# Multiobjective Optimization of an Industrial Nylon-6 Semibatch Reactor System Using Genetic Algorithm

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Received 30 June 1998; accepted accepted 25 August 1998

**ABSTRACT:** Multiobjective Pareto optimal solutions for three different grades of nylon-6 produced in an industrial semibatch reactor are obtained by using the adapted Nondominated Sorting Genetic Algorithm (adapted NSGA). The two objective functions minimized are the total reaction time and the concentration of undesirable cyclic dimer in the product, while simultaneously attaining desired values of the monomer conversion and the number average chain length. The control variables used are the fractional valve opening f(t) and the jacket fluid temperature  $T_{J}$ . The study shows a marked improvement over current industrial operation. It is found that the optimal values of the cyclic dimer concentration in the product are worse (higher) when the reactor-control valve system is studied than when the reactor is considered alone. This is because the control valve leads to additional constraints. The technique used is quite general and can be used to study other reactor systems as well. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 729–739, 1999

**Key words:** multiobjective optimization; nylon-6; industrial semibatch reactor system; adapted nondominated sorting genetic algorithm; genetic algorithm; monomer conversion; number average chain length

## INTRODUCTION

Extensive work has been reported<sup>1-3</sup> on the simulation and optimization of nylon-6 reactors in the past with an in-depth study of the effects of various operating variables like water concentration, temperature, etc., on the molecular characteristics of the polymer formed. This system offers tremendous scope for optimal design of reactors because of the conflicting nature of objective functions involved. Hoftyzer et al.<sup>4</sup> initiated studies

along this direction, and reported some semiquantitative optimal solutions. Reimschuessel and Nagasubramanian<sup>5</sup> optimized a two-stage isothermal reactor using only the three major reactions of the kinetic scheme of nylon-6 formation. Naudin ten Cate<sup>6</sup> optimized two-stage tubular reactors, whereas Mochizuki and Ito<sup>7</sup> optimized a single-stage tubular reactor. Our group also has been actively engaged in the optimization of ideal batch and industrial nylon-6 reactors using different techniques of optimization, like the sequential quadratic programming,<sup>8</sup> Pontryagin's minimum principle,<sup>9</sup> and the genetic algorithm.<sup>10</sup> In all these studies, the focus of optimization has been the reactor alone, and not the reactor system. For example, the control valve at the outlet of the industrial reactor (see Fig. 1) studied by Wajge et al.<sup>11</sup> plays a crucial role by regulating the outflow of the vapor mixture of

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Contract grant sponsor: Research Center, Gujarat State Fertilizers Co. Ltd., Vadodara, India.

Journal of Applied Polymer Science, Vol. 73, 729-739 (1999)

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nitrogen, monomer, and water vapor. It is possible that the optimal vapor release rates (in mol/h)  $V_T(t)$  (t is time in hours) predicted by the previous studies are not the true optimal solutions because the characteristics of the control valve, which is an integral part of the reactor system, are not incorporated in the model equations. With more powerful and robust optimization techniques and with faster and larger computers available, one can now study the optimization of the more complex polymerization reactor systems. The present study is an attempt along this direction, and considers the optimization of the combination of an industrial nylon-6 reactor and a control valve as a system. To the best of our knowledge, this is the first attempt in polymerization reaction engineering that focuses on optimization of polymerization systems, albeit simple ones.

The optimization technique used in the present study is an adaptation of a very robust and popular optimization technique, called the genetic algorithm (GA) from the realm of artificial intelligence. GA is found to be very easily programmed on a computer, and is found to converge to the global optimum even in the presence of several local optima. Details of this genetic algorithm and its numerous adaptations are available in the literature<sup>10,12–16</sup> and are not repeated here.

Optimal solutions obtained herein for the industrial nylon-6 reactor show considerable improvement over the current operation. Changes in the operating variables made on the lines suggested by this study have been found to lead to improved industrial operation. The technique used is quite general and can easily be used for any other reactor assembly.

## FORMULATION

The industrial nylon-6 reactor<sup>11</sup> studied herein is shown in Figure 1. The reactor is a jacketed vessel with a low speed anchor or ribbon agitator to mix the highly viscous polymer mixture. Heat transfer to the polymerizing mixture is provided by condensing vapors at temperature  $T_J$  in the jacket (in degrees Kelvin), which does not vary with time t. Polymerization of the liquid mixture takes place above about 220°C with some vaporization of water W and monomer M ( $\epsilon$ -caprolactam). The pressure of the vapor above the liquid is manipulated using a control valve that releases a vapor mixture of water, inert (nitrogen), and



**Figure 1** Schematic diagram of the industrial semibatch nylon-6 reactor-control valve system.  $R_{v,m}$  and  $R_{v,w}$  are the rates of vaporization of monomer and water at any time (mol/hr).

monomer at a prescribed rate. The vapors so released are taken to a condensor, where a pressure drop of about 13.6 kPa (~2 psi) takes place. The vapor release rate  $V_T(t)$  is related to the fractional valve opening f(t) by the following relation<sup>17</sup> (valid for subcritical gas flows):

$$V_T = 5661.4C_0 f(p\Delta p/M_{av})^{1/2}$$
(1)

where  $C_0$  is the flow constant characterizing the control valve, f(t) is the fractional opening of the valve at time t,  $M_{av}$  is the average molecular weight of the vapor mixture flowing through at any time, p is the upstream valve pressure (in kPa or atm) at time t, and  $\Delta p$  is the pressure drop across the control valve ( $\equiv p - p_1$  in Fig. 1). It is ensured that f and  $V_T$  are zero when  $p < p_1 (p_1 = 13.6 \text{ kPa gage})$ . The value of  $C_0$  is taken as 14.0. This leads to values of  $V_T$ , which are of the same order of magnitude as present in the industrial reactor under current operating conditions. In this study, the *function*, f(t), and the *value*,  $T_J$ , are taken as the control variables,  $\mathbf{u}(t)$  ( $\mathbf{u}$  is the vector of control variables) since these can easily be manipulated in the plant.

Before embarking on any optimization study, one must have a good mathematical model. Wajge et al.<sup>11</sup> have provided details of the model and have shown that predictions of the "tuned" model agree very well with three independent sets of data on the industrial reactor. The equations for  $V_T$  at the beginning of Table 4 in ref. 11 need to be replaced by eq. (1) in this paper.

### Table I Kinetic Scheme for Nylon-6 Polymerization<sup>1-3,11</sup> and Corresponding Rate Parameters

1. Ring opening

$$C_1 + W \xrightarrow{k_1} S_1$$
$$k_1' = \frac{k_1}{K_1}$$

2. Polycondensation

$$S_n + S_m \xrightarrow{k_2} S_{m+n} + W; \quad n, m = 1, 2, \cdots$$
 $k'_2 = \frac{k_2}{K_2}$ 

3. Polyaddition

$$S_n+C_1 \xrightarrow{k_3} S_{n+1}; \quad n=1, 2, \cdots$$
  
 $k_3'=rac{k_3}{K_3}$ 

4. Ring opening of cyclic dimer

$$C_2 + W \xrightarrow{k_4} S_2$$
$$k_4' = \frac{k_4}{K_4}$$

5. Polyaddition of cyclic dimer

$$S_n+C_2$$
  $\xrightarrow{k_5}$   $S_{n+2}; n=1, 2, \cdots$   
 $k_5'=rac{k_5}{K_5}$ 

$$\begin{split} k_i &= A_i^0 \text{exp}(-E_i^0/RT) \,+\, A_i^c \text{exp}(-E_i^c/RT) \Sigma_{n=1}^{\infty}([S_n]) \,=\, k_i^0 \,+\, k_i^c \,\, \Sigma_{n=1}^{\infty}([S_n]) \\ K_i &= \text{exp}[(\Delta S_i \,-\, \Delta H_i/T)/R], \quad i \,=\, 1,\, 2,\, \dots,\, 5 \end{split}$$

i	$A_i^0$ (kg/mol-h)	$E_i^0$ (J/mol)	$\begin{array}{c} A_i^c \\ (\mathrm{kg}^2\!/\mathrm{mol}^2\text{-}\mathrm{h}) \end{array}$	$E_i^c$ (J/mol)	$\Delta H_i \; (\text{J/mol})$	$\Delta S_i$ (J/mol-K)
$     \begin{array}{c}       1 \\       2 \\       3 \\       4 \\       5 \\     \end{array} $	$\begin{array}{c} 5.9874 \times 10^5 \\ 1.8942 \times 10^{10} \\ 2.8558 \times 10^9 \\ 8.5778 \times 10^{11} \\ 2.5701 \times 10^8 \end{array}$	$\begin{array}{c} 8.3198 \times 10^4 \\ 9.7389 \times 10^4 \\ 9.5606 \times 10^4 \\ 1.7577 \times 10^5 \\ 8.9141 \times 10^4 \end{array}$	$\begin{array}{c} 4.3075\times10^{7}\\ 1.2114\times10^{10}\\ 1.6377\times10^{10}\\ 2.3307\times10^{12}\\ 3.0110\times10^{9} \end{array}$	$\begin{array}{c} 7.8703 \times 10^{4} \\ 8.6504 \times 10^{4} \\ 7.5733 \times 10^{4} \\ 1.5652 \times 10^{5} \\ 8.5374 \times 10^{4} \end{array}$	$\begin{array}{c} +8.0268\times 10^{3} \\ -2.4883\times 10^{4} \\ -1.5231\times 10^{4} \\ -4.0176\times 10^{4} \\ -1.3263\times 10^{4} \end{array}$	$\begin{array}{c} -3.2997\times10^{1} \\ +3.9496\times10^{0} \\ -2.9068\times10^{1} \\ -6.0766\times10^{1} \\ +2.4384\times10^{0} \end{array}$

Note:  $k_i$ , forward rate constant of *i*th reaction;  $k'_i$ , reverse rate constant of *i*th reaction;  $K_i$ , equilibrium constant for *i*th reaction;  $S_n$ , linear *n*-mer;  $A_i^0$  and  $A_i^c$ , frequency factors for *i*th reaction in the absence (0) and in the presence (*c*) of catalytic effect (kg mol<sup>-1</sup> h<sup>-1</sup> or kg<sup>2</sup> mol<sup>-2</sup> h<sup>-1</sup>);  $E_i^0$  and  $E_i^c$ , activation energies for the *i*th reaction in the absence (0) and in the presence (*c*) of catalytic effect (J/mol); *R*, gas constant (J/mol-K); *T*, temperature (K);  $\Delta S_i$ , entropy change for the *i*th reaction (J mol<sup>-1</sup> K<sup>-1</sup>);  $\Delta H_i$ , enthalpy of *i*th reaction (J/mol).

The kinetic scheme for nylon-6 polymerization, given in Table I,<sup>2,11</sup> incorporates the three main reactions (ring opening, polycondensation, and polyaddition), as well as two important reactions involving the cyclic dimer  $C_2$ . Reactions involving the higher cyclic oligomers are not incorporated because of the nonavailability of precise rate constants associated with them. This is not a handicap because the major share of the undesirable

cyclic compounds in the reaction mass is the cyclic dimer. The rate and equilibrium constants for this scheme are also presented in Table I. Mass and energy balances, and the appropriate moment equations,<sup>11</sup> can easily be written for this reactor. It is found that the performance of this reactor can be described by fifteen variables  $\mathbf{x}$  that characterize the "state" of this system ( $\mathbf{x}$  is the vector of state variables  $x_i$ ), and the equations

for these state variables are found to have the following general form:

$$dx_i/dt = f_i(\mathbf{x}, \mathbf{u}); \quad i = 1, 2, \dots, 15$$
 (2)

The exact equations are given in ref. 11 and are not repeated here.

The coupled algebraic correlations required to complete the model (for viscosity, heat and mass transfer coefficients, activity coefficients, etc.) are also available in ref. 11. Equation (2) can be combined with eq. (1) to provide the model for the reactor system considered in this study. The DO2EJF subroutine of the NAG library is used to integrate the ODE-IVPs (ordinary differential equations-initial value problems), for a given  $\mathbf{u}(t)$  and initial conditions (indicated by subscript zero). The DO2EJF subroutine uses Gear's technique<sup>18</sup> with a tolerance, TOL, varying between  $10^{-5}$  and  $10^{-3}$ . If the integration of the ODEs fails for any value of TOL, the simulation package automatically increases its value by a factor of 10 and the integration is resumed from the value of t until which converged results had been obtained. This subroutine is combined with an optimization code for performing multiobjective function optimization.

The multiple objectives that are minimized in this study are

- 1. the final (or total) reaction time  $t_f$ , and
- 2. the dimer concentration in the final product  $[C_2]_f$  (brackets in this article indicate concentration in mol/kg mixture).

Both of these objectives are conflicting in nature and provide a good example for multiobjective optimization. The control vector  $\mathbf{u}(t)$  comprises of the fractional control valve opening f(t) and the jacket fluid temperature  $T_J$ . One of these is a *function* of time, while the other is a constant *value*. These are based on the possibilities available in the industrial system. The optimization problem can be represented mathematically as follows:

$$\min_{f(t),T_J} \mathbf{I} = [I_1, I_2]^T$$
(3a)

$$I_{1} = (t_{f}/t_{f,\text{ref}}) + w_{1}(1 - \mu_{n,f}/\mu_{n,f,\text{ref}})^{2} + w_{2}(1 - x_{m,f}/x_{m,f,\text{ref}})^{2}$$
(3b)

$$\begin{split} I_2 &= (C_2] / [C_2]_{f,\text{ref}}) + w_1 (1 - \mu_{n,f} / \mu_{n,f,\text{ref}})^2 \\ &+ w_2 (1 - x_{m,f} / x_{m,f,\text{ref}})^2 \quad (3c) \end{split}$$

subject to

$$\frac{d\mathbf{x}}{dt} = \mathbf{f}(\mathbf{x}, \mathbf{u}); \quad \mathbf{x}(t=0) = \mathbf{x}_0$$
(3d)

$$\mathbf{u}_{\min} \le \mathbf{u} \le \mathbf{u}_{\max}$$
 (3e)

In eq. (3), **I** is the vector of objective functions  $I_m$  (m = 1,2),  $t_f$  is the total reaction time (in h),  $w_1$  and  $w_2$  are weightage factors,  $x_m$  is the monomer conversion,  $\mu_n$  is the number average chain length of the polymer, **f** is the vector of functions  $f_i$  in state variable equations, subscript f indicates the "final" or product values, subscript ref indicates reference values, i.e., values associated with the current operation (before optimization), and subscripts min and max refer to minimum and maximum values, respectively. These terms are defined below:

$$x_m(t) = 1 - (F[C_1] + \zeta_1) / (F_0[C_1]_0)$$
(4a)

$$\mu_n(t) = \mu_1/\mu_0 \tag{4b}$$

$$\boldsymbol{x}_{m,f} = \boldsymbol{x}_m(t_f) \tag{4c}$$

$$\mu_{n,f} = \mu_n(t_f) \tag{4d}$$

*F* is the mass of liquid in the reactor at time *t* (in kg),  $C_1$  is caprolactam, and  $\zeta_i$  is the total mol of *m* (*i* = 1), *w* (*i* = 2), or both (*i* = 3) vaporized until time *t* (mol).  $\mu_k$  (*k* = 0, 1) is the *k*th moment of the

chain length distribution, (  $\equiv \sum_{n=1}^{\infty} n^k [S_n]$ ). Use of constant reference values  $t_{f,ref}$ ,  $[C_2]_{f,ref}$ ,  $\mu_{n,f,ref}$ , and  $x_{m,f,ref}$  to nondimensionalize the several variables is necessary for proprietary reasons, but does not reduce the value of this study. The forms of  $I_1$  and  $I_2$  used in eqs. 3(b) and (c) ensure that the final values,  $\mu_{n,f}$  and  $x_{m,f}$ , attain the desired values,  $\mu_{n,f,ref}$  and  $x_{m,f,ref}$ , which are associated with current operation. This end-point constraint ensures that the downstream processing of the polymer product from the reactor is not affected by changes in reactor operation, and that product properties are unchanged. The polydispersity of the polymer is not important for nylon-6 because its final value is close

$C_0 = 14$ (Eq. 1)
$N_{\rm ga} = 10$
$N_{P}^{-} = 40$
$N_{ m str}=7$
$N_{\rm sim} = 100$
q = 15
lpha=2
$p_{c} = 0.8$
$p_m = 0.01$
$N_{g,\max} = 50$
$N_{\rm chr} = (10 + 1) \times 7 = 77$
$w_1 = w_2 = 0.25 \times 10^6$
$f_k^{\min} = 0, f_k^{\max} = 1.0; k = 1, 2, \dots, N_{\text{ga}}$
$T^{\min} = 220.0^{\circ}C$

This Study ( $[W]_0 = 3.45\%$ )

270.0°C

Table II Computational Parameters<sup>10</sup> Used in

Note:  $N_P$ , number of chromosomes in the population;  $N_{\rm str}$ , number of binary digits representing each of the control variable values;  $N_{\rm sim}$ , number of f values after interpolation; q, desired number (approx) of Pareto points required to be generated;  $\alpha$ , exponent controlling the sharing effect;  $p_c$ , crossover probability;  $p_m$ , mutation probability;  $N_g$ , generation number;  $N_{\rm chr}$ , total number of binary digits in chromosome =  $(N_{\rm ga} + 1) \times N_{\rm str}; f_k$ , fractional valve opening at (digitized) time  $t_k$ . See Ref. 10 for details.

to 2.0 in the reference as well as optimal cases. In eq. 3, the end-point constraints on  $\mu_{n,f}$  and  $x_{m,f}$  are incorporated as penalty functions in both the objective functions with large weightage factors,  $w_1$  and  $w_2$ , and for the optimal solutions finally obtained, these penalties will be negligible, and  $I_1$  and  $I_2$  will be equal to  $t_f / t_{f,ref}$  and  $[C_2]_f / [C_2]_{f,ref}$ , respectively. A popular adaptation of the simple genetic al-

gorithm  $(SGA)^{12-14}$  useful for solving multiobjective optimization problems involving control variables that are not functions is the nondominated sorting genetic algorithm (NSGA) developed by Srinivas and Deb.<sup>19</sup> This technique has been further adapted by our group<sup>10</sup> to solve multiobjective optimization problems involving control variables that are functions of time. Reference 10 gives the details of this algorithm, as well as a flow chart. In this technique, the continuous function f(t) is digitized into  $N_{ga}$  values (which are constrained to be continuous at any value of t) and then NSGA obtains the optimal values of  $N_{\rm ga}$ + 1 "values." Several "chromosomes" (solutions) are generated, and the "population" of chromosomes evolves over the "generations" to give, finally, the optimal solutions (based on the Darwinian principle of survival of the fittest).

### **RESULTS AND DISCUSSION**

In order to ensure that the computer code was free of errors, time histories of  $x_m$ ,  $[C_2]$ ,  $\mu_n$ , etc., were generated for a few individual chromosomes and were found to be the same as those obtained by the simulation code<sup>11</sup> using the same values of f(t) and  $T_{J}$ . This gave confidence that at least a major part of the computer program was correct. The code for the adapted NSGA was then implemented with values of the (computational) parameters given in Table II. The fractional valve opening, one of the control variables, can vary between 0.0 and 1.0. The window used for the jacket temperature<sup>10</sup> was taken as  $220^{\circ}C \leq T_{J}$  $\leq$  270°C . The CPU time on a HP8000S/950 supermini mainframe computer to generate 50 generations of solutions of the adapted NSGA technique was found to be 10.5 s.

Figure 2 shows all the feasible solutions [i.e., those satisfying the end-point constraints on  $x_{m,f}$  and  $\mu_{n,f}$  in Eqs. 3(b) and (c)] in "front" 1 in the initial population (generation number = 0). It also shows how the feasible points evolve over the several generations. Figure 3 shows the optimal (and feasible) points in generation no. 49. Not many changes in these points take place after this generation. This set of points are said to form a Pareto optimal set. (Paretos are defined to be a set of points on the  $I_1$  versus  $I_2$  diagram, such that when we go from any one point to another on this set, one objective function improves, but one or



**Figure 2** Feasible points in front 1 in the different generations for  $[W]_0 = 3.45\%$ .



**Figure 3** Pareto optimal set (for generation 49) for  $[W]_0 = 3.45\%$ . Utopia  $(U_3)$  and preferred solution  $(O_3)$  indicated. Geometrical construction often used to locate the preferred solution also shown.

more other objective functions worsen. Thus, these are equally good, or noninferior, optimal points.) Converged optimal Pareto sets for  $[W]_0 = 2.52$  and 4.43 % are given in Figures 4 and 5. It may be noted that the same value of  $[C_2]_{f,ref,3}$  (the current or reference value for  $[W]_0 = 3.45\%$ ) is used to normalize  $[C_2]_f$  in all of these three cases so that the values of  $[C_2]_f$  can be compared for the



**Figure 4** Pareto optimal set (for generation 50) for  $[W]_0 = 2.52\%$ . Utopia  $(U_2)$  and preferred solution  $(O_2)$  indicated.



**Figure 5** Pareto optimal set (for generation 50) for  $[W]_0 = 4.43\%$ . Utopia  $(U_4)$  and preferred solution  $(O_4)$  indicated.

different values of  $[W]_0$  easily. Additional points on the Pareto could have been generated by taking larger values of  $N_p$ , but these would have required much larger computer times, and were not found necessary. It may be reemphasized that the valve can open only when the dimensionless pressure  $\Pi [\equiv (p - p_0)/(p_{\max, ref} - p_0)]$  in the reactor (inlet of the control valve) exceeds 0.0227 so that there is a driving force for flow to take place through the control valve to the inlet of the condensor. This is true for all values of  $[W]_0$ .

An interesting aspect in the case of multiobjective optimization is to study the two asymptotes of the Pareto set. These are shown in Figures 3-5 and are generated by solving the optimization problem [eq. (3)] twice, using only one objective function at a time (and not both, see ref. 10). The intersection of the two lines is referred to as utopia<sup>8,10</sup> (point  $U_i$ , with i = 2, 3, 4 indicating  $[W]_0$ = 2.52, 3.34, and 4.43%). The point nearest to  $U_i$ (geometrically) is often (but not always) used as the "best" operating points (called the preferred solution) and is denoted by  $O_i$  (see Fig. 3). Obviously, the *exact* location of the preferred solution depends on the scales chosen for the abscissa and the ordinate, and so there is a considerable degree of arbitrariness in selecting these points using this method. We have chosen the preferred solutions for the three values of  $[W]_0$  at the locations  $O_i$  indicated in Figures 3–5. These points were selected from among the feasible points given by



**Figure 6** Jacket fluid temperatures corresponding to different points on the three Paretos of Figures 3–5. Water concentration refers to  $[W]_{0}$ .

*our algorithm*, such that they were near the geometrically obtained utopia. The best method for selecting the preferred solution<sup>20</sup> requires discussions with several plant personnel (called decision makers), who need to use their "judgments" to choose the best or preferred points from among the Pareto optimal (equally good) points shown to them. Obviously, the existence of the Pareto set helps channelize the thinking of the decision maker.

We now look at the optimal conditions of operation of the industrial reactor at some of (or all) the points on the Pareto. Figure 6 shows the optimal jacket fluid temperature  $T_{J}$  corresponding to the different points on the Pareto for all three values of  $[W]_0$ . Figures 7–9 show the optimal function f(t) for a few points on the Pareto set. The points for which f(t) are plotted are identified in Figures 3–5. Points  $O_i$  (i = 2, 3, or 4 for  $[W]_0 = 2.52$ , 3.45, and 4.43%, respectively) are the preferred solutions. The associated vapor release rate histories  $V_T/V_{T,\text{max,ref,3}}$  (where the normalizing constant used is the same for all three values of  $[W]_0$ ) are shown in Figures 10–12 for the points  $O_3$ ,  $O_2$ , and  $O_4$ , respectively. A striking observation from these figures is that the vapor release starts quite early for the optimal solutions, in contrast to the current histories. The corresponding dimensionless pressure histories  $\Pi (t/t_{f,ref})$ , corresponding to points  $O_3, O_2$ , and  $O_4$  in Figures 3–5, are compared with current variations in Figure 13. Much lower pressures are indi-



**Figure 7** Variation of fractional valve opening with dimensionless time corresponding to different points,  $A_3$ ,  $O_3$ , and  $B_3$  (see Fig. 3), on the Pareto ( $[W]_0 = 3.45\%$ ).

cated for optimal operations. These are consistent with the early opening of the control valve and early vapor release rates. Figure 14 shows the corresponding (dimensionless) temperature histories  $\theta(t/t_{f,\text{ref}})$  [ $\theta$  is the dimensionless temperature,  $\equiv (T - T_0)/(T_J - T_0)$ ]. Lower temperatures associated with higher vaporization during the early stages of reaction are observed under optimal conditions. The early vapor release leads to a more



**Figure 8** Variation of fractional valve opening with dimensionless time corresponding to different points,  $A_2$ ,  $O_2$ , and  $B_2$  (see Fig. 4), on the Pareto ( $[W]_0 = 2.52\%$ ).



**Figure 9** Variation of fractional valve opening with dimensionless time corresponding to different points,  $A_4$ ,  $O_4$ , and  $B_4$  (see Fig. 5), on the Pareto ( $[W]_0 = 4.43\%$ ).

rapid increase in  $\mu_n$  with time, as shown in Figure 15. The optimal  $\mu_n$  histories increase continuously without showing any plateau. Also, the conversion of monomer (see Fig. 16)  $x_m$  increases more gradually when compared to the current histories, which have a steep rise at about  $t/t_{f,ref} = 0.2$ . Similar *qualitative* behavior was observed in the previous study<sup>10</sup> where the operation of the nylon-6 reactor *alone* was optimized. Figure 17 shows how the cyclic



**Figure 10** Variation of the dimensionless vapor release rate with dimensionless time for the current and optimal (preferred solution,  $O_3$ ) cases;  $[W]_0 = 3.45\%$ .



**Figure 11** Variation of the dimensionless vapor release rate with dimensionless time for the current and optimal (preferred solution,  $O_2$ ) cases;  $[W]_0 = 2.52\%$ .

dimer concentration builds up under optimal conditions to its drastically reduced values. Again, the same normalizing values (corresponding to  $[W]_0$ = 3.45%) for  $[C_2]_{f,ref}$  are used for all the three curves, so that one can easily compare the  $[C_2](t)$  values.

The effect of varying the several computational parameters given in Table II are similar to those obtained by Mitra et al.<sup>10</sup> and are not



**Figure 12** Variation of the dimensionless vapor release rate with dimensionless time for the current and optimal (preferred solution,  $O_4$ ) cases;  $[W]_0 = 4.43\%$ .



**Figure 13** Variation of the dimensionless pressure histories with dimensionless time for the current and optimal (preferred solutions) cases, for  $[W]_0 = 2.52$ , 3.45, and 4.43%. Vertical indicators with 2, 3, and 4 marked indicate the end of the optimal curves for  $[W]_0 = 2.52$ , 3.45, and 4.43%, respectively. The  $t_f$  for  $[W]_0 = 4.43\%$  is slightly lower than that for 2.52%, even though the vertical arrow indicators for these cases do not show this.

being presented for the sake of brevity. The only new parameter in this study is the valve constant  $C_0$  [eq. (1)]. Figure 18 shows how the



**Figure 15** Variation of the degree of polymerization with dimensionless time for the current and optimal (preferred solutions) cases for  $[W]_0 = 2.52$ , 3.45, and 4.43%.

Pareto changes when the value of  $C_0$  is varied by  $\pm 10$  % around the value given in Table II. This diagram shows the complex interplay of several physicochemical phenomena that play important roles in deciding the optimal solutions.



**Figure 14** Variation of the dimensionless temperature with dimensionless time for the current and optimal (preferred solutions) cases for  $[W]_0 = 2.52, 3.45$ , and 4.43%. Other details are the same as in Figure 13.



**Figure 16** Variation of the monomer conversion with dimensionless time for the current and optimal (preferred solutions) cases for  $[W]_0 = 2.52, 3.45, \text{ and } 4.43\%$ . Other details as in Figure 13.



**Figure 17** Variation of the dimensionless dimer concentration (using  $[C_2]_{f,\text{ref}}$  for  $[W]_0 = 3.45\%$  as the normalizing parameter for all three cases) with dimensionless time for the current and optimal cases (preferred solutions) for  $[W]_0 = 2.52$ , 3.45, and 4.43%.

A comparision of the Pareto sets for the system, reactor + control valve (solid lines in Fig. 19), with those obtained earlier<sup>10</sup> for the nylon-6 reactor *alone* (dotted lines), is shown in Figure 19. It is observed that the values of the optimal  $[C_2]_f$  in the present case are slightly higher (worse). This emphasizes the importance of studying optimization of *systems* rather than of individual units. It



**Figure 18** Effect of the valve constant  $C_0$  on the Pareto set for  $[W]_0 = 3.45\%$ .



**Figure 19** Comparision of the Pareto solutions obtained in the present study (full lines: for the system reactor + valve) with those obtained by Mitra et al.<sup>10</sup> (dotted lines: for the reactor alone).

was found in our previous study<sup>10</sup> that  $V_T / V_{T,\max,ref}$  should be nonzero at and near t = 0 for the preferred solutions. This is not feasible in the *real* reactor because the driving force for vapor flow is a change in the pressure  $[\Delta p$  in eq. (1)], there being no vacuum system present. Introduction of this constraint in the present optimization study leads to a worsening of the optimal solution and indicates the usefulness of the study.

# CONCLUSIONS

In this study we have carried out multiobjective optimization of an industrial nylon-6 reactor system (reactor-cum-control valve) using an adapted NSGA technique. The two control variables used in this study are the fractional control valve opening f(t)and the jacket fluid temperature  $T_{J}$ . Pareto optimal solutions have been obtained for all three initial water concentrations used in industry to manufacture three different grades of polymer. The total reaction time and the cyclic dimer concentration in the product are both much smaller than under current conditions. This is primarily due to the early release of vapor from the reactor. However, the optimal solutions obtained for the reactor-valve system are worse than those obtained for the reactor alone, because of the incorporation of real-life constraints in the former. We have indications that significant improvements in the operation of the industrial reactor have indeed been achieved by using the optimal pressure histories. The techniques used are quite general and can be used for other reactor *systems* as well.

This work has been partly supported by a grant from the Research Center, Gujarat State Fertilizers Co. Ltd., Vadodara, India. The correspondence author also gratefully acknowledges the hospitality, kindnesses, and the stimulating academic environment and infrastructure that he is currently enjoying as a Visiting Professor at the National University of Singapore, where the manuscript was revised.

#### REFERENCES

- Reimschuessel, H. K. J Polym Sci Macromol Rev 1977, 12, 65.
- Tai, K.; Tagawa, T. Ind Eng Chem Prod Res Dev 1983, 22, 192.
- Kumar, A.; Gupta, S. K. J Macromol Sci Revs Macromol Chem Phys C 1986, 26, 183.
- Hoftyzer, P. J.; Hoogschagen, J.; Van Krevelen, D. W. In Proceedings of the 3rd European Symposium on Chemical Reaction Engineering, Amsterdam; Sept. 15–17, 1964; p 247.
- 5. Reimschuessel, H. K.; Nagasubramanian, K. Chem Eng Sci 1972, 27, 1119.
- 6. Naudin ten Cate, W. F. H. In Proceedings of the International Congress in Use of Elec Comp in Chemical Engineering, Paris, April 1973.

- Mochizuki, S.; Ito, N. Chem Eng Sci 1978, 33, 1401.
- Sareen, R.; Gupta, S. K. J Appl Polym Sci 1995, 58, 2357.
- Kohli, N. K.; Sareen, R.; Gupta, S. K. J Appl Polym Sci 1996, 62, 1219.
- Mitra, K.; Deb, K.; Gupta, S. K. J Appl Polym Sci 1998, 69, 69.
- Wajge, R. M.; Rao, S. S.; Gupta, S. K. Polymer 1994, 35, 3722.
- Holland, J. H. Adaptation in Natural and Artificial Systems; University of Michigan Press: Ann Arbor, MI, 1975.
- Goldberg, D. E. Genetic Algorithms in Search, Optimization and Machine Learning; Addison-Wesley: Reading, MA, 1989.
- Deb, K. Optimization for Engineering Design: Algorithms and Examples; Prentice Hall of India: New Delhi, 1995.
- Chakravarthy, S. S. S.; Saraf, D. N.; Gupta, S. K. J Appl Polym Sci 1997, 63, 529.
- Garg, S.; Gupta, S. K.; Saraf, D. N. J Appl Polym Sci., 1999, 71, 2101.
- Smith, C. A.; Corripio, A. B. Principles and Practices of Automatic Process Control; Wiley: New York, 1985.
- Gupta, S. K. Numerical Methods for Engineers; New Age Pub: New Delhi, India, 1995.
- 19. Srinivas, N.; Deb, K. Evolut Comput 1995, 2, 3.
- Chankong, V.; Haimes, Y. Y. Multiobjective Decision Making: Theory and Methodology; North Holland: New York, 1983.