



Optimal Grade Transition for Polymerization Using a Novel Sequential Evolution Algorithm

Z.S. FEI, B. DUAN, Q.H. CHI and J. LIANG*

State Key Lab of Industrial Control Technology, Department of Control Science and Engineering, Zhejiang University, Hangzhou 310027, P.R. China

*Corresponding author: Tel/Fax: +86 571 87953883; E-mail: jliang@iipc.zju.edu.cn

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In order to reduce off-specification polymer products, it is important to obtain the optimal trajectories of manipulated variables during the grade transition process. A real-coded genetic algorithm based sequential evolution algorithm is proposed, wherein the population evolves in each dimension gradually based on the introduced evolution points and a grouped evolution strategy is used in each subpopulation. The Lee-Ramirez bioreactor case test showed that the sequential evolution algorithm is high-effective and is quite suitable for solving dynamic optimization problem. Then the sequential evolution algorithm is applied to solve the grade transition optimization problem in a gas phase fluidized-bed polyethylene reactor, where the different situations of multiple grades change over, various constraints, model mismatch and process disturbance are considered respectively. The results demonstrated that the optimal profiles could be determined precisely with short computing time.

Key Words: Grade transition, Optimization, Polymerization, Genetic algorithm.

INTRODUCTION

Polymer has a wide range of applications in industrial products and everyday life. To satisfy diverse market demands, polyolefin companies often have to produce different grades of polymer products in the same plant. During the grade transition process, quite a lot of off-specification products that don't satisfy the quality requirements would yield. Thus, it is important to perform grade transition operations in an optimal way so that the off-specification products can be minimized. Often optimal open-loop policies for accomplishing grade changeovers were determined by dynamic model based optimization^{1,2}. Furthermore, Chatzidoukas *et al.*³ had ever used the mixed integer dynamic optimization approach to compute the closed-loop control configuration and optimal grade transition policies considering the influence that the control structure configuration had on process operability and product quality. Biegler *et al.*⁴ studied the optimal grade transition problem in large-scale high-impact polystyrene (HIPS) plant and computed the off-line dynamic optimal grade transition trajectories among unstable open-loop operating points. Considering the great impact of model mismatch and process disturbances on optimization results, Bovin *et al.*^{5,6} proposed a measure-based approach called NCO tracking in which a decentralized control framework was used. However, in the previous studies the gradient based algorithms such as sequential quadratic programming (SQP) were constantly used to solve the optimal grade transition problem. In gradient based

algorithm, a great deal of gradient information needs to be provided and the algorithm will often be trapped in local optima⁷. Moreover when the required gradient information could not be given, the algorithm will be invalid.

Genetic algorithm (GA) is an intelligent algorithm that can avoid the local optimal trapping and need no gradient information. Considering the high-dimensional characteristic and the huge computing burden in dynamic optimization solving, a novel evolution algorithm named sequential evolution algorithm (SEA) that can obtain the global optima is proposed. The sequential evolution algorithm is a real-coded genetic algorithm based evolution strategy in which the population evolves in each dimension gradually. The entire population is divided into subpopulations in each dimension. All the subpopulations evolve independently but are also connected with each other by introducing the evolution point. Then the sequential evolution algorithm is implemented to the optimal grade transition process of polyethylene. The cases of multiple grades transitions, various constraints, model mismatch and the process disturbance are all considered. The results show that the optimal transition trajectories can exactly achieved and the computation burden is greatly reduced. When model mismatch and process disturbance exist, the product quality trajectories deviate significantly from the normal optimal trajectory.

Grade transition optimization problem: In this study, the polymerization of ethylene in a fluidized-bed reactor⁵ with

a heterogeneous Ziegler-Natta catalyst is considered. Ethylene, hydrogen, nitrogen and catalyst are fed continuously to the reactor. The gas phase consisting of ethylene, hydrogen and nitrogen provides the fluidization of the polymer bed and transports heat out of the reactor through a recycling system. The recycle gases are pumped back into the bottom of the reactor through a heat exchanger. The fresh feeds are mixed with the recycle stream before entering the reactor. Excessive pressure and impurities are removed using a bleed stream at the top of the reactor. Fluidized polymer product is removed from the base of the reactor through a discharge valve. The overall diagram of the fluidized-bed reactor is showed in Fig. 1.

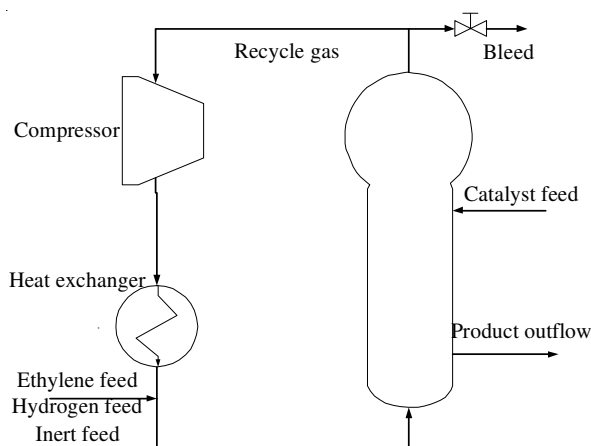


Fig. 1. Diagram of polyethylene fluidized-bed reactor

The melt index (the amount of melted polymer that can be squeezed through a standard orifice in 10 min) and density are often used as the specification of polyolefin products. Due to McAuley's work⁸, a simplified first-principles model of a fluidized-bed polyethylene reactor could be determined as follows:

$$MI_i = \exp\left\{k_4\left(\frac{1}{T} - \frac{1}{T_0}\right)\right\} \cdot \left\{k_1 + k_2 \frac{[H_2]}{[M_1]} + k_3 \frac{[M_2]}{[M_1]}\right\}^{k_5} \quad (1)$$

$$D_i = p_1 + p_2 \cdot \ln(MI_i) - \left\{p_3 \frac{[M_2]}{[M_1]}\right\}^{p_4} \quad (2)$$

$$\frac{dMI_c^A}{dt} = \frac{1}{\tau} \cdot MI_i^A - \frac{1}{\tau} \cdot MI_c^A \quad (3)$$

$$\frac{d\frac{1}{D_c}}{dt} = \frac{1}{\tau} \cdot \frac{1}{D_i} - \frac{1}{\tau} \cdot \frac{1}{D_c} \quad (4)$$

where, MI_i and D_i denote instantaneous melt index and density, MI_c and D_c are cumulative melt index and density, τ is the polymer-phase residence time in the reactor. In eqn. (3), the special parameter A is often set to -0.286 by experiments. And k_i ($i = 1 \dots 5$), p_j ($j = 1 \dots 4$) are coefficients to be determined.

The goal of the optimization of the grade transition operation is to analyze and characterize the grade transition for gas-phase fluidized-bed reactors from the point of view of minimizing the transition time or the amount of off-specification

polymer. In order to minimize the off-specification polymer during the grade transition operation, the following objective function penalizing the deviations from targets during the time period of interest is used.

$$J = \int_{t_0}^{t_f} \left[\omega_1 \left(\frac{MI_c(t) - MI_f}{MI_f} \right)^2 + \omega_2 \left(\frac{D_c(t) - D_f}{D_f} \right)^2 \right] dt \quad (5)$$

where, MI_f and D_f are target values of melt index and density separately, ω_1 and ω_2 denote weighting factors.

Sequential evolution algorithm

Algorithm construction: The sequential evolution algorithm is a real-coded genetic algorithm based evolution strategy, in which the population is divided into some subpopulations and evolves in each dimension gradually. To calculate the fitness values of individuals for each subpopulation the evaluation point is introduced to store the feasible solution in each iterative step.

Encoding: In standard genetic algorithm, the binary coding is often used, which is more similar with the composition of chromosomes and can make the crossover and mutation operations easy. However, for high-dimensional optimization problems, binary coded genes will be too long and will decrease the algorithm efficiency greatly. Thus, in sequential evolution algorithm the real code is used.

Suppose that the dimensionality of the optimization variables is m and the number of individuals in the population is n . Let x_t^k represents the k th-dimension subpopulation in the t th generation, $k \in \{1, 2, \dots, m\}$. Real-coded method is used here and each subpopulation is consist of n real numbers, *i.e.* $x_t^k \in \mathbb{R}^n$. So x_t^k could be expressed as a n -dimensional vector, $x_t^k = (x_t^{k(1)} x_t^{k(2)} \dots x_t^{k(n)})^T$ and the population of the t th generation X_t is expressed as a $n \times m$ -dimensional matrix, $X_t = (x_t^1 x_t^2 \dots x_t^m)$. In the initial population $X_0 = (x_0^1 x_0^2 \dots x_0^m)$, the row vectors are not the same and all the individuals in each subpopulation are different, *i.e.* if $i \neq j$ ($i, j \in \{1, 2, \dots, m\}$) then $x_t^{k(i)} \neq x_t^{k(j)}$.

Fitness function: The evolution point is introduced to calculate the fitness function in sequential evolution algorithm. Evolution point is a m -dimensional vector used to store the present feasible solution for the whole population. Let $Q_t = (q_t^1 q_t^2 \dots q_t^m)$ denotes the evolution point, where q_t^k represents the k th point in the t th generation, $k \in \{1, 2, \dots, m\}$. The evolution point plays the role of providing the other ($m-1$) dimensional variables when the k th-dimensional subpopulation evolve. After evolution operation of the k th-dimensional subpopulation is finished, q_t^k is substituted by the optimal individual. And the initial evolution point $Q_0 = (q_0^1 q_0^2 \dots q_0^m)$ is randomly given within the feasible region of the optimization variables.

In sequential evolution algorithm, the fitness value for each subpopulation is determined by the specific individual and the evolution point and has nothing to do with the other subpopulations. Let $x_t^{k(i)}$ represent the i th individual in the k th-dimensional subpopulation of the t th generation. $x_t^{k(i)}$ and other ($m-1$) elements in the evolution point except q_t^k together form a candidate solution, $u_t^{k(i)} = (q_t^1 q_t^2 \dots q_t^{k-1} x_t^{k(i)} q_t^{k+1} \dots q_t^m)$. And the fitness function can be computed using the objective function in the following statement.

$$\text{Fit}[f(u_t^{k(i)})] = f(u_t^{k(i)}) \tag{6}$$

where $f(\cdot)$ is objective function of the considered optimization problem.

Genetic operators: In normal genetic algorithm, genetic operators selection, crossover and mutation are generally used under binary encoding. After the selection operation by roulette wheel method, the selected individuals carry out crossover and mutation operations at single or multiple intersection points. But in sequential evolution algorithm, each subpopulation evolves independently and each subpopulation searches in single-dimensional space. The grouped-evolution strategy is implemented in each subpopulation. In the grouped-evolution strategy, the subpopulation is divided into groups randomly after calculating the fitness function of each individual in the k th subpopulation. Then the optimal individuals selected by fitness value in each group are used to cross with other individuals. The expressions for crossover are stated as,

$$s_1 = p_1 + \alpha(p_2 - p_1) \tag{7}$$

$$s_2 = p_1 + (1 - \alpha)(p_2 - p_1) \tag{8}$$

in which p_1, p_2 , are parents and s_1, s_2 , are offspring. Based on the fitness of s_1, s_2 , only the better one of the two offspring is kept. And the selected offspring and original optimal individuals together make up the new group.

After the evolution is finished of the k th subpopulation, the optimal individual is used to substitute the element q_t^k in the evolution point. For the $(k+1)$ th subpopulation the fitness is calculated using the optimal individuals of former subpopulations (from 1 to k). Hence each subpopulation evolves just in single dimension independently and seeks for the global optima together with the other subpopulations. Evolution point approaches to the global optimal point gradually through the iterative evolution for each subpopulation.

The sequential evolution algorithm approach is just like living beings' evolution, where the same species living in different regions reproduce independently but connect indirectly. The evolution of species in one place can impact the evolution of other places. Species in all the places will eventually evolve through the corresponding evolution of different regions. Geometrically, sequential evolution divide the original complex m -dimension searching problem into a serial of one-dimension searching problems. Evolution point forges ahead only in one dimension at each step and reaches the optimal value after iterative evolution. As the evolution algorithm is used in each dimension, the sequential evolution algorithm can obtain the global optima to some extent. Considering the two-dimensional optimization problem, the diagram of sequential evolution process is illustrated in Fig. 2, where x_0 is the starting point.

Sequential evolution algorithm procedures for dynamic optimization: In order to solve the dynamic optimization problem using the proposed sequential evolution algorithm approach, it is often needed to discretize the corresponding variables firstly. Let us consider a dynamic optimization problem as follows

$$\begin{aligned} \min_{u(t)} \int_{t_0}^{t_f} \Phi[z(t), u(t)] dt \tag{9} \\ \text{s.t. } \frac{dz}{dt} = f[x(t), u(t)], z(t_0) = z_0 \end{aligned}$$

where, $z(s \times 1)$ denote the state variables and $u(m \times 1)$ are the control variables to be optimized.

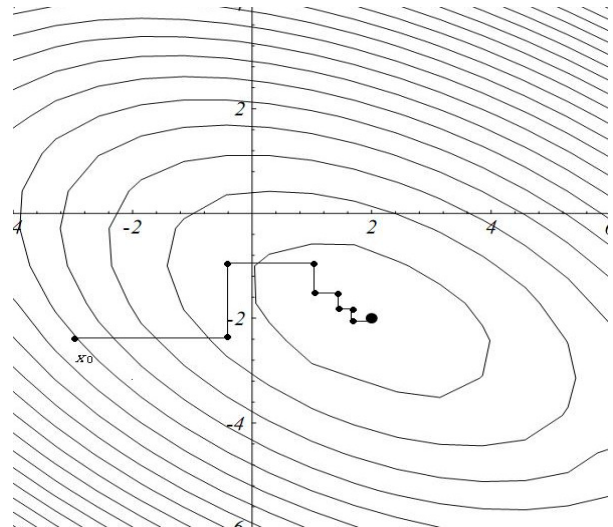


Fig. 2. A simple illustration of sequential evolution

In this work, the control variables are discretized by piecewise constants. The time duration of the process $[0, t_f]$ is divided into N parts, in each time interval element the control variables are kept at constant values. And then the state variables are calculated based on the discretized control variables using numerical integration algorithms, such as Runge-Kutta method. Now the fitness function values in sequential evolution algorithm can be computed consequently.

To solve the dynamic optimization problem, the procedures using sequential evolution algorithm is expressed as follows. And the overall diagram of the proposed algorithm is shown in Fig. 3.

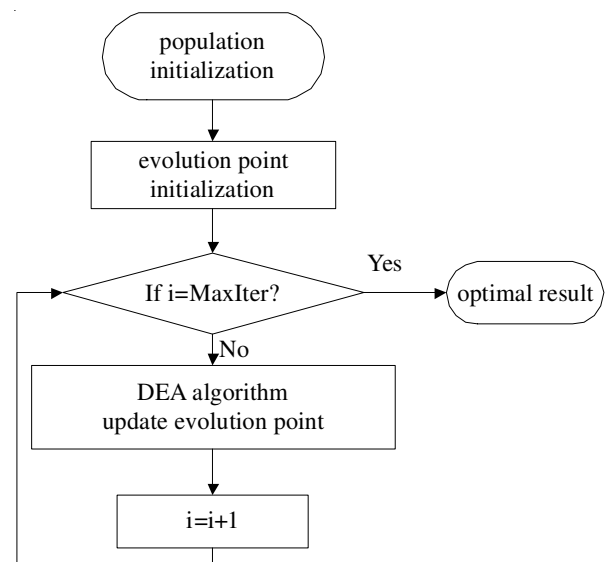


Fig. 3. Dynamic optimization procedure by sequential evolution algorithm

STEP1: Given the individual number of the population n , the boundary of control variable $[lb, ub]$, the max iterative number and the segment number N . After discretization, the number of variables to be optimized is $L = m \times N$, where m is the number of control variables.

TABLE-1
RESULTS OF LEE-RAMIREZ MODEL USING DIFFERENT ALGORITHMS

Authors	Year	Method	Max J	Evaluations	Time(s)
Tholudur	1996	DP ⁹	0.803	-	-
Roubos <i>et al.</i>	1999	GA ¹⁰	0.8149	1000000	-
Luus	2000	IDP ¹¹	0.8164	-	291-510
Jayaraman <i>et al.</i>	2001	CACO ¹²	0.8095	26763	-
Sarkar and Modak	2003	ANNSA ¹³	0.8166	1338401-2120801	-
Zhang <i>et al.</i>	2006	SACA ¹⁴	0.8158	120000	-
Pu <i>et al.</i>	2008	CAMACO ¹⁵	0.816	8340-58020	-
Lin <i>et al.</i>	2008	Hopt-AiNet ¹⁶	0.8165	4235	150.84
This Work	2011	Sequential evolution algorithm	0.8166	3200	93

STEP2: Generate the initial population X_0 randomly within the control variable boundary, $X_0 = (x_0^1, x_0^2, \dots, x_0^L)$. Choose an arbitrary individual as the initial evolution point $Q_0 = (q_0^1, q_0^2, \dots, q_0^L)$.

STEP3: For t th generation, $X_t = (x_t^1, x_t^2, \dots, x_t^L)$, $Q_t = (q_t^1, q_t^2, \dots, q_t^L)$. Considering the first subpopulation x_t^1 , for each individual $x_t^{1(i)}$ ($i = 1, 2, \dots, n$) computing the objective function value using the candidate solution $(x_t^{1(i)}, q_t^2, \dots, q_t^L)$. Then the subpopulation evolves using the above proposed grouped-evolution strategy. The evolution point element q_t^1 is substituted with the best individual.

STEP4: Continue the similar procedure as STEP3 until all the subpopulations have evolved.

STEP5: The population and the evolution point are all updated and set $X_{t+1} = X_t^{\text{new}}$, $Q_{t+1} = Q_t^{\text{new}}$.

STEP6: If the maximum number of iterations is reached, stop the procedure and display the optimal result; else set $t = t+1$ and return to step 3.

Algorithm test: Here the optimal control problem for Lee-Ramirez biology reactor^{9,10} is used to test the proposed algorithm. In the Lee-Ramirez biology reactor, induced foreign protein is produced by recombinant bacteria. And there are seven state variables and two control variables. The details of the optimal control problem can be found in previous work¹⁰. This problem is commonly used as a test case for other optimization algorithm. The optimization algorithm, such as dynamic programming (DP)⁹, real-coded genetic algorithm (GA)¹⁰, iterative dynamic programming (IDP)¹¹, continuous antcolony optimization (CACO) algorithm¹², the hybrid algorithm combined by artificial neural network and simulated annealing algorithm (ANNSA)¹³, sequential antcolony algorithm (SACA)¹⁴, continuous multi antcolony optimization (CMACO) method¹⁵, hybrid optimal artificial immune network (Hopt-AiNet) *et al.* have ever been used to solve the optimal control problem for Lee-Ramirez biology reactor.

In order to solve this optimal control problem using sequential evolution algorithm, the process duration is divided into 10 parts, each time element is 1 h and the four-order Runge-Kutta method is used to determine the state variable value in each segment. As there are two control variables, the dimensionality of the discretized optimization problem is 20. And the population number is chosen as 8, iterative number is 20, the two control variables vary in the domain $[-1, 2]$ with the initial value $[0, 0]$. The proposed algorithm is running in the environment of Matlab 7.6.0 edition under Microsoft XP system. And the computer hardware platform consists of a 1.6 GHz Pentium processor and 1 GB RAM. The result of the

new algorithm is compared with former algorithms in literature, which is showed in Table-1.

From the Table-1, it is observed that the global optimal value can be found by the proposed sequential evolution algorithm. Comparing to latest Hopt_aiNet method, the evaluations for the objective function is decreased by 29 % and the time elapse is decreased by 38 %. The sequential evolution algorithm is faster and is more suitable to solve the dynamic optimization problem. The optimal profiles for the inducer feeding rate is presented in Fig. 4. And the trajectory of the objective function in iteration is also showed in Fig. 5.

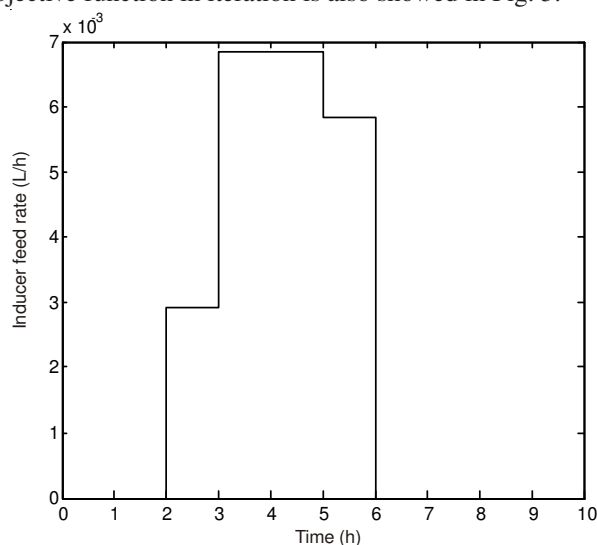


Fig. 4. Optimal profile of inducer feed rate

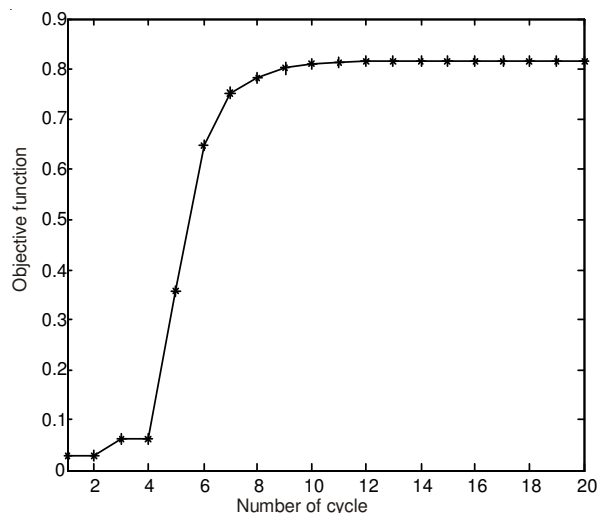


Fig. 5. Values of objective function

Grade transition optimization and discussion: In the optimization of polyethylene grade transition in gas-phase reactor, the molar ratio of hydrogen to ethylene ($[H_2]/[M_1]$) and the molar ratio of comonomer to ethylene ($[M_2]/[M_1]$) in the cycle gas are used as control variables. The proposed sequential evolution algorithm approach is used to solve the polyethylene grade transition optimization problem. The results for different situations of multiple grades changeover, different discretizations, various constraints, model mismatch and process disturbance will be stated respectively. The programs are running in MATLAB 7.6.0 on the platform of 1.6 GHz Pentium processor, 1 GB RAM and Windows XP operating system.

Multiple grades transition operation: In continuous producing process of polyethylene, the switching operation of $A \rightarrow B \rightarrow C$ is considered. The quality index of the three grades are stated in Table-2. And the initial values and constraints of the control variables are given in Table-3.

TABLE-2 QUALITY INDEX OF DIFFERENT GRADES		
Grade	Melt index, MI ($g\ 10^{-1}\ min^{-1}$)	Density, D ($g\ cm^{-3}$)
A	1.0	0.918
B	2.8	0.939
C	5.0	0.934

TABLE-3 INITIAL VALUES AND CONSTRAINTS OF THE CONTROL VARIABLES			
	Temperature (K)	$[H_2]/[M_1]$	$[M_2]/[M_1]$
Initial value	360	0.1615	0.3635
Low bound	353	0	0
Upper bound	373	0.8	0.8

For solving the grade transition optimization problem, the proposed sequential evolution algorithm is compared to the conventional control vector parameterization^{1,7,17} (CVP) method. The results of switching from grade A to grade B is showed in Fig. 6 (solid line, sequential evolution algorithm; dotted line, CVP). The computing time elapses for sequential evolution algorithm method is about 357.655805s while for control vector parameterization method is about 415.61s.

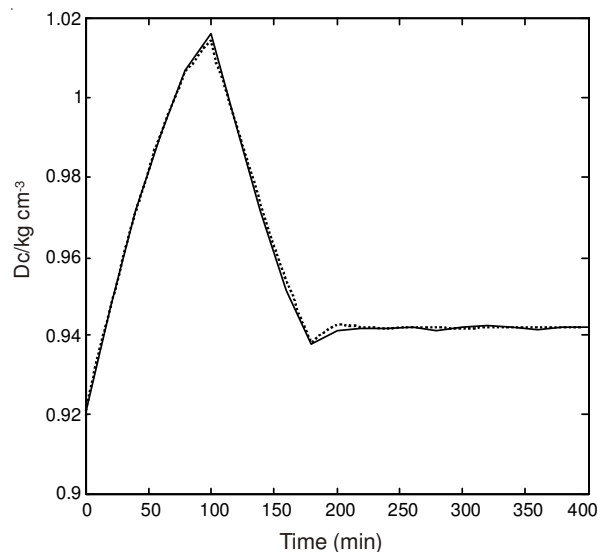
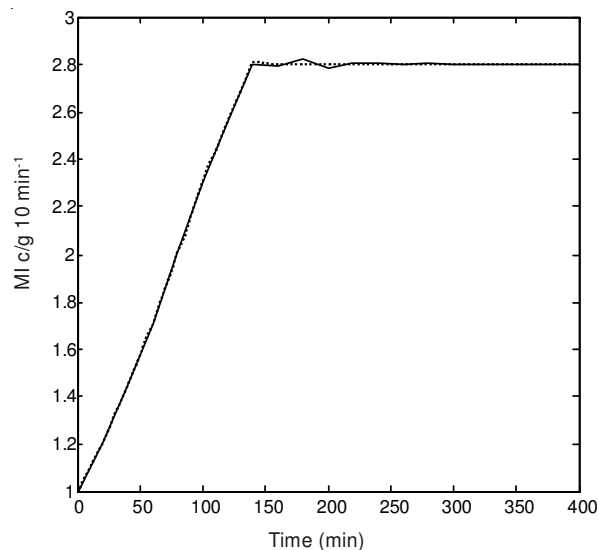
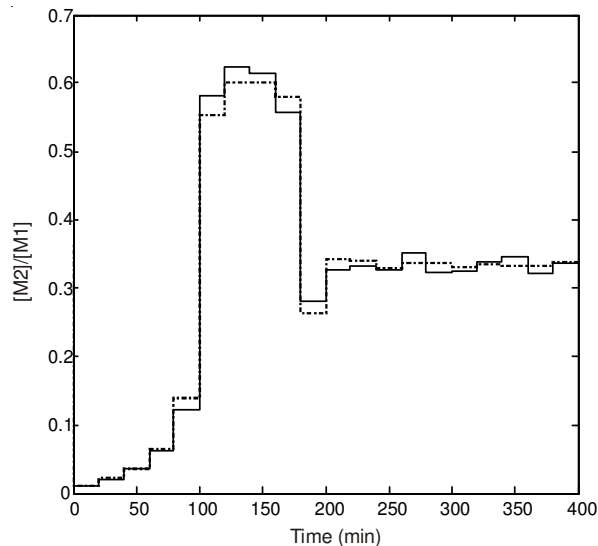
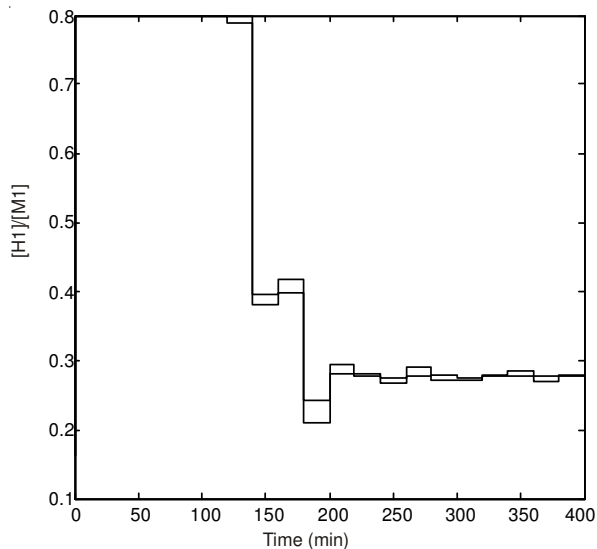


Fig. 6. Optimal profiles for switching from grade A to grade B

The results of switching from grade B to grade C is shown in Fig. 7 (solid line, sequential evolution algorithm; dotted line, CVP). And the computing time elapses for sequential evolution algorithm method is about 363.365663s

while for control vector parameterization method is about 912.962390s.

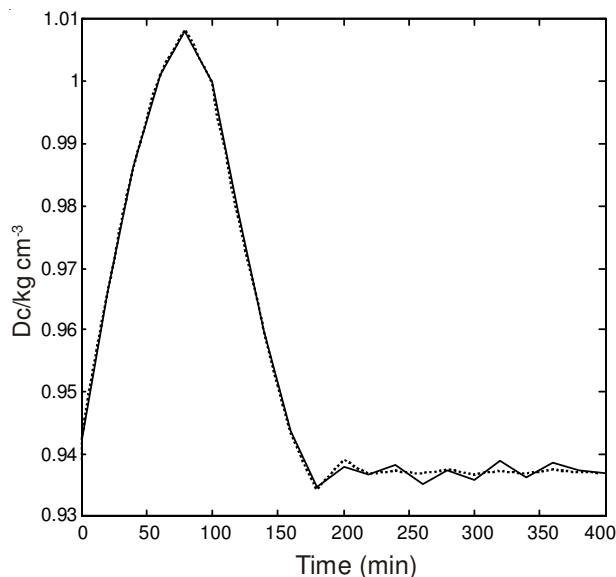
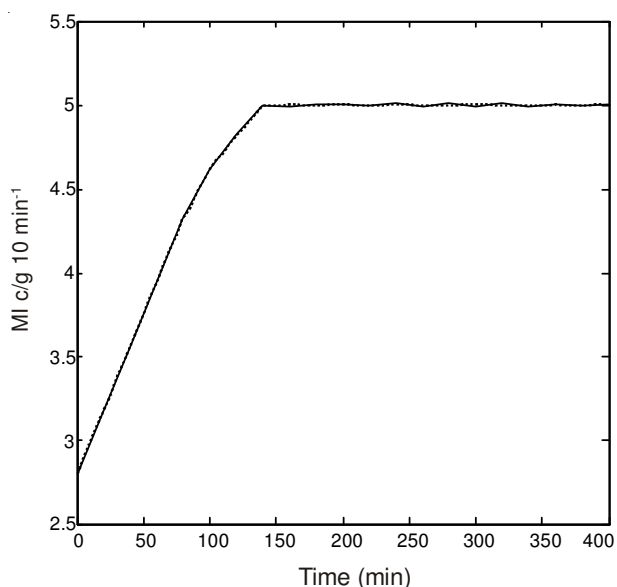
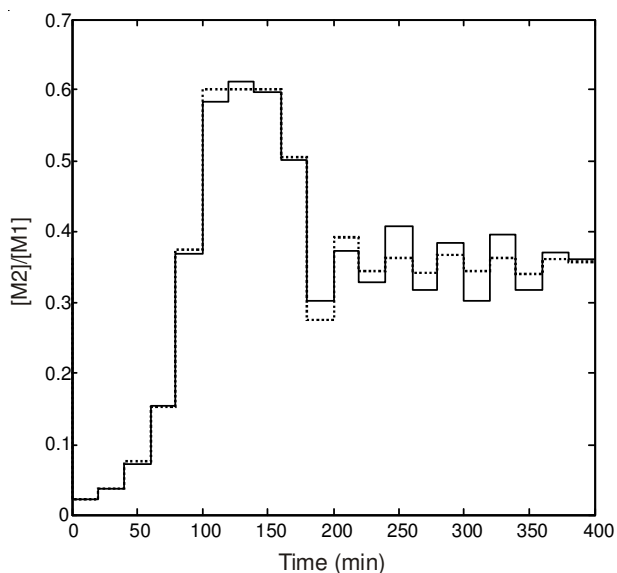
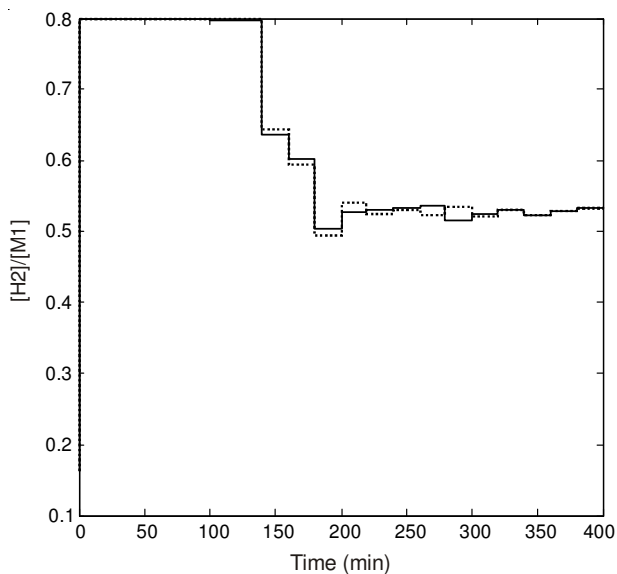


Fig. 7. Optimal profiles for switching from grade B to grade C

For the optimal polyethylene grade transition problem, the obtained optimal results are almost the same using the two different methods of sequential evolution algorithm and control vector parameterization. In order to increase the MI value, it is necessary to increase $[H2]/[M1]$ or decrease $[M2]/[M1]$. But decreasing the $[M2]/[M1]$ will increase the product density. So in optimal operation of control variables, the $[H2]/[M1]$ is kept at the upper boundary at first, while the $[M2]/[M1]$ is kept at the low value. For the whole switching process the control vector parameterization method cost about 1337.57s, while the proposed sequential evolution algorithm method needs only 721.01s (reduce about 46 %). It can be inferred that the proposed sequential evolution algorithm compute faster and can ensure the accuracy at the same time.

Different constraints of control variables: Decided by process safety and mechanism, there are often have boundary constraint during the grade transition process for the control variables $[H2]/[M1]$ and $[M2]/[M1]$. Different constraint conditions can also give rise to different optimal results. For the sake of comparing to the constraint in Table-3, the following constraint stated in Table-4 is also considered. And the corresponding results are given in Fig. 8. The lines with asterisk points are the results of constraint in Table-4 while the line with circle points denote the results of constraint in Table-3.

TABLE-4 ANOTHER CONSTRAINT OF THE CONTROL VARIABLES			
	Temperature (K)	$[H2]/[M1]$	$[M2]/[M1]$
Initial value	360	0.1615	0.3635
Low bound	353	0.1	0.1
Upper bound	373	0.6	0.6

As the new constraint in Table-4 restricts the operation more strictly, the feasible search region of control variable will be smaller. So the transition time of melt index increases to 250 min while it is only 150 min under the original constraint. The longer transition time will result in more off-specification cost during the grade transition process. But at the

same time the overshoot of melt index and density become less, which can make the process more stable. As enlarging the region of control variables can accelerate the transition process, the larger constraint boundary is more preferable.

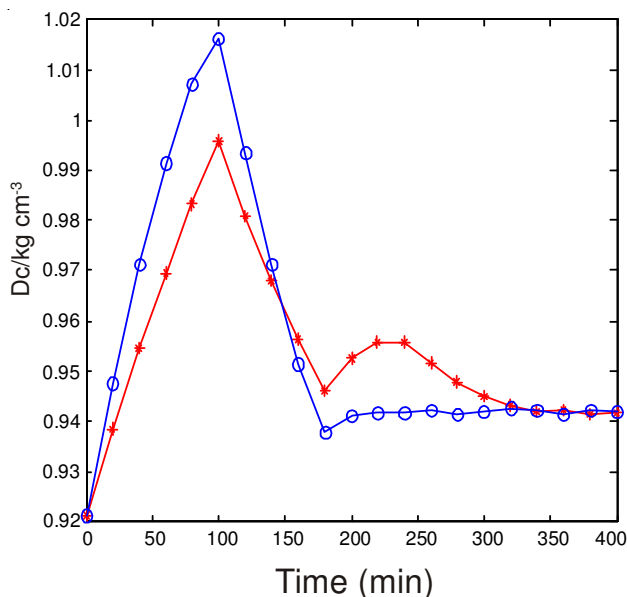
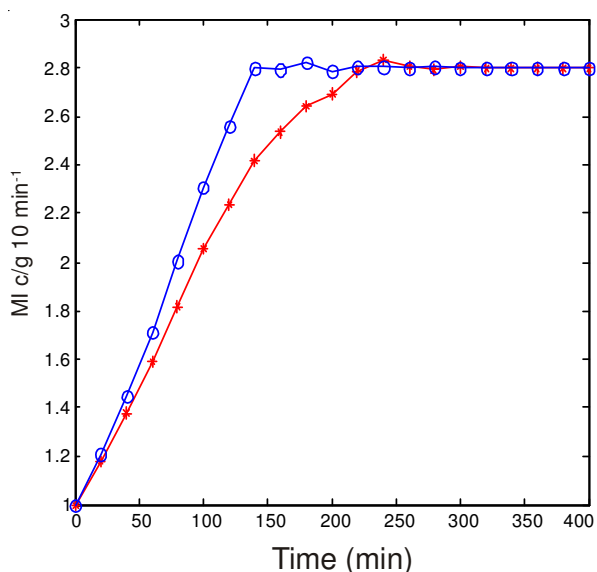
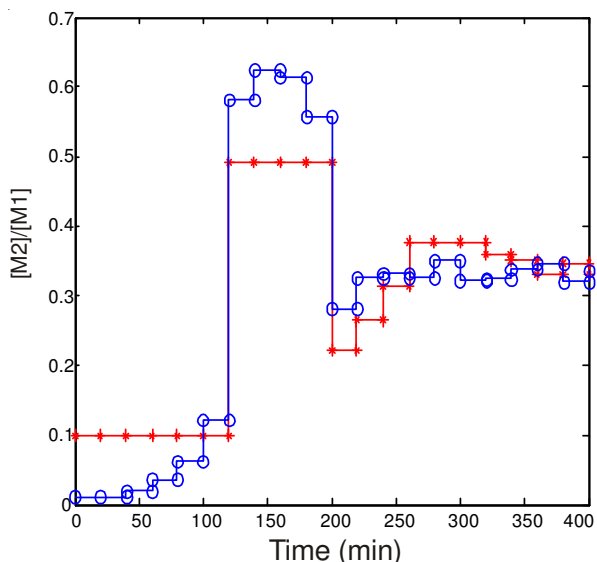
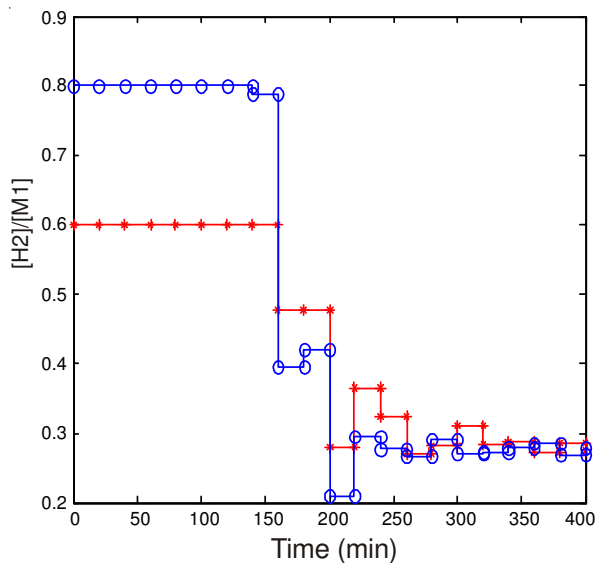
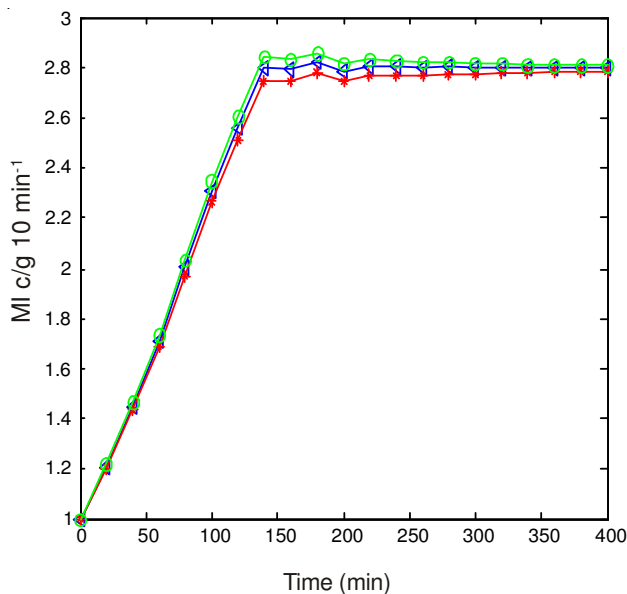


Fig. 8. Optimal trajectories with different constraints

Optimization considering model mismatch: In practical industrial process, model mismatch is inevitably existing. And model mismatch could result in bad impact on the grade transition optimization. Here the mismatch problem is simulated by changing the parameter A ($A \pm 10\%$). The switching profiles of melt index and density with the same optimal control variable profiles under model mismatch are studied and the results are given in Fig. 9.

When the control variable profiles in Fig. 6 are used as the input of the process, the obtained profiles of melt index are slightly different and the profiles of density are almost the same under the model mismatch (by changing parameter A). For the melt index profile, both adding A by 10% and reducing A by 10% will give rise to little residual error from the objective value of melt index. From the result, it can be found that the model mismatch of changing parameter A can just result in quite a little impact on the grade transition operation. However influences of additional model mismatch for other reasons need more else study.



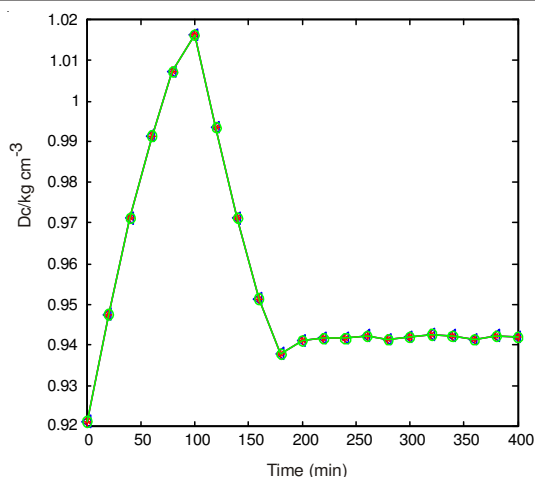


Fig. 9. Switch profiles of MI and density under model mismatch

Optimization considering disturbance: Process disturbance exist in producing process because of variations of operation conditions and environment change. Here the temperature of the reactor is considered as the disturbance of the considered process and the resulting profiles for melt index and density is illustrated in Fig. 10, where the lines with triangle points denote the profiles without disturbance while lines with circle points and lines with asterisk points denote the profiles adding positive and negative disturbance to the temperature respectively.

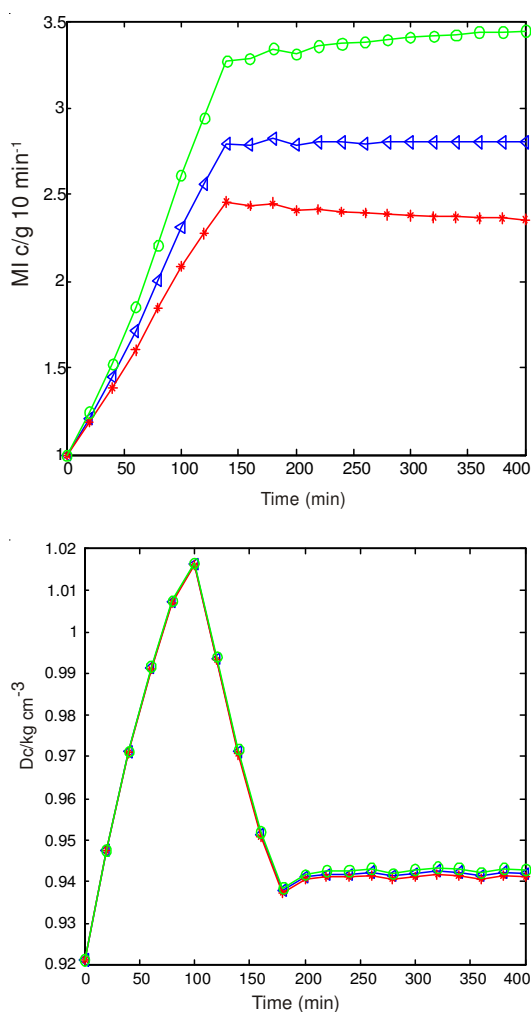


Fig. 10. Profiles of MI and density with disturbance

We can see that temperature disturbance has great impact on melt index. Under temperature disturbance, the melt index could not reach the final product value and the transition operation will fail or even result in unsafe situation. So it is quite important to reduce the disturbance for practical operation.

Conclusion

A real-coded genetic based sequential evolution algorithm (SEA) is proposed, in which the original parallel evolution strategy is substituted by sequential evolution strategy, a novel evolution point is added into the evolving process and the grouped evolution strategy is used for the subpopulation evolution. In the case test of Lee-Ramirez model, the sequential evolution algorithm can obtain the global optimum exactly and the computing burden is reduced by 29 % and the computing time is reduced by 38 % comparing to the Hopt-AiNet method. Then the sequential evolution algorithm is applied to solve the polyethylene grade transition optimization problem. The optimal policies can be achieved by sequential evolution algorithm while the computing time is greatly reduced. Besides, for the grade transition problem, the situations of multiple grades transitions, various constraints, model mismatch and the process disturbance are also considered. The results indicate that model mismatch and process disturbance would give rise to the result that the product quality trajectories deviating significantly from the normal optimal trajectory.

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REFERENCES

1. K.B. McAuley and J.F. MacGregor, *AIChE J.*, **38**, 1564 (1992).
2. M. Takeda and W.H. Ray, *AIChE J.*, **45**, 1776 (1999).
3. C. Chatzidoukas, J.D. Perkins, E.N. Pistikopoulos and C. Kiparissides, *Chem. Eng. Sci.*, **58**, 3643 (2003).
4. A. Flores-Tlacuahuac, L.T. Biegler and E. Saldivar-Guerra, *Ind. Eng. Chem. Res.*, **45**, 6175 (2006).
5. D. Bonvin, L. Bodizs and B. Srinivasan, *Chem. Eng. Res. Design*, **83**, 692 (2005).
6. J.V. Kadam, W. Marquardt, B. Srinivasan and D. Bonvin, *AIChE J.*, **53**, 627 (2007).
7. L.T. Biegler and I.E. Grossmann, *Comput. Chem. Eng.*, **28**, 1169 (2004).
8. K.B. McAuley and J.F. MacGregor, *AIChE J.*, **37**, 825 (1991).
9. A. Tholudur and W.F. Ramirez, *Biotechnol. Progr.*, **12**, 302 (1996).
10. J.A. Roubos, G. van Straten and A.J.B. van Boxtel, *J. Biotechnol.*, **67**, 173 (1999).
11. W. Mekarapiruk and R. Luus, *Ind. Eng. Chem. Res.*, **39**, 84 (2000).
12. V.K. Jayaraman, B.D. Kulkarni, K. Gupta, J. Rajesh and H.S. Kusumaker, *Biotechnol. Progr.*, **17**, 81 (2001).
13. D. Sarkar and J.M. Modak, *Chem. Eng. Sci.*, **58**, 3131 (2003).
14. B. Zhang, H. Yu and D. Chen, *J. Chem. Eng. Chin. Univ.*, **20**, 120 (2006).
15. L. Pu, Y. Huanjun and C. Dezhao, *J. Chem. Eng. Chin. Univ.*, **22**, 871 (2008).
16. K. Lin, Y. He and C. Dezhao, *J. Zhejiang Univ. (Eng. Sci.)*, **42**, 2181 (2008).
17. V.S. Vassiliadis, R.W.H. Sargent and C.C. Pantelides, *Ind. Eng. Chem. Res.*, **33**, 2111 (1994).