

Application of Genetic Algorithm in Kinetic Modeling and Reaction Mechanism Studies

Fatemi, Shohreh⁺ and Masoori, Mohammad*

Department of Chemical Engineering, University of Tehran, I.R. IRAN

Bozorgmehry Boozarjomehry, Ramin

Department of Chemical & Petroleum Engineering, Sharif University of Technology, I.R. IRAN

ABSTRACT: *This study is focused on the development of a systematic computational approach which implements Genetic Algorithm (GA) to find the optimal rigorous kinetic models.*

A general Kinetic model for hydrogenolysis of dibenzothiophene (DBT) based on Langmuir-Hinshelwood type has been obtained from open literature. This model consists of eight continuous parameters (e.g., Arrhenus and Van't Hoff parameters) and six discrete parameters representing the order of the reaction with respect to each concentration.

The optimal value of these parameters have been obtained based on Genetic Algorithm. Furthermore, the best type of Genetic operators and their corresponding parameters for this type of problems have been obtained based on a comprehensive study of the effect of these parameters on the efficiency of the Genetic Algorithm.

The study shows that the optimum parameters corresponding to Genetic Algorithms depends on the type of operators used in GA. Due to flexibility and generality of Genetic Algorithms, it seems that GA is a useful technique with lots of potentials in determination of optimum kinetic model corresponding to a set of complex reactions.

KEY WORDS: *Genetic algorithm, Kinetic model, Optimization, Hydrogenolysis of DBT,*

INTRODUCTION

Research on chemical kinetics of heterogeneous catalytic reactions often requires rigorous kinetics because of complicated reaction mechanism and adsorption rate limiting steps occurred by reactants, intermediates and products.

By mechanism illustration, these rate equations are derived as non-separable and non-linear functions of

concentration and temperature [1-3].

Mathematical modeling of these complex chemical kinetics leads to non-linear parameter estimation problems in which the experimental data frequently contain more than one optimum. The optimization algorithms, which are based on traditional gradient based methods or direct search methods have the limitation of getting trapped

* To whom correspondence should be addressed.

+E-mail: shfatemi@ut.ac.ir

1021-9986/05/4/37

10/\$/3.00

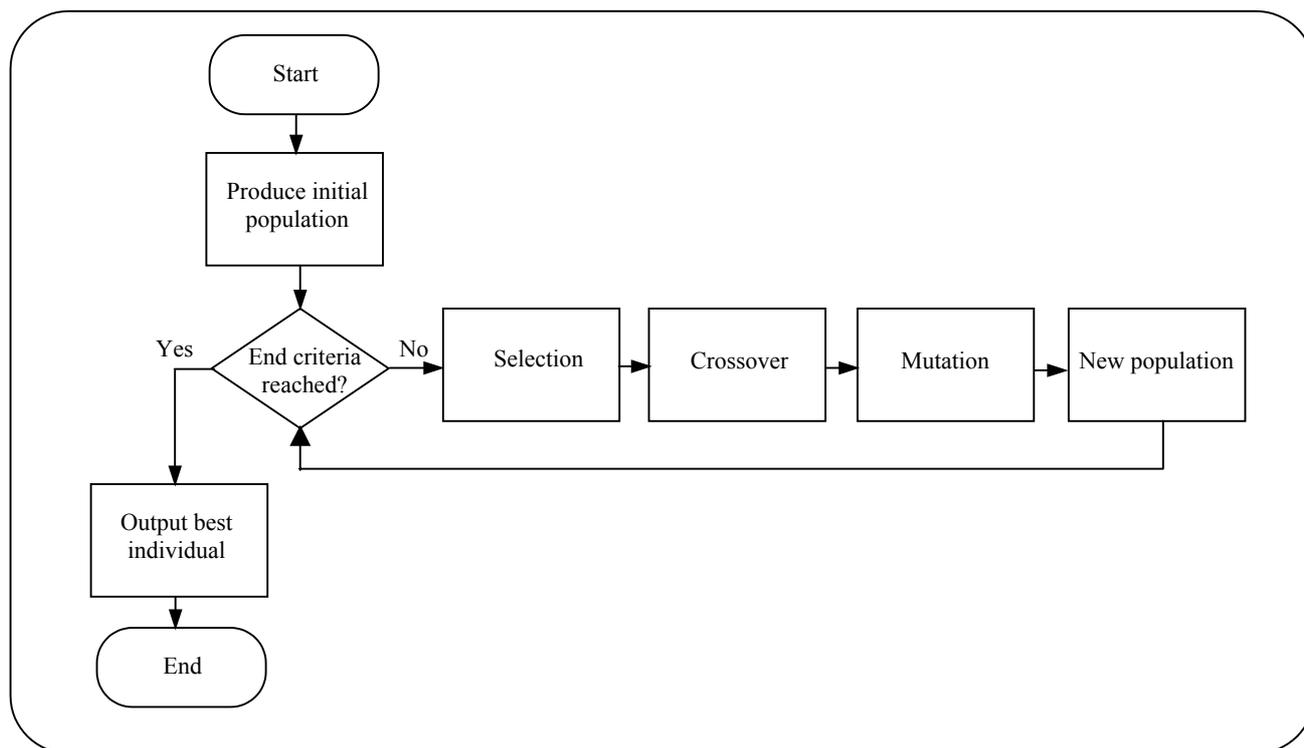


Fig. 1 : The flow chart of Genetic Algorithm.

in local optima. In these methods finding the appropriate initial estimates which lead to convergence to the global optimum can be difficult [4].

To overcome these limitations various approaches based on evolutionary algorithms have been recently used for optimization purposes. One of these algorithms is Genetic Algorithm which is based on the evolutionary process encountered in nature, and can be used as a novel optimization algorithm [5-7]. The application of GA in various scientific and engineering disciplines including chemistry have recently increased[8].

There are a few article published about kinetic modeling using GA, [8,9], but most of them are based on implementation of GA in prediction of good initial estimates for further application in iterative gradient based methods [10]. A few of the published papers implemented a hybrid GA method instead of pure GA for determination of kinetic parameters [11].

The aim of this work is introduction of GA as a robust method for kinetic modeling of complex reaction mechanisms. In this research a GA is used to find the global optimum without using any other auxiliary optimization method.

This work focuses on kinetic modeling of hydro-

desulfurization of heavy sulfur compounds contained in petroleum cuts. Unlike the previous work, a general and complex model of hydrogenolysis reaction rate of dibenzothiophene (DBT), as the model compound, with continuous and discrete unknown parameters is selected. By using a pure GA, the kinetic model and its parameters are optimized, directly.

In this research, attempts have been made to derive the best values of available parameters in GA to increase the efficiency of the algorithm.

Genetic Algorithm

In Genetic algorithms, the solution procedure starts with an initial set of random candidate solutions called population. Each individual in the population is called a chromosome, representing a potential solution of the problem. A chromosome can be represented by a binary string, each part of this binary string represents one of the decision variables.

The chromosomes evolve through successive iterations, called *generation*. During each *generation*, the chromosomes are compared against each other according to a measure called fitness. To create the next *generation*, new chromosomes called offspring, are formed through

the following procedures:

a) Merging two chromosomes from current *generation* using a *crossover* operator.

b) Modifying a chromosome using a *mutation* operator.

In the new *generation* chromosomes with poor fitness are replaced by the obtained offsprings. In this procedure those chromosomes with better fitness have priority to participate in the creation of offsprings [12]. The general flowchart of the GA is presented in Fig. 1. Various stages of GA are elaborated in the following sections:

Initialization

To create initial population, a set of chromosomes is randomly generated. Each chromosome is a binary string in which each gene can take a value of zero or one. Each decision variable in the original optimization problem is mapped to a set of genes whose length depends on the feasible range and the precision of the decision variable. As an example, for a decision variable like x_i whose value is between a_i and b_i and its precision is p_i , the number of required genes can be calculated through the following equation:

$$n_i = \text{int} \left\{ \frac{\log \frac{b_i - a_i}{p_i}}{\log 2} \right\} + 1 \quad (1)$$

Then the total number of genes in a chromosome (n_t) is calculated by following equation:

$$n_t = \sum n_i \quad (2)$$

To convert the encoded parameters (genotypes) to the real parameters (phenotypes) a decoding mechanism by which the set of genes are converted to its corresponding variables is used [13].

Parent Selection

The chromosomes for the next generation are obtained by mating various pairs of chromosomes from current generation. These chromosomes are called parent and the results of mating are called offsprings. In order to keep the diversity of the offsprings, the parents are randomly selected from a set of chromosomes of current generation called mating pool. However, in order to let

the chromosomes with higher fitness have more offsprings than those chromosomes with lower fitness, the chromosomes with higher fitness have more samples in mating pool than the other ones. Implementation of this approach is necessary for the enforcement of "Survival of Fittest" principle, which is the main objective of the Genetic Algorithms.

Crossover

Crossover is one of the main genetic operators, in which two chromosomes are selected block of genes are switched between these two chromosomes. The performance of genetic algorithms depends, to a great extent, on the performance of the *crossover* operator used in GA. Various types of *crossover* operator have been used in GA's some of these types are as follows [14]:

- 1- Singlepoint
- 2- Doublepoint
- 3- Multipoint

Tables 1, 2 and 3 illustrate different examples of *crossover* operators.

The *crossover* rate (p_c) is defined as the ratio of the number of offspring produced in each *generation* to the population size (N). This ratio controls the expected number of chromosomes ($P_c \times N$) undergoing the *crossover* operation. A higher *crossover* rate increases the exploitation of solution space.

Mutation

Mutation is a background operator which produces spontaneous random changes in various chromosomes. A simple way to achieve *mutation* would be to alter the value of one or more genes. *Mutation* serves the crucial role of exploration of search space and generation of sufficient variety in the chromosomes being handled in GA.

The *mutation* rate (P_m) is defined as the percentage of the total number of genes at each generation whose values are flipped. The smaller the mutation rate; the less variety in the candidate solution exists and the less amount of exploration will occur [15].

Fitness Evaluation

In this step each chromosome is first decoded to the corresponding decision variables, and then its fitness which can be considered as the degree of suitability of each

Table 1: Singlepoint Crossover.

Chromosome 1	1001 010000011110
Chromosome 2	1100 011110000111
Offspring 1	1001 011110000111
Offspring 2	1100 010000011110

Table 2: Doublepoint Crossover.

Chromosome 1	1001 01000 0011110
Chromosome 2	1100 01111 0000111
Offspring 1	1001 01111 0011110
Offspring 2	1100 01000 0000111

Table 3: Multipoint Crossover.

Chromosome 1	1001 010 00 001 1110
Chromosome 2	1100 011 11 000 0111
Offspring 1	1001 011 00 000 1110
Offspring 2	1100 010 11 001 0111

chromosome is calculated. In a maximization problem, the fitness can be assumed to be the value of the objective function, where as in a minimization problem it can be used as the opposite sign of objective function [16].

Kinetic model

Hydrogenolysis of DBT is a reaction in which C-S bond is dissociated to produce H₂S and biphenyl in presence of hydrogen on the surface of Co-Mo/ γ -Al₂O₃ catalyst.

The experimental data are derived at temperature range of 548- 598 k and constant pressure of 1.8×10^7 Pa in a differential reactor with different concentrations of DBT, H₂ and H₂S [17]. There are fifty experimental data of DBT reaction rate present at different temperatures and concentrations. The detailed experiment and statistical analysis of the experimental data are presented elsewhere [17,18].

A general kinetic model is selected by using reasonable reaction mechanisms found in literature [1-3,17,19]. These models are based on Langmuir-Hinshelwood or Hougen-Watson model which can cover most type of hydrogenolysis rate equations for heavy sulfur compounds. Most of these equations are presented in Table 4.

According to Table 4 a general model with eight unknown continuous parameters and six discrete parameters (concentrations' powers) was selected as equation (3). This model can be used instead of different types of kinetic model observed in literature. In this equation the rate and adsorption constants are illustrated by Arrhenus and Van't Hoff type equation, in which the order of reaction with respect to hydrogen, hydrogen sulfide and DBT concentrations are unknown. In this general equation, hydrogen concentration is exhibited at two different parts of denominator depending whether hydrogenation occurs on the same site of hydrogenolysis reaction or another site [3].

The unknown powers and parameters (decision variables) should be calculated and optimized using GA.

Decision variables (phenotypes) used in this study with their corresponding valid intervals are shown in Table 5.

A population size of fifty chromosomes ($N=50$) was selected in this study. Because of uncertainty in model parameters, large intervals are selected for frequency factors and energetic parameters. As it is shown in Table 5, the adsorption enthalpy of hydrogen (ΔH_{H_2}) is selected with a very large interval from negative to positive magnitude. This is due to the lack of reliable estimate for this parameter in hydrogenolysis reaction.

In mechanisms proposed for HDS reactions, the powers of the species concentration are usually integer numbers, although sometimes some of them may be one half if there is possibility of dissociation of molecule and atomic adsorption on the catalytic site. So the interval and resolution of discrete parameters are selected as shown in Table 5 to be able to adapt to the mechanism of the reaction.

In this study, three *crossover* operators are implemented at the constant *crossover rate* (P_c) of 100%. Different *mutation rates* ($0 \leq P_m \leq 1$) are used in the program to check the effect of this parameter on the results and determine the optimum value.

Table 4: Kinetic models of hydrogenolysis reaction of DBT.

No.	Kinetic Model	Ref.
1	$-r_{\text{DBT}} = \frac{kK_{\text{DBT}}K_{\text{H}_2}C_{\text{DBT}}C_{\text{H}_2}}{(1 + K_{\text{DBT}}C_{\text{DBT}} + K_{\text{H}_2\text{S}}C_{\text{H}_2\text{S}})^2}$	19
2	$-r_{\text{DBT}} = \frac{kK_{\text{DBT}}K_{\text{H}_2}C_{\text{DBT}}C_{\text{H}_2}}{(1 + K_{\text{DBT}}C_{\text{DBT}} + K_{\text{H}_2}C_{\text{H}_2} + K_{\text{H}_2\text{S}}C_{\text{H}_2\text{S}})^2}$	1
3	$-r_{\text{DBT}} = \frac{kK_{\text{DBT}}K_{\text{H}_2}C_{\text{DBT}}C_{\text{H}_2}}{(1 + K_{\text{DBT}}C_{\text{DBT}} + K_{\text{H}_2\text{S}}C_{\text{H}_2\text{S}})^2(1 + K_{\text{H}_2}C_{\text{H}_2})}$	17
4	$-r_{\text{DBT}} = \frac{kK_{\text{DBT}}K_{\text{H}_2}C_{\text{DBT}}C_{\text{H}_2}}{(1 + K_{\text{DBT}}C_{\text{DBT}} + K_{\text{H}_2\text{S}}C_{\text{H}_2\text{S}}(1 + K_{\text{H}_2}C_{\text{H}_2})^{0.5})^3}$	2
5	$-r_{\text{DBT}} = \frac{kK_{\text{DBT}}K_{\text{H}_2}C_{\text{DBT}}C_{\text{H}_2}}{(1 + K_{\text{DBT}}C_{\text{DBT}} + (K_{\text{H}_2\text{S}}C_{\text{H}_2\text{S}})^{0.5})^2(1 + K_{\text{H}_2}C_{\text{H}_2})}$	17
6	$-r_{\text{DBT}} = \frac{kK_{\text{DBT}}K_{\text{H}_2}C_{\text{DBT}}C_{\text{H}_2}}{(1 + K_{\text{DBT}}C_{\text{DBT}} + K_{\text{H}_2}C_{\text{H}_2} + K_{\text{H}_2\text{S}}C_{\text{H}_2\text{S}})}$	1
7	$-r_{\text{DBT}} = \frac{kK_{\text{DBT}}K_{\text{H}_2}C_{\text{DBT}}C_{\text{H}_2}}{(1 + K_{\text{DBT}}C_{\text{DBT}} + K_{\text{H}_2\text{S}}C_{\text{H}_2\text{S}})(1 + K_{\text{H}_2}C_{\text{H}_2})}$	3

Table 5: Unknown parameters of the model with boundaries and resolution.

Variables	Lower boundary	Upper boundary	Resolution
K_0 , kmol / kgcat.s	10^4	10^7	10^{-3}
E_0 , kJ / kmol	10	10^9	1
K_{DBT} , m^3 / kmol	0	15	10^{-6}
ΔH_{DBT} , kJ / kmol	-10^8	-10^3	1
K_{OH} , m^3 / kmol	10	10^4	10^{-4}
ΔH_{H} , kJ / kmol	-10^9	10^9	0.5
$K_{\text{0,HS}}$, m^3 / kmol	0	20	10^{-6}
ΔH_{HS} , kJ / kmol	-10^8	-10^3	1
α	0	2	0.5
β	0	2	0.5
δ	0	1	0.5
γ	0	1	1
ω	1	3	1
η	0	2	1

$$-r_{\text{DBT}} = \frac{k_0 e^{\frac{E_0}{RT}} K_{0,\text{DBT}} e^{-\frac{\Delta H_{0,\text{DBT}}}{RT}} K_{0,\text{H}_2} e^{-\frac{\Delta H_{0,\text{H}_2}}{RT}} C_{\text{DBT}} C_{\text{H}_2}^\alpha}{(1 + K_{0,\text{DBT}} e^{-\frac{\Delta H_{0,\text{DBT}}}{RT}} C_{\text{DBT}} + \gamma (K_{0,\text{H}_2} e^{-\frac{\Delta H_{0,\text{H}_2}}{RT}} C_{\text{H}_2})^\beta + (K_{0,\text{H}_2\text{S}} e^{-\frac{\Delta H_{0,\text{H}_2\text{S}}}{RT}} C_{\text{H}_2\text{S}})^\delta)^{\gamma_0} (1 + K_{0,\text{H}_2} e^{-\frac{\Delta H_{0,\text{H}_2}}{RT}} C_{\text{H}_2})^\eta} \quad (3)$$

The fitness function of this program is defined as the negative value of average absolute relative deviations (AARD) of the calculated reaction rates with respect to the experimental rates by the following equation:

$$\text{AARD} = \frac{1}{m} \sum_{i=1}^m \left| \frac{r_{\text{exp},i} - r_{\text{cal},i}}{r_{\text{exp},i}} \right| \quad (4)$$

The convergence criterion used in the GA is to get to a constant fitness value for 10000 consecutive generations

RESULTS AND DISCUSSION

GA control parameters

Three *crossover* operators were implemented at different *mutation rates* ($0 \leq P_m \leq 1$) with total *crossover* rate to compare the number of *generations* and required time to reach to the optimum. These results are presented in Fig. 2 for the number of *generations* and in Fig. 3 for the required time to reach to a fitness higher than -15%. It is concluded that for different *crossover* operators there are different optima of P_m .

The results of this model show that, at some higher P_m , it is possible to converge to the optimum more rapidly than the lower ones.

The optimum value of P_m for different *crossover* methods is presented in Table 6. Crossover rate of 100% can converge to the optimum with minimum required time of 281 seconds, using double point *crossover*.

It should be noted that the number of generations and the time required for calculations severely depend on the type of model and the number of unknown parameters with their defined intervals and resolution.

Another part of the results are focused on the study of the required time for the completion of first generation. It seems that the time required for one generation is a linear

function of *mutation rate*, as shown in Fig.4.

Kinetic Model Validation

With respect to the different possible hydrogenolysis kinetic mechanisms a general model was selected with eight unknown rate and energetic parameters and six discrete unknown order parameters presented in equation (3). This general model exhibits adsorption term of DBT, H₂S and H₂ in denominator of rate equation. The effect of hydrogen as an inhibitor was not approved in previous studies of hydrogenolysis kinetics [17]. To discover this effect by GA, H₂ adsorption term is selected into two different categories in the selected general equation of (3) as following:

a) The first choice is presence of H₂ as inhibitor with one of the following conditions:

○ If $\gamma=0$ then η should be none zero. By this condition the inhibition effect of hydrogen will appear as a separate term in denominator, it means that hydrogenation and hydrogenolysis occur on different sites.

○ If $\gamma \neq 0$ then η should be zero. By this condition the inhibition effect of hydrogen will appear non-separable in denominator, it means hydrogenation occurs on the same site as hydrogenolysis.

By the choice of (a), the result of optimization program will certainly show hydrogen inhibition effect by presence of one of the above conditions.

Equation (5) represents the optimum model and its parameters are presented in Table 7. AARD of the experimental rates and model is calculated 14.29%.

b) The second choice is the use of the above two parameters (η, γ) without any restriction. In this case, the GA program can lead to the best magnitude for both η and γ , the optimum value of these parameters may be

$$-r_{\text{DBT}} = \frac{k_0 e^{\frac{E_0}{RT}} K_{0,\text{DBT}} e^{-\frac{\Delta H_{0,\text{DBT}}}{RT}} K_{0,\text{H}_2} e^{-\frac{\Delta H_{0,\text{H}_2}}{RT}} C_{\text{DBT}} C_{\text{H}_2}}{[1 + K_{0,\text{DBT}} e^{-\frac{\Delta H_{0,\text{DBT}}}{RT}} C_{\text{DBT}} + (K_{0,\text{H}_2\text{S}} e^{-\frac{\Delta H_{0,\text{H}_2\text{S}}}{RT}} C_{\text{H}_2\text{S}})^{0.5}] (1 + K_{0,\text{H}_2} e^{-\frac{\Delta H_{0,\text{H}_2}}{RT}} C_{\text{H}_2})} \quad (5)$$

Table 6: The optimum mutation rate to convergence to lower than 15% AARD.

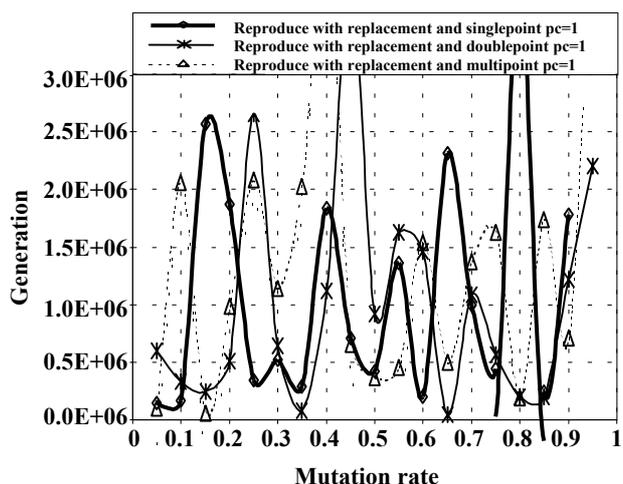
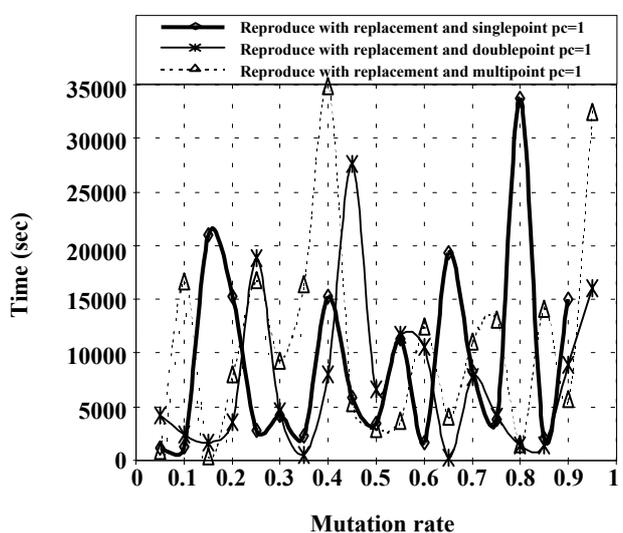
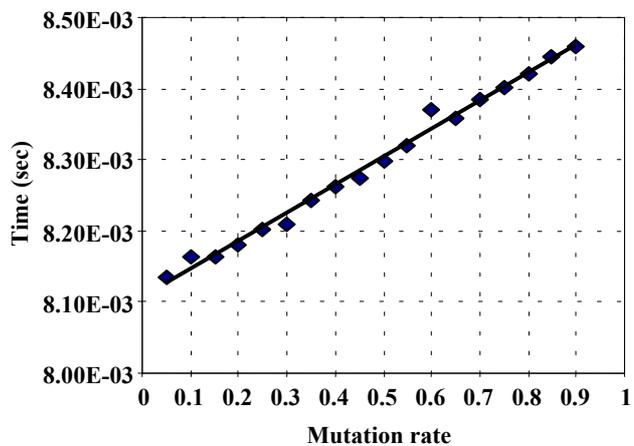
Crossover method	$P_{m,opt}$	No. generation	Time(sec)
Singlepoint	0.05	139906	1138
Doublepoint	0.65	39086	281
multi-point	0.15	53977	439

Table 7: Parameters estimation of the model (Eq. 5).

Variables	Calculated
K_0 , kmol / kgcat.s	1.07204×10^4
E_0 , kj / kmol	6.96038×10^4
K_{0DBT} , m^3 / kmol	9.00934
ΔH_{DBT} , kj / kmol	-2.81924×10^4
K_{0H} , m^3 / kmol	1.31559×10^2
ΔH_H , kj / kmol	-9.80517×10^4
K_{0HS} , m^3 / kmol	6.69337
ΔH_{HS} , kj / kmol	-6.54093×10^4
α	1
β	1.5
δ	0.5
γ	0
ω	1
η	1
AARD	%14.2927

Table 8: Parameters estimation of the model (Eq. 6).

Variables	Calculated
K_0 , kmol / kg.cat.s	2.83810×10^5
E_0 , kj / kmol	3.56821×10^2
K_{0DBT} , m^3 / kmol	3.42035×10^{-1}
ΔH_{DBT} , kj / kmol	-5.14766×10^4
K_{0HS} , m^3 / kmole	1.47123×10^1
ΔH_{HS} , kj / kmol	-7.8362×10^4
α	1
β	0.5
δ	0.5
γ	0
ω	1
η	0
AARD	%12.7534

**Fig. 2 : Number of Generations vs. different Mutation rates to converge to less than 15% AARD.****Fig. 3 : Time required to converge to less than 15% AARD vs. different Mutation rates.****Fig. 4 : Time required for one generation against Mutation rate increase.**

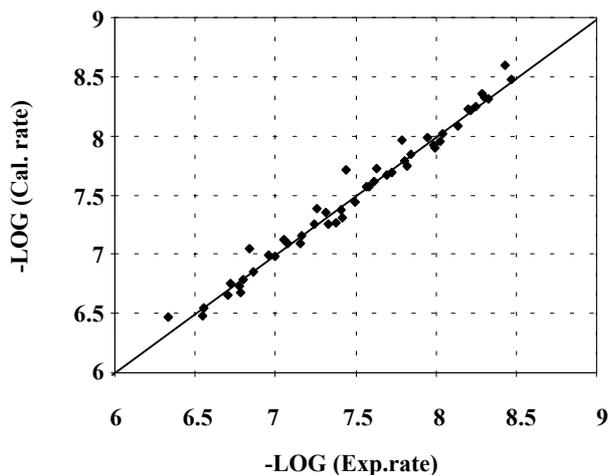


Fig. 5: Experimental rate of DBT reaction vs. Calculated rate, model no.(5).

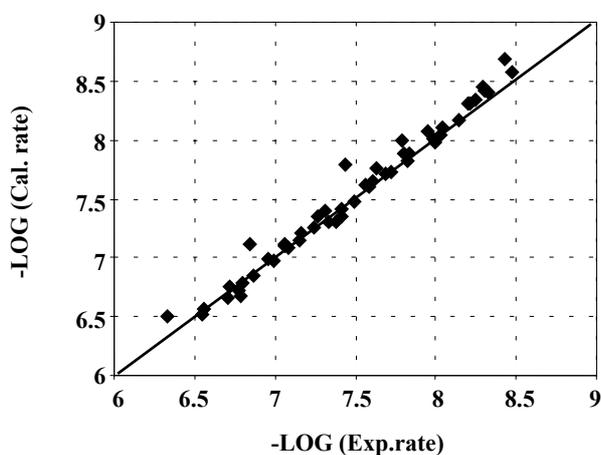


Fig. 6: Experimental rate of DBT reaction vs. Calculated rate, model no.(6).

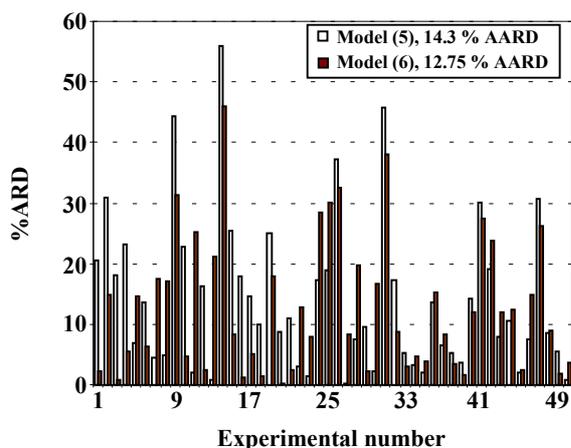


Fig. 7 : Comparison of ARD% for each experimental point of two different model.

both zero or none-zero. In fact in this case, the effect of H_2 on the surface of catalyst, can be obtained according to the results found by GA.

This category exhibits improvement of the results in comparison to the previous choice with the AARD of 12.75%. Equation (6) shows the optimum model with its parameters presented in Table 8. In this equation both η and γ are zero at the optimum point obtained by GA, this means there is no inhibition effect of hydrogen in hydrogenolysis reaction.

Implementation of GA with respect to the experiments and determination of the optimum parameters concludes reliable results of no inhibiting effect of hydrogen on the catalyst surface because of the lower AARD for equation (6).

$$-r_{DBT} = \frac{k_0 e^{-\frac{E_0}{RT}} K_{0,DBT} e^{-\frac{\Delta H_{0,DBT}}{RT}} K_{0,H_2} e^{-\frac{\Delta H_{0,H_2}}{RT}} C_{DBT} C_{H_2}}{[1 + K_{0,DBT} e^{-\frac{\Delta H_{0,DBT}}{RT}} C_{DBT} + (K_{0,H_2S} e^{-\frac{\Delta H_{0,H_2S}}{RT}} C_{H_2S})^{0.5}]}$$
 (6)

In both models obtained in this study, the optimum power H_2S concentration is calculated as 0.5, which means dissociation of H_2S on the surface of the catalyst. This is similar to the results reported by other researchers [17].

Comparison of the calculated and experimental rate of reactions are shown in Fig. 5 and 6. Furthermore, Fig. 7 shows the absolute Relative Deviations of both models for all experimental data.

CONCLUSION

Unlike traditional gradient based methods one of the most important characteristic of Evolutionary Algorithms such as GA is their effectiveness and robustness when they are used for problems uncertainty, insufficient information and noise. In this approach minimum human effort and little insight into the details of the chemical mechanism is required to generate the optimum value for the reaction rate coefficients. Despite the flexibility and robustness of GA, its efficiency heavily depends on the type of genetic operators used in the algorithm and their corresponding parameters. In this study the appropriate type of genetic operators and their parameters have been studied and obtained.

Due to flexibility and generality of Genetic Algorithms, it seems that GA is a useful technique with lots of potentials in determination of optimum kinetic model corresponding to a set of complex reactions.

Acknowledgement

The authors would like to thank Dr. Amir Mansoor Pezeshk and Dr. Ali Babakhani for their help and valuable comments in this research. The financial support of the University of Tehran is gratefully acknowledged.

Nomenclature

a_i	Lower boundary of domain of a specific variable
b_i	Upper boundary of domain of a specific variable
C_{DBT}	Concentration of DBT, (kmol/m ³)
C_{H_2}	Concentration of H ₂ , (kmol/m ³)
C_{H_2S}	Concentration of H ₂ S, (kmol/m ³)
E_0	Activation Energy, (kj/kmol)
$\Delta H_{0,DBT}$	DBT Enthalpy of adsorption, (kj/kmol)
$\Delta H_{0,H_2}$	H ₂ Enthalpy of adsorption, (kj/kmol)
$\Delta H_{0,H_2S}$	H ₂ S Enthalpy of adsorption, (kj/kmol)
k_0	Frequency factor of rate equation, (kmol/kgcat.s)
$K_{0,DBT}$	Frequency factor of DBT adsorption, (m ³ /kmol)
K_{0,H_2}	Frequency factor of H ₂ adsorption, (m ³ /kmol)
K_{0,H_2S}	Frequency factor of H ₂ S adsorption, (m ³ /kmol)
m	Total number of experimental data
N	Population size
n_i	Number of bits in a specific variable
n_t	Total number of bits for a chromosome
p_c	Crossover rate
p_i	Precision of a specific variable
p_m	Mutation rate
R	Gas constant
r_{DBT}	DBT reaction rate
T	Temperature (K)

Received : 11th October 2004 ; Accepted : 18th April 2005

REFERENCES

- [1] Edvinsson, R., Irandoust, S., Hydrodesulfurization of Dibenzothiophene in monolithic Catalyst Reactor, *Ind. Eng. Chem. Res.*, **32**, 391 (1993).
- [2] Froment, G. F., Vanrysselberghe, V. Hydrodesulfurization of Dibenzothiophene on a Co-Mo/ γ -Al₂O₃ Catalyst: Reaction Network and Kinetics, *Ind. Eng. Chem. Res.*, **35**, 3311 (1996).
- [3] Massoth, F.E., Studies of Mo/Alumina Catalysts VI. Kinetics of Thiophene Hydrogenolysis, *J. Catalysis*, **47**, 316 (1977).
- [4] Marquardt, D. W., An Algorithm for Least-Squares Estimation of Nonlinear Parameters, *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963).
- [5] Brunette A., A fast precise genetic algorithm for a non-linear fitting problem, *Computer physics communications*, *Elsevier science* (2000).
- [6] Goldberg, David E., "Genetic Algorithms in Search, Optimization and Machine Learning", Addison-Wesley Pub. Co. (1989).
- [7] Bentley, P. J., *Evolutionary Design by Computers*, Morgan Kaufmann, Publisher, Inc., (1999).
- [8] Balland, L., Estel, L., Cosmao, J. M., Mouhab, N., A Genetic Algorithm with Decimal Coding for the Estimation of Kinetic and Energetic Parameters, *Chemometrics and Intelligent Laboratory Systems*, **50**, p. 121 (2000).
- [9] Elliot, L., Inghen, D. B., Kyne, A. G., Mera, N. S., Pourkashanian, M., Wilson, C.W., Genetic Algorithms For Optimization of Chemical Kinetic Mechanisms, *Prog. Ener. Comb. Sci.*, **30**, 297 (2004).
- [10] Moros, R., Kalies, H., Rex, H. G., Schaffarczyk, S., A Genetic Algorithm from Generating Initial Parameter Estimations for Kinetic Models of Catalytic Processes, *Comp. Chem. Eng.*, **20**, 1257 (1995).
- [11] Froment, G. F. and Park, T. Y., A Hybrid Genetic Algorithm for the Estimation of Parameters in Detailed Kinetic Models, *Comp. Chem. Eng.*, **22**, S103 (1998).
- [12] Michalewicz, Z., "Genetic Algorithms+ Data Structures", Evolution Programs, Springer-Verlag, New York (1996).
- [13] Goldberg, David E., "The Design of Innovation: Lessons from and for Competent Genetic Algorithms", Boston, MA., Kluwer Academic Publishers, (2002).
- [14] Langdon W. B., Riccardo Poli, William B. Langdon "Foundations of Genetic Programming", Springer-

Verlag publication, (2001).

- [15] Schmitt, L. M., Fundamental study theory of genetic algorithms, *Theoretical Comp. Sci.*, **259**, 1 (2001).
- [16] Mitchell, M., An Introduction to Genetic Algorithms (Complex Adaptive Systems), Bradford Books, 06 February, Paperback (1998).
- [17] Broderick, D. H. and Gates, B. C., Hydrogenolysis and Hydrogenation of Dibenzothiophene Catalyzed by Sulfided Co-Mo/Al₂O₃ : The Reaction Kinetics, *AIChE J.*, **27**, 663 (1981).
- [18] Nag, N.K., Spare, A. V., Brodrick, D. H., and Gates, B. C., Hydrodesulfurization of Polycyclic Aromatics Catalyzed by Sulfided Co-Mo/g-Al₂O₃: The relative reactivities, *J. Catal.*, **57**, 509 (1979).
- [19] Vrinat, M. L., The Kinetics of HDS Process- A Review, *Appl. Catal.*, **6**, 137 (1983).