Multi-Objective Dynamic Optimization of Semi-Batch Polymerization Processes

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Summary: An improved evolutionary algorithm is proposed to perform multi-objective dynamic optimization of a semi-batch styrene polymerization process. The target is to determine the optimal feeding trajectories and the reactor operating temperature, which maximize the monomer conversion rate and minimize the initiator residue concentration in the final product. The optimization problem has been formulated as a multi-objective mixed-integer nonlinear problem (MOMINLP). The proposed approach allows the effective computation of the optimal operating strategies for the production of polymers with the average molecular weight and the polydispersity index required.

Keywords: evolutionary algorithms; high performance polymers; multi-objective optimization; processing; semi-batch polymerization

Introduction

Fine chemicals and other high value products are usually processed in semi-continuous reactors. Despite being widely used, batch and semi-batch reactors are often still operated heuristically, based on experience. The industrial acceptance of optimization techniques for such systems is still incipient. In contrast to continuous processes, which have been rigorously studied, the optimization of semi-continuous processes stems from the limited availability of detailed dynamic models, whose development and validation are often quite expensive. The adjustment of time-varying conditions in order to achieve product quality targets and improve process efficiency remains a challenging area of research.

In polymerization systems, the typical highly nonlinear dynamic behavior makes the precise control of the process a difficult task. The lack of appropriate on-line control methodologies and instrumentation to monitor polymer properties can lead to undesirable characteristics of the final product, such as low resistance to shrinkage and distortion at high temperatures and discoloration due to decomposition of initiator residues and oxidation of leftover monomers [1]. Monitoring

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techniques for the evaluation of polymer properties include density, viscosity, surface tension, refractive index, composition, light scattering and chromatographic methods. Despite the recent developments in this field, some of these methods are still rather time consuming and require very expensive instruments [2]. The measurements of polymer properties, in most of them, are carried out off line. Therefore, the unreliability on these methods is still high for industrial environment.

Optimal operating strategies are essential to improve the productivity and profitability of semi-continuous processes by avoiding possible reactor overheating as well as underfeeding or overfeeding. Much effort has been done to determine optimal operating policies for polymerization and copolymerization processes [3-8].

Due to their inherent transience, the optimization of semi-continuous systems requires the calculation of time dependent trajectories rather than the determination of one single set of optimal operating conditions. Changes in the feeding policy and reactor temperature, however, may influence the polymerization performance in opposing ways. Multi-objective optimization techniques have been successfully used to deal with conflicting behaviors. In recent years, several works have been reported on multi-objective dynamic optimization of batch and semi-batch polymerization processes [1, 9-16]. However, most of them are restricted to scalar approaches. In this contribution, a heuristic multi-objective optimization method is adopted to determine the optimal operating strategies for a semi-batch styrene polymerization process. The proposed approach allows the formulation of the problem as a multi-objective mixed-integer nonlinear problem (MOMINLP).

Multi-objective Optimization

Real-world engineering problems usually involve the simultaneous optimization of several targets, even though some of which may be in conflict. In order to face this contradiction, a multi-objective approach is required. The multi-objective optimization procedure consists in a search for non-dominated solutions. The concept of non-dominance refers to the solutions that are superior to the others on all objectives. The optimization progress is guided by the fitness evaluation. The process continues until no improvements can be obtained in any objective without deteriorating at least one of the other objectives. In multi-objective optimization, there may not exist a global solution that is the best concerning all objectives. The optimal solution constitutes a family of non-

dominated points called Pareto optimal front. All points in this front equally satisfy the set of objective functions. Therefore, any point constitutes an acceptable solution of the problem. The choice of one solution over the others requires additional knowledge of the problem.

Evolutionary computation techniques have been widely applied to optimize complex problems, regarding their potential as multi-objective optimizers. Evolutionary algorithms are robust stochastic methods for global and parallel optimization. These methods are founded on the principles of natural genetics, in which the fittest species survive and propagate while the less successful tend to disappear. The evolution strategy consists of performing the population with genetic operators to produce the next generation. The basic genetic operators simulate the processes of selection, crossover and mutation. As in nature, pairs of individuals are selected for reproduction. Selection is based on the survival potential, which is expressed by the fitness function. Crossover involves random exchange of characters between pairs of individuals, or parents, in order to generate one or two offspring. Mutation is an occasional change in a randomly chosen character of an individual, originating a new individual. It introduces diversity to a model population. These operators are activated according to pre-established probabilities.

An important characteristic of the evolutionary methods is that they are able to cope with ill-behaved problem domains, such as the ones presenting multimodality, discontinuity, time-variance, randomness and noise. Several studies on multi-objective evolutionary optimization methodology are presented in the literature [17-20].

The Proposed Algorithm

A multi-objective optimization algorithm based on evolutionary strategies has been proposed to generate optimal operating policies for the styrene polymerization process. In this algorithm, the concept of population ranking initially suggested by Goldberg [21] has been extended to treat multidimensional problems. The probability of reproduction has been determined by a fitness function, which takes into account the rank level and the populational density on the rank. In the ranking procedure, points are categorized into groups according to their non-dominance levels. The closer to the Pareto set a group of points is, the higher its probability to propagate to the next generation.

A penalty function method based on fuzzy logic theory has been adopted to incorporate the

constraints into the fitness function. New operators have been introduced to enhance the algorithm performance: (a) a niche operator, which prevents genetic drift and maintains a uniformly distributed population along the optimal set; (b) a Pareto-set filter, which avoids missing optimal points during the evolution process; (c) an elitism operator, which insures the propagation of the best result of each individual objective function. Real codification, which provides better computational performance and stability in converging to global optima, is also adopted. The detailed algorithm is presented in a previous work [22].

The niche operator controls the replacement of individuals. It determines which individuals go to the next generation by evaluating each child produced by crossover in the domain of the previous population. The replacement of the parents only occurs if the children' superior fitness exceeds the best fitness of the parents. Otherwise, the parents go to the next generation. The niche operator helps to prevent the population to become clustered at certain regions, as a result of stochastic errors associated with the genetic operators and the use of finite size populations.

The Pareto set filter operator is an mechamism to store the non-dominated solutions. This filter is dynamically updated at each iteration: the solutions assigned rank 1 at the current generation are added to the filter and compared with the ones previously stored. All solutions are re-evaluated and the dominated ones are discarded. If the file is full, the most similar points in the Pareto set file are replaced. Such procedure maintains an even distribution of the points in the file. At the end of the optimization process, the solutions stored in the Pareto set file constitute the optimal solution set.

The elitism operator is responsible for the propagation of the best solutions to the next generation. At each iteration, the best solution for each individual objective function is updated. These solutions will randomly replace some of the individuals originated by the crossover and mutation procedures. This operator increases the algorithm robustness and the convergence of the optimization process.

In this contribution, the algorithm has been modified to operate simultaneously in continuous and discrete variable space, in order to treat multi-objective mixed-integer nonlinear problems (MOMINLP). The operators were reformulated to deal with a varying number of decision variables, which is required to solve the optimization case II.

Polymerization Process

The case study consists of a semi-batch styrene polymerization process. Styrene is considered one of the most important monomers produced worldwide. It is mainly used in the production of polystyrene and acrylonitrile-butadiene-styrene resins (ABS), as well as a variety of polymers in the petrochemical industry [23].

The styrene polymerization process is conducted in a semi-batch reactor, using benzoyl peroxide as chemical initiator and toluene as solvent. The operation time is set on 7 h and the initiator is drip-fed periodically to the system, at equal intervals of time. The scheme of the process unit is illustrated in Figure 1.

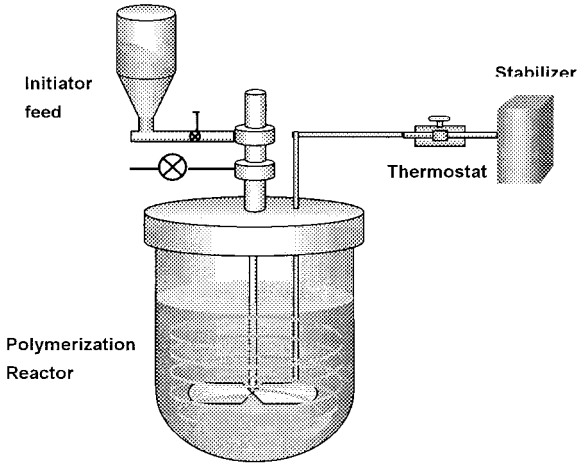

Figure 1. Scheme of the semi-batch polymerization process

Mathematical Modeling

The classical mechanism of free-radical polymerization is used to describe the process. The mathematical model consists of the following differential algebraic system resulting from component mass balances [24]:

$$\frac{dI}{dt} = I_{Fi} - k_d I \tag{1}$$

$$\frac{dS}{dt} = -\frac{k_{fs}}{V} S\lambda_o \tag{2}$$

$$\frac{dM}{dt} = -\frac{(k_p + k_{fm})}{V} M\lambda_o \tag{3}$$

$$\frac{d\mu_o}{dt} = \frac{k_{fm}M + k_{fs}S}{V}\lambda_o + \frac{k_{td}}{V}\lambda_o^2 + \frac{k_{tc}}{2V}\lambda_o^2 \tag{4}$$

$$\frac{d\mu_2}{dt} = \frac{k_{fm}M + k_{fs}S}{V}\lambda_2 + \frac{k_{tc} + k_{td}}{V}\lambda_o\lambda_2 + \frac{k_{tc}}{V}\lambda_1^2 \tag{5}$$

$$\mu_1 = M_o x_M \tag{6}$$

where I, S and M are the initiator, solvent and monomer concentration, respectively. M_o is the initial monomer concentration and I_F is the initiator feed. μ_o and μ_2 are the moments of dead polymer distribution. k_d, k_p, k_{fs}, k_{tc}, k_{td} and k_{fm} are the reaction rate constants and λ_o, λ_1 and λ_2, the three leading moments of the live polymer molecular distribution:

$$\lambda_o = \sqrt{\frac{2\left(k_{dm}M^3V^{-1} + k_d f_e IV\right)}{k_{tc} + k_{td}}} \tag{7}$$

$$\lambda_1 = \lambda_o + \frac{k_p M\lambda_o}{k_{fm}M + k_{fs}S + k_t\lambda_o} \tag{8}$$

$$\lambda_2 = \lambda_o + \frac{k_p M\lambda_o + 2k_p M\lambda_1}{k_{fm}M + k_{fs}S + k_t\lambda_o} \tag{9}$$

The reactor volume is described as a function of the initial reactor volume, the monomer concentration and a volume contraction factor as follows:

$$V = V_o\left[1 + \varepsilon_v\left(\frac{M}{M_o}\right)\right] \tag{10}$$

The following assumptions were made in the kinetic model, aiming to simplify the mathematical formulation of the problem [24, 25]: (a) all reactions are elementary and irreversible; (b) the rates of reaction are independent of chain length; (c) there are no temperature gradients in the reactor, perfect mix is assumed. The mathematical model is based on a lab scale reactor unit. Due to its reduced dimensions, it is assumed that the reactor operates isothermically, with efficient mechanisms of agitation and refrigeration [24].

The average molecular weight, M_w, and the polydispersity, P_d, are calculated using the equations of moments presented above

$$M_w = \frac{PM_{mon}\mu_2}{M_o x_M} \tag{11}$$

$$P_d = \frac{\mu_o \mu_2}{(M_o x_M)^2} \tag{12}$$

The gel effect is included in the termination rate constant, k_t:

$$k_t = k_{to}(c_1 + c_2 x_M + c_3 x_M^2)^2 \tag{13}$$

where $c_1 = 0{,}5093$, $c_2 = 2{,}4645$ and $c_3 = -3{,}7473$

Simulation of the Mathematical Modeling

The set of differential and algebraic equations was solved by the numerical integrator DASSL [26]. In order to investigate the multi-objective behavior of the system, simulations of the polymerization process were conducted for the range of temperature from 310 to 400 K and total initiator feed from 0.02 to 0.2 mol/l. The model parameters and physical properties of the process are summarized in Tables 1 and 2. The initiator residue concentration in the product and the monomer conversion are plotted in Figures 2 and 3 as functions of temperature and total initiator feed. The profiles of the polydispersity index and the molecular weight are illustrated in Figures 4 and 5. The total initiator feed corresponds to the sum of ten periodical feeds. The simulations were conducted using equal concentrations of initiator in all feeds.

Table 1. Kinetic parameters and physical chemistry properties

$k_p = 1{,}051\times10^7 \exp(-7.060/RT)$ (l/mol s) [8]	$k_{fs} = 5{,}92\times10^8 \exp(-17.210/RT)$ (l/mol s) [8]
$k_{fm} = 2{,}31\times10^6 \exp(-12.670/RT)$ (l/mol s) [8]	$k_{to} = 1{,}255\times10^9 \exp(-1.680/RT)$ (l/mol s) [8]
$k_d = 7{,}12\times10^{13} \exp(-29.589/RT)$ (s^{-1}) [27]	$k_{dm} = 2{,}190\times10^5 \exp(-27.440/RT)$ ($l^2/mol^2 s$) [28]
$\rho_M = (0{,}8075 + 1\times10^{-3}\times T)^{-1}$	ε_v = -0,1506-4,436×10^{-4} (T-273,15) [29]
$\rho_S = (1{,}047 + 4{,}9\times10^{-4}\times T)^{-1}$	f_e = 0,72 (-) [30]

Table 2. Operational parameters of styrene polymerization

Parameter		Parameter	
M_{wD} (kg/mol)	1x10^5	P_{dref} (-)	1,5
x_{MD} (-)	0,7	V_0 (ml)	1000

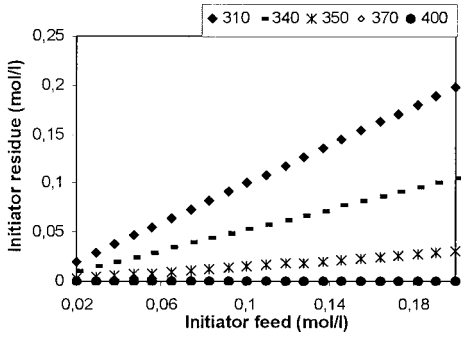

Figure 2. Simulation of the behavior of the initiator residue concentration

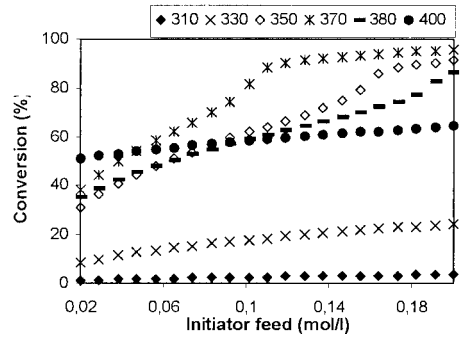

Figure 3. Simulation of the behavior of the monomer conversion

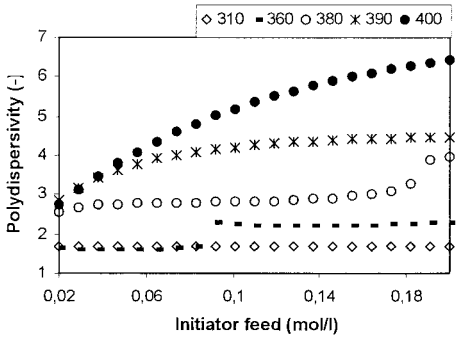

Figure 4. Simulation of the behavior of the polydispersity index

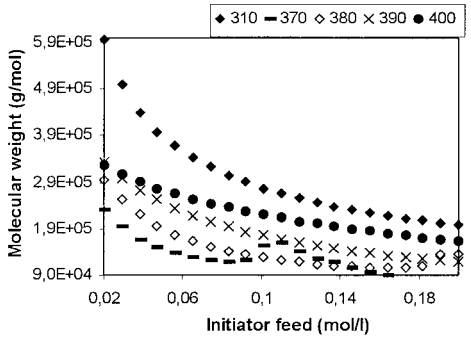

Figure 5. Simulation of the behavior of the molecular weight

It can be observed that the initiator residue concentration is inversely proportional to the temperature and directly proportional to the amount of initiator fed. At high temperatures, however, the initiator is totally consumed, independently of the amount of initiator fed.

High levels of monomer conversion are reached at intermediate temperatures. A slight increase in the conversion is observed when the amount of initiator added to the system is increased. This influence is stronger at intermediate temperatures.

In case of polydispersity index, the simulation shows that low levels of this parameter are obtained under the conditions of low temperature and low initiator concentration.

The molecular weight is inversely proportional to the initiator concentration. The effect of the temperature, in contrast, is not linear. High molecular weights are obtained at extreme values of temperature, both high and low ones.

The opposing behaviors observed for all these parameters make the process suitable to be optimized by using a multi-objective approach.

Formulation of the Multi-objective Optimization Problem

Two different optimization problems are formulated for the styrene polymerization system in order to establish the optimal operating strategies.

Optimization problem – case I

The focus in this case is to maximize the monomer conversion, x_M, up to 100 % and minimize the

residual initiator, I, in the final product. As constraints, an average molecular weight, M_w, greater than 100,000 and a polydispersity index, P_d, inferior to 2.0 are required. Initiator is added at intervals of 42 minutes, totalizing ten additions. The decision variables include the reactor operating temperature, T, and the initiator feeding concentrations, $I_F(i)$, (i = 1, 10). Thus, eleven decision variables are manipulated. The formulation of the optimization problem is as follows:

minimize $f_1 = I(t_f)$ (14)

$f_2 = [1.0 - x_M(t_f)]^2$ (15)

subject to the constraints g_1: $M_w(t_f) \geq 1 \times 10^5$ g/mol (16)

g_2: $1.0 \leq P_d(t_f) \leq 2.0$

and the limits $308.15 \leq T \leq 393.15$ K

$0 \leq I_F(i) \leq 1 \times 10^{-1}$ mol/l

Results and Discussion - Case I

The optimization of the polymerization process was conducted using the parameters listed in Table 3. A thousand iterations were required to generate the Pareto optimal set, illustrated in Figure 6.

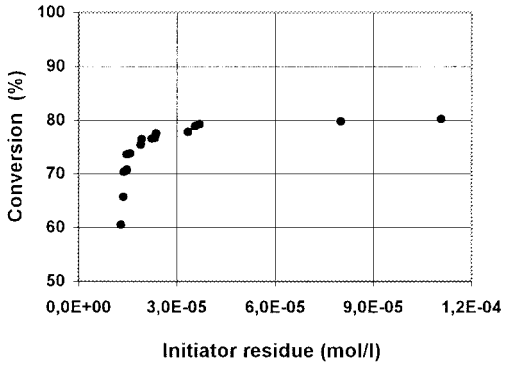

Figure 6. Pareto optimal set for the polymerization process – case I

Table 3. Parameters of algorithm configuration

Population size	20 individuals	Mutation probability	5 %
Crossover probability	75 %	Number of children /crossover	1

Table 4 shows the optimization results for the objective functions - initiator residue and monomer conversion; and the constraints - polydispersity index and molecular weight, as well as the optimal values of the decision variables - reactor temperature and total initiator feed. It can be observed that the optimal solutions followed the limits of the constraints established in the equations (16).

Table 4. Results of the optimization of the polymerization process – case I

Initiator residue (mol/l)	Conversion (%)	Temperature (K)	Total initiator feed (mol/l)	Polydispersity index (-)	Molecular weight (g/mol)
1.30×10^{-5}	60.55	368.68	7.25×10^{-2}	1.99	1.26×10^{5}
1.37×10^{-5}	65.71	368.67	8.61×10^{-2}	1.90	1.20×10^{5}
1.38×10^{-5}	70.41	368.67	1.08×10^{-1}	1.94	1.17×10^{5}
1.46×10^{-5}	70.76	368.67	1.02×10^{-1}	1.91	1.17×10^{5}
1.46×10^{-5}	70.77	368.67	1.02×10^{-1}	1.91	1.17×10^{5}
1.46×10^{-5}	70.79	368.67	1.02×10^{-1}	1.91	1.17×10^{5}
1.46×10^{-5}	70.80	368.67	1.02×10^{-1}	1.91	1.17×10^{5}
1.47×10^{-5}	73.69	368.66	1.12×10^{-1}	1.97	1.18×10^{5}
1.53×10^{-5}	73.72	368.66	1.11×10^{-1}	1.96	1.18×10^{5}
1.58×10^{-5}	73.84	368.66	1.12×10^{-1}	1.97	1.18×10^{5}
1.89×10^{-5}	75.48	368.64	1.48×10^{-1}	1.91	1.19×10^{5}
1.93×10^{-5}	76.50	368.64	1.52×10^{-1}	1.94	1.21×10^{5}
2.24×10^{-5}	76.62	368.62	1.78×10^{-1}	1.92	1.20×10^{5}
2.32×10^{-5}	76.71	368.62	1.77×10^{-1}	1.92	1.20×10^{5}
2.36×10^{-5}	77.59	368.62	1.85×10^{-1}	1.94	1.22×10^{5}
3.34×10^{-5}	77.80	368.49	1.59×10^{-1}	1.94	1.23×10^{5}
3.56×10^{-5}	78.87	368.48	1.84×10^{-1}	1.96	1.25×10^{5}
3.68×10^{-5}	79.28	368.47	1.85×10^{-1}	1.98	1.27×10^{5}
8.01×10^{-5}	79.78	368.10	1.82×10^{-1}	1.97	1.28×10^{5}
1.11×10^{-4}	80.20	367.89	1.81×10^{-1}	1.97	1.29×10^{5}

Under the optimal feeding strategies, it is possible to produce polymers of high molecular weight and reduced polydispersity, with a monomer conversion of 80.2% and initiator residue concentration of 1.1×10^{-4} mol/l. By emphasizing the minimization of the initiator residue in the final product, it is possible to produce polymers with an initiator concentration of 1.3×10^{-5} mol/l and monomer conversion of 61%.

In Figures 7 and 8, the optimal feeding strategies corresponding to the best value of each objective function - maximum monomer conversion and minimum initiator residue, are illustrated.

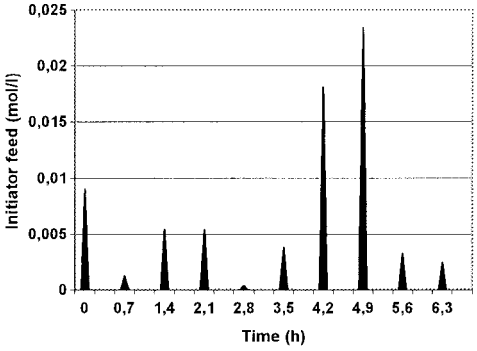

Figure 7. Optimal feeding strategy for the maximum monomer conversion – case I

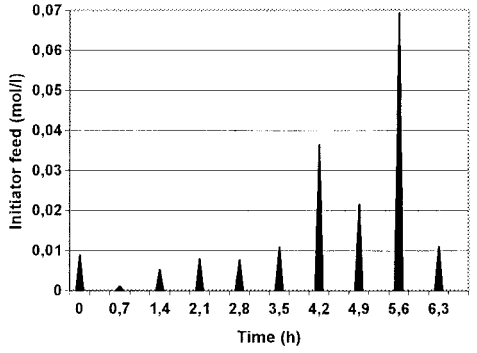

Figure 8. Optimal feeding strategy for the minimum initiator residue – case I.

Optimization problem – case II:

In this case, an additional decision variable is considered: the number of times the initiator is fed to the system. The aim is to find the reactor temperature, T, the number of initiator feeds, n_F, ($1 \leq n_F \leq 20$) and the feeding concentrations, $I_F(i)$, ($i = 1, n_F$). The total number of optimized variables will result from the optimization process itself and may be different for each individual of the population. The objective functions and the constraints are the same of the previous case. The mathematical statement is described by equations (14) to (16).

Results and Discussion - Case II

The preceding parameters of the algorithm configuration, presented in Table 3, are used in this case as well. The number of generations required was 2500 iterations. Figure 9 shows the Pareto optimal set obtained.

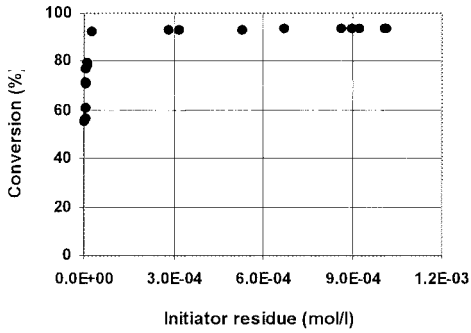

Figure 9. Pareto optimal set for the polymerization process – case II

Table 5 presents the results of the objective functions - initiator residue and monomer conversion; the decision variables - temperature, number of initiator feeds and total initiator feed; and constraints - the polydispersity index and molecular weight. Figures 10 and 11 show the optimal feeding strategies for maximum monomer conversion and minimum initiator residue.

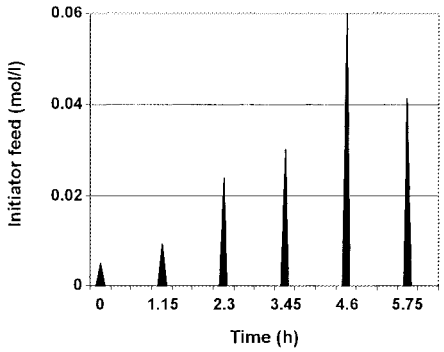

Figure 10. Optimal feeding strategy for the maximum monomer conversion – case II

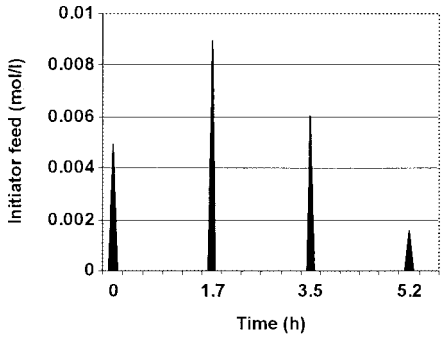

Figure 11. Optimal feeding strategy for the minimum initiator residue – case II

Table 5. Results of the optimization of the polymerization process – case II

Initiator residue (mol/l)	Conversion (-)	Tempera-ture (K)	# feeds (-)	Total initiator feed (mol/l)	Polydis-persity index (-)	Molecular weight (g/mol)
1.99×10^{-6}	55.34	370.92	4	2.15×10^{-2}	1.93	1.45×10^{5}
2.20×10^{-6}	56.38	370.61	5	2.56×10^{-2}	1.94	1.40×10^{5}
2.60×10^{-6}	56.51	370.60	5	2.61×10^{-2}	1.94	1.40×10^{5}
3.46×10^{-6}	57.06	370.44	5	2.81×10^{-2}	1.92	1.40×10^{5}
3.73×10^{-6}	61.12	374.04	6	1.58×10^{-1}	1.99	1.49×10^{5}
4.18×10^{-6}	71.19	371.09	3	5.22×10^{-2}	1.96	1.25×10^{5}
4.73×10^{-6}	71.91	371.12	4	1.11×10^{-1}	1.84	1.27×10^{5}
5.58×10^{-6}	77.28	369.57	7	1.29×10^{-1}	1.96	1.28×10^{5}
8.71×10^{-6}	78.16	368.62	7	1.14×10^{-1}	1.94	1.27×10^{5}
9.41×10^{-6}	79.40	368.45	7	1.16×10^{-1}	2.00	1.31×10^{5}
2.51×10^{-5}	92.66	366.62	7	1.59×10^{-1}	1.92	1.02×10^{5}
2.83×10^{-4}	93.12	366.55	7	1.58×10^{-1}	1.94	1.04×10^{5}
3.18×10^{-4}	93.22	366.57	7	1.59×10^{-1}	1.94	1.03×10^{5}
5.30×10^{-4}	93.29	366.53	6	1.75×10^{-1}	1.91	1.04×10^{5}
6.70×10^{-4}	93.52	366.38	6	1.85×10^{-1}	1.91	1.03×10^{5}
8.63×10^{-4}	93.53	366.03	6	1.65×10^{-1}	1.95	1.04×10^{5}
8.96×10^{-4}	93.59	365.96	6	1.65×10^{-1}	1.96	1.04×10^{5}
9.22×10^{-4}	93.71	365.92	6	1.70×10^{-1}	1.96	1.03×10^{5}
1.01×10^{-3}	93.80	365.80	6	1.69×10^{-1}	1.97	1.02×10^{5}
1.01×10^{-3}	93.82	365.80	6	1.69×10^{-1}	1.97	1.02×10^{5}

Better results are obtained when optimizing the feeding frequency besides the temperature and feeding concentrations. A monomer conversion of 93.8% can be reached with an initiator residue

of 1.0 x10^{-3} mol/l. On the other hand, it is possible to obtain an initiator residue concentration of 2.0 x 10^{-6} mol/l in the final product with a monomer conversion of 55.3%. It can be noticed that wider ranges of optimal results are obtained for both objective functions, as a higher degree of freedom is used in this case.

Moreover, it is worth to emphasize that easier conditions of operation are obtained in this case, as the number of initiator additions is reduced and less consumption of initiator is required.

Conclusions

In this contribution, a multi-objective optimization method based on evolutionary strategies has been developed to determine the optimal operating policies of a styrene polymerization process. The objectives are to maximize the monomer conversion and minimize the residual initiator in the final product. High average molecular weight and low polydispersity index are also required. Two different formulations of the problem were analyzed: the first one involving eleven decision variables, and the second one, a variable number of decision variables, which is dependent of the optimization process. In this case, the number of times the initiator is fed to the reactor is also optimized, resulting in distinct number of variables for each individual of the population. The algorithm has been implemented to operate simultaneously in continuous and discrete variable space in order to solve multi-objective mixed-integer nonlinear problems.

The results show that an improved end-product quality can be obtained by increasing the degree of freedom of the optimization process. These results also confirm the efficiency of the proposed optimization approach to solve semi-continuous polymerization problems involving a large number of decision variables.

Notation

f	objective function
f_e	initiator efficiency factor
g	constraint of the problem formulation
I	initiator concentration
k_d	rate constant of initiator decomposition
k_{fm}	rate constant of chain transfer to monomer
k_{fs}	rate constant of chain transfer to solvent
k_p	propagation rate constant
k_t	termination rate constant
k_{tc}	termination rate constant by combination reaction

k_{td}	termination rate constant by disproportionation reaction
M	monomer concentration
M_w	average molecular weight
n_F	number of initiator additions
P_d	polydispersity index
S	solvent concentration
T	reactor temperature
t_f	final time of reaction
V	reactor volume

Greek Symbols

ε_v	volume contraction factor
$\lambda_o, \lambda_1, \lambda_2$	three leading moments of the live polymer molecular distribution
μ_o, μ_2	moments of dead polymer distribution
ρ	density

Subscripts

D	desirable
F	feed
M	monomer
ref	reference
S	solvent

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