversible reactions. If k_2 is small, then the usual one-term constitutive equation can be used in the design of the reactor. If k_2 is significantly different from zero, the use of a two-term constitutive equation should be considered.

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