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Multiobjective optimization of an industrial wiped film poly(ethylene terephthalate) reactor: some further insights

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Abstract

Multiobjective optimization of an industrial third-stage, wiped-film poly(ethylene terephthalate) reactor is carried out, using a pre-validated model. The two objective functions minimized are the acid and vinyl end group concentrations in the product. These are two of the undesirable side products produced in the reactor. The optimization problem incorporates an end-point constraint to produce polymer having a desired value of the degree of polymerization (DP). In addition, the concentration of the di-ethylene glycol end group in the product is constrained to lie within a certain range of values. The possible decision variables for the problem are the reactor pressure, temperature, catalyst concentration, residence time of the reaction mass in the reactor and the speed of rotation of the agitator. The nondominated sorting genetic algorithm (NSGA) is used to solve this multiobjective optimization problem. It is found that this algorithm is unable to converge to the correct solution(s) when two or more decision variables are used, and we need to run the code several times over (with different values of the computational variable, S_r, the seed for generating the random numbers) to obtain the solutions. In fact, this is an excellent test problem for future multiobjective optimization algorithms. It is found that when temperature is kept constant, Pareto optimal solutions are obtained, while, when the temperature is included as a decision variable, a global unique optimal point is obtained.

Keywords: Multiobjective optimization; Polyethylene terephthalate; Genetic algorithm; Wiped-film reactor; Pareto sets; Fibre grade polyester

Nomenclature

a	specific interfacial area per unit volume of the melt (m^{-1})
a_o	coefficient in the polynomial relating χ_1 to polymer concentration
A	acetaldehyde
A_l	cross-sectional area of the melt in the reactor (m^2)
b_o	coefficient in the polynomial relating χ_1 to polymer concentration
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

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$\boldsymbol{I}$	vector of objective functions, I_i
k_1–k_9	forward reaction rate constants for Eqs. (1)–(9) in Table 1
k'_1, k'_5, k'_7, k'_8	reverse reaction rate constants for Eqs. (1), (5), (7) and (8) in Table 1
k_{2o}, k_{9o}	frequency factors of reactions (Eqs. (2) and (9)) (Table 1), respectively
k_l	overall liquid phase mass transfer coefficient (m min^{-1})
K_1, K_5, K_7, K_8	equilibrium constants for Eqs. (1), (5), (7) and (8) in Table 1
l_{chrom}	chromosome length
L	length of the reactor (m)
N	speed of the agitator, (rpm)
N^*	dimensionless value of N ($\equiv N/N_{ref}$)
N_g	number of generations in NSGA
N_{gen}	maximum number of generations in NSGA
N_p	number of chromosomes in the population, in NSGA
p_c	crossover probability in NSGA
p_m	mutation probability in NSGA
P	pressure of the reactor (mmHg or kPa)
P_e	penalty value in Eqs. (5a) and (5b)
Q	volumetric flow rate of liquid in the reactor, (m^3 min^{-1})
S_r	seed for the random number generator in NSGA
T	temperature (K)
$\boldsymbol{u}$	vector of decision variables, u_i
w_1, w_2, w_3	weighting factors used in the objective functions
W	water
$\boldsymbol{x}$	vector of state variables, x_i
z	dimensionless axial location in reactor ($\equiv$ axial position/L)
Z	di-ester groups

Greek alphabets

α	exponent describing the effect of agitator speed on k_la
α_{sh}	exponent controlling the sharing effect in NSGA
θ	residence time ($\equiv A_lL/Q$) (min)
θ^*	dimensionless value of θ ($\equiv \theta/\theta_{ref}$)
σ	maximum normalized distance in $\boldsymbol{u}$ space between any two points in NSGA
χ_1	Flory parameter describing vapor–liquid equilibrium

Symbols

[*]	concentration in the melt, kmol m^{-3} (unless otherwise specified)

Subscripts/superscripts

d	desired value
f	feed value
out	outlet value
0	value at $z = 0$ (inlet of reactor)
ref	reference conditions, as in Bhaskar et al. (2000a)

1. Introduction

Multiobjective optimization has created immense interest in engineering in the last two decades. Polymerization processes are quite complex in nature and offer themselves as excellent candidates for the application of multiobjective optimization. The quality of the polymer produced is normally described in terms of several experimentally measured indices, e.g. stiffness, tenacity, strength, etc. Fortunately, several of these experimental properties can be related to 'molecular' parameters that can be predicted using mathematical models of the reactors. These include the average molecular weight, polydispersity index, degree of short-chain branching, concentration and distribution of functional groups, etc. The operating (and design) variables of a polymerization reactor system influence these 'molecular' measures of the product in interesting and, often, conflicting ways. This is why multiobjective optimization is of considerable interest for polymerization systems. In this study, we focus our attention on the multiobjective optimization of polyethylene terephthalate (PET) reactors. PET, usually referred as polyesters, is one of the most widely used polymers in practice, and is extensively used in the manufacture of fibres, films, bottles, etc.

A recent review on the applications of multiobjective optimization in chemical engineering (Bhaskar, Gupta & Ray, 2000b) suggests that several interesting studies have been reported on the multiobjective optimization of polymerization reactors. Tsoukas, Tirrell and Stephanopoulos (1982), Fan, Landis and Patel (1984), Farber (1986, 1989), Butala, Choi and Fan (1988), Choi and Butala (1991) carried out multiobjective optimization of copolymerization reactors. These early studies used the parametric method or the ε-constraint method (Chankong & Haimes, 1983) to obtain Pareto optimal sets of non-dominant solutions. A Pareto set is defined such that when we go from any one point to another, at least one objective function improves and at least one other worsens (Chankong & Haimes, 1983). Wajge and Gupta (1994) obtained optimal temperature histories corresponding to different points on the Pareto optimal sets for a non-vaporizing nylon-6 batch reactor, using similar techniques. Sareen and Gupta (1995) obtained optimal pressure *histories* and optimal *values* of the jacket-fluid temperature at different points on the Pareto set for an industrial, semi batch nylon-6 reactor. In this reactor, monomer and water vaporize, and a control valve releases the vapors in a manner that a desired pressure history is maintained. More recently, our group (Chakravarthy, Saraf & Gupta, 1997; Mitra, Deb & Gupta, 1998; Garg & Gupta, 1999; Garg, Gupta & Saraf, 1999; Gupta & Gupta, 1999) has carried out multiobjective optimization studies on nylon-6 and polymethyl methacrylate (PMMA) reactors using the very robust genetic algorithm (GA). An adaptation of GA was used for multiobjective optimizations. This is the nondominated sorting genetic algorithm (NSGA), as developed by Srinivas and Deb (1995) for problems where the decision variables can take on optimal *values*. This technique has been further adapted by Mitra et al. (1998) to apply for problems involving decision variables that are *functions* of time or space. Pareto sets of non-dominated solutions were obtained in all these studies. The Pareto sets usually obtained in multiobjective optimization help channelize the thinking of a decision-maker since they narrow down the choices from among which he or she can choose the 'preferred' solution. This is usually done using intuition or experience, information that is often non-quantifiable (Chankong & Haimes, 1983).

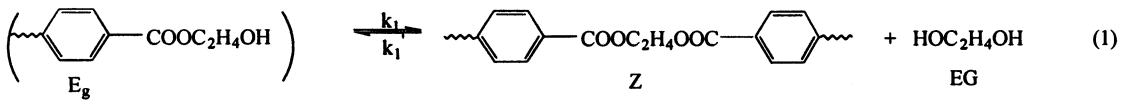
It may be emphasized that multiobjective optimization of real-life systems is quite complex and each new application may require the development of several adaptations of optimization algorithms to obtain meaningful solutions, irrespective of which mathematical procedure is used for the purpose. Indeed, a few such adaptations of GA have been developed in earlier studies (Goldberg, 1989; Deb, 1995).

Recently, Bhaskar, Gupta and Ray (2000a) have carried out the multiobjective optimization of reactors producing fiber-grade PET. Indeed, any amount of lowering of costs indicated by such studies is of tremendous help in the polyester industry. Commercially, PET is manufactured in three stages, using continuous reactors. The first (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). Our study is based on the PTA route that is now quite popular. PTA and EG are usually processed in a series of CSTRs or a plug flow reactor with a recycle in the first stage. A polycondensation catalyst, antimony trioxide, is injected in small concentrations (0.03–0.05 wt.%) into the oligomer stream leaving this reactor. The second (prepolymerization) stage is carried out either in one or two agitated vessels under reduced pressures, at about 2–4 kPa (15–30 mmHg) and 270–280°C. The degree of polymerization (DP) attains a value of about 30–40 in the second stage. The prepolymer so produced undergoes final polycondensation in a finishing (or third stage, wiped film) reactor in which the pressure is maintained quite low at 0.133–0.266 kPa (1–2 mmHg), and temperatures are maintained at about 285–295°C. Since the reaction mass is extremely 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 vapor in a jacket.

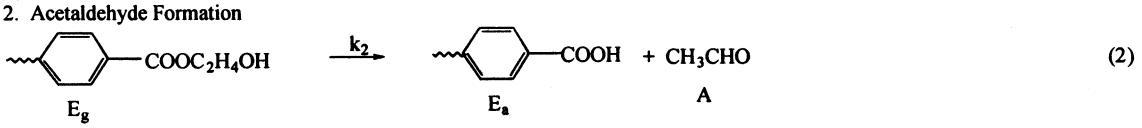
Table 1
Kinetic scheme

1. Ester interchange reaction (Main Polycondensation)

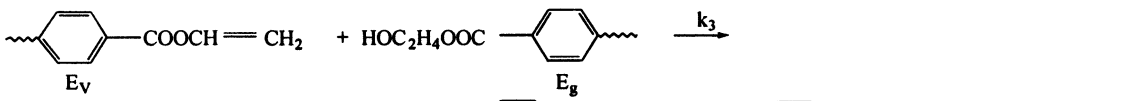


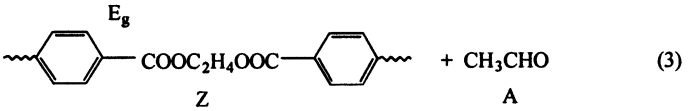
(1)

2. Acetaldehyde Formation



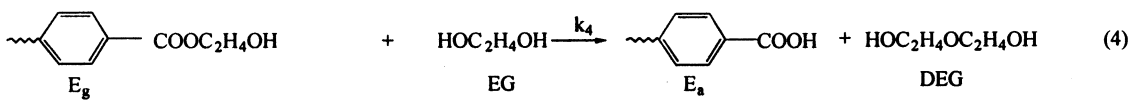
(2)



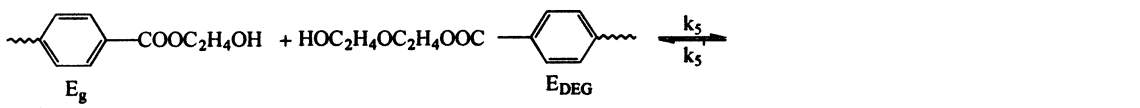


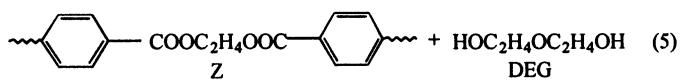
(3)

. Diethylene Glycol Formation

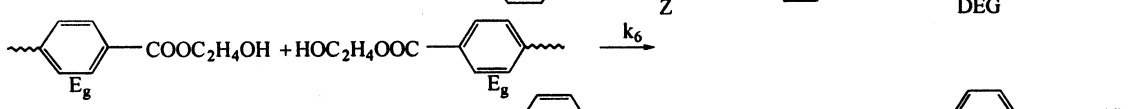


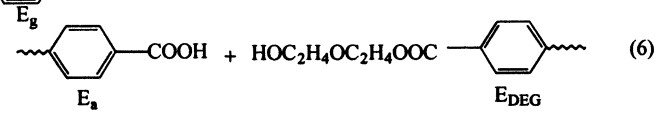
(4)





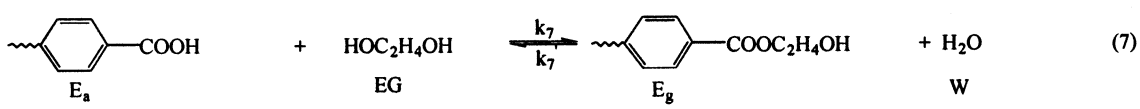
(5)



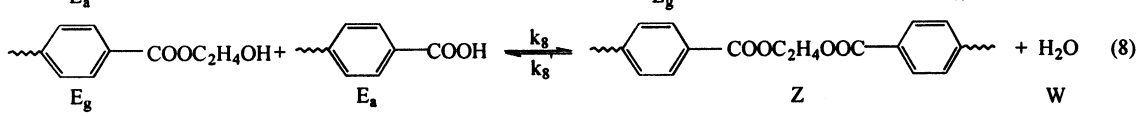


(6)

4. Water Formation

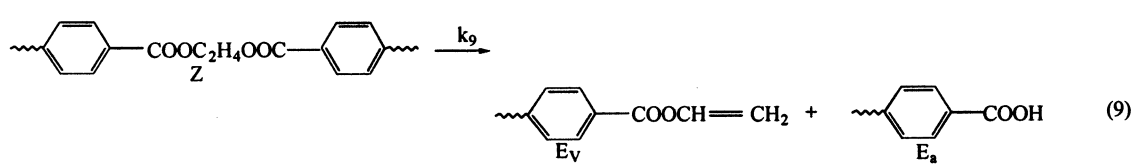


(7)



(8)

. Degradation of Diester group



(9)

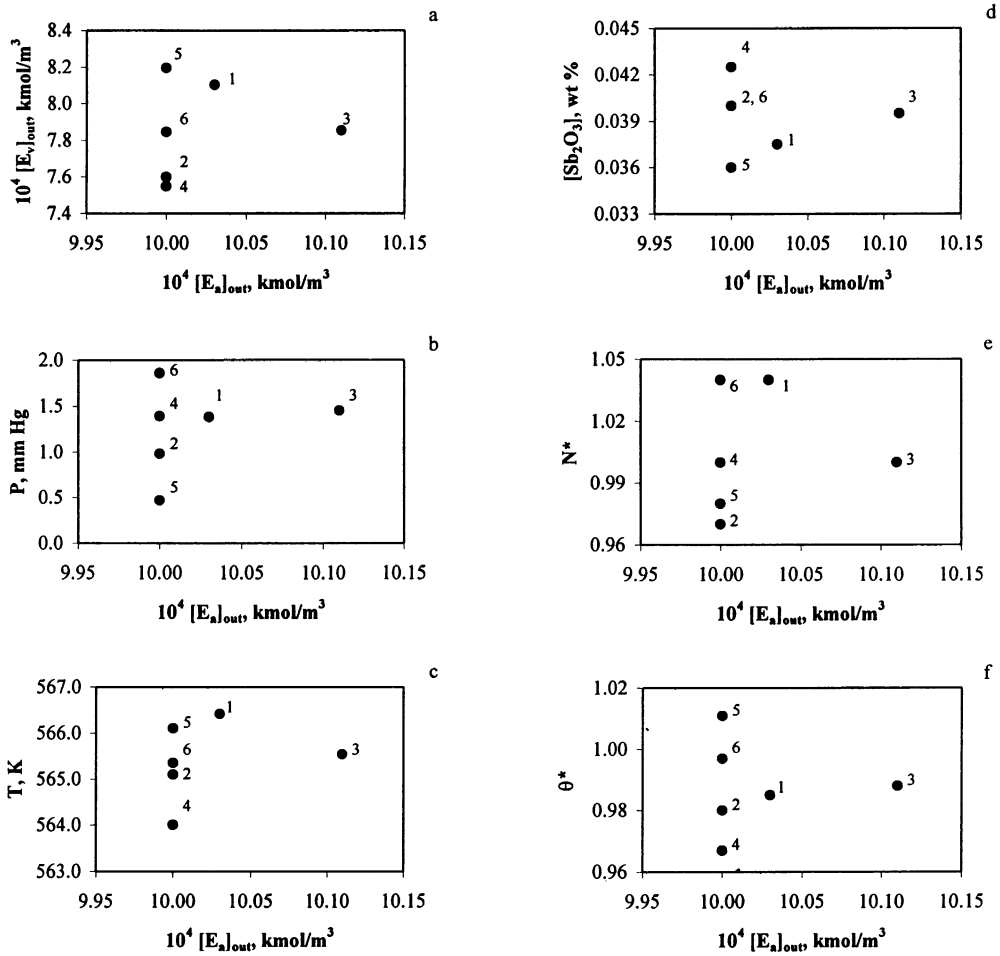


Fig. 1. Optimum values of $[E_a]_{out}$ vs. $[E_v]_{out}$ for several values of S_r (Table 4) for the five-decision variable problem of Eqs. (4a), (4b), (4c), (4d) and (4e) (a). The points correspond to those given in Table 4. Corresponding values of the decision variables are also shown.

Several studies on the modeling and simulation of the different stages of PET manufacture have been reported, as reviewed by Ravindranath and Mashelkar (1986a,b). In contrast, only a few studies (Kumar, Sharma & Gupta, 1984a,b; Kumar, Sukthankar, Vaz & Gupta, 1984; Immanuel & Gupta, 2000) have appeared in the open literature on the optimization of PET reactors. In our earlier study (Bhaskar, Gupta & Ray, 2001), we modified the model of Laubriet, LeCorre and Choi (1991) and simulated an *industrial* wiped film reactor. We '*tuned*' the model parameters using three sets of industrial data available with us. The tuned model, without any changes in the model parameters, predicted the fourth set of data extremely well. Thus, we believe that we have a model that represents the important physico-chemical phenomena in the reactor quite well, and that we could use it for optimizing its performance. Appendix A gives a summary of the model equations and parameters used (Bhaskar et al., 2000a; Bhaskar et al., 2001).

There are two important objectives in this polymerization. These are the minimization of the acid and the vinyl end group concentrations, $[E_a]$ and $[E_v]$, respectively, in the product (represented by subscript, 'out'). The acid end group makes the polymer susceptible to hydrolysis (Besnoin & Choi, 1989) during the downstream operations and leads to breakage of the filaments during spinning, where the humidity is high. The vinyl end groups have been shown to be responsible for the coloration of PET (Besnoin & Choi, 1989; James & Packer, 1995) because of reactions not too well understood right now, and not included in our kinetic scheme shown in Table 1. Hence, the minimization of these two end groups improves the quality of the polymer product. The reduction of $[E_a]$ simultaneously increases the rate of polymerization of the acid end group catalyzed polycondensation reaction, and helps maximize the throughput (this catalytic effect is also not *directly* incorporated in the model). The important end-point constraint is to produce polymer having a desired value of DP. An important side product is the diethylene glycol (DEG) end groups. Its presence affects the crystallinity and hence the melting point of the polymer unfavorably. However, these end groups im-

prove the dyeability of the fiber. Therefore, it is preferred to have a certain allowable *range* for the concentration of DEG end groups in the fiber-grade polyester produced. An inequality constraint is, therefore, imposed for the DEG end group concentration in the product. In addition, a further inequality constraint on the maximum allowable limit for the acid end group concentration is imposed to ensure that it is not only minimized, but also lies below an upper limit.

In our earlier optimization study (Bhaskar et al., 2000a) of the wiped film PET reactor we used five decision variables, viz. the reactor pressure (P), temperature (isothermal, T), catalyst concentration ($[Sb_2O_3]$), residence time (θ) of the polymeric reaction mass inside the reactor, and the speed (N) of the wiped-film agitator. All of these variables can easily be changed in any industrial, wiped-film reactor for PET manufacture, including the one being studied here. We found that the multiobjective optimization problem described above had a unique optimum solution (no Pareto set of several equally good, non-dominating points was obtained). Also, we found that several minima in the decision-variable space were present, where the values of the two objective functions were almost identical (Fig. 1a) for all practical purposes. This result, though interesting, was somewhat unexpected and so we attempted to explore this problem further to develop more insight. This paper presents the results of this detailed study.

2. Modeling and simulation of the wiped-film reactor

We give a short summary of the model used (Bhaskar et al., 2001) in this section. In the third-stage wiped-film PET reactor, the main reaction is polycondensation. This is accompanied by several other reactions, and the entire set of reactions (kinetic scheme) is given in Table 1 (Ravindranath & Mashelkar, 1984). The side reactions considered are the formation of hydroxyl end groups, acid end groups, vinyl end groups and DEG end groups. EG, water (W) and DEG are the volatile by-products of the process.

We have used an adaptation of the two-phase reactor model of Laubriet et al. (1991), as described by Bhaskar et al. (2000a). The model (state variable) equations can be written in the form

$$\frac{d\boldsymbol{x}}{dz} = \boldsymbol{f}(\boldsymbol{x}, \boldsymbol{u}); \quad \boldsymbol{x}(z=0) = \boldsymbol{x}_0 \tag{1}$$

where $\boldsymbol{x}$ is the vector of state variables, defined by

$$\boldsymbol{x} = [[E_g], [E_a], [Z], [E_v], [E_{DEG}], [EG], [W], [DEG]]^T \tag{2}$$

and $\boldsymbol{u}$ is the vector of control or decision variables. In Eq. (1), z represents the (dimensionless) axial position in the wiped-film reactor. The model equations (a set of ordinary differential equations, ODEs and given in Appendix A) are solved using the IMSL subroutine, DIVPAG, which uses Gear's method (Gupta, 1995). 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}), EG, W and DEG, as a function of the axial position in the reactor.

Model tuning and validation was performed using the industrial data given in Table 2. A tuning of nine parameters, k_La_{ref}, a_o, b_o, K_1, K_5, K_8, k_{2o}, k_{9o} and α, was carried out using three of the four sets (reference set 1, and sets 3 and 4) of industrial data given in Table 2. An IMSL subroutine DBCPOL (Nelder–Mead method) was used. The following equation was used to relate k_La to the speed of the agitator, N, (with the volume of the melt remaining unchanged).

$$k_La = k_La_{ref}\left(\frac{N}{N_{ref}}\right)^{\alpha} \tag{3}$$

In Eq. (3), subscript, ref, refers to the value of k_La at the reference conditions (set 1, Table 2). In the present case, the value of α is expected to be higher than 0.5 (Higbie's penetration theory) as kinetic effects are coupled with mass transfer. The values of the tuned parameters are given in Table 2. It is observed from this

Table 2
Industrial data and predicted values at the outlet end for the four data sets

Set[a]	Operating conditions	Product property	Industrial value	Model predicted value[b]
1	Reference (ref)[a]	DP_{out}	82.00	82.00
		$[E_{DEG}]_{out}$ (kmol m^{-3})	0.17	0.1692
		$[E_a]_{out}$ (kmol m^{-3})	1.038×10^{-3}	1.038×10^{-3}
2	$T_{ref}+1$ K	DP_{out}	82.60	82.56
3	$P_{ref}-0.5$ mmHg	DP_{out}	82.70	82.69
4	$N_{ref}+0.1$ rpm	DP_{out}	82.30	82.30

[a] $T_{ref} = 566.15$ K; $P_{ref} = 2.0$ mmHg; $[Sb_2O_3]_{ref} = 0.04$ wt.%; $\theta^* = 1.0$; $N^* = 1.0$; for the other three sets, only one of these values is different, as indicated. Sets 1, 3 and 4 used for tuning; set 2 used for validation.

[b] Tuned values of parameters, $k_La_{ref} = 2.6875$; $a_o = 1.0378$; $b_o = 2.1838$; $K_1 = 6.1835$; $K_5 = 5.143\times10^{-2}$; $K_8 = 11.87$; $k_{2o} = 4.7674\times10^{7}$; $k_{9o} = 0.2215\times10^{9}$; $\alpha = 2.6647$.

Table 3
Computational variables used in this study/Bounds and reference values of the possible decision variables

Weighting factors (Eqs. (5a) and (5b))	GA parameters (ref)		
$w_1 = w_3 = 10^4$ $w_2 = 10^8$ $P_e = 10^4$	$N_{gen} = 50$ $N_p = 50$ $p_c = 0.65$ $p_m = 0.004$ $\sigma = 3.0 \times 10^{-2}$ $\alpha_{sh} = 2.0$ $l_{chrom} = 32$ bits		
Variables/units	Lower bound	Upper bound	Reference value
P, kPa (mmHg)	0.05 (0.4)	0.266 (2.0)	0.266 (2.0)
T (K)	564.15	570.15	564.15
$[Sb_2O_3]$ (wt.%)	0.03	0.045	0.04
θ^*	0.90	1.06	1.00
N^*	0.93	1.05	1.00

table that the model-predicted values of the product properties agree quite well with industrial values, not only for the three sets used for tuning (sets, 1, 3 and 4) but also for set 2, when these parameters are used.

3. Multiobjective optimization

Five decision variables were used for multiobjective optimization in our previous study (Bhaskar et al., 2000a). These are P, T, $[Sb_2O_3]$, θ, and N. The multiobjective function optimization problem described earlier is described mathematically by

$$\mathrm{Min}\boldsymbol{I}(P, T, [Sb_2O_3], \theta^*, N^*) \equiv [I_1, I_2]^T = [[E_a]_{out}, [E_v]_{out}]^T \quad (4a)$$

subject to

$$DP_{out} = DP_d \quad (4b)$$

$$[E_a]_{out} \leq 1.038 \times 10^{-3} \text{ kmol m}^{-3} \quad (4c)$$

$$0.1660 \leq [E_{DEG}]_{out} \leq 0.17 \text{ kmol m}^{-3} \quad (4d)$$

$$\frac{d\boldsymbol{x}}{dz} = \boldsymbol{f}(\boldsymbol{x}, \boldsymbol{u}); \quad \boldsymbol{x}(z=0) = \boldsymbol{x}_0 \quad (4e)$$

In Eqs. (4a), (4b), (4c), (4d) and (4e), subscripts 'out' and 'd' refer to the values at the outlet of the reactor and the desired values of the product property, respectively. The variables, θ^* and N^*, represent dimensionless values, θ/θ_{ref} and N/N_{ref}, where θ_{ref} and N_{ref} (reference values) are the values being used *currently* in the industrial reactor being studied. These values are confidential and are not being provided due to proprietary reasons. Meaningful bounds have been chosen on the five decision variables, $\boldsymbol{u}$, based on industrial practice. These are given in Table 3.

A few important points need to be mentioned here. We have used the catalyst concentration as a decision variable for the optimization of stage 3, even though the catalyst is added (in the form of the glycolate) at the inlet of stage 2. This has been done because the catalyst concentration used affects the operation of stage 3 far more significantly than stage 2, and remains unconsumed. The feed to the wiped-film reactor is assumed to be constant while carrying out the optimization, even though we have taken θ^* as a decision variable. A different value of θ^* would require a higher flow rate in the wiped-film reactor, as well as in the previous reactors (we assume that a change in θ^* is achieved by a change in the flow rate in the wiped-film reactor, rather than the liquid hold up). This is justified since stage 2 is equilibrium-controlled (Ravindranath & Mashelkar, 1982), and its output concentrations depend *only* on its temperature and pressure, and are independent of the flow rate in it.

Both the equality and the inequality constraints (Eqs. (4b), (4c) and (4d)) are incorporated in the objective functions as penalty functions and they can be represented mathematically as

$$\mathrm{Min}\ I_1^* = w_1[E_a]_{out} + w_2\left(1 - \frac{DP_{out}}{DP_d}\right)^2 + P_e \quad (5a)$$

$$\mathrm{Min}\ I_2^* = w_3[E_v]_{out} + w_2\left(1 - \frac{DP_{out}}{DP_d}\right)^2 + P_e \quad (5b)$$

An additional large 'penalty' value, $P_e(=10^4)$, is added to the objective functions, I_1^* and I_2^*, if either of the two inequality constraints in Eqs. (4c) and (4d) are violated. If these constraints are satisfied, then the value of P_e in Eqs. (5a) and (5b) is taken as zero. This ensures that bad chromosomes in the genetic algorithm used for optimization do not get reproduced in the successive generations even if several chromosomes violating these constraints exist in the initial population (i.e. the chro-

mosomes violating Eqs. (4c) and (4d) are 'killed' almost instantaneously using P_e). Minimization of I_1^* and I_2^* leads to a decrease in the acid and vinyl end group concentrations, while simultaneously giving preference to solutions satisfying the several requirements discussed above. The use of a penalty to 'kill' chromosomes when important physical constraints are violated is one of the adaptations made in the basic algorithm (NSGA) in this study.

4. Results and discussion

A computer program was written in FORTRAN 90 and debugged using several test problems (Deb, 1995). The solution of the multiobjective optimization problem described in Eqs. (4a), (4b), (4c), (4d) and (4e) was then obtained using the computational parameters and bounds of the decision variables given in Table 3. The CPU time taken for one optimization run in SGI Origin 2000 super computer varied from 0.521 to 0.872 s depending on the number of decision variables used. The value of DP_d was taken as 82.0, the same as the value for the reference case (set 1 in Table 2) for the industrial reactor *simulated* earlier. This enables one to explore if changes in the operating variables could improve the performance of the *existing* industrial reactor (which was simulated by us, Bhaskar et al., 2001). A *unique* optimal point (solution) was obtained, using $S_r = 0.8887$ (where S_r is the seed used for generating random numbers in the code) as given below (Bhaskar et al., 2000a).

$$[E_a]_{out} = 10.0 \times 10^{-4} \text{ kmol m}^{-3} \quad (6)$$

$$[E_v]_{out} = 7.549 \times 10^{-4} \text{ kmol m}^{-3}$$

The corresponding values of the decision variables are

$$P = 0.18 \text{ kPa (1.39 mmHg)}; \quad T = 564.01 \text{ K};$$

$$[Sb_2O_3] = 0.0425 \text{ wt.\%}; \quad (7)$$

$$\theta^* = 0.967; \quad N^* = 1.0$$

This point is shown as point 4 in Fig. 1.

We then ran our computer program for several values of S_r. Unique points were *always* obtained, irrespective of the value of S_r. The results are shown in Fig. 1 for six values of S_r given in Table 4. It is observed from Fig. 1a that NSGA converges to different (though unique) local optimal points, and is unable to converge, in general, to the global optimal solution (point 4 (obtained using $S_r = 0.8887$), and given in Eqs. (6) and (7)). The failure of NSGA for *this* multiobjective optimization problem contrasts with the almost overwhelming success of this technique for several other complex Chemical Engineering problems studied by our group recently (Bhaskar et al., 2000b; Chan, Aatmeeyata, Gupta & Ray, 2000). Indeed, Goldberg (1989) has indicated that even though GAs are quite efficient in reaching the global-optimum *region*, they are not guaranteed to reach the *precise location* of the global-optimum *point(s)*, particularly for complex problems. The PET wiped film reactor optimization problem, thus, could be an excellent example for testing newer multiobjective optimization algorithms. It may be added that NSGA/GA has certain advantages over other popular gradient-based techniques like NLP/SQP. Lexicographic approach works on the principle of ranking the objective function based on the importance a priori. The disadvantage with lexicographic approach is that the solution is very sensitive to the ranking of the objectives by the decision-maker (DM) and, therefore, one should be careful in applying this technique to objectives having almost equal importance. Different results may be obtained for such cases depending upon the ranking of such objectives by the DM (Chankong & Haimes, 1983). Ranking of objective functions a priori is also a difficult task. The evolutionary algorithms are far superior compared with gradient search techniques in handling discrete search space problems. NSGA has been found to be a highly robust and successful technique for obtaining the optimal solutions for several complex multi-objective optimization problems in chemical engineering. Interestingly, it fails for the PET reactor problem unless adaptation as mentioned in this manuscript is used.

An interesting point suggested by Fig. 1 is that even for near-identical values of the two objective functions, $[E_a]_{out}$ and $[E_v]_{out}$, as for example, points 2 and 4 (corresponding to values of S_r of 0.8887 and 0.6237), the optimal values of the decision variables differ significantly. This reflects the nature of the 'terrain' and indicates the presence of multiple (local) minima having almost equal depths. The presence of such multiple optimal points and the failure of NSGA to give the global (or all the) optimal solution(s) in a single application, are to be noted since this could happen in other optimization problems as well.

We also solved modified versions of the multiobjective optimization problem described in Eqs. (4a), (4b), (4c), (4d) and (4e), which had fewer decision variables. This was done to develop further insight into the multiobjective optimization problem. In the first such problem, we

Table 4
Values of S_r used for the five-decision variable problem

#	S_r
1	0.3500
2	0.6237[a]
3	0.8000
4	0.8887[a] (ref)
5	0.9000
6	0.9500

[a] Multiplicity observed in these cases. Correspond to best optimal solutions.

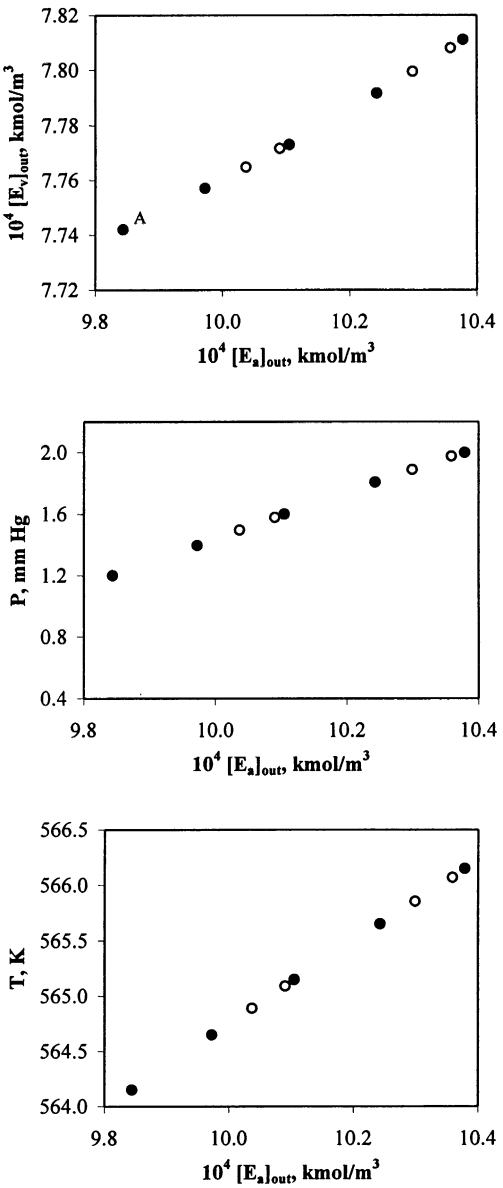


Fig. 2. Optimum solutions for a single-decision variable (P) optimization problem (Eq. (8)) at different values of T (filled circles). Unfilled circles represent the optimal solutions for the two-decision variable (P, T) problem (Eq. (9)) for different S_r. $[Sb_2O_3] = 0.04$ wt.%; $\theta^* = 1.0$; $N^* = 1.0$ for both cases.

used *only one* decision variable, the pressure, P, and kept the other decision variables at constant values (*mostly*, at their reference values given in Table 3). The modified problem is described mathematically by

$$\text{Min } \boldsymbol{I}(P) \equiv [I_1, I_2]^T = [[E_a]_{out}, [E_v]_{out}]^T$$

s.t. Eqs. (4b), (4c), (4d) and (4e) and

$$T = C_1$$

$$[Sb_2O_3] = C_2$$

$$\theta^* = C_3$$

$$N^* = C_4 \quad (8)$$

The bounds on P are taken to be the same as in Table 3. Unique optimal solutions were found for this problem, too, for all the choices of the constants, C_1–C_4. Interestingly, use of different values of S_r for any specified values of C_1–C_4, did not give different optimal solutions in this case, in contrast to what we experienced with Eqs. (4a), (4b), (4c), (4d) and (4e). Fig. 2 (filled circles) shows the unique optimal solutions of Eq. (8) for $[Sb_2O_3] = 0.04$ wt.%, $\theta^* = 1$ and $N^* = 1.0$, i.e. for several different (constant) values of T in the range 564.15 K $\leq T \leq$ 566.65 K. Each constant value of T gives a single unique optimal

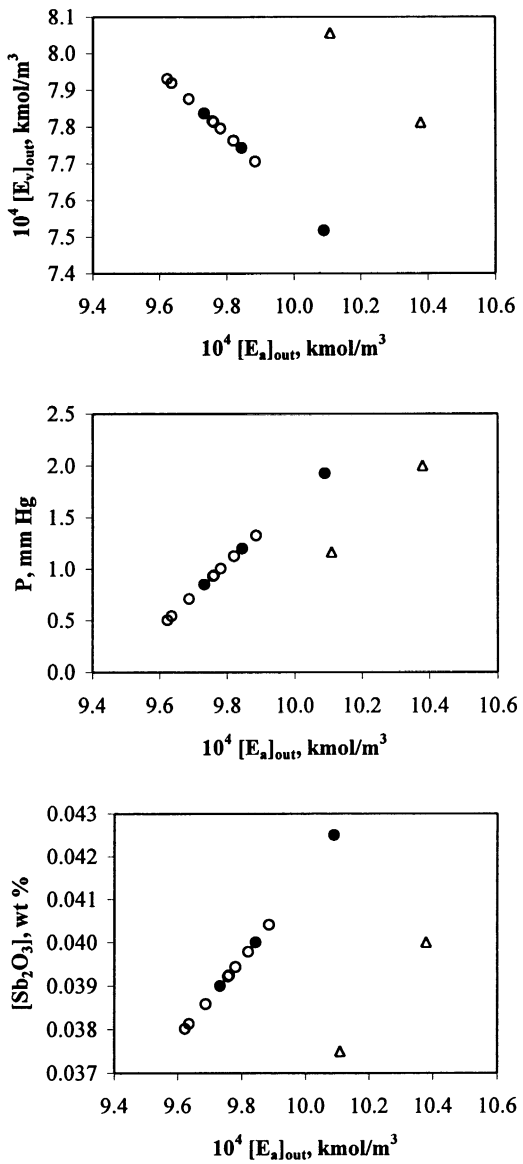


Fig. 3. Optimum solutions for a single-decision variable (P) optimization problem (Eq. (8)) at 564.15 (filled circles) and 566.65 K (unfilled triangles), for different constant values of $[Sb_2O_3]$. Unfilled circles represent the optimal solutions for the two-decision variable (P, $[Sb_2O_3]$) optimization problem for different S_r. $\theta^* = 1.0$; $N^* = 1.0$ for all cases.

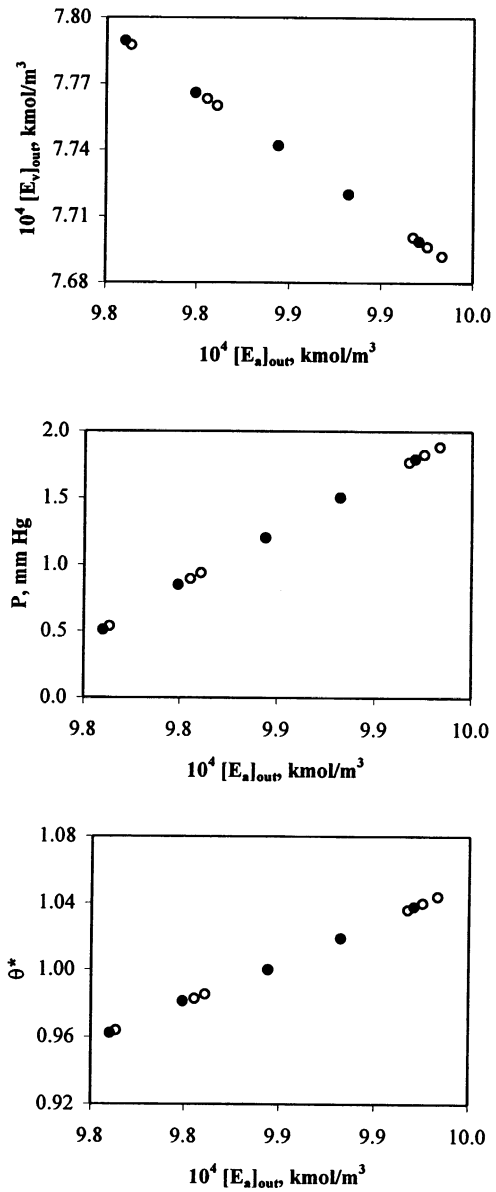


Fig. 4. Optimum solutions for the single-decision variable (P) optimization problem (Eq. (8)) (filled circles) for different constant values of θ^*. Unfilled circles represent the optimal solutions for the two-decision variable (P, θ^*) optimization problem for different S_r. $T=$ 564.15 K; $[Sb_2O_3] = 0.04$ wt.%; $N^* = 1.0$ for all cases.

solution in the $[E_a]_{out}$ versus $[E_v]_{out}$, plane. This diagram shows that temperature affects both $[E_a]_{out}$ and $[E_v]_{out}$ in a similar manner. This is expected since both $[E_a]_{out}$ and $[E_v]_{out}$ are products of degradation reactions. Clearly, point A in Fig. 2a is the best point among all those obtained, dominating over all the other points shown. We should, therefore, expect to obtain point A as the unique global optimum solution if we use NSGA to solve the following multiobjective optimization problem with two decision variables, P and T.

$$\text{Min } \boldsymbol{I}(P, T) \equiv [I_1, I_2]^T = [[E_a]_{out}, [E_v]_{out}]^T$$

s.t. Eqs. (4b), (4c), (4d) and (4e) and

$$[Sb_2O_3] = C_2 = 0.04\%$$

$$\theta^* = C_3 = 1.0$$

$$N^* = C_4 = 1.0 \quad (9)$$

with bounds on P and T as given in Table 3. Fig. 2 (open circles) gives the optimal solutions for this problem for different values of S_r. We obtain unique solutions for each value of S_r. This means that as soon as we move from a one-decision variable problem to one

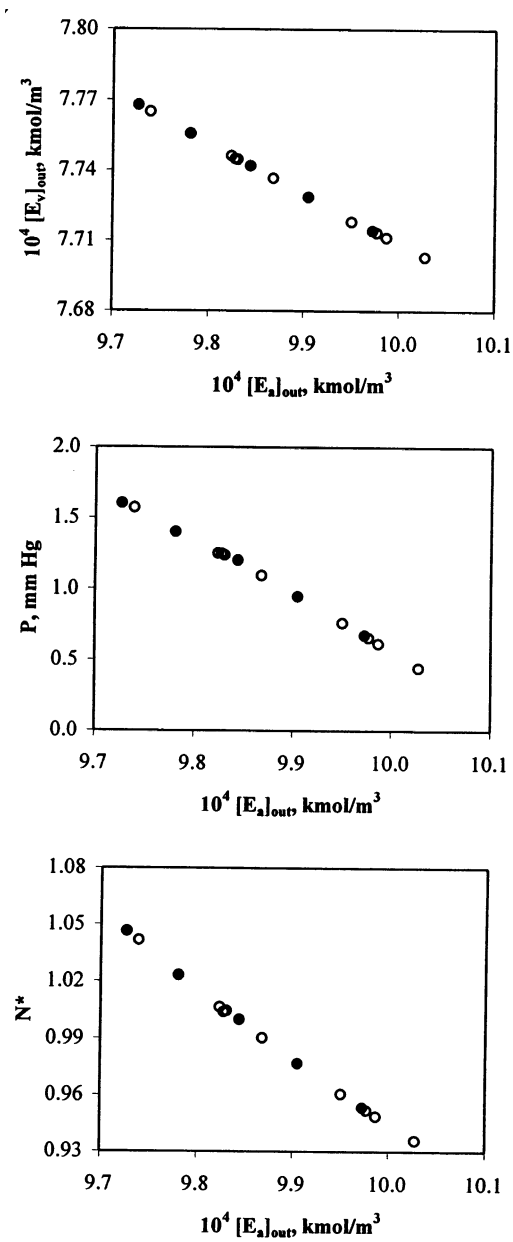


Fig. 5. Optimum solutions for the single-decision variable (P) optimization problem (Eq. (8)) (filled circles) for different constant values of N^*. Unfilled circles represent the optimal solutions for the two-decision variable (P, N^*) optimization problem for different S_r. $T=$ 564.15 K; $[Sb_2O_3] = 0.04$ wt.%; $\theta^* = 1.0$ for all cases.

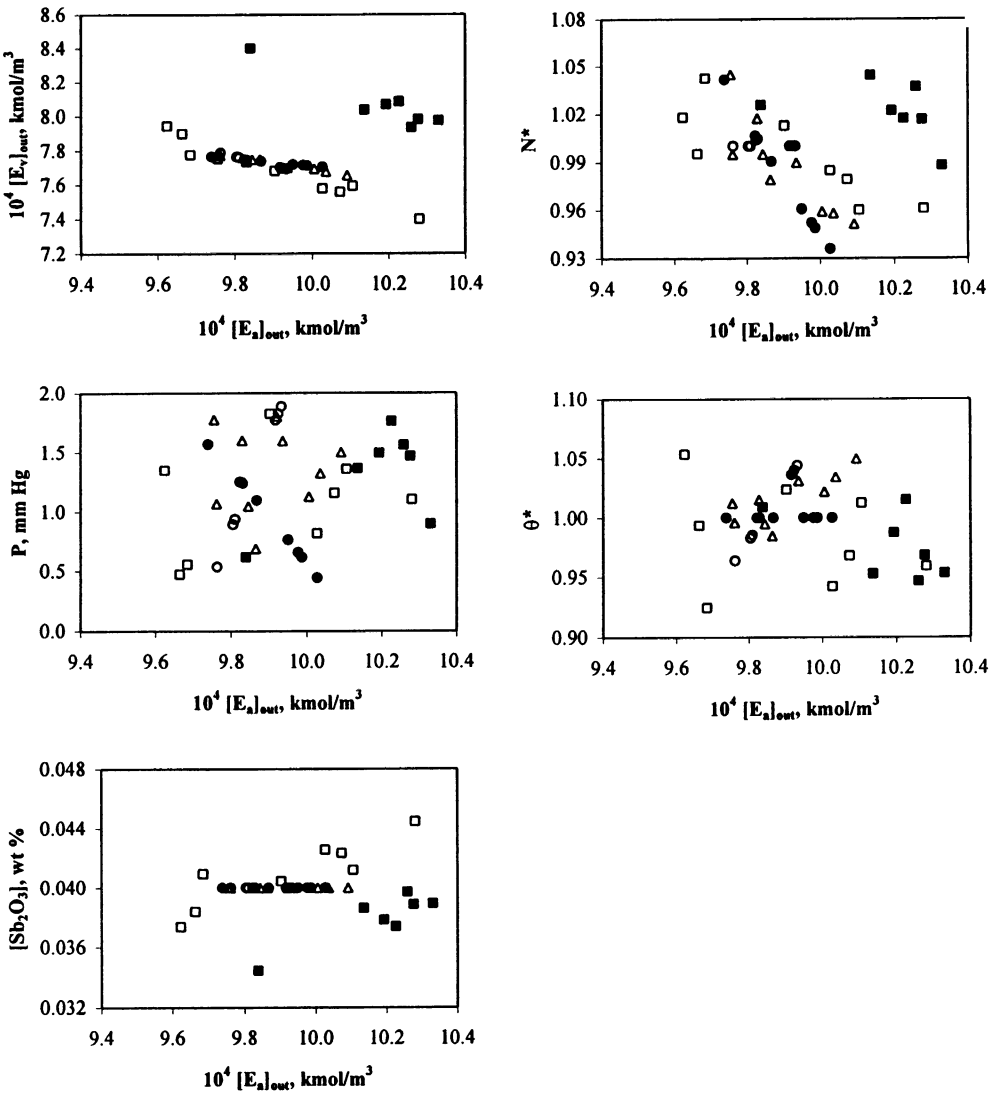


Fig. 6. Optimum solutions of several problems not involving T as a decision variable. The decision variables used are: filled circles, P, N^*; unfilled circles, P, θ^*; unfilled triangles, P, θ^*, N^*; unfilled squares, P, [Sb_2O_3], θ^*, N^*; all for $T = 564.15$ K. Filled squares are for $T = 566.65$ K with decision variables as P, [Sb_2O_3], θ^*, N^*. Reference values (Table 3) used for the operating variables held constant.

involving two decision variables in the PET wiped film reactor optimization problem, NSGA fails to give the global optimal point in a single application. However, multiple applications of this technique with several different values of S_r could be used to obtain the complete and correct solution.

We now study the one decision variable optimization problem in Eq. (8) with $T = 564.15$ K, $\theta^* = 1.0$, $N^* = 1.0$ and with different (*but constant*) values of [Sb_2O_3]. Fig. 3 (filled circles) shows the results. The unfilled triangles in Fig. 3 show similar results, but for $T = C_1 = 566.65$ K. In contrast to what was observed in Fig. 2, Pareto sets are obtained at both the temperatures studied (as well as at other intermediate values of temperature, not shown in Fig. 3). The Pareto for $T = 564.15$ K is superior to that for $T = 566.65$ K. We used NSGA to solve the two objective function problem with $T = 564.15$ K, and with P and [Sb_2O_3] as the decision variables. Again, a *unique* optimal solution was obtained for any value of S_r, instead of the expected Pareto set, indicating the failure of NSGA. Optimal solutions were generated for the two-decision variable problem using several values of S_r, and these are shown (unfilled circles) in Fig. 3. Interestingly, these solutions superpose quite well with those obtained at $T = 564.15$ K using one decision variable, and suggest a means of obtaining meaningful solutions with NSGA (by running NSGA for several values of S_r).

Figs. 4 and 5 show the optimal solutions (filled circles) for the single-decision variable (P) problem (Eq. (8)), for different values of θ^* (Fig. 4) and N^* (Fig. 5). Each run leads to a unique solution, but by varying the appropriate decision variable, we obtain Pareto sets for these two

cases too, as in Fig. 3. The dominating Pareto, once again, was found to correspond to $T = 564.15$ K (Paretos were obtained for higher values of T too, but are not shown here). For this value of T, NSGA is used to obtain the optimal solutions for the two-decision variable multiobjective optimization problem (P and θ^* for Fig. 4; P and N^* for Fig. 5). Once again, NSGA gives only unique points as the optimal solution, and is unable to 'catch' the Pareto sets. Only when we use several values of S_r, are we able to obtain the Paretos indicated by the simpler and equivalent one decision variable problem. It appears (from Figs. 3–5) that running NSGA several times with different S_r helps in obtaining solutions of the PET reactor optimization problem, at least for the three sets of the two-decision variable problems.

Based on our observations in Figs. 2–5 we infer that the multiobjective optimization problem with a single decision variable (Eq. (8)) offers the greatest amount of insight in understanding the effects of the decision variables on the objective functions. Also, it is safest to start from optimal solutions of these simple problems, and *then* attempt to generate optimal solutions to problems involving more than one decision variable. NSGA can still be used to generate solutions for the *present* problem, but only through the use of several applications with different values of S_r (each of which gives only a single, unique optimal point rather than the entire Pareto set, even if the latter is the correct solution). It is interesting to note that we obtain Pareto solutions for *all* the two decision variable multiobjective optimization problems studied until now, except for the first case

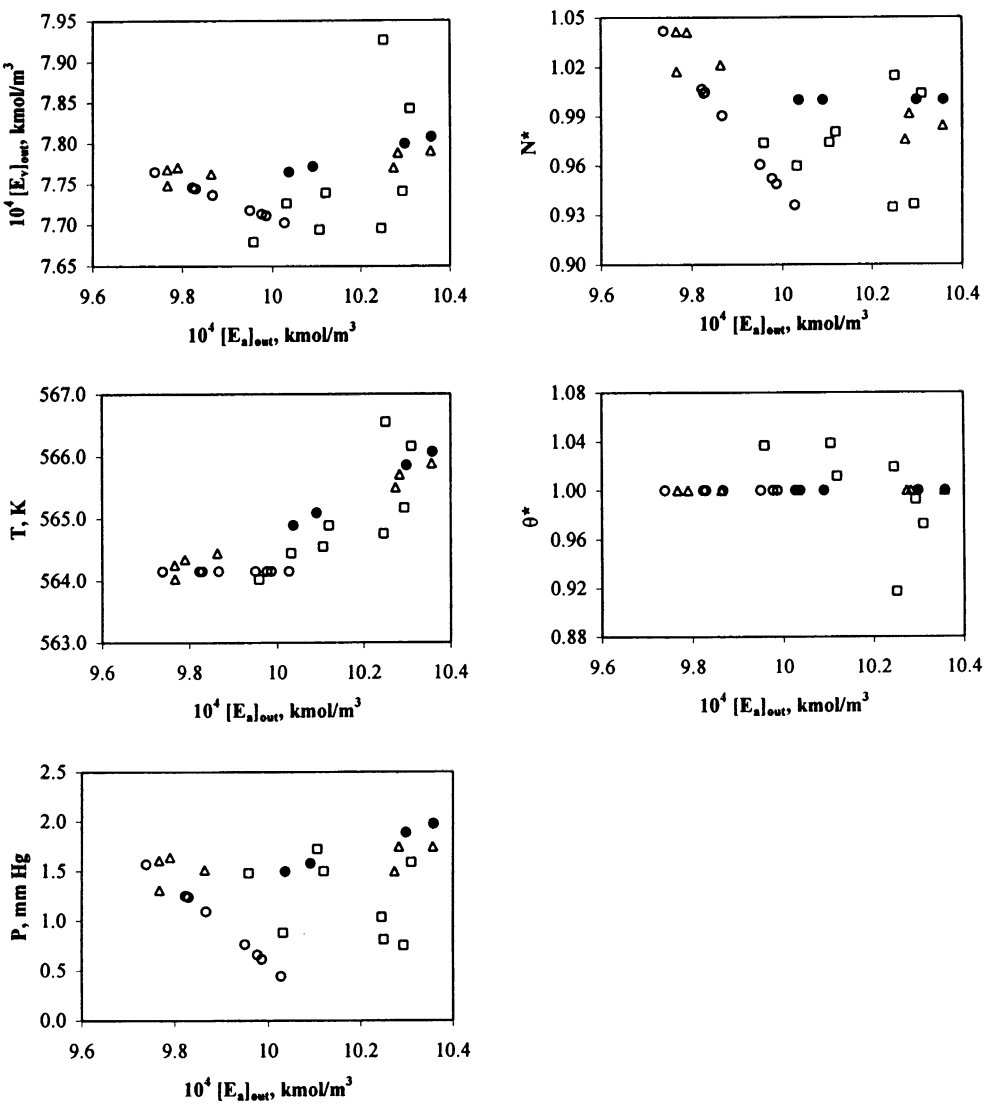


Fig. 7. Optimum solutions of several multiobjective optimization problems. The decision variables used are: filled circles, P, T; unfilled circles, P, N^*; unfilled triangles, P, T, N^*; unfilled squares, P, T, θ^*, N^*. $[Sb_2O_3] = 0.04$ wt.% in all cases. Reference values (Table 3) used for the operating variables held constant.

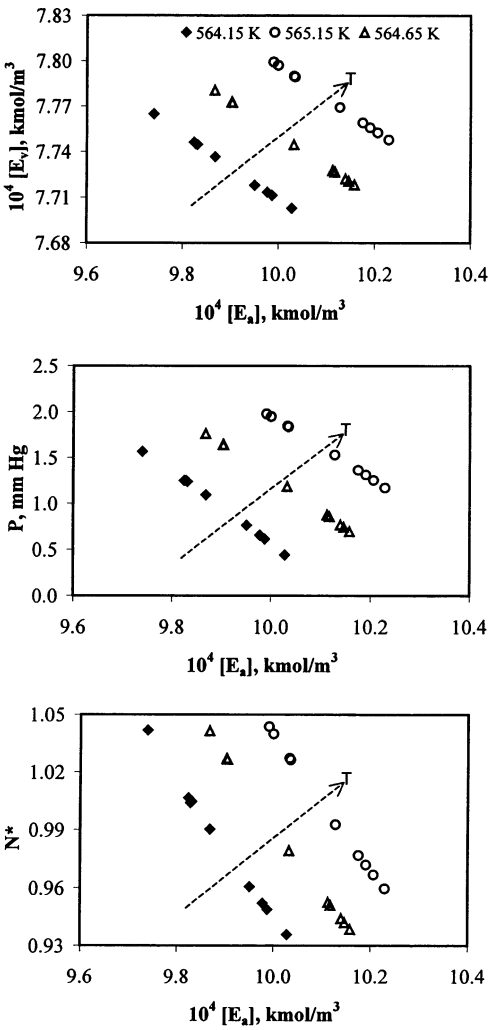


Fig. 8. Optimum solutions for the two-decision variable (P, N^*) optimization problem at three different values of T. $[Sb_2O_3] = 0.04$ wt.%; $\theta^* = 1.0$.

when P and T are the decision variables, where a unique global optimum solution is indicated. Yet another interesting point to note is that Figs. 2–5 do *not* show much scatter, something that confounded us in our earlier optimization study of this reactor (Bhaskar et al., 2000a).

We now present solutions of a few multiobjective optimization problems with three and four decision variables. In these cases, too, NSGA fails to 'catch' the Pareto solutions or the dominating solution, and gives only single optimal points, depending on the value of S_r used. Fortunately, in these cases too, multiple applications of NSGA with different values of S_r gives the complete and correct picture.

Fig. 6 shows the solutions obtained using two, three and four decision variables. None of these sets of decision variables involved T, which was kept constant at 564.15 K. It is observed that as soon as the number of decision variables increases beyond two, scatter is manifested in the plots of the decision variables, even though there is a reasonable amount of overlap (and only a small amount of scatter) in the Pareto solutions obtained in all the cases. The scatter is *particularly* large in the plots of the optimal values of P and θ^* when three or four decision variables are used for optimization. This makes such plots very inconvenient to use in industry. The scatter is associated with the fact that the decision variables compensate for each other and give similar values of $[E_a]_{out}$ and $[E_v]_{out}$. Fig. 6 shows that we also obtain Pareto sets (using several runs of NSGA with different values of S_r) at a constant temperature of 566.65 K. Based on the Pareto sets obtained with four decision variables, P, $[Sb_2O_3]$, θ^*, and N^*, at the two temperatures (564.15 and 566.65 K), we expect that if we use all five decision variables, we would obtain the same optimal solution as the Pareto at 564.15 K and with four decision variables. However, this does not happen and the moment we add on temperature as the fifth decision variable, the Pareto vanishes (see Fig. 1) and we have a global optimum point.

Fig. 7 shows another set of results with several sets of decision variables. This time, *the temperature is included as one of the decision variables, in (almost) all cases*. In this case, Paretos are definitely not obtained (we believe that this is the effect of including T in the set of decision variables), and a single dominating optimal point exists. However, NSGA is again unable to converge to this correct solution in any of the cases and gives single but incorrect optimal solutions. Several runs with different values of S_r were made again to seek out the correct unique solution. Fig. 7 shows that a considerable amount of scatter exists in the optimal solutions when *four* decision variables are used. It is clear that the effect of temperature is most dominant whenever it is included as a decision variable, and unique optimal points are obtained in all such cases. Lower temperatures lead to lower values of *both* $[E_a]_{out}$ and $[E_v]_{out}$, and a unique optimal solution is expected physically. However, we were unable to rationalize all these observations earlier (Bhaskar et al., 2000a) because of lack of sufficient insight developed here.

It is to be emphasized that NSGA was unable to obtain either Pareto optimal solutions or the unique global optimal point, in a single application in the present study. This is in sharp contrast to our earlier studies on multiobjective optimization of steam reformers (Rajesh, Gupta, Rangaiah & Ray, 2000), cyclone separators (Ravi, Gupta & Ray, 2000)and PMMA reactors (Zhou, Gupta & Ray, 2000), systems that are equally complex. We did solve several other (simpler) multiobjective optimization test problems (Deb, 1995) with the *same* code, and were able to obtain the correct Pareto solutions in a single run. This confirms that our code is free of errors. It appears that the present multiobjective optimization problem is an excellent test problem for checking the efficiency of future optimization algorithms and adaptations.

It must be added that we found two solutions with almost identical values of $[E_a]_{out}$ and $[E_v]_{out}$ (points 2 and 4 in Fig. 1) for the optimization problem with five decision variables, but having very different values of the decision variables. We were unable to obtain similar multiple solutions with almost equal values of the objective functions, in problems involving three or four decision variables, even though we made several trial runs.

Since we obtained Pareto sets of non-dominated solutions for several cases, we decided to develop a few correlations that could be used for industrial application (for the reactor being studied). We selected three problems, each involving two decision variables, P and N^*. This was done because multiobjective optimization

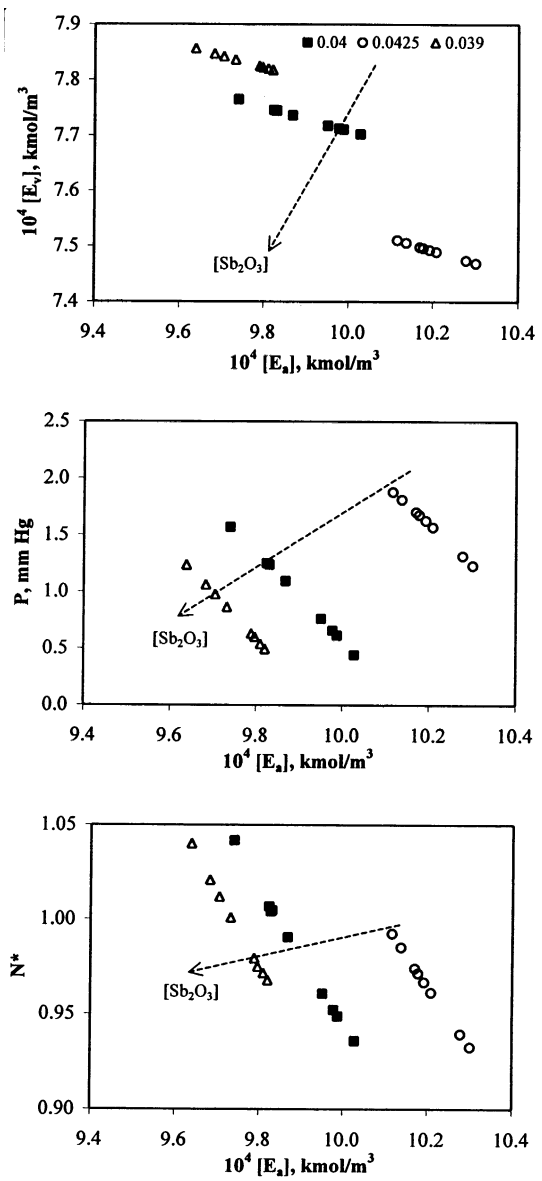


Fig. 9. Optimum solutions for the two-decision variable (P, N^*) optimization problem at three different values of $[Sb_2O_3]$. $T = 564.15$ K; $\theta^* = 1.0$.

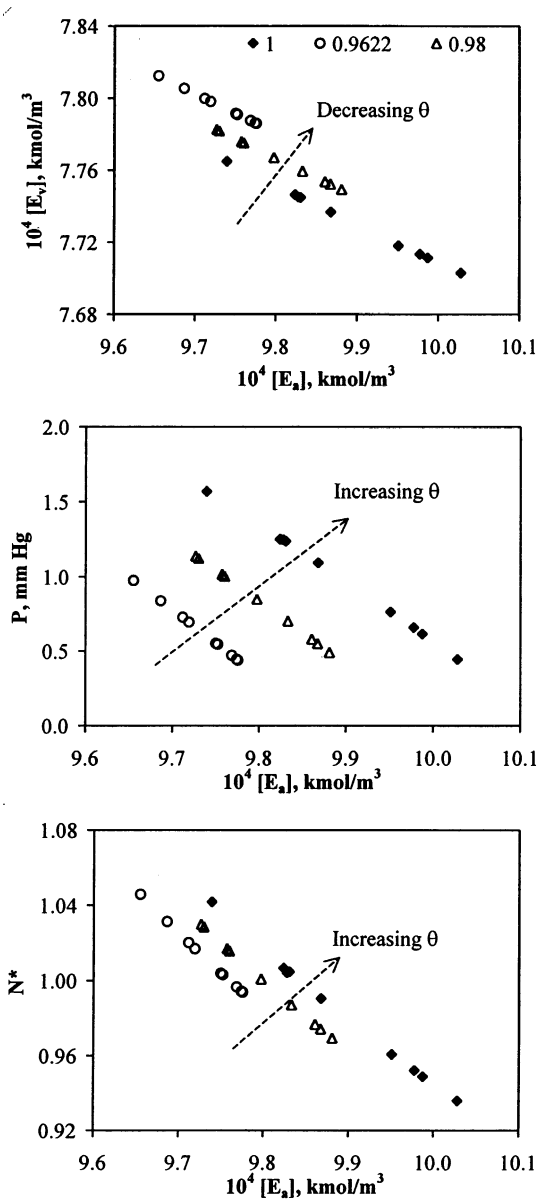


Fig. 10. Optimum solutions for the two-decision variable (P, N^*) optimization problem at three different values of θ^*. $T = 564.15$ K; $[Sb_2O_3] = 0.04$ wt.%.

problems having more than two decision variables showed considerable scatter, and fitting correlations would be meaningless. The reason why we selected P and N^* was because these were the most commonly varied decision/operating variables used in industrial wiped-film PET reactors. The results are shown in Figs. 8–10. The Pareto sets are observed to be well described by straight lines in all these cases. Table 5 gives the correlations. Once the decision-maker decides upon a preferred solution (a preferred value of, say, the acid end group concentration) and selects say, a reactor temperature, the correlations given in Table 5 could be used to obtain the optimal values of pressure, N^* and the vinyl end group concentration.

5. Conclusions

An improved and validated model for the wiped-film finishing reactor for PET manufacture is used to solve an optimization problem involving two objective functions and some end-point constraints. The concentrations of the side products, $[E_a]_{out}$ and $[E_v]_{out}$, are minimized, while ensuring that the product has certain desired characteristics (DP_{out}, $[E_a]_{out}$ and $[E_{DEG}]_{out}$,). The highly successful technique (based on our earlier experiences), NSGA, fails to give correct solutions in a single application, particularly when several decision variables are used. One needs to study several *simpler* optimization problems with fewer decision variables, and also apply NSGA several times over (using different values of S_r) in order to be able to obtain the correct solutions. It is found that for the PET wiped film reactor, Pareto solutions of non-dominating solutions are obtained whenever temperature is kept constant and is *not* used as a decision variable. In contrast, a globally unique optimal point is obtained when the temperature is taken as one of the decision variables, because its effect on the two objective functions dominates.

Appendix A. Complete set of model equations used in this study

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

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

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

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

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

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

$$\frac{1}{\theta}\frac{d[EG]}{dz} = R_1 - R_4 - R_7 - k_1a([EG] - [EG^*])]$$

$$\frac{1}{\theta}\frac{d[W]}{dz} = R_7 + R_8 - k_1a([W] - [W^*])]$$

$$\frac{1}{\theta}\frac{d[DEG]}{dz} = R_4 + R_5 - k_1a([DEG] - [DEG^*])]$$

where

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

$$R_2 = k_2[E_g]$$

$$R_3 = k_3[E_v][E_g]$$

$$R_4 = 2k_4[E_g][EG]$$

$$R_5 = k_5[E_g][E_{DEG}] - 4k'_5[Z][DEG]$$

$$R_6 = k_6[E_g]^2$$

$$R_7 = 2k_7[E_a][EG] - k'_7[E_g][W]$$

$$R_8 = k_8[E_g][E_a] - 2k'_8[Z][W]$$

$$R_9 = k_9[Z]$$

Vapor–liquid equilibrium correlations.

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

Table 5
Correlations for predicting optimal pressure, speed of the agitator and vinyl-end group concentrations for $DP_d = 82.0$[a]

Decision Variables			Correlations
T (K)	$[Sb_2O_3]$ (wt.%)	θ^*	
564.15–566.15	0.04	1.0	$P_{opt} = 1.393\ T - 3.666[E_a]_{out} - 748.4$ $N^*_{opt} = -0.3546[E_a]_{out} + 0.09483\ T - 49.01$ $[E_v]_{out,opt} = 0.08864T - 0.2153[E_a]_{out} - 40.15$
564.15	0.039–0.0425	1.0	$P_{opt} = 721.2447[Sb_2O_3] - 3.843808[E_a]_{out} + 10.15276$ $N^*_{opt} = 37.69[Sb_2O_3] - 0.3616[E_a]_{out} + 3.052$ $[E_v]_{out,opt} = -69.267[Sb_2O_3] - 0.21743[E_a]_{out} + 12.6551676$
564.15	0.04	0.9623–1.0	$P_{opt} = 26.623876\theta^* - 4.061131[E_a]_{out} + 14.551311$ $N^*_{opt} = 0.8404\theta^* - 0.3799[E_a]_{out} + 3.9019$ $[E_v]_{out,opt} = -0.78\theta^* - 0.21563124[E_a]_{out} + 10.64471844$

[a] P in mmHg; $[E_a]_{out}$, $[E_v]_{out}$ in kmol m^{-3}.

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

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

$$\ln P_{EG}^o = 49.703 - \left(\frac{8576.7}{T}\right) - 4.042 \ln T$$

$$\ln P_W^o = 18.568 - \frac{4047.606}{T - 33.3}$$

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

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

$j = \text{EG, W, DEG}$

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

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

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

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

$$\chi_1 = a_o + b_o \left(1 - \frac{U_v}{U_v^o}\right)$$

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

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

Kinetic parameters (Laubriet et al., 1991; Martin & Choi, 1991) $([Sb_2O_3] = 0.04$ wt.%$)^+$.

Reaction number, i	Type of reaction	Rate constant $k_i = k_{io} \exp(-E_i/RT)$		Equilibrium constant
		k_{io} (m^3 mol^{-1} min^{-1})	E_i (J mol^{-1})	
1	Reversible	1.09×10^3	4418	6.1835
2	Irreversible	4.7674×10^7*	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	0.2215×10^9*	9028	

+, 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 Laubriet et al. (1991); Martin and Choi (1991).

*, min^{-1}.

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