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MODELING OF AN INDUSTRIAL WIPED FILM POLY(ETHYLENE TEREPHTHALATE) REACTOR

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ABSTRACT

An improved two-phase model has been developed for a wiped film (third stage) polyester reactor. The model accounts for all the important main and side reactions and incorporates the effect of vaporization of four low molecular weight volatile species. Industrial data under three different operating conditions are used to obtain best-fit (tuned) values of the model parameters. When these values are used unchanged in the model, the latter predicts industrial operation under a fourth set of operating condition. This indicates that the 'tuned' model accounts for all the physico-chemical phenomena present in the reactor. A sensitivity study reveals the importance of some parameters and suggests that these should be determined experimentally using more basic experimental studies rather than by tuning industrial data wherein several additional physical phenomena are present.

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INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the most widely used polymers in the fiber and engineering plastics industry. In the past two decades, PET has gained sufficient commercial importance to inspire a considerable amount of research in the area of modeling and simulation of the several reactors used in its manufacture. The early 1980s saw work in the open literature in this area primarily from two groups, ours (Kumar et al., 1982 a, b; 1983) as well as that of Ravindranath and Mashelkar (1982 a, b). After a short period of reduced interest, this area again started attracting considerable interest from groups led by Choi (Besnoin and Choi, 1989; Lei and Choi, 1990; Laubriet et al., 1991; Cheong and Choi, 1995, 1996), Ray (Jacobsen and Ray, 1992a; Hipp and Ray, 1996) and Doherty and Malone (Steppan et al., 1990) Several reviews have also appeared over these last two decades in this area (Gupta, 1983; Ravindranath and Mashelkar, 1986 a, b; Jacobsen and Ray, 1992b). However, there is a dearth of studies on the optimization of PET reactors. The very few studies (Kumar et al., 1984 a, b, c), on the optimization of PET reactors in the open literature are preliminary in nature and are not directed towards *industrial* reactors. In this study, we present a mathematical model that describes a third stage, wiped film industrial PET reactor. Industrial data are used to obtain 'best-fit' (tuned) parameters used in the model, using the optimization technique of Nelder and Mead (1965). This 'tuned' model can then be used to obtain optimal operating conditions for this reactor, using multiple objective functions and end point constraints. The technique used in this study is quite general, and parallels similar work on the modeling of an industrial nylon-6 semibatch reactor (Wajge et al., 1994).

Commercially, PET is manufactured in three stages using continuous reactors. The first stage (esterification stage) is carried out at atmospheric pressure and at 270–280°C. The raw materials commonly used are a molar excess of ethylene glycol (EG) and either purified terephthalic acid (PTA) or dimethyl terephthalate (DMT). PTA and DMT have their own advantages and disadvantages. Nowadays, DMT is not usually preferred because of the problems in handling methanol, a by-product in the first stage. The use of PTA posed a problem earlier because its solubility in EG is low. But it has good solubility in BHET (bis-hydroxy ethylene terephthalate), a product of the first stage reactor, and the use of a recycle stream (or back mixing) in the first stage can overcome this drawback. PTA and EG are now usually processed in a series of CSTRs or a plug flow reactor with a recycle in the first (or esterification) stage. A polycondensation catalyst, antimony trioxide, is injected in small concentrations (0.03–0.05 percent by weight) into the oligomer stream exiting from this reactor. The second stage (pre-polymerization) is carried out either in one or two agitated vessels under reduced pressures, at about 15–30 mm Hg and 270–280°C. The degree of polymerization, DP, reaches a value of about 30–40 in this stage. The prepolymer so produced undergoes final polycondensation in a finishing (or third stage) reactor in which the pressure is maintained quite low at 1–2 mm Hg, at a temperature of about 280–290°C. Since the reaction mass is very viscous under these conditions, the finishing reactor has a special construction to enhance mass transfer and the removal of the by-product, ethylene glycol, so as to drive the reaction in the forward direction and to give a product having a high value of DP. The finisher is usually a jacketed cylindrical vessel with a horizontal agitator, with large screens mounted on the latter. The reaction mass in the third-stage reactor is usually heated by condensing Dowtherm™ vapors in a jacket. The desired DP of the product (textile grade) from this reactor is above about 80.

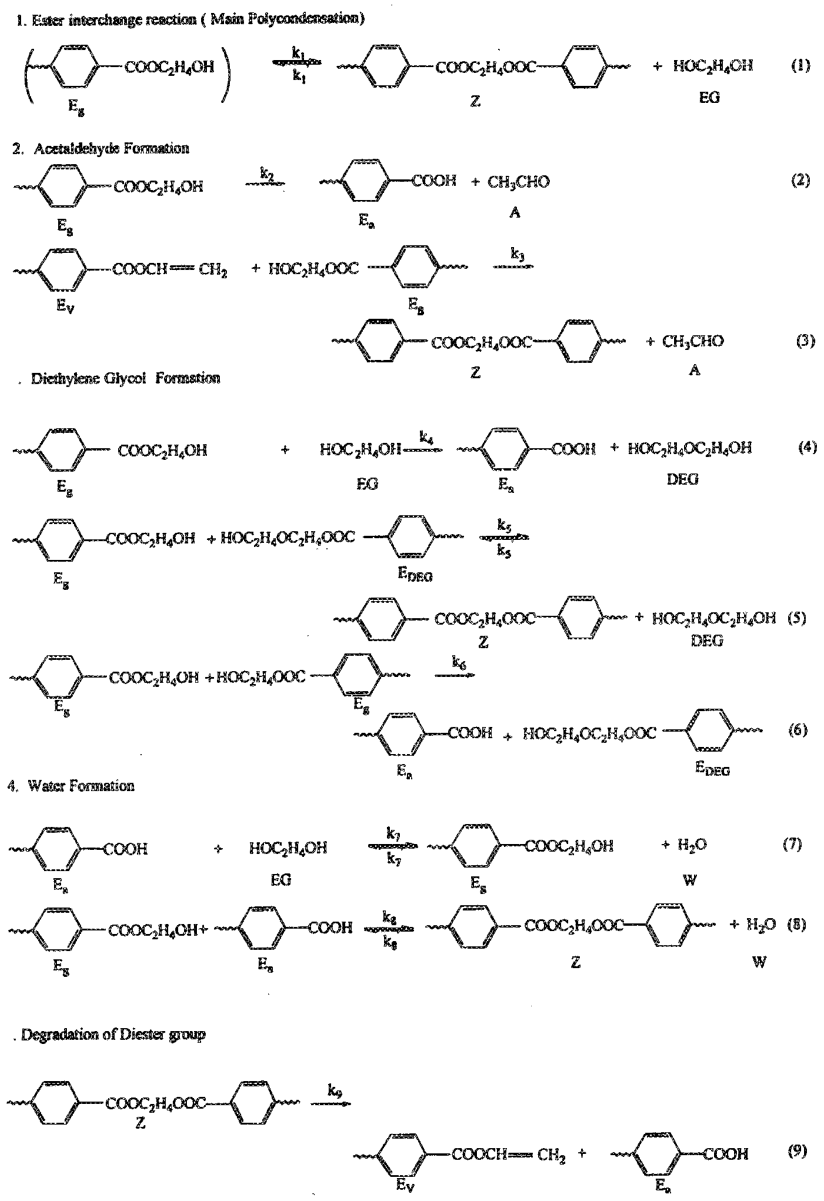
The finishing reactor for PET poses interesting problems in modeling due to the coupling of the mass-transfer and kinetic effects. In the past few years, several attempts have been made to develop models for this reactor. These vary in their levels of sophistication, from the earliest and simplest models (Secor, 1969; Hovenkamp, 1971; Amon and Denson, 1980; Ravindranath and Mashelkar, 1982c, 1984; Ghosh et al., 1983; Gupta et al., 1984; Kumar et al., 1984a) to more recent ones (Laubriet et al., 1991; Cheong and Choi, 1995, 1996; Jacobsen and Ray, 1992a; Hipp and Ray, 1996) incorporating not only the main reactions but also several side reactions taking place in the reactors. Secor (1969) was the first to use penetration theory to explain mass transfer effects in a finishing reactor. The calculations use a value of 1.0 for the equilibrium constant for the polycondensation reaction. Hovenkamp (1971) made use of the Flory-Huggins (Flory, 1953) model instead of Raoult's law, to predict the activity coefficients of the different vaporizing species, EG, as well as other low molecular weight compounds produced by the side reactions, namely, water (W) and diethylene glycol (DEG). Amon and Denson (1980) proposed a simplified analysis for the performance of wiped film reactors. Gupta et al. (1983) and Kumar et al. (1984) made modifications in this model and extended it for predicting the poly-dispersity index of the polymer using moment-closure techniques (Gupta and Kumar, 1987). Ravindranath and Mashelkar (1982) developed an effective flash procedure for determining the interfacial concentration of the volatile species along the length of the finisher. Disc-ring reactor models and axial dispersion plug flow models were proposed by Dietze and Kunhe (1969) and Ravindranath and Mashelkar (1982) for describing the performance of these reactors. Laubriet et al. (1991) proposed a two-phase model for the finishing reactor for the polycondensation of PET. This model has the advantage of being independent of the specific reactor geometry, since it uses a single variable, k_La, to describe the mass transfer effects in the reactor. Cheong and Choi (1995, 1996) proposed a multi-compartment model for the continuous rotating disc polycondensation reactors. This model does not consider the side reactions that occur in the reactor. A detailed kinetic modeling study has been done by and Ray (1992a) who solve the equations using their CAD package, POLYRED. Hipp and Ray (1996) have developed a dynamic model for polycondensation in tubular reactors.

In the present study, we extend the comprehensive, two-phase model proposed by Laubriet et al. (1991), and apply it to an industrial reactor in the manufacture of PET (PTA route) for which some data is available with us. The model parameters are first 'tuned' so as to describe the available industrial data, and then detailed results are presented so as to obtain a better understanding of the operation of this reactor. Such an intuitive understanding is essential before one can undertake a meaningful optimization study involving several objective functions (often conflicting) and end-point constraints associated with the requirement of product property specifications. It is well established from our earlier similar optimization studies on nylon-6 (Wajge and Gupta, 1994; Mitra et al., 1998) and poly methyl methacrylate (PMMA) (Chakravarthy et al., 1997) that one must have such an intuitive 'feel' of the system behavior in order to be able to 'guide' *any* optimization code used towards the optimal point or points, because of the narrow 'windows' for the optimal solutions. We believe that this work is the *first* attempt in the *open* literature to tune a model for PET wiped film reactors against real-life *industrial* data under *a few different sets of operating conditions.*

FORMULATION

The kinetic scheme and the kinetic parameters used in the present work are presented in Table 1. Apart from the main polycondensation reaction, the side reactions considered are the formation of acetaldehyde (A), DEG, water (W) and the degradation of di-ester groups (Z). The reactions taking place in the finishing reactor are quite complex. Unfortunately, kinetic information is not available for many of the side reactions, and even for the main reactions, is at best, unreliable. The choice of the side reactions is based on the objectives of modeling and on the level of sophistication we wish to have in predicting the product properties. We have considered all the main reactions (Equations 1–9, Table 1). These have *also* been used for modeling by earlier workers (Ravindranath and Mashelkar, 1984, Laubriet et al., 1991), but without them using any industrial data to tune the model parameters. Indeed, we have had to tune some of the rate constants of the main reactions (and have found their values to lie within the *ranges* suggested in the literature, but different than those used by the groups of Mashelkar and Choi). The concentrations of several of the other by-products are extremely low under conditions of interest and therefore, in all engineering applications and for *computational ease,* one has usually ignored them. For example, cyclic oligomers have been ignored by Ravindranath and Mashelkar, (1986a) and Laubriet et al., (1991). The steady-state model equations are quite similar to those presented by Laubriet et al. (1991) and the complete set is summarized in Table 2. It is assumed that the flow of the liquid down the reactor is plug-flow and that the vapor phase is well mixed. Also, it is assumed that there is no mass transfer resistance in the vapor

Table 1. Kinetic Scheme and Model Equations



(*continued*)

Table 1. Continued

Kinetic parameters (Laubriet et al. 1991; Saint Martin and Choi, 1991)([Sb2O3] = 0.04 wt%)+

Reaction No., i	Type of reaction	Rate constant $k_i = k_{io} \exp(-E_i/RT)$ k_{io} ($m^3\ mol^{-1}$)	 E_i ($Jmol^{-1}$)	Equilibrium constant
1	Reversible	1.09×10^3	4418	6.1835
2	Irreversible	$4.7674 \times 10^{7*}$	7117	
3	Irreversible	1.09×10^3	4418	
4	Irreversible	8.32×10^4	7117	
5	Reversible	1.09×10^3	4418	$5.143\ 10^{-2}$
6	Irreversible	8.32×10^4	7117	
7	Reversible	2.08×10^3	4203	2.5
8	Reversible	2.08×10^3	4203	11.87
9	Irreversible	$0.2215 \times 10^{9+}$	9208	

+Values of K_1, K_5, K_8, k_{2o}, and k_{9o} are those obtained in the present study, and differ from those in Refs of Laubriet et al., 1991; Saint Martin and Choi, 1991. *min^{-1}

Table 2. Complete Set of Model Equations Used in This Study

Balance equations for the liquid phase (Laubriet et al. 1991)

$$\frac{1}{\theta}\frac{d[E_g]}{dz} = [-2R_1 - R_2 - R_3 - R_4 - R_5 - 2R_6 - R_7 - R_8]$$

$$\frac{1}{\theta}\frac{d[E_a]}{dz} = [R_2 + R_4 + R_6 + R_7 + R_8 + R_9]$$

$$\frac{1}{\theta}\frac{d[Z]}{dz} = [R_1 + R_3 + R_5 + R_8 + R_9]$$

$$\frac{1}{\theta}\frac{d[E_v]}{dz} = [-R_3 + R_9]$$

$$\frac{1}{\theta}\frac{d[E_{DEG}]}{dz} = [-R_5 + R_6]$$

$$\frac{1}{\theta}\frac{d[EG]}{dz} = R_1 - R_4 - R_7 - k_l a([EG] - [EG^*])$$

$$\frac{1}{\theta}\frac{d[W]}{dz} = R_7 + R_8 - k_l a([W] - [W^*])$$

$$\frac{1}{\theta}\frac{d[DEG]}{dz} = R_4 + R_5 - k_l a([DEG] - [DEG^*])$$

where:

$R_1 = k_1[E_g]^2 - 4k'_1\,[Z][EG]$
$R_2 = k_2[E_g]$

(continued)

Table 2. Continued

$R_3 = k_3[E_v][E_g]$
$R_4 = 2k_4[E_g][EG]$
$R_5 = k_5[E_g][E_{DEG}] - 4k'_5[Z][DEG]$
$R_6 = k_6[E_g]^2$
$R_7 = 2k_7[E_a][EG] - k'_7[E_g][W]$
$R_8 = k_8[E_g][E_a]2k'_8[Z][W]$
$R_9 = k_9[Z]$

Vapor-liquid equilibrium correlations:

$$c_j^* = \left(\frac{c_{poly}}{1 - \sum_j x_j^*}\right) x_j^*; \; + \; c_j^*[EG^*], [W^*], [DEG^*]$$

$$C_{poly} = \frac{[E_g] + [E_a] + [E_v] + [E_{DEG}]}{2}$$

$$x_j^* = \frac{Py_j}{p_y^o \gamma_j}; \; j = EG, W, DEG$$

$$\ln P_{EG}^o = 49.703\,(8576.7/T) - 4.042 \ln T$$

$$\ln P_W^o = 18.568 - \frac{4047.606}{T - 33.33}$$

$$\ln P_{DEG}^o = 17.0326 - \frac{4122.52}{T} - 122.5$$

$$y_j = \frac{\int_0^1 k_l a(C_j - C_j^*)dz}{\sum_j \int_0^1 k_l a(C_j - C_j^*)dz + \int_0^1 (k_2[E_g] + k_3[E_v][E_g])dz} \; j = EG, W, DEG$$

$$\gamma_j = \frac{1}{m_j} exp\left(1 - \frac{1}{m_j} + \chi_1\right); j = EG, W, DEG$$

$$m_j = \frac{V_p \, \rho_j}{M_j}; j = EG, W, DEG$$

$$U_v = \sum_j \frac{M_j C_j}{\rho_j}; j = EG, W, DEG$$

$$V_p = \frac{1 - U_v}{C_{poly}}$$

$$x_1 = a_o + b_o \left(\frac{1 - U_v}{U_v^o}\right)$$

$$k_l a = k_l a_{ref} \left(\frac{N}{N_{ref}}\right)^a$$

$$DP = \left(\frac{([E_g] + [E_a] + [E_v] + [E_{DEG}] + 2[Z])_{feed}}{[E_g] + [E_a] + [E_v] + [E_{DEG}]}\right)$$

phase. Flory-Huggins' theory (Flory, 1953) is used to describe the activity coefficients of the volatile species, EG, W and DEG. Acetaldehyde is assumed to vaporize as soon as it is produced in the liquid phase. Most of the details of the model development are available in the literature (Laubriet et al., 1991) and are not repeated here. However, we have had to make a few modifications in the model in order to obtain meaningful results for the industrial reactor. These are

1. A linear relationship was assumed between the Flory-Huggins' interaction parameter, χ_I, and the volume fraction of the polymer in the melt phase

   $$\chi_I = a_o + b_o\,[1 - (U_v/U_v^o)] \tag{1}$$

   where a_o and b_o are (curve-fit) constants and U_v and U_v^o are the volume fractions of the low molecular weight (volatile) components at any axial location and at the feed end of the third-stage reactor, respectively.
2. The acetaldehyde formed in the melt phase is assumed to go into the vapor phase instantaneously. The assumption that acetaldehyde is instantly removed as soon as it is formed is valid because of the fact that the vapor pressure of acetaldehyde is very high at polycondensation temperatures. The rate at which acetaldehyde is produced by chemical reaction in the entire reactor is given by

   $$\text{Rate of vaporization of A} = \int_0^1 (k_2[E_g] + k_3[E_v][E_g])dz \tag{2}$$

These modifications are incorporated in Table 2 and their effects are discussed in the Results and Discussion section.

The model equations for the reactor are a set of ordinary differential equations (ODEs) as given in Table 2. These are to be integrated using appropriate values of the feed conditions, given in Table 3. The concentration of the acid and DEG end groups in the feed, as used in this study, are in close agreement with the values given by David and Lawrence (1995). The IMSL subroutine, DIVPAG, was used to solve these equations. The subroutine uses Gear's algorithm (Gupta, 1998) with a tolerance of 10^{-8}. An iterative solution is necessary because the liquid and vapor phases have different kinds of flow (plug and well mixed). Values for the average mole fractions of the volatile species in the vapor phase, y_j, are assumed (see Table 4 for the starting guess values) and then the ODE's are integrated from the dimensionless value of $z = 0$ (feed end) to $z = 1$ (product end). The vapor phase values of y_j are then re-evaluated and used as the guess values for the next iteration. This method of successive substitutions (Picard iteration) (Gupta, 1998) is continued till the sum of the squares of the y_j does not change between two successive iterations by more than 1×10^{-12}. Typically, convergence is achieved in one iteration, if we use the guess values given in Table 4. The pro-

Table 3. Feed Conditions and Reactor Operating Conditions

Feed concentrations ($kmol/m^3$) and densities (kg/m^3) of pure liquid components	
$[E_g]_f = 4.0 \times 10^{-1}$	$[E_{DEG}]_f = 0.17$
$[E_a]_f = 2.57 \times 10^{-3}$	$[EG]_f = 6.5 \times 10^{-3}$
$[Z]_f = 11.2$	$[W]_f = 4.6 \times 10^{-4}$
$[Ev]_f = 1.17 \times 10^{-3}$	$[DEG]_f = 4.0\ 10^{-4}$
$\rho EG = 1108$; ρw 1000; ρ_{DEG} 118	
Reactor operating and final conditions (reference values used wherever not specified):	
***Set 1:* (*Reference Values*)**	
P = 2.0 mm Hg	***Set 2:***
T = 566 K	T = 567 K
θ† = ***	***Set 3:***
N† = ***	P = 1.5 mm Hg
$[Sb_2O_3] = 0.04$ wt%	***Set 4:***
$DP_f = 40$	$N = N_{ref}$ 0.1 rpm

† Values not provided for proprietary reasons

gram was run on a Cray J916 super computer on a UNICOS platform. The CPU time required for one converged run is 0.05s. Convergence was also attained though in more iterations when other guess values were used, but the values in Table 4 are used to save computer time during the 'tuning' process. The model provides values of DP and the concentrations of the hydroxyl end groups (E_g), acid end groups (E_a), di-ester end groups (Z), vinyl end groups (E_v), DEG end groups (E_{DEG}), ethylene glycol (EG), water (W) and di-ethylene glycol (DEG), as a function of the axial position in the reactor after convergence is achieved.

The program was checked for several conditions to ensure that it was error-free. Simulations were carried out for the input conditions and parameters used by Laubriet et al. (1991) and the results were found to be identical to those reported by these workers. Also, the model equations were solved manually using Euler's (Gupta, 1998) method for a few iterations. The results thus obtained matched well with the values provided by the computer code.

Having obtained a working computer code for the third stage PET reactor, we now turn our attention to the main aim of the present study, viz., to make the model suitable for simulating the available industrial data. The industrial data for DP was available in 'chart units' (related to the melt viscosity of the polymer). These data were converted from chart units to DP using a calibration chart. The details of the calibration chart are proprietary and are not provided here. Four sets of industrial data were available to us:

Set 1. For one known set of operating conditions (pressure, temperature, residence time, speed of the agitator, catalyst concentration), referred

Table 4. Parameter Values Used In This Study

Initial guess values used for y_j:

$Y_{EG} = 0.90 \quad y_w = 0.05 \quad y_{DEG} = 0.04$

Bounds and final turned values for the decision variables:

Bounds	Tuned values
$1.0 < k_L a_{ref} < 10.0$	2.6875
$0.5 < a_o < 2.0$	1.0378
$2.0 < b_o < 6.0$	2.1838
$0.5 < K_1 < 10.0$	6.1835
$0.001 < K_5 < 1.0$	5.1430×10^{-2}
$2.0 < K_8 < 40.0$	11.870
$1.664 \times 10^7 < k_{2o} < 8.32 \times 10^7$	4.7674×10^7
$7.2 \times 10^9 < k_{9o} < 7.2 \times 10^9$	0.2215×10^9
$0.02 < \alpha < 5.0$	2.6647

Weight factors used in eqs. 3, 4 and 6:

$w_{11} = w_{13} = w_{14} = 10^5;\ w_{21} = w_{31} = 10^3$

Industrial and predicted values at the outlet end for the 4 sets:

Set #	Product property	Industrial value	Model predicted value	Model predicted value
			$\alpha = 2.6647$	$\alpha = 0.5$
1	DP	82.00	82.00	82.09
	$[E_{DEG}]$, kmol/m^3	0.17	0.1692	0.1691
	$[E_a]$, kmol/m^3	1.038×10^{-3}	1.038×10^{-3}	1.036×10^{-3}
2	DP	82.60	82.56	82.54
3	DP	82.70	82.69	82.68
4	DP	82.30	82.30	82.06

to as the reference case, several product properties {DP, DEG concentration (both as [DEG] and $[E_{DEG}]$) and $[E_a]$} were available. These are given in Tables 3 and 4 (except a few values indicated by ***, which are not being provided in order to ensure confidentiality of proprietary information). These represent standard (non-pathological) operation of the industrial third stage reactor studied here.

Set 2. The DP of the polymer product was available for the case when the temperature was 1°C higher than the reference case. All other operating conditions were at their reference values.

Set 3. The DP of the polymer product was available when the pressure in the reactor was 0.5 mm Hg lower than the reference value. All other operating conditions were at their reference values.

Set 4. The DP of the polymer product was available when the agitator speed was 0.1 rpm higher than the reference value. Again, all other operating conditions were at their reference values.

At this point, it is to be emphasized that we have adapted the model of Laubriet, Choi and co-workers (1991), and have used the (small amount of) *industrial* data available to us, under a few different operating conditions (some normal, some *slightly* pathological, which had to be corrected by changing the operating conditions) from an industrial, wiped film reactor producing PET of $DP_{out} = 82$. The variation of the product properties is studied in the range in which the kinetic model is tested to be *really* trustworthy (as extrapolation of a model for a complex process could be a little dangerous).

In order to obtain best-fit (tuned) values of the parameters in the model, an error function, I, is defined. This comprised of a sum of square errors between the model predicted and industrial values:

$$I(\underline{u}) = \sum_{i,j} w_{ij} \left[1 - \frac{S_{ij,m}}{S_{ij,ind}} \right]^2 \tag{3}$$

where S_{ij} is the value of the ith property at the output (or product) end for set no. j, the subscripts, m and ind, represent values predicted by the model (for any set of parameters, $\mathbf{u}$) and the industrial values, respectively, and w_{ij} are the weight factors indicating the emphasis to be accorded any error of the ith property of set no. j. The method of Nelder and Mead (Nelder and Mead, 1965) was used to obtain the values of the model parameters which minimize the error, I. The IMSL subroutine DBCPOL (polytope method) with a tolerance of 1×10^{-5} was used. This subroutine uses the complex direct search algorithm based on comparing the objective function values. Several sets of parameters were tried in this study till a reasonable tuning of the model was accomplished. These are described in the next section.

RESULTS AND DISCUSSION

The model of Laubriet et al. (1991) (without the two modifications described earlier) was tested for the reference case. The same (constant) value of χ_1 was used for all the three vaporizing species, EG, W and DEG. Similarly, a single value of k_La was used for all the three volatile species. The values suggested by Laubriet et al. (1991) ($\chi_1 = 0.5$, $k_La = 3$ min^{-1}) were used in the simulation program for the input conditions of the industrial reactor being studied. It was found that the model underestimated the DP and the DEG end group concentration and over-estimated the acid end group concentration at the product end. The unmodified model was, thus, found to be unsuccessful in predicting the industrial values.

A review of the literature showed that there exists a discrepancy in the values of the Flory-Huggins' interaction parameter, χ_1, used in the models for the finishing reactor for PET production. Ravindranath and Mashelkar (1982, 1984) have used a value of 0.5 in their studies. Saint Martin and Choi (1991), on the other hand, have studied the effect of χ_1 on the DP of the product. They have calculated the value of χ_1 using the solubility parameter data provided by Brandrup and Immergut (1989). The calculated value of χ_1 of 1.3 was used in their subsequent research studies (Cheong and Choi, 1995, 1996). The value of χ_1 is very important, since the overall rate of the removal of EG is a strong function of the interfacial concentration of EG, which, in turn, is a function of χ_1. Larger values of χ_1 favor the vaporization of ethylene glycol. This leads to higher values of DP. It is also well established that χ_1 is a strong function of the volume fraction of the polymer, $(1 - U_v)$, particularly at higher values of the latter, and the values go far beyond the dilute (poor) solution values of 0.5 assumed by Ravindranath and Mashelkar (1984) and Laubriet et al. (1991). Plots of χ_1 *vs.* volume fraction of the polymer for some of the polymer systems indicate that χ_1 increases extremely rapidly as the volume fraction of the polymer increases (Flory, 1953; Seymour and Carraher, 1981). Since the volume fraction of the polymer is quite high in the finishing PET reactor (approximately above 0.99) we decided to use a linear dependence of χ_1 on U_v in our model (see Eq. 1). Also, in view of the uncertainty in the value of χ_1 and non-availability of the experimental values of χ_1 for PET, we decided to treat the constants, a_o and b_o, in Eq. 1 as curve-fit parameters, using industrial data.

The estimation of k_La_{ref} (= k_La used for sets 1, 2 and 3) is, similarly, not too well documented in the open literature even though the value used by a few workers (Ravindranath and Mashelkar, 1982; Rafler et al., 1987) is in the order of 0.01 sec^{-1} at high conversions of PET polymerization. Since k_La_{ref} depends on the exact geometry of the finishing reactor, it has to be obtained by curve fitting industrial data.

The reference set 1 was first used for curve-fitting these three parameters (a_o, b_o, k_La_{ref}), using values of the rate constants as given by Laubriet et al. (1991). The objective function used was

$$I = w_{11}\left(1 - \frac{DP_{1,m}}{82.00}\right)^2 + w_{21}\left(1 - \frac{[E_{DEG}]_{1,m}}{0.17}\right)^2 + w_{31}\left(1 - \frac{[E_a]_{1,m}}{1.038 \times 10^{-3}}\right)^2 \tag{4}$$

The parameters, a_o, b_o and k_La_{ref}, were tuned for set 1 by minimizing I. It was found that product property specifications of the polymer could not be met, i.e., the industrial data for the reactor being studied here could not be explained by the model, even after using a linear dependence of χ_1 on the volume fraction of the polymer, as well as k_La_{ref}, and treating these as curve-fit parameters. This indicated that at least some of the other model parameters need to be re-tuned.

A thorough search of the literature was made at this stage. It was found that some controversy does, indeed, exist in the values of the rate constants used by various workers. Experimental studies by several workers (Koepp and Werner, 1959; Challa, 1960; Fontana, 1968; Hovenkamp and Munting, 1970; Chelgoya et al., 1979; Reimschussel and Debona, 1979) indicate that the value of the equilibrium constant for the polycondensation reaction is in the range of 0.4 – 1.0. However, Fontana (1968) has observed that the equilibrium constant is close to 0.5. For model calculations, the earlier studies (Gupta, 1983, Ravindranath and Mashelkar, 1986) estimated the kinetic and mass transfer data by curve fitting industrial or pilot plant data. Laubriet et al. (1991) have used the same order of magnitude values in their work. Unfortunately, these values could not explain the industrial data available to us. The experimental value of $[E_{DEG}]$ for our industrial reactor was almost independent of the axial position while in earlier studies, a drastic decrease in $[E_{DEG}]$ was exhibited down the length of the reactor. Also, the concentration of the acid end group in the industrial reactor being studied here decreased and reached a very low value in the product. In contrast, the values predicted in the earlier studies (Ravindranath and Mashelkar, 1984 and Laubriet et al., 1991) were quite high in comparison with the specifications of the product for our system. Therefore, it was considered necessary to re-tune the kinetic parameters of the model.

Several simulations were performed to study the effect of the several rate and equilibrium constants used in this work, individually. The equilibrium constants, K_1, K_5 and K_8, and the frequency factors (k_{2o} and k_{9o}) of the rate constants, k_2 and k_9, were found to affect $[E_{DEG}]$ and $[E_a]$ of the product most significantly. A tuning of these parameters was carried out using three of the four sets of data (reference set, sets 3 and 4) on the industrial reactor studied herein. The reason why set 1 is used is because it provides information on several commercially important product properties. Set 3 is selected because pressure is the most important operating and control variable in the industrial reactor. Set 4 is the only information available which accounts for the change of k_La with the rotational speed, N, of the agitator. The following equation is used to relate k_La to the speed of the agitator, N, provided the volume of the melt remains unchanged:

$$k_La = k_La_{ref}\,(N/N_{ref})^{\alpha} \tag{5}$$

where the subscript, ref, refers to the value of k_La at the reference conditions (set 1). The value of α used in some earlier studies is in the range of 0.33 to 0.5. Higbie's penetration theory gives $\alpha = 0.5$. This theory is based on mass transfer in the absence of chemical reaction. But in the present case, the value of α is expected to be higher as the kinetic effects are coupled with mass transfer. The value of α is also obtained by curve-fitting industrial data in this work, since use of α = 0.33–0.5 did not give good results.

The objective function used finally is, thus, given by

$$I = w_{II}\left(1 - \frac{DP_{1,m}}{82.00}\right)^2 + w_{21}\left(1 - \frac{[E_{DEG}]_{1,m}}{0.17}\right)^2 + w_{31}\left(1 - \frac{[E_a]_{1,m}}{1.038 \times 10^{-3}}\right)^2 + w_{13}\left(1 - \frac{DP_{3,m}}{82.70}\right)^2 + w_{14}\left(1 - \frac{DP_{4,m}}{82.30}\right)^2 \tag{6}$$

The parameters to be tuned are k_La_{ref}, a_0, b_0, K_1, K_5, K_8, k_{2o}, k_{9o} and α. Table 4 lists the upper and lower bounds as well as the final tuned values (using sets 1, 3 and 4) of these parameters. A similar tuning of rate constants as well as a few other parameters have been reported by Zabisky et al. (1992), for an industrial LDPE reactor. The weight factors were chosen by trial and error, to achieve the best curve-fit. The values of the weight factors used are also given in Table 4. The FORTRAN 90 program was run on an SGI Origin2000 computer.

The parameters so obtained could explain the three sets of industrial results (sets 1, 3 and 4) used for tuning, very well. These are then used *without change*, to *predict* the effect of a change in temperature (set 2). Very good agreement of the value of DP of the product for this case was obtained (see Fig. 1 and Table 4). The fact that the parameters were obtained using three sets of industrial data, and then the model predicted another set of industrial data well, *without re-tuning of these parameters*, indicates that the model accounts for all the physico-chemical phenomena actually present in the industrial reactor quite well.

Fig. 1 shows the fit of the predicted values of the DP of the polymer product, with industrial values. Also indicated are the values of DP of the product when α is fixed at 0.5. The values of k_La_{ref} are in the range used by earlier workers, even though the value of α is fairly high. Fig. 1 shows that the values of DP of the product obtained, when α is fixed at 0.5 do not agree too well with industrial values, even though a curve-fit has been performed. Fig. 2 shows how the error, I, changes with the iteration number during the tuning process. The error is seen to decrease to an asymptotic value in 1961 iterations. The CPU time required for convergence is 0.860s. It may be added that the initial guess values for y_j for each simulation in the tuning operation are taken to be the same as given in Table 4.

A sensitivity analysis is now performed by varying one parameter at a time with other parameters fixed at their reference values (given in Table 4). Such a study gives an intuitive feel of the reactor behavior, information that is useful in studies involving reactor optimization and control. The effect of temperature is

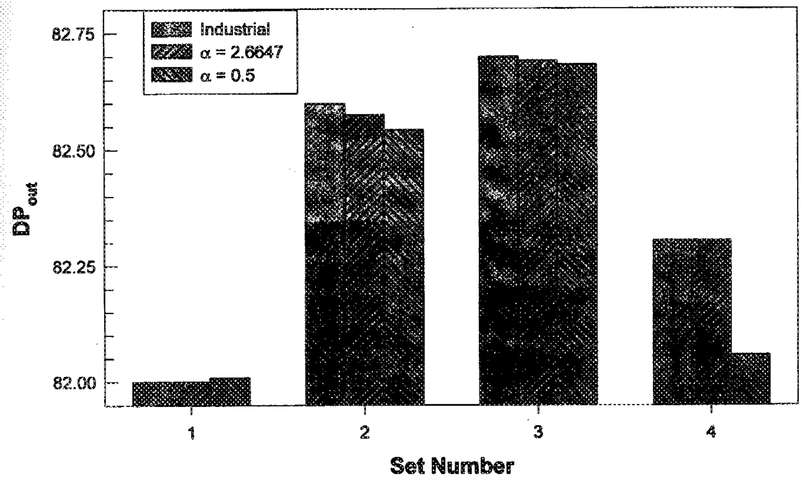


Figure 1. Prediction of industrial values of DP of the product with model values using the best-fit value of α of 2.6647 as well as for α = 0.5.

considered first. The concentration profiles of the side products and the variation of DP along the axial position, z, of the finishing reactor for three different temperatures (564 K, 566 K and 569 K) are presented in Figs. 3-10. Fig. 3 shows the effect of the reactor temperature on the DP of the polymer. It is observed that as the temperature goes up from 564 to 569 K, the value of the DP of the product

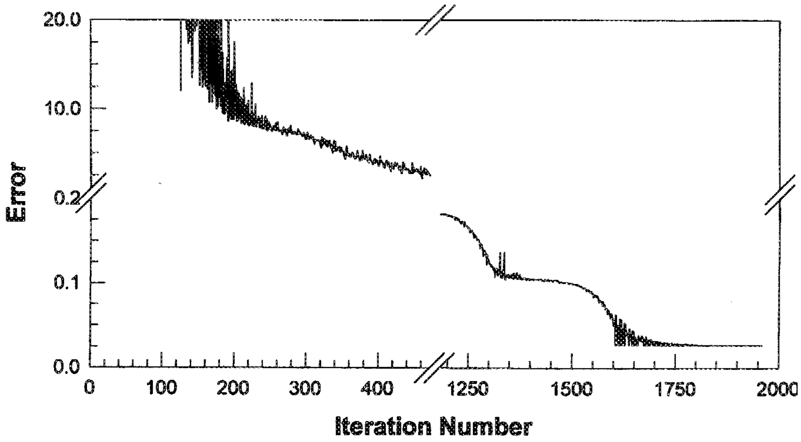


Figure 2. Plot of error, I *vs.* iteration number for the tuning of sets 1, 3 and 4.

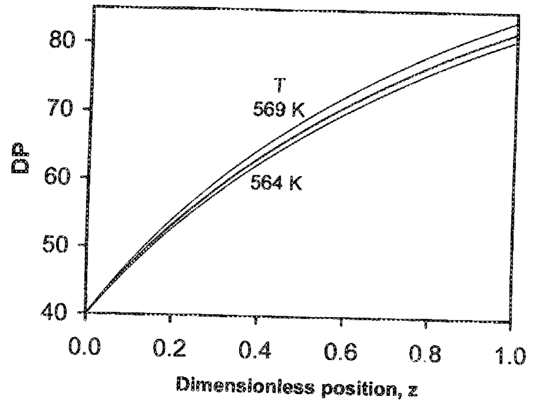


Figure 3. Effect of temperature on the DP of the polymer as a function of the dimensionless axial position in the reactor, z. The unmarked curve represents the variation of DP *vs.* z at the reference temperature of 566 K.

increases from 80.90 to 83.65. This is the combined effect of temperature on the rate constants, as well as on the equilibrium interfacial concentration, C_j^* (through P_j^o), of the volatile species. It is assumed that χ_1 as well as k_La_{ref} are not much influenced by such a change in temperature. The DP of the polymer increases primarily because of the faster rate of the main (No. 1) reaction in Table 1 at higher

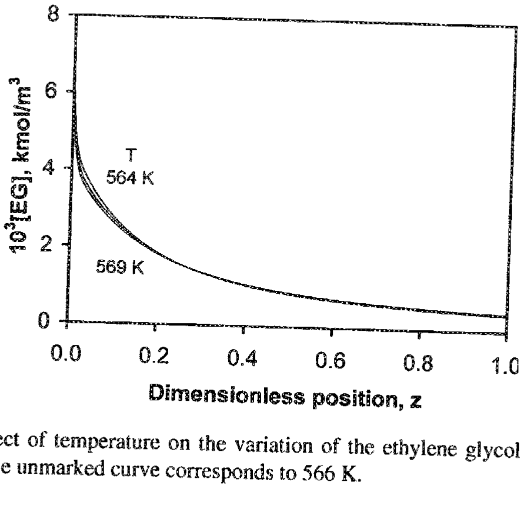


Figure 4. Effect of temperature on the variation of the ethylene glycol concentration, [EG], with z. The unmarked curve corresponds to 566 K.

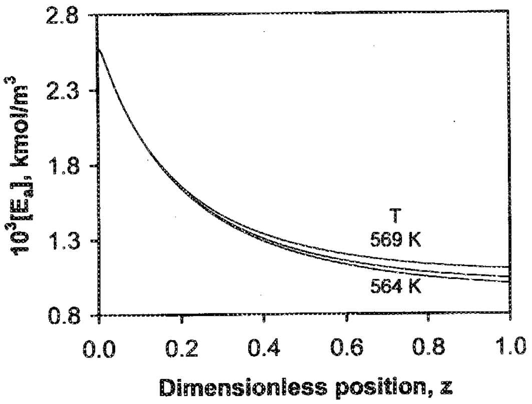


Figure 5. Effect of temperature on the variation of the acid end group concentration, $[E_a]$, with z. The unmarked curve corresponds to 566 K.

temperatures, which leads, simultaneously, to a faster rate of vaporization of EG, the concentration of which is lower in the melt (Fig. 4). The degradation reaction (No. 9, Table 1) is found to be strongly influenced by temperature. Both the acid end group concentration, $[E_a]$, as well as the vinyl end group concentration, $[E_v]$, increase with an increase in the temperature (see Figs. 5 and 6). These effects agree well with observations made in industry. The vinyl end groups lead to the

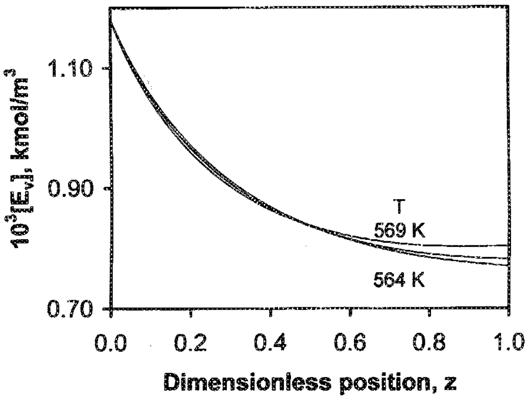


Figure 6. Effect of temperature on the variation of the vinyl end group concentration, $[E_v]$, with z. The unmarked curve corresponds to 566 K.

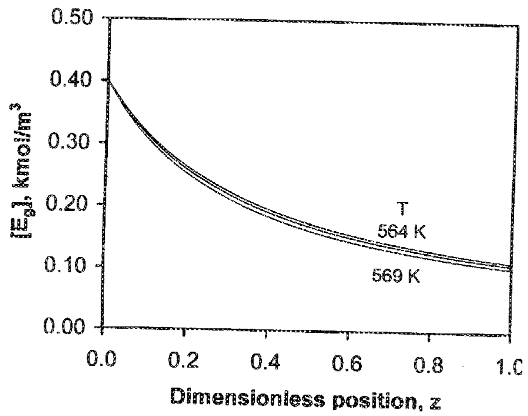


Figure 7. Effect of temperature on the variation of the hydroxyl end group concentration, $[E_g]$, with z. The unmarked curve corresponds to 566 K.

formation of anhydrides and network structures, and so need to be kept low. Figs. 7-9 show that $[E_g]$ and the concentrations of the other vaporizing species, [W] and [DEG], decrease with increasing temperature. $[E_g]$ decreases because the rate of the main reaction (No. 1) increases. The concentrations of [W] and [DEG] are lower at higher temperatures because of higher rates of vaporization, as was the case with EG. Lower operating temperatures are preferred in industrial operations to avoid high concentrations of $[E_a]$, which is known to affect the hydrolytic

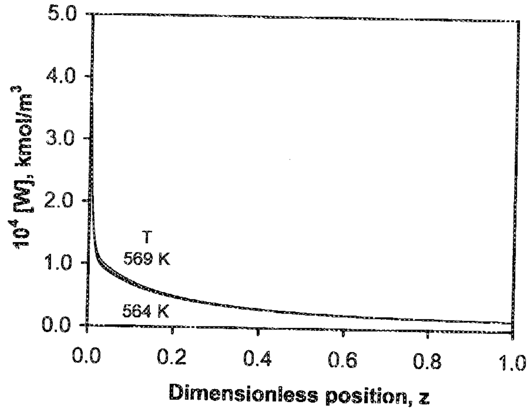


Figure 8. Effect of temperature on the variation of the water concentration, [W], with z. The unmarked curve corresponds to 566 K.

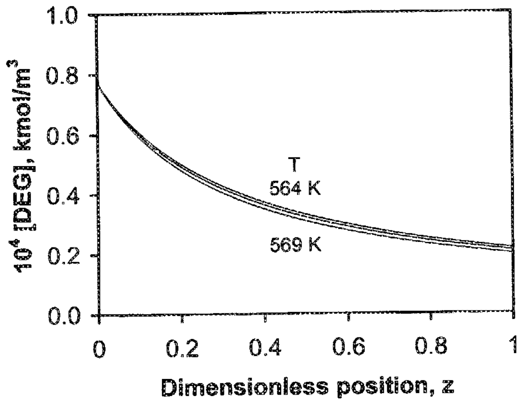


Figure 9. Effect of temperature on the variation of the DEG concentration, [DEG], with z. The unmarked curve corresponds to 566 K.

stability of the polymer product. High concentrations of [E_a] lead to problems during the spinning and drawing stages in fiber manufacture due to the use of moist air and water in these operations. Lower temperatures also favor lower values of [E_v]. Fig. 10 shows that increasing temperature leads to higher concentrations of E_{DEG} at the outlet of the reactor. This is in contrast to the trend observed for the concentration of the volatile species, DEG, the concentration of which is

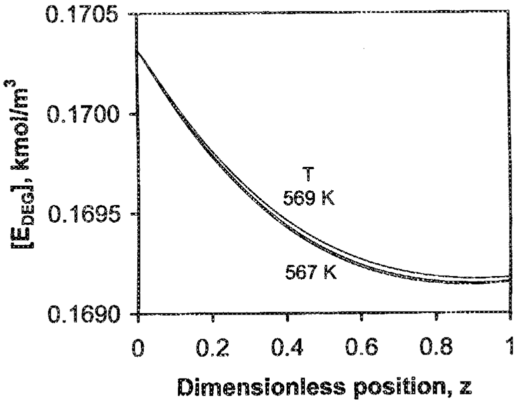


Figure 10. Effect of temperature on the variation of the DEG end groups concentration, [E_{DEG}, with z. The unmarked curve corresponds to 566 K.

far lower due to its vaporization. The increase of $[E_{DEG}]$ with increasing temperatures is, indeed, observed for the industrial reactor being studied, and is opposite to the effect observed by Laubriet et al. (1991). The concentration of E_{DEG} in the final polymer determines its degree of crystallinity and hence its dyeability, and it is important to have a model which predicts the right trends.

Fig. 11 shows plots of the rate of vaporization of the four volatile species per unit dimensionless length, per unit volume of melt, as a function of z. The area under any curve between z and z + dz gives the rate (mol/min) of any species, j, vaporizing per unit total volume (A_1L) of the melt in the reactor in this distance. Thus, the total area under any curve in Fig. 11 gives the total rate of vaporization in the entire reactor, divided by the volume of the melt. It is clear that EG vaporizes the most, as expected and the vaporization of EG is dominant in the early part of the reactor. It must be emphasized that the DEG concentrations in the liquid and vapor phases are not too different and one must be careful to ensure that the concentration of DEG in the vapor phase is lower than [DEG*] in order to have vaporization at all axial locations.

Table 5 summarizes the effects of varying the different operating conditions and parameters on the values of the concentrations of the various side products, as well as the DP at the outlet of the reactor. It is observed that the pressure in the reactor has a strong influence on the DP of the product. The DP of the polymer at the reactor outlet increases from about 82 to 84 as the pressure decreases from 2.0

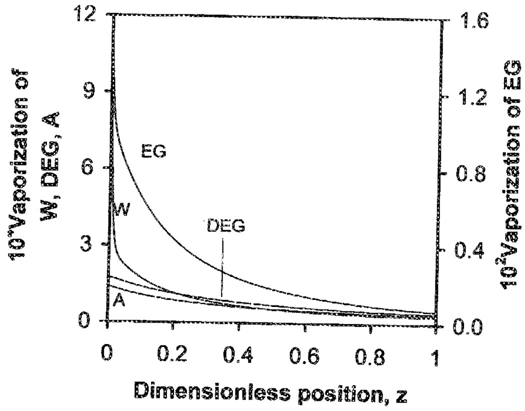


Figure 11. Plot of the rate of vaporization (per unit volume of melt, per unit z) of EG, W, DEG and A as a function of z. For EG, W and DEG, the ordinate is $k_La(Cj\text{-}Cj^*)$, while for A it is $k_2[E_g] + k_3[E_v][E_g]$. Reference condition (set 1) is used. The total vaporization rates (mol/m^3 melt-min) over the entire reactor (area under the curves) are EG: 2.735×10^{-3}, W: 8.281×10^{-5}, DEG: 8.104×10^{-5} and A: 6.360×10^{-5}.

Table 5. Sensitivity Analysis

		Concentration of various species at the reactor outlet in kmol/m^3							
Parameter	value	$[E_g]_{out}$	$10^3[E_a]_{out}$	$10^4[E_v]_{out}$	$[E_{DEG}]_{out}$	$10^4[EG]_{out}$	$10^5[W]out$	$10^5[DEG]_{out}$	DP_{out}
Temperature, K	564	0.1131	1.0025	7.7010	0.1691	4.6150	1.4562	2.1681	80.89
	566	0.1091	1.0380	7.8117	0.1692	4.4660	1.4915	2.0923	82.00
	569	0.1036	1.0991	8.0342	0.1693	4.2550	1.5539	1.9842	83.65
P, mm Hg	0.50	0.1048	1.0042	7.8908	0.1668	3.0453	1.1468	1.9240	84.06
	1.00	0.1062	1.0154	7.8647	0.1675	3.5106	1.2597	1.9791	83.38
	1.50	0.1077	1.0267	7.8384	0.1683	3.9841	1.3746	2.0351	82.69
	2.00	0.1091	1.0380	7.8117	0.1692	4.4660	1.4915	2.0923	82.00
θ/θ_{ref}	0.92	0.1152	1.0498	7.8302	0.1692	4.8033	1.5707	2.2039	80.29
	0.96	0.1121	1.0435	7.8190	0.1692	4.6274	1.5295	2.1464	81.17
	1.00	0.1091	1.0380	7.8117	0.1692	4.4660	1.4915	2.0923	82.00
	1.04	0.1064	1.0332	7.8080	0.1692	4.3180	1.4565	2.0413	82.82
$10^2[Sb_2O_3]$, wt%	3.00	0.1276	1.0049	8.7019	0.1687	4.7587	1.6426	2.4252	77.04
	3.50	0.1174	1.0215	8.2288	0.1690	4.6062	1.5582	2.2415	79.72
	4.00	0.1091	1.0380	7.8117	0.1692	4.4660	1.4915	2.0923	82.00
	4.25	0.1056	1.0462	7.6024	0.1693	4.4011	1.4632	2.0278	83.03
$a_o/a_{o,ref}$	0.90	0.1090	10400	7.8100	0.1690	4.4800	1.5000	2.1000	82.00
	1.00	0.1091	1.0380	7.8117	0.1692	4.4660	1.4915	2.0923	82.00
	1.05	0.1091	1.0377	7.8129	0.1691	4.4585	1.4896	2.0909	82.03
	1.25	0.1090	1.0400	7.8200	0.1690	4.4300	1.4800	2.0900	82.10
$b_o/b_{o,ref}$	1.00	0.1091	1.0380	7.8117	0.1692	4.4660	1.4915	2.0923	82.00
	1.05	0.1086	1.0338	7.8205	0.1689	4.2798	1.4464	2.0711	82.25
	1.15	0.1077	1.0265	7.8359	0.1684	3.9600	1.3691	2.0347	82.68
	1.25	0.1070	1.0200	7.8500	0.1680	3.7000	1.3100	2.0000	83.00
k_1a_{ref}, min^{-1}	2.00	0.1139	1.1051	7.6692	0.1697	5.5071	1.9371	2.1894	80.47
	2.50	0.1102	1.0526	7.7796	0.1693	4.6882	1.5856	2.1139	81.66
	2.69	0.1091	1.0380	7.8117	0.1692	4.4660	1.4915	2.0923	82.00
K_1	4.0	0.1183	1.0210	7.5692	0.1689	4.5326	1.5664	2.2590	79.49
	5.0	0.1132	1.0301	7.7027	0.1691	4.4960	1.5246	2.1661	80.88
	6.2	0.1091	1.0380	7.8117	0.1692	4.4660	1.4915	2.0923	82.00
	7.0	0.1070	1.0400	7.8700	0.1692	4.4500	1.4700	2.0600	82.60
K_5	0.05	0.1091	1.0380	7.8117	0.1692	4.4660	1.4915	2.0923	82.00
	0.06	0.1089	1.0385	7.8178	0.1683	4.4528	1.4895	2.4087	82.33
	0.07	0.1090	1.0400	7.8200	0.1670	4.4400	1.4900	2.7700	82.70
	0.10	0.1080	1.0400	7.8400	0.1650	4.3900	1.4800	3.7800	83.80
K_8	5.00	0.1092	1.4021	7.8088	0.1692	4.4683	1.4992	2.0931	81.89
	10.00	0.1090	1.0900	7.8100	0.1692	4.4700	1.4900	2.0900	82.00
	11.87	0.1090	1.0380	7.8117	0.1692	4.4660	1.4915	20923	82.00
	13.00	0.1090	1.0100	7.8100	0.1692	4.4700	1.4900	2.0900	82.00
10^7k_{2m}, min^{-1}	2.50	0.1100	0.7910	7.8000	0.1692	4.4900	1.2200	2.1000	82.00
	4.74	0.1091	1.0380	7.8117	0.1692	4.4660	1.4915	2.0923	82.00
	5.82	0.1090	1.1500	7.8200	0.1692	4.4500	1.6200	2.0900	82.00
	8.32	0.1085	1.4240	7.8257	0.1692	4.4283	1.9072	2.0793	82.10
10^9k_{9m},min^{-1}	0.22	0.1091	1.0380	7.8117	0.1692	4.4660	1.4915	2.0923	82.00
	0.36	0.1091	1.1295	9.3938	0.1692	4.4617	1.5911	2.0907	81.96
	0.72	0.1089	1.3676	13.5070	0.1692	4.4499	1.8496	2.0867	81.84
	1.44	0.1084	1.8449	21.7400	0.1692	4.4265	2.3645	2.0787	81.59

to 0.5 mm Hg. Decreasing pressures facilitate the removal of EG from the bulk melt phase and enhance the growth of the polymer chains. The concentration of DEG in the product decreases as the pressure is lowered. This effect is similar to what happens with increasing temperatures. The value of $[E_a]$ is not affected much by changing pressures, in sharp contrast to the behavior with increasing temperatures. The effect of decreasing pressure on $[E_V]$ in the product is, again, much less than the effect of temperature. It is clear that lower pressures are used to produce higher molecular weight polymer since they compensate the effects of lower temperatures that are required to keep the other product properties within prescribed limits. These trends would be useful in optimization studies in the future.

Table 5 shows that the DP of the final product increases as the residence time is increased. This is associated with a faster depletion of hydroxyl end groups. The other side product concentrations are not affected much by a change in the residence time. Again, one would like to minimize the residence time in any optimization study, while producing polymer having the same values of DP. It is clear that lower pressures and lower temperatures need to be used to minimize the residence time, thereby increasing the throughput.

Table 5 shows that while a_o, the value of χ_1 at the feed end of the reactor does not influence the DP of the product much, b_o does, indeed, have some effect. b_o is also seen to affect the value of $[E_{DEG}]$. Though the tuned values of a_o and b_o were able to predict the industrial results fairly well, the sensitivity of DP and $[E_{DEG}]$ to b_o suggests the importance of obtaining better correlations for χ_1.

An increase in k_La_{ref} leads to increasing DP values, while it decreases $[E_a]$, both being desirable objectives. The value of $[E_{DEG}]$ decreases with an increase in k_La_{ref}, which may not be desirable. An increase in k_La could be achieved by a better design of the agitator, an increase in the speed of the agitator, or by altering the level of the melt in the reactor. The first of these cannot be achieved except at the design stage. Lowering the level of the melt in the finisher simultaneously, leads to an increase in the residence time, which counteracts the advantages attained because of lower rates of production. The manipulation of the agitator speed, N, is, therefore, a more preferred control-action in industry, particularly if the reduction of pressure is not sufficient to achieve an objective. In fact, a modification of pressure and/or the speed of the agitator are most often used for negating the effects of unplanned disturbances affecting the DP of the product in actual reactor operations.

An increase in the catalyst concentration from 0.03 or 0.0425% leads to a significant increase in the DP of the product and a simultaneous significant reduction in the vinyl end group concentration, both desirable attributes. Indeed, changes in the catalyst concentration and temperature are used as the final recourse in industrial practice when changes in both pressure and the speed of the agitator are unable to negate the effect of disturbances on the DP of the polymer product. Unfortunately, the time lags associated with both these corrective control actions (catalyst concentration and temperature) are large, and this is why these actions are used only when the other means (pressure and the speed of the agitator) have failed.

The catalyst concentration also affects the color of the polymer produced. Barkley and Predmore (1970) and Chimaru et al. (1973) have suggested that the Sb^{3+} in the Sb_2O_3 catalyst gets reduced to metallic Sb^0 during the reaction. David and Lawrence (1995) have found experimentally that there is a non-linear dependence of the L-color (a measure of the luminosity or the whiteness) of the polymer on the concentration of Sb^0. In fact, increasing Sb_2O_3 concentrations leads to an undesirable greying of the polymer (lower L-color). Since our kinetic model does not incorporate this phenomenon, we should constrain the concentration of the catalyst so as to achieve a balance between the L-color and the two other properties of the polymer (DP and $[E_v]$) which are strongly influenced by the catalyst concentration.

Since several rate and equilibrium constants have been 'tuned' in this study to achieve a good fit, it is important to see the sensitivity of the results to these parameters. Table 5 shows that of the four equilibrium constants present in the reaction scheme, the DP of the polymer product is more significantly influenced by K_1 and K_5. An increase in K_5 also leads to a significant decrease in $[E_{DEG}]$. Indeed, K_5 was used as a tuning parameter in this study, primarily to achieve a better curve-fit of the industrial $[E_{DEG}]$ value. An increase in K_8 leads to a desirable lowering of the acid end group concentration. Table 5 also shows that increasing k_{2_0} leads to an increase of the acid end group concentration, while an increase in k_{9_0} results in a decrease of DP but a *substantial* increase in $[E_a]$, $[E_v]$ and $[W]$, which is highly undesirable. It is clear from this sensitivity study that one needs to get better estimates for the rate and equilibrium constants using experimental data under more ideal reaction conditions, rather than from industrial data where several additional physical phenomena are present. It may be added that tuning of the rate and equilibrium constants to explain *industrial* data has been used for other polymerization systems as well, e.g., LDPE (Zabisky et al., 1992) and nylon 6 (Wajge et al., 1994).

CONCLUSIONS

An improved model for the finishing reactor in PET manufacture is developed. Optimal values of the parameters of the model are estimated using industrial data available with us. Data involving commercially important product properties like DP and the concentrations of the DEG and acid end groups have been used.

The parameters tuned are k_La_{ref}, the Flory-Huggins' interaction parameter, χ_1, the equilibrium constants, K_1, K_5 and K_8, the frequency factors of two-rate constants, k_2 and k_9, and α, a parameter associated with the effect of the rpm of the agitator on k_La. These parameters are tuned using three sets of industrial data. The tuned parameters are then used unchanged to predict the concentration of the various side products and the DP for a different operating temperature. It is found that the model predicts these values very well. A sensitivity analysis is then performed using the tuned values of the model parameters, and the effect of several operating variables as well as parameters on the important physical properties is studied. Conflicting trends are observed from the model and insights developed can now be used to formulate and obtain meaningful solutions to problems on the optimization as well as control of this industrial reactor. This study brings out the importance of having accurate kinetic data, as well as of values of χ_1 and k_La.

NOMENCLATURE

A	Acetaldehyde
a	Specific interfacial area per unit volume of the melt, m^{-1}
A_1	Cross-sectional area of the melt in the reactor, m^2
a_o, b_o	Parameters in the equation describing χ_1
C_j	Concentration of the volatile species, j, in the melt (= [j]), $kmol/m^3$
C_j^*	Equilibrium concentration of the volatile species, j, in the melt at the interface, $kmol/m^3$
C_{poly}	Total concentration of the polymeric species in the melt and at the interface, $kmol/m^3$
DEG	Di-ethylene glycol
DP	Degree of polymerization or the number average chain length of the polymer
E_a	Acid end groups
E_{DEG}	DEG end groups (excluding those on pure DEG)
E_g	Hydroxyl end groups (excluding those on pure EG)
EG	Ethylene glycol
E_v	Vinyl end groups
k_1 to k_9	Forward reaction rate constants for eqs. 1–9 in Table 1
K_1, K_5, K_7, K_8	Equilibrium constants for reactions 1,5,7,8, respectively
k_1', k_5', k_7', k_8'	Reverse reaction rate constants for reactions 1,5,7,8, respectively
k_{2o}, k_{9o}	Frequency factors of reactions 2 and 9 (Table 1), respectively
k_L	Overall liquid phase mass transfer coefficient, m/min
L	Length of the reactor, m
M_j	Molecular weight of the volatile species, j
m_j	Ratio of liquid-phase molar volumes of the polymer and pure species, j
N	Speed of the agitator, rpm

P	Pressure of the reactor, mm Hg
P_j^0	Vapor pressure of species j, mm Hg
Q	Volumetric flow rate of liquid in the reactor, m^3/min
R	Universal gas constant = 8.314 J/(mol-K)
R_1 to R_9	Reaction rate terms
S_{ij}	Value of i^{th} property at product-end for set no. j
T	Temperature, K
$\mathbf{u}$	Vector of parameters
U_v	Volume fraction of volatile material in the melt
U_v^0	Volume fraction of volatile material in the melt at $z = 0$
V_p	Molar volume of pure liquid polymer, kmol/m^3
W	Water
W_{ij}	Weight factors used in the objective function
x_j^*	Melt phase mole fraction of the volatile species, j, at the interface (at equilibrium)
y_j	Equilibrium mole fraction of the volatile species, j, in the vapor space
z	Dimensionless axial location (• axial position/L)
Z	Di-ester groups

Greek Letters

α	Exponent describing the effect of agitator speed on k_1a
θ	Residence time, min ($\equiv A_1L/Q$)
χ_1	Flory-Huggins' polymer-solvent interaction parameter
γ_j	Activity coefficient of the volatile species, j
ρ_j	Density of the pure liquid species, j, kg/m^3

Subscripts/Superscripts

f	Feed-end of reactor
ind	Industrial
m	Model
ref	Reference value (set 1)

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