

A Hybrid Genetic Algorithm for the Estimation of Polyesterification Kinetic Parameters

By Feng Guangzhu*, Li Fasong, Li Heping, Qu Hai, and Cui Yingde

DOI: 10.1002/ceat.200600012

A simple genetic algorithm (SGA) has been improved in this paper. The resulting hybrid genetic algorithm (HGA) was used to estimate the kinetic parameters of polyesterification between dimer fatty acid and ethylene glycol. The acid values of product predicted by the kinetic model match well with experimental data at different material proportions and conversion ratios. The kinetic model was proven to be effective. The hybrid genetic algorithm was compared with the simple genetic algorithm, and the result indicated that the improved genetic algorithm has higher efficiency, stronger ability on local searches, better precision, and a wider search range.

1 Introduction

Polyesterification is a complex reaction system because it contains products of different molecular weights [1] and the detailed study of the reaction kinetic is difficult. Flory produced the assumption of equal activity [2], and supposed the activity of the end groups of components with different molecular weights were equivalent under conditions where the viscosity was low and the reactant was homogeneous over the whole reaction. The assumption simplified the kinetics of polyesterification, and the reaction model could be concluded. Different people have introduced several rate equations based on this assumption, including Flory [3], Lin [4], Wu [5], and so on. Some people also explained that the activities of the end groups were not equivalent. For example, Zetterlund, et al. [6] considered the activities of hydroxyl on the monomers and polymers were unequal, and produced a new kinetic model.

The integral of the rate equation and the estimation of parameters is a difficult problem in kinetics of unequal activities. Some computer methods and software such as Runge-Kutta, Monte Carlo, Excel, Easy-Fit [7], and Genetic algorithms may be used. Genetic algorithms are estimation methods which are independent of the starting point and able to search in the entire space. They have been the subject of several studies, particularly in the field of chemical engineering [8]. The use of genetic algorithms in reaction kinetics was introduced by L. Elliot, detailed in [9]. This paper presents an improved genetic algorithm which is used to estimate the kinetic parameters of polyesterification between dimer fatty acid and ethylene glycol catalyzed by *p*-Toluene sulfonic acid. The assumption of unequal end-group activity

between monomers and polymers was introduced into the reaction kinetic model.

2 Materials and Methods

2.1 Materials

Dimer fatty acid (DA) purchased from Fujian Liancheng Baixin Science and Technology Co., Ltd. in China with 98.2 % purity (monomer 0.2 %, dimer 98.2 %, trimer 1.6 %) and an acid value of 196.8 mgKOH g⁻¹ was used. Ethylene glycol (EG) produced by Luoyang reagent factory and *p*-Toluene sulfonic acid purchased from China National Pharmaceutical Group Corporation are analytically pure. Nitrogen gas was used in the synthesis of the polymers to protect the reactants from oxygen.

2.2 The Hybrid Genetic Algorithm

The simple genetic algorithm (SGA) contains ordinary operators in coding, selection, crossover, and mutation, and it has disadvantages such as being premature, inefficient and lacking ability in local searches [10]. These SGA shortcomings were improved in this paper and a new type of hybrid genetic algorithm (HGA) was obtained. The operators of the HGA are as follows:

- I. Coding: The binary representation traditionally used in the SGA has some drawbacks when applied to multi-parameter, high precision and wide range numerical problems. So real coding was used with the aim of improving precision and the search range.
- II. The calculation of fitness value: The fitness value of each individual can be calculated as Eq. (1)¹⁾:

$$f = \frac{1}{\sum_{t=1}^n (AV_{Pred} - AV_{Expe})^2} \quad (1)$$

- 1) List of symbols at the end of the paper.

[*] G. Feng (author to whom correspondence should be addressed, fgzhu@haut.edu.cn), School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450052, PR China, and School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, PR China; F. Li, H. Li, H. Qu, School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450052, PR China; Y. Cui, Zhongkai University of Agriculture and Technology, Guangzhou 501225, PR China.

AV_{Pred} is an acid value predicted by the reaction kinetic model, AV_{Expe} is the experimental acid value of the sample during the progress of the reaction, and t is the sampling time. The Runge-Kutta method was used to integrate the rate equations and concentrations of each component over time, and subsequently the acid value was calculated from the concentrations. The fitness value corresponds to the adaptation of the individual to “survive” in the new generations [11], The higher the fitness value is, the more likely the individual will be kept during the selection step.

III. Selection operator: The roulette wheel selection was used as a selection operator. The Elitist model was used to eliminate worse individuals and preserve better individuals. The selection of parent generations was done according to their adaptability; the larger the adaptability, the greater the opportunity of being selected.

The Elitist model was ameliorated to enhance the ability of local searches. First, the best and the worst individuals in the current generation were determined, then the best individual in the current generation was compared with the best individual until the current generation, and the better one was saved to replace the best individual until current generation. Finally, the best individual until the current generation was changed slightly and replaced the worst individual in the current generation.

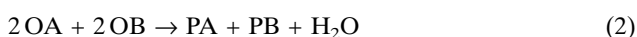
IV. Crossover operator: One-point crossover was selected as the crossover operator of the HGA. Two parent individuals were chosen randomly from the selected individuals. The codes after the random point of the two individuals were swapped with a certain probability to create two new children. The crossover point was selected at the connection of the parameters in the chromosome.

V. Mutation operator: Uniform mutation was selected for the operator. Each gene in the chromosome was replaced by a random gene with a certain probability.

VI. Operation constant: The number of individuals is eighty; the total generation is five hundred; the probability of crossover is 0.5; and the probability of mutation is 0.1.

2.3 Derivation of the Kinetic Model

The end groups in the reactant were separated into four types: hydroxyl on the monomer (OB), carboxyl on the monomer (OA), hydroxyl on the polymers (PB), and carboxyl on the polymers (PA). The reaction between the components can be described as in Eqs. (2–5):



The reverse reaction was ignored because the forward reaction was so quick at the beginning of the reaction, and the water produced was removed by vacuumizing after 30 min of reaction. The side reactions were not considered in the derivation of the model.

The rate equations were obtained as in Eqs. (6–11):

$$\frac{dc_{\text{OA}}}{dt} = -2k_{\text{OAOB}}c_{\text{OA}}^m c_{\text{OB}}^n - 2k_{\text{OAPB}}c_{\text{OA}}^m c_{\text{PB}}^n \quad (6)$$

$$\frac{dc_{\text{OB}}}{dt} = -2k_{\text{OAOB}}c_{\text{OA}}^m c_{\text{OB}}^n - 2k_{\text{PAOB}}c_{\text{PA}}^m c_{\text{OB}}^n \quad (7)$$

$$\begin{aligned} \frac{dc_{\text{PA}}}{dt} = & k_{\text{OAOB}}c_{\text{OA}}^m c_{\text{OB}}^n + k_{\text{OAPB}}c_{\text{OA}}^m c_{\text{PB}}^n - k_{\text{PAOB}}c_{\text{PA}}^m c_{\text{OB}}^n \\ & - k_{\text{PAPB}}c_{\text{PA}}^m c_{\text{PB}}^n \end{aligned} \quad (8)$$

$$\begin{aligned} \frac{dc_{\text{PB}}}{dt} = & k_{\text{OAOB}}c_{\text{OA}}^m c_{\text{OB}}^n + k_{\text{PAOB}}c_{\text{PA}}^m c_{\text{OB}}^n \\ & - k_{\text{OAPB}}c_{\text{OA}}^m c_{\text{PB}}^n - k_{\text{PAPB}}c_{\text{PA}}^m c_{\text{PB}}^n \end{aligned} \quad (9)$$

$$AV = \frac{(c_{\text{OA}} + c_{\text{PA}} + c_c) \times 56.1}{d} \quad (10)$$

$$\frac{dc_{\text{OA}}}{dt} + \frac{dc_{\text{PA}}}{dt} = \frac{dc_{\text{OB}}}{dt} + \frac{dc_{\text{PB}}}{dt} \quad (11)$$

k_{OAOB} , k_{OAPB} , k_{PAOB} , and k_{PAPB} are the rate constants of the reaction between OA and OB, OA, and PB, PA and OB, and PA and PB, respectively, c_{OA} , c_{OB} , c_{PA} , and c_{PB} are the concentrations of OA, OB, PA, and PB, respectively, m is the reaction order of carboxyl and n the reaction order of hydroxyl ($n = 1$ in this paper). AV is the acid value of the sample, c_c the concentration of the catalyst, d the density of the reactant, and c_d the difference between the concentrations of carboxyl and hydroxyl.

The estimation of the parameters was carried out in three steps. First of all, the order of reaction (m and n) was confirmed using the assumption of equal activity. Secondly, experiments were designed to estimate the parameters of k_{OAPB} and k_{PAOB} . Excess monomer was supplemented into the reactant after it had reacted for several hours with the materials proportion of 1:1, and the reactions could be ignored except for the added monomer and the polymers. Finally, m , n , k_{OAPB} , and k_{PAOB} were introduced into the rate equations to obtain the values of k_{OAOB} and k_{PAPB} .

2.4 Preparation of the Polymers

28.1 g (0.05 mol) of dimer fatty acid, 3.11 g (0.05 mol) of ethylene glycol and 0.5 % of *p*-Toluene sulfonic acid as the catalyst were placed into a round bottom flask (three necks),

which was equipped with a dephlegmator and a pipe for the nitrogen. Nitrogen was introduced into the flask to remove the oxygen and prevent the oxidation of the materials. The flask was placed into an oil bath with a temperature of 170 °C. After 30 min reaction the nitrogen was stopped and vacuum pumping was used to remove the water from reactant. The reaction continued 8–10 h in vacuum. The acid value of the reactant was measured at certain reaction times during the progress of the reaction.

3 Results and Discussion

3.1 The Result of Kinetic Parameters

The parameters of the kinetic model were obtained using the hybrid genetic algorithm. They are shown in Tab. 1.

Table 1. The results for the kinetic parameters.

parameters	value	parameters	value
m	2.019	k_{OAPB}	0.09035
n	1.0	k_{PAOB}	1.665
k_{OAOB}	0.0268	k_{PAPB}	0.743

The parameters were introduced into the model, and the predicted values were obtained using the method of Runge-Kutta. The results are shown in Figs. 1 and 2.

The figures show that the predicted values match well with the experimental data. The result indicates that the reaction order is 2.019 with respect to carboxyl and 1 with respect to hydroxyl in the polyesterification using dimer acid and ethylene glycol as the reactant materials and catalyzed by *p*-Toluene sulfonic acid. This is different to the conclusions of Folry, but the model prediction matches well with experimental data at different conversion ratios and material proportions in the whole reaction. It is obvious that the kinetic model can be used to predict this reaction.

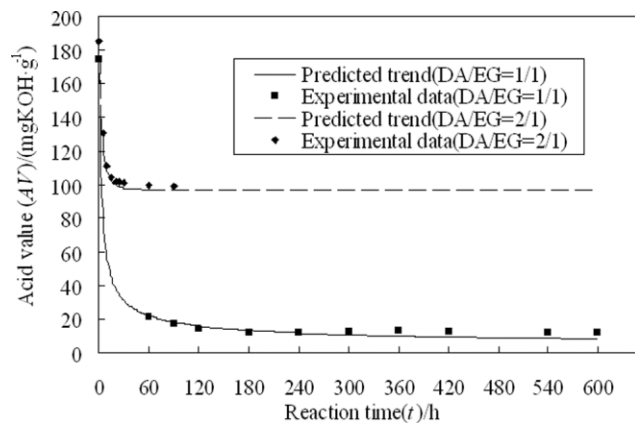


Figure 1. The predicted and the experimental acid values.

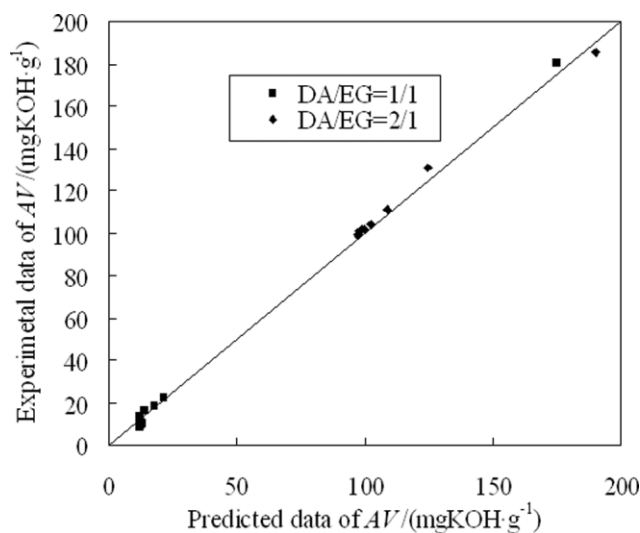


Figure 2. The comparison of the predicted and experimental acid values.

3.2 Comparison between the SGA and HGA

Improvement of the SGA is necessary for the solution of complex kinetic problems. Fig. 3 shows the evolution progress of the SGA and HGA.

Fig. 3 shows that the HGA has the advantages of rapidness and precision. A high fitness value can be obtained in fewer than two hundred generations, and the fitness value of the HGA is higher than for the SGA.

The estimation results from the SGA and HGA are shown in Tab. 2. It also indicates that the HGA is better than SGA.

The improvements increased the efficiency of the program, extended the search range, and enhanced the ability of local searches.

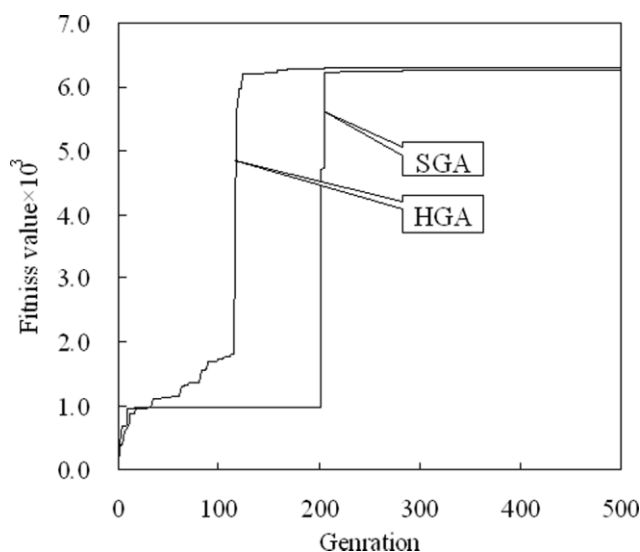


Figure 3. Generation progress of the parameter estimation.

Table 2. Results of parameter estimation.

Para	SGA		HGA	
	k_{OAOB}	k_{PAPB}	k_{OAOB}	k_{PAPB}
I	0.0271	0.516	0.0268	0.0268
II	0.0272	0.455	0.0268	0.743
III	0.268	0.539	0.0268	0.743

4 Conclusions

It is preferable to use the HGA for the estimation of kinetic parameters. It is better than the SGA on the efficiency, precision, ability of local search, and search range etc. The kinetic model prediction matches well with the experiment at different conversion ratios and material proportions when the parameters estimated by HGA were introduced into the model. It also proves that the model is useful for the polyesterification of dimer acid and ethylene glycol catalyzed by *p*-Toluene sulfonic acid.

Acknowledgements

The authors gratefully acknowledge the financial support of this work granted by Henan Provincial Natural Science Foundation of China (Grant No. 0511021000).

Received: January 8, 2006

Symbol used

SGA	[-]	simple genetic algorithm
HGA	[-]	hybrid genetic algorithm
DA	[-]	dimer fatty acid
EG	[-]	ethylene glycol
AV	[mgKOH g ⁻¹]	acid value of the sample
AV_{Pred}	[mgKOH g ⁻¹]	predicted acid value by the reaction kinetic model
AV_{Expc}	[mgKOH g ⁻¹]	experimental acid value of the sample in progress of reaction
t	[s]	sampling time

OB	[-]	hydroxyl on the monomer
OA	[-]	carboxyl on the monomer
PB	[-]	hydroxyl on the polymers
PA	[-]	carboxyl on the polymers
k_{OAOB}	[mol L ⁻¹ min ⁻¹]	rate constant of the reaction between OA and OB
k_{OAPB}	[mol L ⁻¹ min ⁻¹]	rate constant of the reaction between OA and PB
k_{PAOB}	[mol L ⁻¹ min ⁻¹]	rate constant of the reaction between PA and OB
k_{PAPB}	[mol L ⁻¹ min ⁻¹]	rate constant of the reaction between PA and PB
c_{OA}	[mol L ⁻¹]	concentration of OA
c_{OB}	[mol L ⁻¹]	concentration of OB
c_{PA}	[mol L ⁻¹]	concentration of PA
c_{PB}	[mol L ⁻¹]	concentration of PB
m	[-]	reaction order of carboxyl
n	[-]	reaction order of hydroxyl ($n = 1$ in this paper)
c_c	[mol L ⁻¹]	concentration of the catalyst
d	[g cm ⁻³]	density of the reactant (this is an approximation, treated as invariable in each reaction, for the change is tiny)
c_d	[mol L ⁻¹]	difference between the concentration of carboxyl and hydroxyl (this is invariable in each reaction).

References

- [1] H. S. Kaufman, J. J. Falctta, *Introduction to Polymer Science and Technology*, John Wiley & Sons, New York **1977**.
- [2] P. J. Flory, *Am. Chem. Soc.* **1939**, *61*, 3334.
- [3] P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, New York **1953**.
- [4] K. H. Lin, J. Hsieh, *Appl. Polym.* **1977**, *21*, 2711.
- [5] K. Nalampang, A. F. Johnson, *Polymer* **2003**, *44*, 6103.
- [6] P. B. Zetterlund, W. Weaver, A. F. Johnson, *Polym. React. Eng.* **2002**, *10*, 41.
- [7] J. Heidarian, N. M. Ghasem, W. M. A. W. Daud, *Chem. Eng. J.* **2004**, *100*, 85.
- [8] L. Bolland, L. Estel, J. M. Cosmao, N. Mouhab, *Chemometr. Intell. Lab.* **2000**, *50*, 121.
- [9] L. Elliott et al., *Prog. Energ. Combust.* **2004**, *30*, 297.
- [10] Z. Ming, S. Shudong, *Genetic Algorithms: Theory and Applications*, National Defence Industry Press (China), Beijing **1999**.
- [11] R. Yao et al., *Chem. Eng. J.* **2003**, *94*, 113.