Empirical Modelling and Scale-up of a Semi-batch Polyestrification Process

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SYNOPSIS

A semi-empirical kinetic model that fits laboratory data and predicts pilot plant data was developed. The model is a modified version of a recently reported third-order kinetic equation for the reaction of nonstoichiometric amounts of hydroxyl and carboxylic groups. The model can be used to quantify the effects of reaction temperature and inert gas flow rate on the reaction rate. The Arrhenius temperature dependence of the rate constant permitted the calculation of the reaction activation energy (53.6 kJ/mol). The gas flow rate dependence is an empirical function of the molar ratio of reactants to inert gas. The same function is simultaneously used as the process scale-up rule. The mathematical model can be potentially used for commercial-sized reactors.

INTRODUCTION

The chemistry of polyestrification has received considerable attention in the literature. Many articles, books, and comprehensive reviews[1,2] have discussed the kinetics of polymerization reactions. The engineering aspect of the problem has not enjoyed similar emphasis. Whereas discussions on temperature effects on reaction rates are not uncommon,[3] analysis of the effects of agitation speed, inert gas flow rate,[4] and mass transfer resistance[5] are scarce. The understanding of both aspects of the system is essential for the successful development of scale-up procedures that transform laboratory-prepared resins into commercially produced polyesters.

In an earlier publication,[6] the large-scale preparation of a novel polyester resin was discussed and the effects of the reaction temperature and inert gas flow rates were presented. In this paper, a semi-empirical kinetic model capable of predicting pilot plant kinetic data from laboratory-scale data is presented. The model incorporates the effects of two process parameters (reaction temperature and inert gas flow rate), both having the advantages of easy practical

alteration and of significant influence on polyestrification. Other process variables are assumed to be restricted by existing design and practical limitations.

BACKGROUND

The reaction of glycols with unsaturated anhydrides is a common method of synthesizing unsaturated polyester resins. The reaction is usually carried out batch-wise in a temperature range of 200–250°C. The reaction is initiated in a lower temperature (approximately 170°C) forming the ester with no water loss. At higher temperatures, the reaction proceeds to form linear polyester molecules. The reversible polyestrification reaction is shifted forward by the continuous removal of water by a stream of inert carrier gas. Polyester quality is monitored by periodically collecting samples from the reactor and measuring the acid number (mg KOH required to neutralize the acid in 1 g sample) that serves as a measure of the degree of polymerization.

Different kinetic models and conclusions of the polyesterification reactions can be found in the literature.[1,2] Flory's[7] original work on stoichiometric ratios of glycols and diacids yielded third- and second-order kinetics for uncatalyzed and catalyzed polyestrification, respectively. Recently, Lin and

Hsieh[8] presented different models for both the catalyzed and uncatalyzed reactions that hold over the whole reaction. Flory's[7] and Lin and Hsieh's[8] models that coincide only in the case of stoichiometric ratios of reactants can be used to show the effect of temperature on reaction rate since their reaction rate constant is a function of temperature. On the other hand, neither these nor other kinetic models available in the literature can be employed to quantify the effects of the inert gas flow rate (G) on the reaction rate despite its tremendous effect on the reaction rate.[6] Hence, these models cannot be used for reaction scale-up since the (G) dependence is not quantified.

In scaling up a process, several approaches are possible.[9] One normally starts from the laboratory-scale reactor, moves to the pilot plant stage, and then from the pilot plant to the commercial unit. In going from one scale to another, similarity principles, mathematical modelling, or both may be used. In this work, a combination of both techniques was utilized. To ensure thermal similarity between the laboratory and the pilot plant reactors, the process heating rates ($1°C/min$) and reaction temperature (200 or $210°C$) were kept the same. In addition, to preserve one important aspect of the dynamic similarity in both reactors,[10] agitators were run at the same tip speed (0.64 m/s). The mathematical modelling aspect of the scale-up work focused on modifying an existing kinetic model to account for the effects of (1) gas flow rate and (2) batch size on the reaction rate.

MODEL DEVELOPMENT

The objective of building a mathematical model for the polyestrification reaction and process is to predict the kinetic data (acid number–time curve) for a large-scale system from a small-scale system, and to provide a basis for the scale-up of the process. It is illustrated here for the laboratory-pilot plant-scale experiments. The data used in evaluating the constants of the model were obtained from the 10-I reactor experiments discussed in an earlier publication.[6]

Prior to creating the model, the measured acid number was expressed in terms of extent of reaction (polymerization). The experimental acid number vs. time sets of data collected from the 10-I scale reaction were fitted into a third-order rate equation. The calculated rate constant (k) was next assumed, on the basis of experimental observations, to be an Arrhenius function of reaction temperature (T) and

an empirical function of the inert gas flow rate (G). Special attention is paid to choosing the functional depenence of G since not only does it reflect the effect of the gas flow rate, it also contains a scale-up rule. Unlike T, G is a size-dependent quantity.

Several functions are available in the literature regarding the effect of gas flow on absorption in gas–liquid systems. Examples include the superficial gas velocity[11] and the gas flow number.[12] In our model, the ratio of the initial number of moles of the reactants to the molar flow rate of inert gas is taken as the term representing the gas flow rate effect and the scale-up rule, simultaneously. Since the number of moles of water generated by the reaction is proportional to the number of moles of reactants, the corresponding ratio of moles of water to moles of carrier gas is expected to be a meaningful quantity, representing the G effect on the reaction rate. The exact form of the functional dependence will be determined empirically from the 10-I reactor data. Finally, the developed model will be used to predict the kinetic data (acid number–time curve) of the pilot plant experiments.

Extent of Reaction

The acid number (AN) measured in accordance with ASTM D 1639 is expressed in terms of the concentration of carboxylic groups in the reaction mixture $([H])$.

$$AN = 56.1[H]. \tag{1}$$

The units of $[H]$ are mol/kg of the reaction mixture. The conversion of carboxylic groups is defined as:

$$P = \frac{H_0 - H}{H_0} = 1 - \frac{H}{H_0}$$

$$= 1 - \frac{[H]M}{[H_0]M_0}, \tag{2}$$

where H_0 and H are, respectively, moles of carboxylic groups available in the reaction time initially and at any other time; M_0 and M are, respectively, the mass of the reaction mixture initially and at any other time. M is smaller than M_0 since water is being removed from the reactor. If one assumes that every mole of water that is produced in the reactor is removed by the inert gas (i.e., zero mass transfer resistance), then it follows that:

$$\frac{M}{M_0} = \frac{1 - 0.018[H_0]}{1 - 0.018[H]}. \tag{3}$$

Combining eqs. (1), (2), and (3) gives:

$$P = 1 - \frac{AN}{AN_0}\left(\frac{1 - 3.2085 \times 10^{-4}AN_0}{1 - 3.2085 \times 10^{-4}AN}\right). \quad (4)$$

Equation (4) relates conversion with the initial and measured acid number. In our case, AN_0 is 248; thus:

$$P = 1 - \frac{3.7115 \times 10^{-3}AN}{1 - 3.2085 \times 10^{-4}AN}. \quad (5)$$

Kinetics

Flory[7] showed that the ("self-catalyzed") polyestrification reaction followed third-order kinetic equation for a stoichiometric mixture, whereas Lin and Hsieh[8] developed the kinetic equation when a nonstoichiometric ratio of the glycols and anhydrides are reacted. In our case, this ratio is 1.062 and thus Lin and Hsieh's equation [eq. (6)] will be used.

$$\frac{d[H]}{dt} = k[H](a + [H])^2, \quad (6)$$

where

$$a = (r - 1)[H_0] \quad (7)$$

and

$$r = [OH_0]/[H_0]. \quad (8)$$

Equation (6) may be integrated to give:

$$\ln -\frac{(r - P)}{(1 - P)} - \frac{(r - 1)}{(r - P}$$

$$= \ln \frac{(r - P_2)}{(1 - P_2)} - \frac{(r - 1)}{(r - P_2)} + ka^2(t - t_2), \quad (9)$$

where $[OH_0]$ is the initial hydroxyl concentration and P_2 is the conversion at time t_2. Lin and Hsieh took t_2 and P_2 as 0 and 0, respectively, which is not true unless the condensation and the reaction temperatures are the same. However, in our case, they are not; t_2 may be small compared with total t for small-scale systems. However, in large-scale systems, t_2 is 10–15% of total reaction time. Condensation starts at $T = 170°C$ ($P_0 = 0$, $t_0 = 0$) and the reaction mixture is heated to $T = 200$ or $210°C$. During this period, P is changing and so is k since

T is changing. What complicates the matter is that, in our case, k is a function of temperature and the gas flow rate (G), which is also changing with temperature. Thus, the lower integration limit of eq. (6) has to be the time (and conversion) at which T and G are held constant.

A computer program was written to check whether our data[6] agreed with Lin and Hsieh's kinetic model. The program reads the acid number–time data, transforms it to polymerization rate data [eq. (5)] and plots the left-hand side (LHS) of eq. (9) vs. $(t - t_2)$. Figure 1 shows such plots for two typical laboratory experiments. The slope of the best line that fits the data is used to calculate k.

Reaction Rate Constant

To quantity the effects of T and G on k, an Arrhenius temperature dependence and an empirical function of the ratio of moles of reactants (n_r) to molar flow rate of gas (n_g) are assumed. In the 10-I experiments, n_r is 65.97 mol, whereas n_g is given by:

$$n_g = \frac{PG}{RT}, \quad (10)$$

where P is the pressure and R is the gas constant. From numerous data sets, the functional dependence of k on the ratio n_r/n_g was found to be:

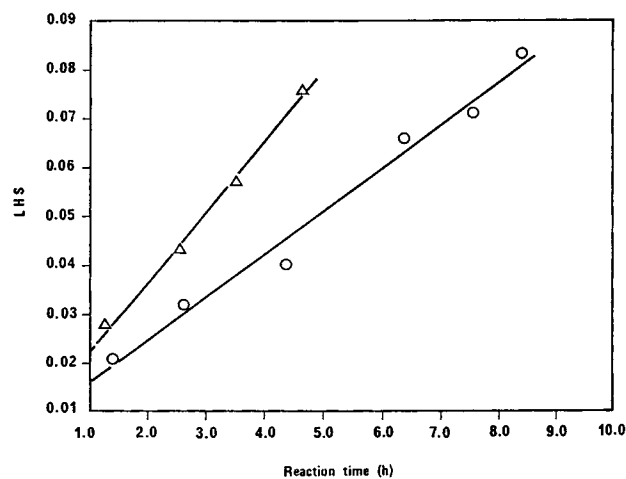$$\ln k \propto \left(\frac{n_r}{n_g}\right)^{1.85}. \quad (11)$$

Figure 1 Third-order kinetics (Lin and Hsieh's equation) of two laboratory batches; $G = 0.06$ m³/h, $T = 200°C$ (O), $T = 210°C$ (△).

Thus, k may be written as:

$$k = k_0 \exp\left(-\frac{k_1}{T}\right) \exp(k_2 N), \qquad (12)$$

where

$$N = \left(\frac{n_r}{n_g}\right)^{1.85} \qquad (13)$$

and k_0, k_1, and k_2 are constants. To illustrate how these constants can be evaluated from the laboratory data, Table I is presented. In Table I, the k values (slope of best fit line divided by a^2) are shown for two temperatures and two gas flow rates. It is straightforward to show that at $T = 473°K$, eq. (12) reduces to:

$$k = 0.17937 \exp[-9.88 \times 10^{-4} N], \qquad (14)$$

whereas at $483°K$, eq. (12) becomes:

$$k = 0.23802 \exp[-4.5194 \times 10^{-4} N] \qquad (15)$$

and, in general,

$$k = 1.5416 \times 10^5 \exp\left(\frac{-6463.1}{T}\right) \exp((5.3606$$
$$\times 10^{-5} T - 2.6344 \times 10^{-2}) N). \qquad (16)$$

Thus, our kinetic model is composed of eqs. (9) and (16), where the latter determines k for a given T and G and the former provides the conversion–time relationship. The equations that were developed from the laboratory data can be directly applied to the pilot plant kinetic data since a scale-up rule (N) is already included.

The operating temperature and gas flow rate for five representative pilot plant experiments are presented in Table II. The corresponding N values were obtained from eqs. (10) and (13) after substituting

Table I   Operating Conditions of Four Laboratory Experiments

T (°K)	G (m³/h)	ng (mol/h)	N	k (kg²/mol² h)
473	0.06	2.4537	441.19	0.116
473	0.09	3.6805	208.38	0.146
483	0.03	1.2268	1590.49	0.116
483	0.06	2.4537	441.19	0.195

Table II   Operating Conditions of Five Pilot Plant Experiments

T (°K)	G (m³/h)	ng (mol/h)	N
473	0.750	30.270	992.629
473	1.125	45.405	468.832
473	1.500	60.540	275.347
483	1.125	45.405	468.832
483	1.500	60.540	275.347

1261.53 mol for n_r. Equations (14) and (15) are used to calculate k and eq. (9) is employed to calculate a set of P values for a set of t values. Finally, eq. (5) is inverted to give AN in terms of P and an acid number–time curve is generated. A comparison of the calculated vs. experimental acid number–time curves is shown in Figures 2–6.

DISCUSSION

Figures 2–6 show good agreement between the experimentally measured and the calculated kinetic curves. Defining percent error as the difference between the calculated and experimental values divided by the experimental value, it was found that the maximum errors (Figs. 2–6) were 6, 7, 12, 17, and 4%, respectively. The corresponding average error (sum of individual errors divided by number of data points) in these figures was 4, 4, 6, 13, and 2%, respectively. Whereas both types of errors are high for Fig. 5, the other four figures reflect reasonably good prediction capabilities of the model. The
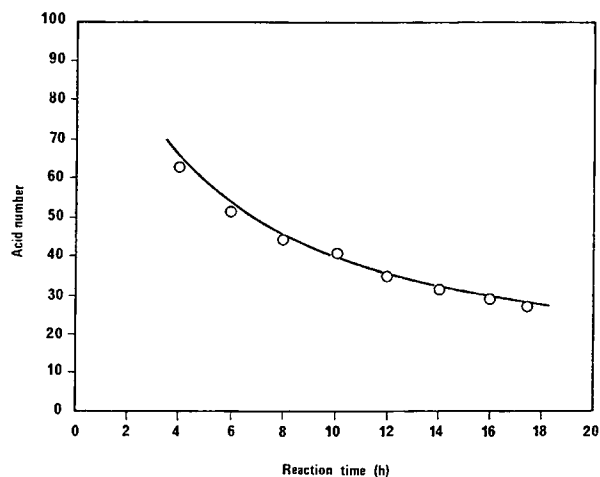

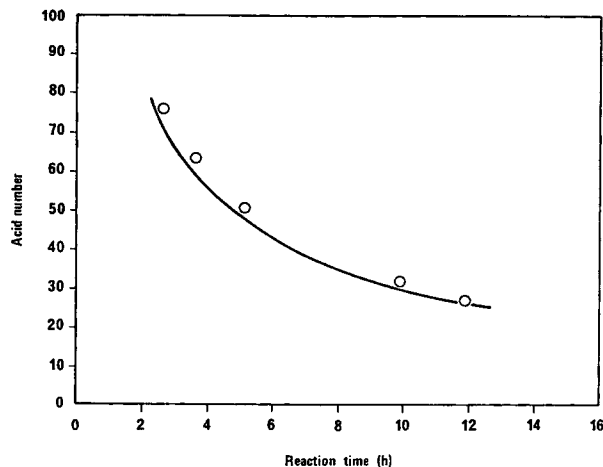**Figure 2** Comparison of calculated (—) and experimentally determined (O) acid number–time curves: $T = 200°C$, $G = 0.75$ m³/h.

Figure 3 Comparison of calculated (—) and experimentally determined (O) acid number–time curves: T = 200°C, G = 1.125 m^3/h.

Figure 5 Comparison of calculated (—) and experimentally determined (O) acid number–time curves: T = 210°C, G = 1.125 m^3/h.

semi-empirical model does a better job in predicting the acid number at the lower range. This is of key importance since a 10% error in the estimation of the acid number in the low acid number range may result in an error of 2–3 h in the calculated reaction time, whereas a 10% error in the estimation of the acid number in the high acid number range may lead to an error of 0.5–1 h only in the calculated reaction time. Our kinetic model was also found to predict the kinetic data of a 10 m^3 reactor. The Kuwait Chemical Manufacturing Company (KCMC) is a producer of several grades of unsaturated polyester resins. In a series of runs on their 10 m^3 reactor, they found that 4 h after operating at a fixed tem-
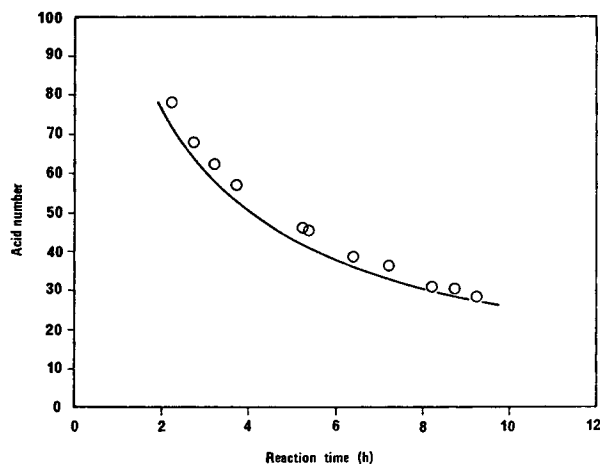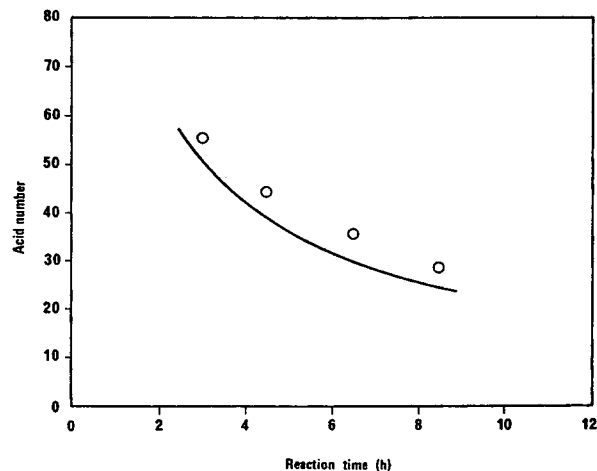
perature and gas flow rate [the required conditions to apply eq. (9)], the acid number dropped from 67.8 to 45.1. Both of these values were obtained by taking the arithmetic average of the acid number of six batches. Our kinetic model predicts a drop from 67.8 to 44.6 during the same time period (4 h). Although this close agreement is fortuitous, it nevertheless gives credibility to the mathematical model.

In deriving our model, several assumptions that needed verification were made. In obtaining eq. (3), zero mass transfer resistance was assumed, i.e., the fluid did not exert any resistance for the water generated by the reaction to be carried away by the
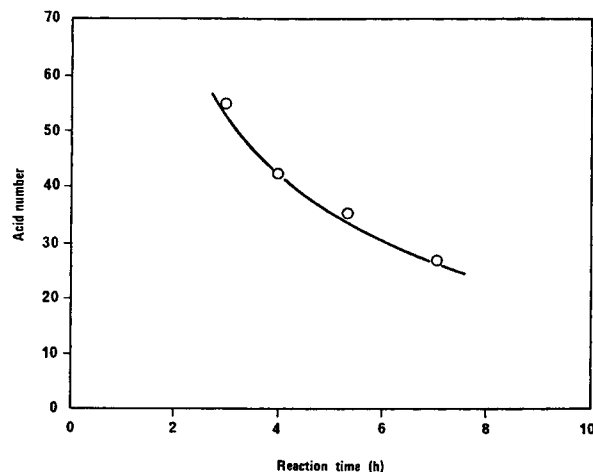

Figure 4 Comparison of calculated (—) and experimentally determined (O) acid number–time curves: T = 200°C, G = 1.5 m^{-3}/h.

Figure 6 Comparison of calculated (—) and experimentally determined (O) acid number–time curves: T = 210°C, G = 1.5 m^3/h.

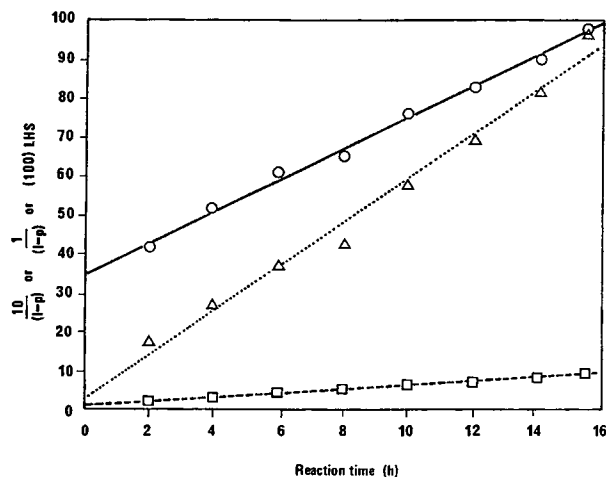**Figure 7** Second- (O) and third-order Flory's (△), Lin and Hsieh's (□) kinetics of a pilot plant run: $T = 200°C$, $G = 0.75 \text{ m}^3/\text{h}$.

inert gas. According to Gupta et al.,[5] this assumption is justified if the degree of polymerization (DP) is less than 30. In our case, the reaction was carried out to about 90% conversion. Thus, the degree of polymerization is approximately eight, as shown in eq. (17). Therefore, the zero mass transfer resistance assumption is valid.

$$DP = \frac{1 + r}{2r(1 - P) + 1 - r}$$

$$= 7.6. \qquad (17)$$

Another assumption was made regarding the reaction kinetics [eq. (6)]. Despite the fact that Lin
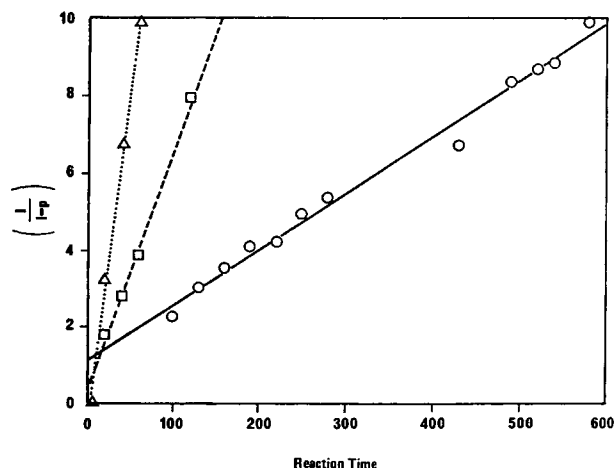

Figure 8 Second-order kinetics of uncatalyzed polyestrification, data taken from Ref. 3 (O), 8 (□), and 13 (△).

Table III   Ratio of Reaction Rate Constants of Laboratory and Pilot Plant Experiments

Run	k_{LH}/k_F	k_{LH}/k_s
1	0.51	0.73
2	0.53	0.71
3	0.52	0.73
4	0.51	0.74
5	0.48	0.76
6	0.49	0.74
7	0.50	0.73
8	0.48	0.77
9	0.47	0.78

and Hsieh's[8] model resulted in a good data fit (Fig. 1), other models were found to almost equally fit our kinetic data. Flory's[7] model gave a good fit (Fig. 7) that was expected since our hydroxyl to carboxylic groups ratio was close to 1. Good agreement between Flory's model and experimental data for $r = 1.1$ was recently reported.[3] What was not expected was that a second-order plot $(1/(1 - P)$ vs. $t)$ would also fit our data. In fact, other researchers' data [3,8,13] on uncatalyzed polyestrification were found to fit a second-order plot up to 90% conversion (Fig. 8). The results and conclusions of our model, therefore, are valid irrespective of the kinetic model used (Flory, Lin and Hsieh, second order). Plotting the data according to each of these models resulted in different k values (Fig. 7). However, the ratio of the values of the Lin and Hsieh's to Flory's rate constants (k_{LH}^*/k_F) and the ratio of the values of the Lin and Hsieh's to second-order rate constants (k_{LH}/k_s) were almost constant (Table III) irrespective of the operating conditions (T and G) and the size of the reactor. The constant ratios implies that the relative temperature and gas flow rate effects are independent of the choice of the theoretical kinetic model.

The third assumption made concerned the functional dependence of k on G. As mentioned earlier, the superifical gas velocity and gas flow number are normally used in continuous gas–liquid mass transfer operations. Using either of these quantities does not eliminate the need of a scale-up rule that relates the value of these parameters in different reactor sizes.[12] The advantage of using N [eq. (13)] is that it combines the scale-up of the functional dependence terms. In addition, it has some physical significant since the amount of water generated by the

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* k_{LH} is the rate constant multiplied by the dissociation rate constant of acid in glycols.[8]

reaction and removed by the inert gas is proportional to the moles of reactants. Keeping the molar ratio of water to gas constant, irrespective of the reactor size, is likely to shift the polyestrification reversible reaction to the right and produces the same reaction rate provided that the reaction temperature is kept the same in these reactors of various sizes and provided that the initial concentration of reactants are unchanged upon scale-up.

A final note must be made regarding the temperature dependence. The Arrhenius relation (k $\sim k_0 \exp E \dfrac{-k_1}{T} F$ permits the calculation of the activation energy of the reaction (E) since:

$$k_1 = \frac{E}{R} . \tag{18}$$

Using the value of k_1 shown in eq. (16), E is found to be 56.6 kJ/mol, which is in the range (52.7 kJ/mol) of activation energies of similar polyestrification reactions.[4] The other term appearing in eq. (16) and containing the temperature dependence comes about as a result of the interaction of the T and G variables.[6]

The same procedure followed in deriving this model was applied to two other resin formulations developed in our laboratories, and similar agreement between calculated and experimental acid number–time curves was obtained.

CONCLUSIONS

A semi-empirical kinetic model that fits the laboratory data and predicts pilot plant data was developed. The model is a modified version of Lin and Hsieh's kinetic equations and is capable of quantifying the effect of the inert gas flow rate. The temperature dependence was assumed to be of the Arrhenius type and the activation energy of the reaction was found to be 53.6 kJ/mol. The gas flow rate dependence was empirically obtained as a function of the ratio of the number of moles of reactants to the molar flow rate of inert gas. This function also served as a scale-up rule. The developed mathematical model is simple and requires minimum information (operating temperature and gas flow rate). However, it does not include terms to account for the geometrical and dynamic aspects of the process. This is partly due to the fact that geometrical quantities such as D/DI where D is the reactor diameter and DI is the impeller diameter were kept constant (0.61 and 0.60, for the laboratory and pilot

plant systems, respectively). The ratio of the reactor diameter to the liquid height (h) was not markedly different in both scales; D/h for the laboratory reactor was 0.78, whereas for the pilot plant reactor, the ratio was 1.07. As for the dynamic variables, the agitator tip speed was kept constant (0.64 m/s) in both reactors, but the type of agitator and its relative positioning in the reactor were different. Not withstanding these limitations, the model is successful in predicting pilot plant data and can be potentially used for larger reactors, as shown from the good agreement between the model calculated and experimentally determined acid number of a commercial-sized reactor. Moreover, the generic form of the model [eqs. (9) and (12)] is applicable to various polyester resin formulations.

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