Study of Parametric Sensitivity in an Autothermal Nylon 6 Reactor

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ABSTRACT: The parametric sensitivity of an industrial autothermal nylon 6 reactor was studied. The sensitivities of the temperature maxima with respect to various parameters of the model are computed numerically. The sensitivity peaks were found to occur (almost) at the same value of the input parameter, thus confirming the generalized nature of the thermal parametric sensitivity criterion. It is shown that this criterion can easily be used to find safer regions of operation of the reactor. The variation of the number-average chain length of the product, μ_{nf}, with the variation of input parameter, W_0, was also studied. A methodology was suggested to obtain the desired ranges of operation of the reactor which represent an optimal balance between the thermal sensitivity and the sensitivity of μ_{nf}. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 333–343, 1999

Key words: parametric sensitivity; nylon 6; polymerization reaction engineering; reactors; industrial reactors

INTRODUCTION

A maximum (called a hot spot) is often exhibited in the steady-state temperature profile in a plug-flow tubular reactor in which an exothermic reaction occurs. For certain operating conditions, this maximum temperature is quite sensitive to small variations of the reactor inlet conditions, as well as to any of the other parameters characterizing the physicochemical aspects of the system. This phenomenon was referred to as "parametric sensitivity" or "runaway" reactor behavior by Bilous and Amundson.[1] Since this situation is clearly undesirable in reactors, various *a priori* criteria have been developed to determine the regions of parametric sensitivity or runaway in the reactor parameter space, so that they can be avoided at the design stage itself or by changing the operating conditions in pathological reactors, if possible.

Several theories have been proposed to determine the boundary between the sensitive and nonsensitive regions of reactor operation. The first *a priori* runaway criterion was proposed by Barkelew,[2] who used a geometric property of the temperature trajectories deduced from an empirical analysis of a large number of solutions of the model. A more convincing and physically sound definition was proposed by Dente and Collina,[3] who defined runaway as the occurrence of a region with a positive second-order derivative before the hot spot in the temperature-reactor length plane. Van Welsenaere and Froment[4] used this same criterion, which they referred to as the "second criterion," their first one being based on the locus of the maxima in the temperature–conversion plane. Hlavacek et al.[5] applied the several criteria proposed by various authors in the context of the thermal explosion theory. The traditional criterion for runaway, that is, ignition or explosion, used in this field (classical work of Semenov[6]) requires the occurrence of a positive second-order derivative before the maximum in the temperature–time plane. This is identical to the

Dente and Collina[3] criterion. Adler and Enig[7] showed that a more suitable criterion is obtained by considering the temperature–conversion plane instead of the temperature–time plane. In 1982, Morbidelli and Varma[8] applied the same criterion to the case of positive-order irreversible reactions, with no limitations on the activation energy or inlet temperature. Morbidelli and Varma[9] proposed a generalized criterion for parametric sensitivity which is not explicitly based on the temperature profile. This theory is based on the rigorous definition of sensitivity, which is defined as the derivative of the maximum temperature with respect to some reactor inlet condition or physicochemical parameter. This sensitivity theory has been successfully applied to various chemical-reaction and reactor systems including fixed-bed catalytic reactors[8] with consecutive and parallel reactions,[9] CSTRs,[10] tubular reactors with cocurrent external cooling,[11] and chain-polymerization reactors.[12,13] This criterion is intrinsic in nature and gives quantitative estimates of sensitivities and is therefore quite elegant. It has been shown that thermal runaway occurs under the condition when the hot-spot sensitivities with respect to each of the parameters attain their maxima *simultaneously*, thus leading to the concept of a generalized sensitivity criterion. So, it can be inferred that the critical condition is the situation when the hot-spot sensitivities with respect to *any* of the parameters attain the maximum value.

Work on the parametric sensitivity of polymerization systems started with the pioneering studies of Biesenberger and coworkers.[14,15] These studies were limited to chain-polymerization and copolymerization systems which do not exhibit the gel or Trommsdorff effect.[16,17] Tjahjadi et al.[12] studied the temperature and molecular weight sensitivities in tubular homopolymerization reactors in the absence of the gel effect, using the approach of Morbidelli and Varma.[8,9] The study provided design constraints for the low-density polyethylene reactor system. Kapoor et al.[13] extended this work to account for the presence of the gel effect in batch or plug-flow reactors. Their mathematical system (model of the reactor) involved several nonlinear, coupled ordinary differential equations (initial value problem, ODE–IVPs) as well as nonlinear algebraic equations. Morbidelli et al.[18] provided a detailed review of work on parametric sensitivity in their recent monograph.

To the best of our knowledge, no studies on the parametric sensitivity of industrial nylon 6 reactors have been reported in the open literature. It

Figure 1 An autothermal reactor configuration.

was reported by Gupta and Tjahjadi[19] and Ramesh and Gupta[20] that temperature maxima do indeed occur in one type of an industrial (autothermal) nylon 6 reactor. Indeed, acute operating problems were faced by the operators of an industrial reactor of this kind (see Fig. 1) in India, because it was designed to operate quite close to the parametrically sensitive zone. This suggests that a study of the parametric sensitivity of such reactors is a worthwhile endeavor. Also, the structure of the modeling equations for the autothermal reactor shown in Figure 1 is quite different from that encountered for the reactors studied earlier. The modeling equations not only comprise of a set of coupled, nonlinear ODEs and nonlinear algebraic equations, but, also, a trial-and-error technique is required to converge to the final results because the equations for the tube side and those of the column side[19] are coupled. The methodology developed herein for studying the parametric sensitivity of such reactors under steady-state conditions can be useful for studying other similar reactors.

The simplest of the models for such reactors, namely, that of Gupta and Tjahjadi,[19] is used. The definition of sensitivity and normalized sensitivity as given by Morbidelli and Varma[8,9] is used in this work. However, the values of the absolute sensitivities and normalized sensitivities for a particular input parameter are calculated *numerically* in this work, rather than by using the formulation of Morbidelli and Varma,[8,9]

Table I   Kinetic Scheme for Nylon 6 Polymerization and Corresponding Rate Parameters[19,22]

1. Ring opening

$$C_1 + W \underset{k_1' = \dfrac{k_1}{K_1}}{\overset{k_1}{\rightleftharpoons}} S_1$$

2. Polycondensation

$$S_n + S_m \underset{k_2' = \dfrac{k_2}{K_2}}{\overset{k_2}{\rightleftharpoons}} S_{m+n} + W; n, m = 1, 2, \ldots$$

3. Polyaddition

$$S_n + C_1 \underset{k_3' = \dfrac{k_3}{K_3}}{\overset{k_3}{\rightleftharpoons}} S_{n+1}; n = 1, 2, \ldots$$

4. Ring opening of cyclic dimer

$$C_2 + W \underset{k_4' = \dfrac{k_4}{K_4}}{\overset{k_4}{\rightleftharpoons}} S_2$$

5. Polyaddition of cyclic dimer

$$S_n + C_2 \underset{k_5' = \dfrac{k_5}{K_5}}{\overset{k_5}{\rightleftharpoons}} S_{n+2}; n = 1, 2, \ldots$$

$$k_i = \bar{A}_i^0 \exp(-\bar{E}_i^0/R\bar{T}) + \bar{A}_i^c \exp(-\bar{E}_i^c/R\bar{T}) \sum_{n=1}^{\infty} ([\bar{S}_n]) = \bar{k}_i^0 + \bar{k}_i^c \sum_{n=1}^{\infty} ([\bar{S}_n])$$

$$K_i = \exp[(\Delta\bar{S}_i - \Delta\bar{H}_i/\bar{T})/R], \ i = 1, 2, \ldots, 5$$

i	$\bar{A}_i^0$ (kg mol^{-1} h^{-1})	$\bar{E}_i^0$ (J/mol)	$\bar{A}_i^c$ (kg^2 mol^{-2} h^{-1})	$\bar{E}_i^c$ (J/mol)	$\Delta\bar{H}_i$ (J/mol)	$\Delta\bar{S}_i$ (J mol^{-1} K^{-1})
1	5.9874×10^5	8.3198×10^4	4.3075×10^7	7.8703×10^4	$+8.0268 \times 10^3$	-3.2997×10^1
2	1.8942×10^{10}	9.7389×10^4	1.2114×10^{10}	8.6504×10^4	-2.4883×10^4	$+3.9496 \times 10^0$
3	2.8558×10^9	9.5606×10^4	1.6377×10^{10}	8.4148×10^4	-1.6923×10^4	-2.9068×10^1
4	8.5778×10^{11}	1.7577×10^5	2.3307×10^{12}	1.5652×10^5	-4.0176×10^4	-6.0766×10^1
5	2.5701×10^8	8.9141×10^4	3.0110×10^9	8.5374×10^4	-1.3263×10^4	$+2.4384 \times 10^0$

even though the latter is quite elegant. This is because numerical computation of sensitivities can easily be done *directly* these days with the availability of very high speed/size computers, and the *analytical* development of equations for the adjoint variables can be avoided.

FORMULATION

The focus of study in this work was the hydrolytic polymerization of ε-caprolactam in an industrial autothermal reactor. The kinetic scheme used is given in Table I along with the rate constants. There are five major reactions: ring opening, polycondensation, polyaddition, ring opening of cyclic dimer, and polyaddition of cyclic dimer. The reactions involving the higher cyclic oligomers are not incorporated into this scheme since precise rate constants are not available. Mass and energy-balance equations for the tube and shell sides of the autothermal reactor are the same as those in the simulation study of Gupta and Tjahjadi.[19]

The equations are given in Table II in dimensionless form. The various dimensionless groups are defined in the Nomenclature section. The model involves eight state variables, $\mathbf{y}$, and six dimensionless parameters, $\boldsymbol{\phi}$ ($\boldsymbol{\phi}$ is a vector), defined by

$$\mathbf{y} = [C_1,\ S_1,\ \mu_0,\ \mu_1,\ \mu_2,\ C_2,\ W,\ T]^T \quad (1a)$$

$$\boldsymbol{\phi} = [T_0,\ W_0,\ B_0,\ \tau,\ \beta,\ \varepsilon]^T \quad (1b)$$

The energy-balance equation involves the algebraic equation representing the change of the specific heat, C_p, with the temperature and concentration of caprolactam. The differential equation corresponding to the energy balance is decoupled by using the algebraic relationship among C_p, T, and C_1. Correlations for the physical properties, ρ and C_p, of the reaction mass are those suggested by Jacobs and Schweigman[21] and are used in our study since they are more general than the correlations of Tai and Tagawa.[22] The model assumes plug flow and neglects radial temperature variations on both the tube and column sides. The former is a fairly good approximation since the presence of column internals usually leads to an almost flat velocity profile. Neglecting the radial gradients may not be entirely justified and is done purely to keep the model simple. Because of some amount of mixing induced by the column internals, it is believed that the radial gradients will be dampened out somewhat. The model involves several other dimensionless parameters than those given in eq. (1b). These are listed in the Nomenclature section. The dimensionless rate constants, activation energy, and heat of reaction parameters are not incorporated into the vector, $\boldsymbol{\phi}$, and it is assumed that they are known quite precisely (and so are unimportant in influencing the reactor runaway condition). So, only six important parameters which characterize the reactor *operation* are used for the sensitivity study and are considered in the vector, $\boldsymbol{\phi}$. It may be mentioned that the ordinary differential equations for the (dimensionless) temperature, T_t (at any x), in the tube involves the temperature, T_c, *at the same physical location but outside* (i.e., at $1 - x$), in the column. This is indicated in Table II. Similarly, the equation for T_c (at x) involves T_t in the tube at $1 - x$. The temperature sensitivity, $s_{\phi j,T^*}$, and its normalized value, $S_{\phi j,T^*}$, with respect to any parameter, ϕ, are defined as[8,9]

$$s_{\phi j,T^*} \equiv \frac{dT^*}{d\phi_j} \quad (2a)$$

$$S_{\phi j,T^*} \equiv \frac{\phi_j}{T^*}\frac{dT^*}{d\phi_j} \quad (2b)$$

where T^* is the maximum value of the dimensionless temperature.

It was demonstrated[19] that the temperature profile in this reactor clearly exhibits a maximum or hot spot under usual operating conditions. The position of the hot spot and the value of T^* vary with the values of the parameters. The sensitivities in eq. (2) can be calculated numerically (see Appendix for details) by varying any ϕ around its desired value, $\phi_{j,\mathrm{ref}}$, and obtaining the values of T^*. The following numerical differentiation algorithm is then used[23]:

$$\frac{dT^*}{d\phi_j} = \frac{T^*(\phi_{j,\mathrm{ref}} + \Delta\phi_{j,\mathrm{ref}}) - T^*(\phi_{j,\mathrm{ref}} - \Delta\phi_{j,\mathrm{ref}})}{2(\Delta\phi_{j,\mathrm{ref}})} \quad (3a)$$

$$\frac{dT^*}{d\phi_j} = \frac{\begin{array}{c} - T^*(\phi_{j,\mathrm{ref}} + 2\Delta\phi_{j,\mathrm{ref}}) \\ + 4T^*(\phi_{j,\mathrm{ref}} + \Delta\phi_{j,\mathrm{ref}}) - 3T^*(\phi_{j,\mathrm{ref}}) \end{array}}{2(\Delta\phi_{j,\mathrm{ref}})} \quad (3b)$$

The normalized sensitivities can then be easily computed using eq. (2b). The above procedure is quite simple and general, and no analytical expression is needed for the adjoint variables as in the formulation of Morbidelli and Varma.[8,9]

Table III gives the reference values of the parameters used in this study. A mainframe computer (DEC Alfa) took around 91 s to generate four sensitivity values for any particular ϕ.

RESULTS AND DISCUSSION

Simulation results obtained from our computer code for the reference conditions defined in Table III, but with $W_0 = 0.014$, are shown in Figures 2–5. The profiles obtained using the value of W_0 as used by Gupta and Tjahjadi[19] are quite close to those reported earlier. Details of the simulation procedure and the several checks on the correctness of the computer code are given in ref. 19 and are not repeated here for the sake of brevity. A maximum is observed on the column side in the temperature profile (Fig. 2). These maxima are identified precisely by using the NAG subroutine D02EJF, and eq. (3) is then used to obtain the values of the sensitivities.

An apparent anomaly can be seen from Figures 3 and 4. Even though the monomer conversion at

Table II   Balance Equations for Tube and Column Sides (Dimensionless Form)

For $x = 0$ to $x = 0.5$ (tube side)

$$\frac{d}{dx}(\rho V_t) = 0$$

$$\frac{dC_1}{dx} = \frac{\tau s}{\beta V_t}[-K_{F1}C_1W + K_{R1}S_1 - K_{F3}C_1\mu_0 + K_{R3}(\mu_0 - S_1)]$$

$$\frac{dS_1}{dx} = \frac{\tau s}{\beta V_t}[K_{F1}C_1W - K_{R1}S_1 - 2K_{F2}S_1\mu_0 + 2K_{R2}W(\mu_0 - S_1) - K_{F3}S_1C_1 + K_{R3}S_2 - K_{F5}S_1C_2 + K_{R5}S_3]$$

$$\frac{d\mu_0}{dx} = \frac{\tau s}{\beta V_t}(K_{F1}C_1W - K_{R1}S_1 - K_{F2}\mu_0^2 + K_{R2}W(\mu_1 - \mu_0) + K_{F4}WC_2 - K_{R4}S_2)$$

$$\frac{d\mu_1}{dx} = \frac{\tau s}{\beta V_t}[K_{F1}C_1W - K_{R1}S_1 + K_{F3}C_1\mu_0 - K_{R3}(\mu_0 - S_1) + 2K_{F5}C_2\mu_0 - 2K_{R5}(\mu_0 - 2S_1) + 2K_{F4}WC_2 - 2K_{R4}S_2]$$

$$\frac{d\mu_2}{dx} = \frac{\tau s}{\beta V_t}\left[K_{F1}C_1W - K_{R1}S_1 + 2K_{F2}\mu_1^2 + \frac{1}{3}K_{R2}W(\mu_1 - \mu_3) + K_{F3}C_1(\mu_0 + 2\mu_1)\right.$$

$$\left. + K_{R3}(\mu_0 - 2\mu_1 + S_1) + 4K_{F5}C_2(\mu_1 + \mu_0) + 4K_{R5}(\mu_0 - \mu_1 + S_2) + 4K_{F4}WC_2 - 4K_{R4}S_2\right]$$

$$\frac{dC_2}{dx} = \frac{\tau s}{\beta V_t}[-K_{F4}C_2W + K_{R4}S_2 - K_{F5}C_2\mu_0 + K_{R5}(\mu_0 - S_1 - S_2)]$$

$$\frac{dW}{dx} = \frac{\tau s}{\beta V_t}[-K_{F1}C_1W + K_{R1}S_1 + K_{F2}\mu_0^2 - K_{R2}W(\mu_1 - \mu_0) - K_{F4}C_2W + K_{R4}S_2]$$

$$\frac{d}{dx}(C_pT_t) = -\tau s(T_t - T_c|_{1-x}) + \frac{\tau s\rho B_0}{\beta}\sum_{i=1}^{5}H_i\Re_i$$

For $x = 0.5$ to $x = 1$ (column side)

$$\frac{d}{dx}(\rho V_c) = 0$$

replace (s/V_t) in the tube-side equations above for **y** (except T) by $(1/V_c)$

$$\frac{d}{dx}(C_pT_c) = \left[\tau sr_0^2(T_t|_{1-x} - T_c) + \frac{r_0\tau}{U_0}(1 - T_c) + \frac{\rho\tau B_0}{\beta}\sum_{i=1}^{5}H_i\Re_i\right]/(\rho V_c)$$

Property correlations

$$\bar{\rho} = \frac{1000}{1.0065 + 0.0123[\bar{C}_1] + (\bar{T} - 495)(0.00035 + 0.00007[\bar{C}_1])}$$

$$\bar{C}_p = 0.6593C_1 + (1 - C_1)(0.4861 + 0.000337\bar{T})$$

Rates of reactions

$$\Re_1 = K_{F1}C_1W_1 - K_{R1}S_1$$
$$\Re_2 = K_{F2}\mu_0^2 - K_{R2}W(\mu_1 - \mu_0)$$
$$\Re_3 = K_{F3}C_1\mu_0 - K_{R3}(\mu_0 - S_1)$$
$$\Re_4 = K_{F4}C_2W - K_{R4}S_2$$
$$\Re_5 = K_{F5}C_2\mu_0 - K_{R5}(\mu_0 - S_1 - S_2)$$

$$K_{Fi} = k_i^0\exp\left\{E_i^0\left(\frac{T-1}{\varepsilon T}\right)\right\} + k_i^c\exp\left\{E_i^c\left(\frac{T-1}{\varepsilon T}\right)\mu_0\right\}; \quad i = 1, 2, \ldots, 5$$

$$K_{Ri} = K_{Fi}/\left[K_{i,j}\exp\left\{H_i\left(\frac{T-1}{H_rT}\right)\right\}\right]; \quad i = 1, 2, \ldots, 5$$

Closure conditions

$$S_2 = S_3 = S_1$$

$$\mu_3 = \frac{\mu_2(2\mu_2\mu_0 - \mu_1^2)}{\mu_1\mu_0}$$

Continuity of state variables[19] are assumed at $x = 0$.

Table III   Values Used for the Various Parameters (Reference Conditions)

$[\bar{C}_1]_0 = 8.8$ mol/kg
$[\bar{W}]_0 = 0.15$ mol/kg
$[\bar{S}_1]_0 = \bar{\mu}_{0,0} = \bar{\mu}_{1,0} = \bar{\mu}_{2,0} = [\bar{C}_2]_0 = 0.0$
$\bar{T}_0 = 488$ K
$\bar{T}_J = 530$ K
$\bar{V}_{t,0} = 200$ m/h
$\bar{L} = 20$ m
$\bar{r}_t = 0.025$ m
$\bar{r}_c = 0.35$ m

$\bar{U}_t = 20.9$ kJ m^{-2} h^{-1} K^{-1}
$\bar{U}_J = 4.18$ kJ m^{-2} h^{-1} K^{-1}
$s = 15$ m/m
$\varepsilon_c = 10^{-3}$
TOL $= 10^{-12}$
$\phi_1 \equiv T_0 = 0.92075$
$\phi_2 \equiv W_0 = 0.017$
$\phi_3 \equiv B_0 = 0.1018$
$\phi_4 \equiv \tau = 0.1349$
$\phi_5 \equiv \beta = 0.19477$
$\phi_6 \equiv \varepsilon = 0.0492$

Figure 3   Monomer conversion as a function of position for $W_0 = 0.014$. The values of the other parameters are given in Table III.

$x = 0.5$ is negligible, the value of μ_n at the same position is nonzero. This is because the kinetic scheme for nylon 6 polymerization does not involve only the polycondensation reaction, but involves ring-opening and polyaddition as well. In the tube side (which is primarily a preheater), an

extremely small amount of C_1 opens up to form S_1 and higher linear oligomers (like S_2, S_3, etc.) and the number-average chain length of this small amount of polymer produced is finite, as shown in Figure 4 (note that C_1 is not included in the com-

Figure 2   Temperature profile along the reactor for $W_0 = 0.014$. The values of the other parameters are given in Table III.

Figure 4   Profile for μ_n for $W_0 = 0.014$. The values of the other parameters are given in Table III.

Figure 5 C_2 as a function of position for $W_0 = 0.014$. The values of the other parameters are given in Table III.

putation of μ_n, unlike what is commonly done for systems involving only the polycondensation reaction).

Figure 6 shows the absolute values of the *normalized* temperature sensitivities [eq. (2b)] for the reference values of ϕ_j given in Table III. While computing S_{W_0,T^*} ($j = 2$), temperature maxima were obtained around the value of W_0 shown on the abscissa. Similarly, while computing the sensitivities with respect to other ϕ_j ($j = 1, 3–6$), W_0 was fixed at any particular value (shown by stars in Fig. 6), and values of ϕ were varied around their reference values at these chosen W_0. Figure 6 shows that the temperature at the hot spot, T^*, is most sensitive to T_0, the dimensionless inlet temperature of the feed. W_0, the dimensionless inlet concentration of water, comes next in importance in terms of influencing T^*. The sensitivity values for the other parameters, B_0, τ, β, and ε, are almost an order of magnitude lower. The results shown in Figure 6 are similar in nature to those reported for nonpolymerizing systems by Morbidelli and Varma.[9] Figure 6 also shows that the various sensitivities peak at *about* the same value of $W_0 \equiv W_{0,c} \cong 0.013$ ($[\overline{W}]_0 \cong 0.123$ mol/kg), indicating the generalized nature of the sensitivity criterion. The small displacements between the several peaks are probably because the sensitivities have been obtained numerically. These peaks occur at the same location when we plot the

Figure 6 Absolute values of the normalized sensitivity as a function of W_0 for various choices of ϕ_j (j: $1 = T_0$, $2 = W_0$, $3 = B_0$, $4 = \tau$, $5 = \beta$, $6 = \varepsilon$). Left-hand scale used for $j = 1, 2$, and 4; right-hand scale used for the other cases. Reference values of the parameters (Table III) are used wherever they are not indicated. For $j = 5$, temperature peaks are not exhibited in the reactor for values of W_0 of about 0.0135.

Figure 7 Absolute values of the normalized sensitivity as a function of T_0 for various choices of ϕ_j (j: $1 = T_0$, $2 = W_0$, $3 = B_0$, $4 = \tau$, $5 = \beta$, $6 = \varepsilon$). Left-hand scale used for $j = 1$ and 4. Other details are the same as for Figure 6. For $j = 5$, temperature peaks are not exhibited in the reactor for values of T_0 of about 0.908.

sensitivities with respect to T_0 (see later in Fig. 7). Kapoor et al.[13] reported similar minor deviations in the sensitivity studies on methyl methacrylate polymerization. From a practical point of view, it is desirable to use values of W_0 in the nonsensitive region, that is, to the left of W_{0c}, in order to avoid large increases caused by errors in the values of W_0. In fact, the value of $[\overline{W}]_0 = 0.15$ mol/kg used by Gupta and Tjahjadi[19] represents a pathological condition, as indeed was the case for the industrial reactor studied by them.

Figure 7 shows plots of the normalized sensitivities (absolute values) with T_0 on the abscissa. The generalized nature of the sensitivities is again to be noted. The sensitivity peaks occur (without displacement, in contrast to observations in Fig. 6) at $T_0 \equiv T_{0c} \cong 0.908$. Again, the values reported by Gupta and Tjahjadi[19] for the industrial reactor are $T_0 = 0.9207$, which lies beyond the value of T_{0c} and represents the pathological operation of the reactor. It may be added that one cannot use values of T_0 which are too far below T_{0c} because no peak is exhibited in this region and the reaction is essentially quenched, resulting in very low values of the monomer conversion and low values of μ_n. The region to the right of the critical value of T_0 is also not recommended for reactor operation, because the reactor

is already in the runaway state with very high temperatures.

An interesting phenomenon exhibited by the autothermal nylon 6 reactor studied here is the fact that the final value, μ_{nf} (=value for the product), of the degree of polymerization varies quite significantly with W_0. Figure 8 shows the effect of varying W_0 on μ_{nf} for different values of T_0. The other parameters are kept at their reference values. A peak (μ_{nf}^*) in μ_{nf} is observed. The existence of peaks in μ_{nf} as in Figure 8 has interesting ramifications in terms of reactor design and operation. Errors in the values of W_0 (e.g., due to careless metering of components in the feed) could result in significant changes in μ_{nf} and, therefore, of the physical properties of the polymer produced, if the operation of the reactor is far away from the μ_{nf} peak. Obviously, these maxima represent the best (least sensitive) operating points, at least as far as μ_{nf} is concerned.

Figure 9 shows plots of μ_{nf}^* versus T_0 and μ_{nf}^* versus W_0 at the peaks of Figure 8. Figure 9 can be used to find T_0 and W_0 associated with this least sensitive (best) operating point for any value of μ_{nf}^*. Figures 8 and 9 are very useful plots. If we wish to design a reactor with, say, $\mu_{nf} = 179.8$, the best design (in terms of the molecular weight criterion *alone*) would correspond to points A in

Figure 8 μ_{nf} values as a function of W_0 for different T_0 (T_0: 1: 0.898, 2: 0.90, 3: 0.915, 4: 0.918, 5: 0.92, 6: 0.925). Reference values of other parameters are used.

these two diagrams ($W_0 = 0.017$, $T_0 = 0.915$). If we consider the sensitivities of T, we find (see Fig. 7) that for $W_0 = 0.017$ the value of $T_0 = 0.915$ lies beyond the sensitivity peak, and so this is *not* a preferred design. If we decide to design/operate the reactor (for $\mu_{nf} = 179.8$) using a higher value

of T_0 (of, say, $T_0 = 0.92075$, for which Fig. 6 is applicable, corresponding to the interpolated point B in Fig. 8), we will have to be very careful about ensuring the value of W_0 at 0.0142 (Fig. 8) since μ_{nf} is sensitive to minor variations in this situation. Figure 6 shows that this value of W_0 again lies beyond the sensitivity peak. This discussion illustrates the procedure of operating existing reactors using several plots simultaneously. For designing new reactors, additional design flexibility is available (e.g., geometrical parameters).

CONCLUSIONS

A detailed discussion of temperature and μ_{nf} sensitivities has been provided for the continuous flow, industrial autothermal nylon 6 reactor. The numerical technique used to develop values of the temperature sensitivities is quite general and can be applied to any industrial reactor configuration. It is shown that for the autothermal nylon 6 reactor constraints on its operation are provided by temperature as well as by μ_{nf}^* sensitivities.

Figure 9 Values of T_0 and W_0 at the peaks, μ_{nf}^*, shown in Figure 8

NOMENCLATURE

$\bar{A}_i^0, \bar{A}_i^c$ frequency factor of ith reaction (uncatalyzed and catalyzed) (kg mol^{-1} h^{-1} or kg^2 mol^{-2} h^{-1})

B_0 dimensionless heat of reaction $= (-\Delta \bar{H}_3 [\bar{C}_1]_0)/(10^3 \bar{C}_{p0} \bar{T}_J)$

C_1 dimensionless concentration of caprolactam $= [\bar{C}_1]/[\bar{C}_1]_0$

$[\bar{C}_1]$ molar concentration of caprolactam (mol/kg)

C_2 dimensionless concentration of cyclic dimer $= [\bar{C}_2]/\bar{C}_1]_0$

C_p dimensionless heat capacity, $\bar{C}_p/\bar{C}_{p0}$

$\bar{C}_p$ heat capacity of reaction mixture (J kg^{-1} K^{-1})

$\bar{E}_i, \bar{E}_i^c$ activation energy of ith reaction (J/mol)

E_i^0, E_i^c $\bar{E}_i^0/\bar{E}_5^0, \bar{E}_i^c/\bar{E}_5^0$

$\Delta \bar{H}_i$ enthalpy of ith reaction (J/mol)

H_i $\Delta \bar{H}_i/\Delta \bar{H}_3$

H_r $R\bar{T}_J/\bar{E}_5^0$

K_i equilibrium constant at $\bar{T}$

$K_{i,J}$ equilibrium constant evaluated at $\bar{T}_J$

k_i, k_i' rate constants for forward and reverse reactions (kg mol^{-1} h^{-1}; kg^2 mol^{-2} h^{-1})

k_i^0, k_i^c $\bar{k}_i^0 (T_J)/\bar{k}_5^0 (T_J), \bar{k}_i^c (T_J)[\bar{C}_1]_0/\bar{k}_5^0 (T_J)$

$\bar{k}_i^0, \bar{k}_i^c$ rate constants for uncatalyzed and catalyzed reaction, defined in Table I

$\bar{L}$ length of the reactor (m)

R gas constant (J mol^{-1} K^{-1})

$\mathfrak{R}_i$ dimensionless rate of ith reaction (Table II)

$\bar{r}$ radius (m)

r_0 $\bar{r}_t/\bar{r}_c$

s actual length of tube in 1 m of column length (m/m)

$\Delta \bar{S}_i$ entropy of ith reaction (J mol^{-1} K^{-1})

S_n $[\bar{S}_n]/[\bar{C}_1]_0$

$[\bar{S}_n]$ molar concentration of linear oligomer (mol/kg)

$s_{\phi j, T*}$ sensitivity of $T*$ to ϕ

$S_{\phi j, T*}$ normalized sensitivity

T dimensionless temperature $= \bar{T}/\bar{T}_J$

$\bar{T}$ temperature (K)

$\bar{U}$ overall heat transfer coefficient (kJ m^{-2} h^{-1} K^{-1})

U_0 $\bar{U}_t/\bar{U}_J$

V $\bar{V}/\bar{V}_{t,0}$

$\bar{V}$ velocity (m/h)

W dimensionless water concentration $= [\bar{W}]/[\bar{C}_1]_0$

$[\bar{W}]$ water concentration (mol/kg)

x dimensionless axial location in reactor $= \bar{x}/2L$

$\bar{x}$ axial position in reactor, $0 \leq \bar{x} \leq 2\bar{L}$

$\mathbf{y}$ state variable vector

Greek Letters

β $2\bar{U}_t/\{\bar{r}_t \bar{\rho}_0 \bar{C}_{p0} [\bar{C}_1]_0 \bar{k}_5^0 (\bar{T}_J)\}$

ε $R\bar{T}_J/\bar{E}_5^0$

μ_k $\bar{\mu}_k/[\bar{C}_1]_0; k = 0, 1, 2, \ldots$

$\bar{\mu}_k$ $\sum_{n=1}^{\infty} n^k [\bar{S}_n]; k = 0,1,2,\ldots$ (mol/kg)

μ_n number-average chain length $= \mu_1/\mu_0$

ρ $\bar{\rho}/\bar{\rho}_0$

$\bar{\rho}$ density of reaction mass (kg/m^3)

τ $4\bar{U}_t\bar{L}/[\bar{C}_{p0}\bar{\rho}_0\bar{r}_t\bar{V}_{t0}]$

ϕ vector of dimensionless parameters

Superscripts

$*$ maximum value

(k) kth iteration

Subscripts

c column side value or critical value

f final value

J jacket side value

0 inlet value

ref   reference value

t tube side value

Symbol

$[\bar{\;}]$ molar concentrations (mol/kg)

APPENDIX: NUMERICAL TECHNIQUE[19]

The initial conditions for the tube side are available at $x = 0$. For the column side, the initial conditions are obtained by applying the continuity equations at the outlet of the tube. For a particular ϕ and for feed conditions, a discretized temperature profile, $T_c^{(0)} (x)$ (usually isothermal) is assumed and the model equations for the tube side are integrated from $x = 0$ to $x = 0.5$ using Gear's method (NAG subroutine D02EBF with double precision). Then, the column-side equations are integrated from $x = 0.5$ to $x = 1$, using

the temperature profile in the tube just generated. This constitutes one iteration of calculations. The computed column temperatures, $T_c^{(k+1)}(x)$, in the kth iteration are compared against the previous values, $T_c^{(k)}(x)$, $k = 0, 1, 2, \ldots$, and if the convergence criterion, $\{| \, T_c^{(k+1)}(x) - T_c^{(k)}(x) \, | \leq \varepsilon_c\}$, is met at all (discretized) positions, no further iteration is required. If not, the values of $T_c^{(k+1)}(x)$ are used in the next iteration. The values of all the state variables are stored at grid points located at $x = 0.01N$ (where N is an integer; $N = 1, 2, \ldots$). The highest value of temperature, T^* (in the column side), is searched from among the stored values. To get the maximum precisely, the state-variable equations are again integrated in the forward direction starting from the grid point just before the maximum, until the condition $dT/dx = 0$ is satisfied to within some tolerance value (NAG subroutine D02EJF with double precision was used for this). The maximum value of the temperature, T^*, for this value of ϕ is stored. The particular input parameter is then changed by small values (both positive and negative $\Delta\phi_j$ could be used), keeping the other parameters constant at their reference values (Table III). The same procedure is repeated to obtain the temperature maxima. The numerical derivatives are calculated using eq. (3a). Different values of $\Delta\phi_j$ are used and the derivatives evaluated. This is continued until the value of $dT^*/d\phi$ becomes constant (not dependent on the variation of $\Delta\phi_j$). The one-sided formula[23] for the derivative [Eq. (3b)] can also be used where required. This is also accurate[23] to $O(\Delta\phi_j)^2$. The values of the sensitivities are normalized to take care of the wide variations in the values of ϕ. The maximum value of μ_{nf} is obtained from the simulation result itself by varying W_0, when other parameters are fixed at their reference values (except T_0). μ_{nf}^* may be obtained for different values of T_0.

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