Chemical Engineering Journal 94 (2003) 113–119

Chemical Engineering Journal

www.elsevier.com/locate/cej

Kinetics research for the synthesis of branch ether using genetic-simulated annealing algorithm with multi-pattern evolution

Ruiqing Yao, Bolun Yang*, Guangxu Cheng, Xianhu Tao, Fanxu Meng

Department of Chemical Engineering. Xi'an Jiaotong University, Shaanxi, Xi'an 710049, PR China

Received 14 August 2002; accepted 6 January 2003

Abstract

To obtain the kinetics parameters for the complex reaction system, a more intellectualized hybrid evolutionary algorithm was developed. In this new method, the normal genetic algorithm (GA) was modified with adaptive multi-annealing crossover and mutation strategies instead of simple strategy. The multi-pattern evolution was also adapted to improve the search efficiency. This hybrid algorithm not only avoids the problem of local optimum, but shows a higher estimating precision and a better convergence than that the normal GA. By using this algorithm, the kinetics parameters for the synthesis of ethyl *tert*-amyl ether from ethanol and *tert*-amyl alcohol over strongly acidic cation exchange resin (Ambelyst 15 (A-15)) as catalyst were successfully estimated. The calculated results using the parameters obtained from the hybrid evolutionary algorithm agree well with the experimental data.

Keywords: Complex reaction; Kinetics; Ethyl *tert*-amyl ether; Genetic algorithm; Simulated annealing; Evolutionary algorithm; Optimization

1. Introduction

Many complex reaction systems involve numerous elementary reactions. The number of the kinetics parameters to be estimated increases very rapidly with the complexity of the physico-chemical model. It is necessary to use a robust estimation method, which allows the whole parameter space to be explored, to determine the global solution to the problem, and not merely a local solution.

Evolutionary algorithms (EAs) were developed in recent years. They are a series of optimization methods that include genetic algorithm (GA), evolution strategy (ES), evolutionary programming (EP) and their variants [1]. Compared with other traditional optimization algorithm, these evolutionary algorithms based on the principles of natural biological evolution to solve real valued optimization have shown some advantages. For examples: the astringency is independence of the setting of initial values, stronger robustness and better search ability in the entire space [2]. Among of them, GA is widely used to solve the optimization problem, it is also used in the field of kinetics research [3–6]. A notable characteristic of GA is that it can find the region of the optimal values quickly; however, the ability of accurate search in this region is not satisfactory for complex system.

Simulated annealing (SA) is an approach to simulate the thermodynamic process of annealing (cooling solid) [7] and it is observed that this approach could be used to search for feasible solutions of an optimization problem, with the objective of converging to an optimal solution [8]. This method can search accurately in certain region; however, it is difficult to explore the whole search space. Although these problems can be solved by the integration of the GA with SA in a simple way, the calculation time will cost much more than before and that must be intolerable for the optimization of a complex multi-parameters system.

A new hybrid algorithm thus is developed which fundamentally differs from the normal GA and SA algorithms by the fact that the adaptive multi-annealing mutation, adaptive multi-annealing crossover and population strategy are introduced into the GA. By this method, the performance of GA is improved and the CPU times are also reduced. Using this new hybrid evolutionary algorithm, the kinetics parameters for the synthesis of ethyl *tert*-amyl ether from ethanol and *tert*-amyl alcohol are explored; the differences between this hybrid evolutionary algorithm and the normal GA are also discussed.

---

* Corresponding author. Tel.: +86-29-2668569; fax: +86-29-3237910.
E-mail address: blunyang@xjtu.edu.cn (B. Yang).

1385-8947/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1385-8947(03)00025-1

Nomenclature

c	components number
C_{CAT}	concentration of catalyst (mol-H^+ m^{-3})
C_i	concentration of component (mol m^{-3})
d	number of tested point
h	generation of heredity
k_i	rate constant of each positive reaction considering the inhibition of water
k_{i0}	rate constant of each positive reaction
k'_i	rate constant of each reverse reaction considering the inhibition of water
k'_{i0}	rate constant of each reverse reaction
K_e	equilibrium constant
K_W	inhibition of water ($m^6\,mol^{-2}$)
n	molar quantities (mol)
P_c	crossover probability
P_m	mutation probability
Q	exchange capacity of catalyst (mol-H^+ (kg-dry resin)$^{-1}$)
r_i	reaction rate (mol (mol-H^+)$^{-1}$ s^{-1})
t	time (s)
t_{GSA}	calculation times of GSA algorithm
T	temperature (K)
V	volume of reaction system (m^3)
V_i	molar volume of component ($m^3\,mol^{-1}$)
$W_{A\text{-}15}$	amount of catalyst A-15 (kg)

Greek letter

ψ	value of adaptability function ($m^6\,mol^{-2}$)

2. Experimental

2.1. Materials

tert-Amyl alcohol (TAA) and ethanol were purchased as analytically pure reagents from Xi'an Chemical Reagent, in Xi'an, China. The purity of the reagents was greater than 99.9 mass percent; Ambelyst 15 (A-15) was supplied by Rohm and Hass Corp. (USA), it was soaked into ethanol and was dried at 368 K in an oven drier with a vacuum pump for 8 h before use. The ion exchange capacity, Q, based on the dry resin is 4.96 (mol-H^+ (kg-dry resin)$^{-1}$).

2.2. Apparatus and procedure

The reactor consisted of a three-necked flat-bottomed flask of 250 ml capacity fitted with a condenser in the central opening, a sampling device and a thermowell. The reaction temperature was controlled by a water bath. The reaction mixture was magnetically stirred at the speed about 600 rpm in all the runs for the reason that the reaction rate was independent of agitation speeds in the range of 200–800 rpm and the particle size that was used in this experiment did not influence the reaction rate, this showed that the external and internal diffusion resistances were not significant. Therefore the internal and external diffusion could be ignored and the process was exclusively controlled by reaction kinetics.

The experiments were carried out at 313, 318, 323 and 328 K. Reactant ratios, C_{EtOH} (mol l^{-1})/C_{TAA} (mol l^{-1}) were 0.5, 1 and 2. At the beginning of experiments, a certain ratio reactants were put into reactor, heat reactor with water bath. When the reactants reached the reaction temperature, certain amount of catalyst was added into the reactor and start to record the time. The concentration of each component was analyzed after an interval.

The concentration of each component was analyzed in a TCD gas chromatograph with 4 m column of Gaskuropack 54 as packing material. The temperature of TCD was 453 K, the temperature of vaporizer was 483 K. Helium was used as the carrier gas with flow rate of (1.5×10)–6 $m^3\,s^{-1}$. Separation had been achieved for all components.

3. Kinetics model

For the synthesis of ethyl *tert*-amyl ether from ethanol and *tert*-amyl alcohol on strong acid cation exchange resin A-15 at atmospheric pressure in liquid phase, following reaction equations can be used to describe this process:

$$\mathrm{EtOH} + \mathrm{TAA} \underset{k'_1}{\overset{k_1}{\Leftrightarrow}} \mathrm{TAEE} + \mathrm{H_2O} \qquad (1)$$

$$\mathrm{TAA} \underset{k'_2}{\overset{k_2}{\Leftrightarrow}} \mathrm{2MB1} + \mathrm{H_2O} \qquad (2)$$

$$\mathrm{TAA} \underset{k'_3}{\overset{k_3}{\Leftrightarrow}} \mathrm{2MB2} + \mathrm{H_2O} \qquad (3)$$

$$\mathrm{2MB1} \underset{k'_4}{\overset{k_4}{\Leftrightarrow}} \mathrm{2MB2} \qquad (4)$$

$$\mathrm{EtOH} + \mathrm{2MB1} \underset{k'_5}{\overset{k_5}{\Leftrightarrow}} \mathrm{TAEE} \qquad (5)$$

$$\mathrm{EtOH} + \mathrm{2MB2} \underset{k'_6}{\overset{k_6}{\Leftrightarrow}} \mathrm{TAEE} \qquad (6)$$

where, Eq. (1) is the main reaction, Eqs. (2)–(6) are side reactions. Each reaction is reversible. Because the boiling point of isoamylene (2MB1 306.20 K; 2MB2 311.60 K) is more higher than the temperature of condenser (243 K), isoamylene is considered to be recovered fully in all of our experiments.

The rate equations of this model can be expressed as follows:

$$r_1 = k_1 C_{TAA} C_{EtOH} - k'_1 C_{TAEE} C_{H_2O} \qquad (7)$$

$$r_2 = k_2 C_{TAA} - k'_2 C_{2MB1} C_{H_2O} \qquad (8)$$

$$r_3 = k_3 C_{TAA} - k'_3 C_{2MB2} C_{H_2O} \qquad (9)$$

$$r_4 = k_4 C_{2MB1} - k'_4 C_{2MB2} \quad (10)$$

$$r_5 = k_5 C_{EtOH} C_{2MB1} - k'_5 C_{TAEE} \quad (11)$$

$$r_6 = k_6 C_{EtOH} C_{2MB2} - k'_6 C_{TAEE} \quad (12)$$

where,

$$k_i = \frac{k_{i0}}{1 + K_w C_{H_2O}}, \quad (i = 1, 2, \ldots, 6) \quad (13)$$

$$k'_i = \frac{k'_{i0}}{1 + K_w C_{H_2O}} \quad (i = 1, 2, \ldots, 6) \quad (14)$$

From Eqs. (7)–(12), we get Eqs. (15)–(20).

$$\frac{dC_{EtOH}}{dt} = C_{CAT}(-r_1 - r_5 - r_6) \quad (15)$$

$$\frac{dC_{TAA}}{dt} = C_{CAT}(-r_1 - r_2 - r_3) \quad (16)$$

$$\frac{dC_{2MB1}}{dt} = C_{CAT}(r_2 - r_4 - r_5) \quad (17)$$

$$\frac{dC_{2MB2}}{dt} = C_{CAT}(r_3 + r_4 - r_6) \quad (18)$$

$$C_{H_2O} = C_{TAA,0} - C_{TAA} - \Delta C_{A\text{-}15(H_2O)} \quad (19)$$

$$C_{TAEE} = C_{EtOH,0} - C_{EtOH} \quad (20)$$

$$\Delta C_{A\text{-}15(H_2O)} = K_w C_{H_2O} C_{CAT} \quad (21)$$

Eqs. (7)–(21) are the kinetics model of this reaction system. There are 13 kinetic parameters k_i must be solved. In Eqs. (13) and (14), a modification is made for the expression of k_i based on the catalyst resin's preferential sorption of water, this interference is considered as the inhibition of water. K_W is a function of temperature [9,10]. $C_{CAT} = Q(W/V)$ [mol-H$^+$ m^{-3}] and expresses the concentration of catalyst, W the amount of catalyst (kg) and V the volume of reaction system (m^3). $\Delta C_{A\text{-}15(H_2O)}$ is the reduction amount of water because of the resin's preferential sorption.

4. Basic theory of hybrid evolutionary algorithm

4.1. A simple integration method of genetic-simulated annealing (GSA) algorithm

In the normal GA, only simple crossover, mutation and selection are used as the genetic operators, the normal GA can not embody a complicated evolutionary process. Because of the limitation of population size and number of generation, the algorithm is easy to form truncation error, which will lead to precocity. For this reason, many researchers have tried to design new hybrid algorithms by combining GA with other optimization algorithms [11,12]. All of these hybrid algorithms can improve the efficiency of genetics algorithm in a certain degree.

SA is a powerful optimization technique, which can theoretically converge asymptotically to the global optimum solution with probability '1' when the initial temperature is high enough and cooling rate is infinitely slow [13]. The process of this evolutionary operation adopts the new values based on Boltzmann rule: when an optimized value is adopted, a depraved value is also adopted with a certain probability. This rule is expressed as the following form:

$$\exp\left(\frac{-\Delta f}{T}\right) \geq \text{random}(0, 1) \quad (22)$$

Here, Δf is the difference of fitness value between the child generation and the parent generation, T the annealing temperature. The main drawback of SA in practice is that the parameters in SA are hard to control. There is a contradiction between optimization efficiency and computation time during the selection of annealing rate: if the cooling rate is excessively fast, the evolutionary operation may miss the extremum. Contrarily, the convergence rate of this algorithm will be very slow. Second, in every temperature, SA can hardly determine if it reaches the balanced state by itself, this means the length of Markov chain can not be controlled easily, and when it is reflected to the algorithm, the times of Metropolis process will not be controlled easily. In addition, the selection of the initial temperature is a difficulty for application of SA as well.

A simple integration method of genetic-simulated annealing (GSA) algorithm is to generate new individuals with GA, then these individuals are processed with SA and the results are used as the initial individuals of the next generation. This process can be illustrated in Fig. 1.

This algorithm has a better searching ability for the global optimal solution in some degree; however, it will increase the CPU time extremely. If the generation number is N, population size is M, the iterations at each temperature in annealing process (length of Markov chain) is between l and L, then the calculation times (t_{GSA}) would be $M \times (1 + N + N \times l) < t_{GSA} < M \times (1 + N + N \times L)$. Obviously, it is unsuitable for estimating the complex reaction kinetics parameters.

4.2. New evolution-simulated algorithm

A hybrid evolution-simulated annealing algorithm with multi-pattern evolution is developed in this paper. In this new algorithm, the SA is introduced into the operations of crossover and mutation instead of annealing processing of the individuals after crossover and mutation. Some different operators are also used in each of the process of crossover and mutation to enhance the searching ability of this algorithm further.

For the more, the population strategy is used. It will bring the individuals to evolve in two different patterns: one is adaptive multi-annealing mutation and adaptive multi-annealing crossover; another is to evolve according to evolution strategy, then, every population takes part in

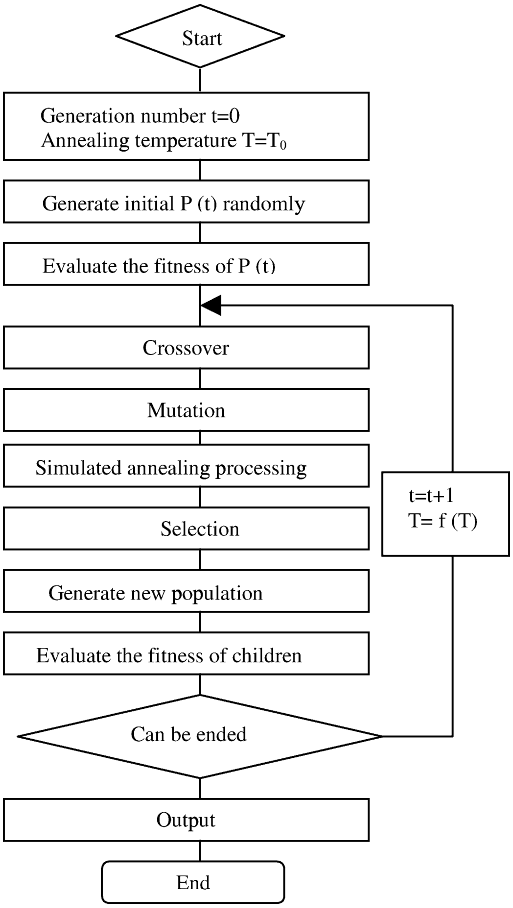

Fig. 1. Flow chart of normal GA–SA.

competition together. This population strategy can prevent the form of some "super individuals", avoid precocity effectively and quicken the calculation speed of algorithm to find the global optimal solutions.

4.3. *Adaptive multi-annealing crossover*

Adaptive multi-annealing crossover can take different crossover strategy act on every individual circularly, and adopts the child generations with a Boltzmann rule. These crossover strategies include: part arithmetic crossover, complete arithmetic crossover and heuristics crossover. Annealing temperature evolution strategy is the fast annealing strategy:

$$T(t) = \frac{T_0}{1+\alpha t} \quad \alpha \in [0, 1] \tag{23}$$

4.4. *Adaptive multi-annealing mutation*

Adaptive multi-annealing mutation is an annealing mutation that uses many different kinds of mutation operators such as nonuniform mutation; Gaussian mutation that based on generation number and multi-step mutation. In each generation, these mutation operators act on every individual circularly, so that, in the beginning of evolution, there will be a high mutation probability. The acceptance criterion is in accordance with Boltzmann rule too.

The functional parameters of GA such as crossover probability P_c and mutation probability P_m will influence the algorithm deeply, but it is difficult to find the optimum values for these parameters. Both of them are adjusted dynamically in the program of this adaptive algorithm, they decrease with the increase of evolutionary generations. With this method, the difficulty of repeated adjusting the value of P_c and P_m can be avoided. This is an attempt to intelligentize the algorithm program. The adaptive function used in this paper is:

$$p = \exp\left(\frac{-\delta \cdot t}{t\_\mathrm{max}}\right) \tag{24}$$

Here, p express P_c or P_m, t is the current generation number, t_max the maximum number of generation, δ a coefficient which expresses the decrease rate of P_c or P_m with the increase of the number of generation. Although δ can be designed as a function relating to the number of generation, distinct advantage for improving the adjusting effect is not shown in this way. Therefore, δ is set to be a constant 1.5 in this paper, and a satisfied result is achieved. By this way, the algorithm is similar to random search in the initial stage of evolution process for the reason that the great probability of crossover and mutation is used; the searching operation thus can reach the whole parameter space. Along with the evolutionary process, the preconditions for adopting child generation individual are more rigorous, algorithm will adopt the excellent new individual in priority, and the algorithm search carefully in certain region, and its local searching capacity is enhanced.

4.5. *Selection*

The $(\mu + \lambda)$-ES is employed as selection strategy. This is a multi point searching method, which uses truncation selection in an extended searching space and can retain the excellent individuals of parent and child generation, this method can improve the convergence efficiency of the new algorithm. The flow diagram for this hybrid evolutionary algorithm is showed as Fig. 2.

4.6. *Apply styles of algorithm*

There are 13 kinetics parameters in this reaction system, which need to be estimated. In the process of evolution operation, encoded mode is real number coding, population size is set as 60 and generation number is 50. Crossover strategy is adaptive multi-annealing crossover. Two patterns are employed as mutation strategy: pattern 1 is adaptive multi-annealing strategy; pattern 2 is the normal mutation that combined with SA as Fig. 2.

The fitness function in this paper is defined as

$$\psi(\bar{K}) = \left(\sum_{i=1}^{c}\sum_{j=1}^{d}[y_i(t_j, \bar{K}) - Y_i(t_j)]^2\right)^{-1} \tag{25}$$

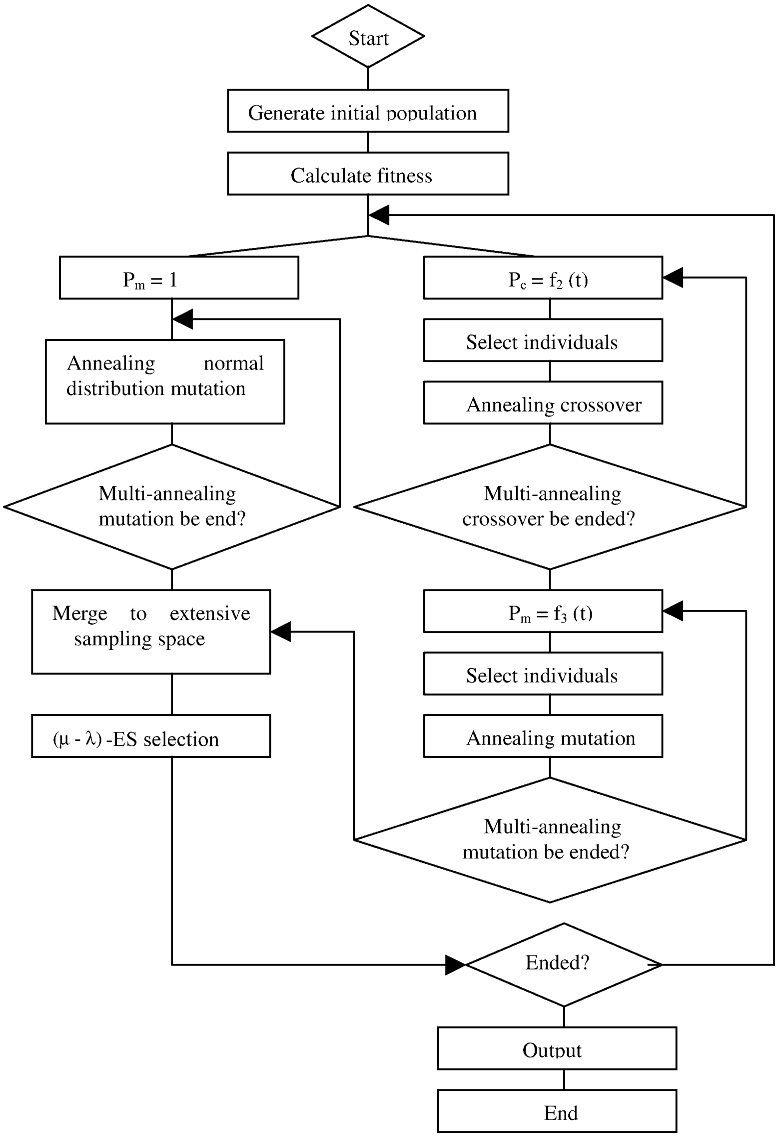

Fig. 2. Sub-flowchart of hybrid evolutionary algorithms.

where $\bar{K}$ is vector of model parameter, c the components number, d the number of tested points, t_j the reaction time, $y(t_j, \bar{K})$ expresses the calculated values of concentration, $Y(t_j)$ expresses the experiment values of concentration. ψ is the value of adaptability function.

5. Results and discussion

5.1. Performance analysis of hybrid evolutionary algorithm

To compare the performance between the new algorithm and normal GA, the same parameter numbers, same encoded mode are employed in these two algorithms. Here, the crossover probability is 0.8; mutation probability is 0.2; the population size is 60, the maximum number of generation is 100. The roulette wheel selection strategy, part arithmetic crossover strategy and uniform mutation strategy are chosen.

Figs. 3 and 4 show the relationship between fitness and the number of generation in normal GA and the new hybrid algorithm, respectively.

Comparing these two figures, it can be known that the normal GA cannot provide satisfied optimization result for such a complicated reaction system as mentioned above. In Fig. 3, when the number of generation is 100, its fitness value is still lower than that when the number of generation is 40 in Fig. 4. For the more, since the normal GA has big mutation probability, the fitness is unsteady and undulate after the 100th generation as shown in Fig. 3. On the contrary, because the truncation selection strategy is used in the hybrid evolutionary algorithm, the average fitness values curve rises smoothly, and it is steady from the 40th generation.

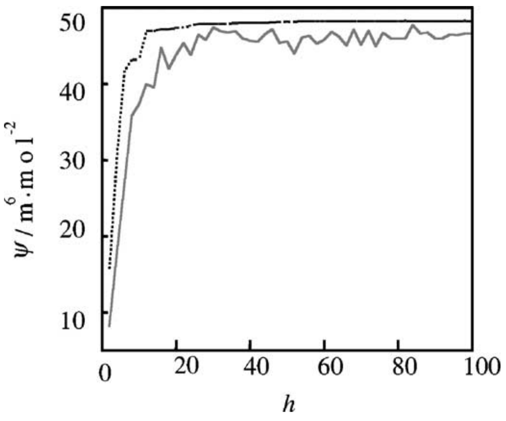

Fig. 3. Fitness profiles in traditional GA: (···) maximum fitness; (—) average fitness.

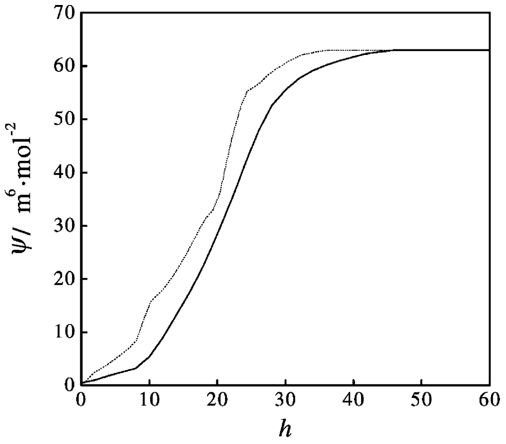

Fig. 4. Fitness profiles in modified GA: (···) maximum fitness; (—) average fitness.

5.2. Calculate the kinetics parameters with the modified evolutionary algorithm

The kinetics parameters of the synthesis of TAEE are estimated with the hybrid evolutionary algorithm and Runge–Kutta method. The relational expressions of k_i and temperature (T) are listed in Table 1.

Table 2
Equilibrium constants for the synthesis of TAEE at different temperature (EtOH:TAA = 1:1 (mol/mol))

T/K	R1	R2	R3	R4	R5	R6
K_e (experimental)						
313	302.5	6.3	73.1	24.3	63.1	7.3
318	299.6	7.1	74.3	21.4	59.1	6.3
323	298.7	8.1	80.3	19.3	48.3	5.6
328	297.6	9.3	90.4	18.3	40.2	4.9
K_e (thermodynamic)						
313	222.1	4.1	49.9	12.0	57.9	4.8
318	221.5	5.1	58.1	11.5	47.0	4.1
323	221.5	6.3	68.4	11.0	38.3	3.5
328	222.2	7.7	80.2	10.6	31.4	3.0

R1–R6 represent reaction (1)–(6).

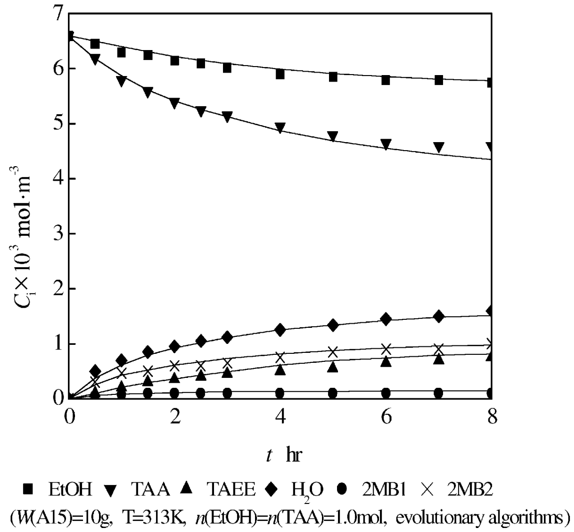

Fig. 5. Concentration profiles with time. EtOH:TAA = 1:1 (mol/mol), $T = 313\,\mathrm{K}$, $W_{\mathrm{CAT}} = 10\,\mathrm{g}$.

Table 1
Results of reaction kinetics parameters calculated by modified evolutionary algorithm

$k_i = f(T)$ (new GA)	$k_i = f(T)$ (R–K)	Unit	E_a (kJ mol^{-1}) (new GA)	E_a (kJ mol^{-1}) (R–K)
$k_{10} = \exp((16.38-8909.41)/T)$	$k_1 = \exp((18.35-8799.37)/T)$	$(\mathrm{m^6\,(mol\,s\,mol\text{-}H^+)^{-1}})$	74.07	73.15
$k'_{10} = \exp((8.32-5423.3)/T)$	$k'_1 = \exp((3.93-4948.13)/T)$	$(\mathrm{m^6\,(mol\,s\,mol\text{-}H^+)^{-1}})$	45.09	41.14
$k_{20} = \exp((23.93-10785)/T)$	$k_2 = \exp((27.98-10389.8)/T)$	$(\mathrm{m^3\,(s\,mol\text{-}H^+)^{-1}})$	89.67	86.38
$k'_{20} = \exp((29.45-11812.1)/T)$	$k'_2 = \exp((28.54-11427.74)/T)$	$(\mathrm{m^6\,(mol\,s\,mol\text{-}H^+)^{-1}})$	98.21	95.01
$k_{30} = \exp((6.36-4930.27)/T)$	$k_3 = \exp((10.05-5067.9)/T)$	$(\mathrm{m^3\,(s\,mol\text{-}H^+)^{-1}})$	40.99	42.13
$k'_{30} = \exp((18.79-9203.17)/T)$	$k'_3 = \exp((18.37-9475.52)/T)$	$(\mathrm{m^6\,(mol\,s\,mol\text{-}H^+)^{-1}})$	76.52	78.78
$k_{40} = \exp((14.57-6779.12)/T)$	$k_4 = \exp((15.17-6992)/T)$	$(\mathrm{m^3\,(s\,mol\text{-}H^+)^{-1}})$	56.36	58.13
$k'_{40} = \exp((18.82-8833.4)/T)$	$k'_4 = \exp((19.02-9208.9)/T)$	$(\mathrm{m^3\,(s\,mol\text{-}H^+)^{-1}})$	73.44	76.56
$k_{50} = \exp((-6.05-821.712)/T)$	$k_5 = \exp((-0.69-788.43)/\mathrm{T})$	$(\mathrm{m^6\,(mol\,s\,mol\text{-}H^+)^{-1}})$	6.83	6.56
$k'_{50} = \exp((-9.97-1027.14)/T)$	$k'_5 = \exp((-9.74-1046.46)/T)$	$(\mathrm{m^3\,(s\,mol\text{-}H^+)^{-1}})$	8.54	8.70
$k_{60} = \exp((3.28-4108.56)/T)$	$k_6 = \exp((6.14-4085.78)/T)$	$(\mathrm{m^6\,(mol\,s\,mol\text{-}H^+)^{-1}})$	34.16	33.96
$k'_{60} = \exp((-0.41-2465.14)/T)$	$k'_6 = \exp((-0.44-2358.15)/T)$	$(\mathrm{m^3\,(s\,mol\text{-}H^+)^{-1}})$	20.49	19.60
$K_w = \exp((-18.24 + 4355.07)/T)$	$k_w = \exp((-17.97 + 4623.4)/T)$	$(\mathrm{m^3\,mol^{-1}})$	–	–

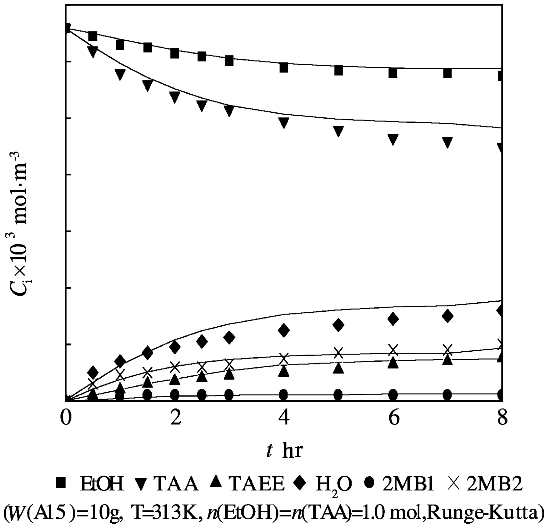

Fig. 6. Concentration profiles with time. EtOH:TAA = 1:1 (mol/mol), $T = 313\,K$, $W_{CAT} = 10\,g$.

The equilibrium constants at different temperature, K_e (exptl), which were obtained from the results in Table 1 are presented in Table 2. For comparison the K_e (thermodyn) calculated from thermodynamic data are included in Table 2. The experimental results K_e (exptl) are higher than K_e (thermodyn).

The relationship between concentration and reaction time is shown in Fig. 5. The scattered symbols express the experimental data and the lines are the calculated values with *k* that was estimated with the new hybrid evolutionary algorithm, obviously both of them agree very well. The lines in Fig. 6 are the calculated concentration values with *k* that was estimated with Runge–Kutta method in the same conditions as in Fig. 6. From the comparison of Figs. 5 and 6, it is proved that the evolution-simulated annealing algorithm with multi-pattern evolution developed fit experimental values with higher precision than Runge–Kutta method.

6. Conclusions

A modified hybrid evolutionary algorithm (evolution-simulated annealing algorithm with multi-pattern evolution) is developed in this paper. The advantages of this hybrid evolutionary algorithm are the quick convergence rate and the better ability to restrain precocity than the normal GA.

The kinetics parameters of synthesis of TAEE are estimated by using the new algorithm. The rate constant values at different temperature for this reaction system are obtained. The expressions of the relationship between rate constants and temperature are established in Arrhenius form. The results accuracy is evidence by a comparison the equilibrium constants from forward and backwards kinetics with those obtained from the thermodynamics. The curves of concentration and temperature that are fitted with these parameters agree well with the experimental results.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (Grant No. 200176044).

References

[1] Z. Michalewicz, M. Schoenauer, Evolutionary algorithms for constrained parameter optimization problems, Evol. Comput. J. 4 (1996) 1–32.
[2] L. Balland, et al., A genetic algorithm with decimal coding for the estimation of kinetic and energetic parameters, Chemomet. Intell. Lab. Syst. 50 (2000) 121–135.
[3] R. Moros, et al., Genetic algorithm for generating initial parameter estimations for kinetic models of catalytic processes, Comput. Chem. Eng. 20 (1996) 1257–1270.
[4] W. Polifke, W. Geng, K. Dobbeling, Optimization of rate coefficients for simplified reaction mechanisms with genetic algorithms, Combust. Flame 113 (1998) 119–134.
[5] S.D. Harris, et al., The optimization of reaction rate parameters for chemical kinetic modeling of combustion using genetic algorithms, Comput. Methods Appl. Mech. Eng. 190 (2000) 1065–1090.
[6] S. Yang, B. Yang, Estimating kinetics parameters in synthesis of ethyl *tert*-butyl ether by using genetic algorithm, J. Chem. Ind. Eng. (China) 53 (2002) 54–59.
[7] N. Metropolic, et al., Equation of state calculations by fast computing machines, J. Chem. Phys. 21 (1953) 1087–1092.
[8] S. Kirkaptrick, C.D. Gelatt, M.P. Vecchi, Optimization by simulated annealing, Science 220 (1983) 671–680.
[9] B. Yang, S. Yang, R. Yao, Synthesis of ethyl *tert*-butyl ether from *tert*-butyl alcohol and ethanol on strong acid cation-exchange resins, React. Funct. Polym. 44 (2000) 167–175.
[10] K. Okamoto, et al., Prevaporation-aided esterification of oleic acid, J. Chem. Eng. Jpn. 26 (1993) 475–481.
[11] D. Gong, M. Gen, G. Yamazaki, Hybrid evolutionary method for capacitated location-allocation problem, Comput. Ind. Eng. 33 (1997) 577–580.
[12] H. Cao, et al., Modeling and prediction for discharge lifetime of battery systems using hybrid evolutionary algorithms, Comput. Chem. 25 (2001) 251–259.
[13] S. Geman, D. Geman, Stochastic relaxation Gibbs distributions and the Bayesian restoration of images, IEEE Trans. Pattern Anal. Machine Intell. 6 (1984) 721–741.