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Which method is better for the kinetic modeling: Decimal encoded or Binary Genetic Algorithm?

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Abstract

Kinetic modeling is an important issue, whose objective is the accurate determination of the rates of various reactions taking place in a reacting system. This issue is a pivotal element for the process design and development particularly for novel processes which are based on reactions taking place between various types of species.

In this paper, the Genetic Algorithms have been used to develop a systematic computational framework for kinetic modeling of various reacting systems. This framework can be used to find the optimum values of various parameters that exist in the kinetic model of a reacting system. The Fischer–Tropsch (FT) reactions have been used as the kinetic modeling bench mark. General kinetic models for FT, Water–Gas-shift (WGS) and overall rates based on Langmuir–Hinshelwood type have been considered and their optimum parameters have been obtained by Genetic Algorithms. The study shows the obtained model outperforms the other alternative models both in generality and accuracy. Furthermore, the performance of Binary and Decimal Genetic Algorithms have been compared. The obtained results show that despite its ease of implementation, Decimal encoding GA has lower performance comparing to Binary encoding GA.

Keywords: Genetic Algorithm; Binary encode GA; Decimal encoding GA; Kinetic modeling; Fischer–Tropsch (FT); Water–Gas-shift (WGS)

1. 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 which often contains more than one minimum among which one is the global minimum and the others are local minima. On the other hand, the gradient-based optimization algorithms usually used in the parameter estimation of these problems suffer from getting trapped in local minima. Furthermore, convergence of these methods can be achieved only if they are initiated with a set of appropriate initial estimates for the decision variables [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. The continuing improvements of the price/performance in these computational systems have made them attractive for various types of optimization problems. In particular, Genetic Algorithms work very well on mixed (continuous and discrete), combinatorial problems. They are less susceptible to getting stuck at local optima than gradient search methods. But they tend to be computationally expensive [5–7]. The application of GA in various scientific and engineering disciplines including chemistry has recently increased [8].

There are a few articles published on kinetic modeling using GA [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.

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Nomenclature

a	reaction rate constant
a_i	lower boundary of domain of a specific variable
b	reaction rate constant
b_i	upper boundary of domain of a specific variable
c	reaction rate constant
d	reaction rate constant
FT	Fischer–Tropsch
K	reaction rate constant
K_p	equilibrium constant Water–Gas-shift
m	total number of experimental data
n_i	number of bits in a specific variable
N	population size
OVL	overall synthesis gas consumption
P	pressure (MPa)
P_c	crossover rate
P_i	precision of a specific variable
P_m	mutation rate
r	reaction rate ($\mathrm{mol\,kg_{catalyst}^{-1}\,s^{-1}}$)
WGS	Water–Gas-shift reaction

Greek letters

α	reaction rate constant
β	reaction rate constant
χ	reaction rate constant
δ	reaction rate constant
ε	reaction rate constant
ϕ	reaction rate constant
γ	reaction rate constant
φ	reaction rate constant
ω	random number between 0 and 1
ξ	random number between 0 and 1

Furthermore, since there are two main approaches in the implementation of Genetic Algorithm (i.e., GA with decimal phenotypic transformation and GA with binary phenotypic transformation) the performance of these two approaches have also been compared in kinetic modeling. Since Fischer–Tropsch reactions have been recently used to obtain clean and environmentally safer fuel in gas-to-liquid (GTL) and olefin in gas to olefin (GTO) processes, Fischer–Tropsch and Water–Gas-shift reactions are used as the kinetic bench mark in this work.

Next section contains a brief overview of both Binary and Decimal encoding Genetic Algorithms. In Section 3, Fischer–Tropsch and Water–Gas-shift reactions and various kinetics published for these reactions are reviewed and the mathematical formulation of the kinetic modeling problem is also explained in this. Section 4 contains the results of kinetic modeling along with the performance of Binary and Decimal encoded Genetic Algorithms.

2. Genetic Algorithm

In Genetic Algorithms, the solution procedure starts with an initial set of random candidate solutions called population. Each individual in the population which is called a chromosome, is a set consists of various segments (called genotypes). Each genotype represents the value of a decision variable (called phenotype). Phenotypic transformation is a function which converts phenotypes into genotypes. This transformation should be invertible in order to get from genotypes to their corresponding phenotypes.

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) mating two chromosomes from current *generation* using the crossover operator;
(b) modifying the chromosome using the *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.

2.1. Initialization

2.1.1. Binary GA

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 0 or 1. 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:

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

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

$$n_t = \sum n_i \tag{2}$$

The inverse of the phenotypic transformation is used to convert the genotypes into their corresponding phenotypes [13].

2.1.2. Decimal GA

In this kind of GA, each chromosome is a decimal string in which each gene can take a decimal number. Therefore, in Decimal GA neither encoding nor decoding step is required.

2.2. 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

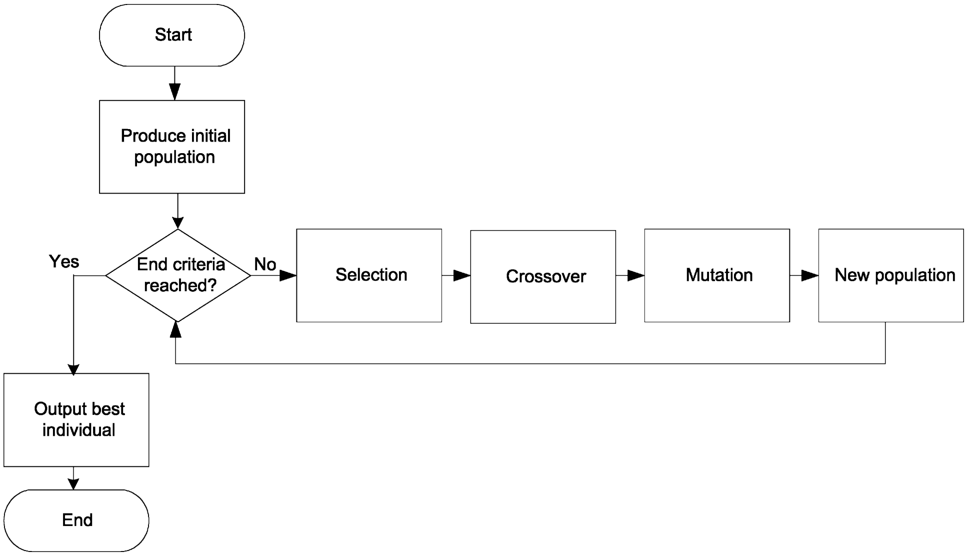

Fig. 1. The flow chart of genetic algorithm.

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. This stage is similar for both Binary and Decimal encoded GA. In order to implement this scenario the mating pool is filled with two copies of the two fittest individuals, and to keep the size of mating pool constant the last two individuals with the least fitnesses do not take apart in the mating mechanism.

2.3. Crossover

Crossover is one of the main genetic operators, in which two chromosomes are selected as parents whose mating results in two new chromosomes called offsprings for the next generation. The performance of Genetic Algorithms heavily depends on the performance of the *crossover* operator used in GA. 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.

2.3.1. Binary GA

In Binary GA at least one randomly selected block of genes are exchanged between parent chromosomes. Various types of *crossover* operator have been used in GA, some of these types for Binary GA are as follows [14]:

1. single point;
2. double point;
3. multi-point.

2.3.2. Decimal GA

In Decimal GA, however, since the chromosome is a bunch of real variables, application of such a scenario is not possible. In this case, one of the most commonly used crossover operator is arithmetic crossover in which the offsprings are obtained through the following equations:

$$\text{Offspring1} = \omega \times \text{Parent1} + (1-\omega) \times \text{Parent2} \tag{3}$$

$$\text{Offspring2} = \omega \times \text{Parent2} + (1-\omega) \times \text{Parent1} \tag{4}$$

2.4. 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 used 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].

In Binary GA, the mutation operator is usually accomplished by random selection of a set of genes and flipping their values from 1 to 0 or vice versa, where as in Decimal GA the mutation is done through the following equation:

$$\text{Mutated gene} = \text{original gene} \times (1-\xi) + \xi \times (b_i - a_i) \tag{5}$$

where η is a positive random number less than one, and a_i and b_i are the interval in which each variable can vary.

2.5. Fitness evaluation

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

Table 1
Kinetic models of Fischer–Tropsch [1,2]

Model	Kinetic equation
FT-I	$\dfrac{kP_{CO_2}^{1/2}P_{H_2O}^{1/2}}{(1+aP_{CO}^{1/2}+bP_{H_2O})^2}$
FT-II	$\dfrac{kP_{CO_2}^{1/2}P_{H_2O}^{3/4}}{(1+aP_{CO}^{1/2}P_{H_2}^{3/4}+bP_{H_2O})^2}$
FT-III	$\dfrac{kP_{CO}^{1/2}P_{H_2}}{1+aP_{CO}^{1/2}+bP_{H_2O}}$
FT-IV	$\dfrac{kP_{CO}P_{H_2}^{1/2}}{(1+aP_{CO}+bP_{H_2O})^2}$
FT-V	$\dfrac{kP_{CO}P_{H_2}}{(1+aP_{CO}+bP_{H_2O})^2}$
FT-VI	$\dfrac{kP_{CO}P_{H_2}}{1+aP_{CO}+bP_{H_2O}}$
FT-VII	$\dfrac{kP_{CO}P_{H_2}^2}{1+aP_{CO}+bP_{H_2O}}$

considered as the degree of suitability of each 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].

3. Kinetic models

Fischer–Tropsch synthesis (FTS), as an alternate process, can convert the synthesis gas (H_2/CO) derived from carbon sources, such as coal, peat, biomass and natural gas, into hydrocarbons and oxygenates. In consideration of the limited reserves of crude oil, today, it continuously attracts renewed interests as an option for the production of clean transportation fuels and chemical feedstocks [3].

There is a significant interest in both the process and the mechanism of Fischer–Tropsch synthesis from the practical and theoretical viewpoints. The FTS produces a considerable variety of products that are mainly hydrocarbons and oxygenated compounds. The operating condition has significant influence upon the product distribution; therefore, it is critically important to control the selectivity of the product. This is closely related to the kinetics and mechanism of the FTS. In the light of the potential economic and environmental importance of FTS, a detailed understanding of the process is highly desirable [2].

Table 2
Kinetic models of Water–Gas-shift [1,2]

Model	Kinetic equation
WGS-I	kP_{CO}
WGS-II	$k(P_{CO}P_{H_2E}-(P_{CO_2}P_{H_2})/K_p)$
WGS-III	$\dfrac{k(P_{CO}P_{H_2O}-(P_{CO_2}P_{H_2}^{1/2})/K_p)}{(1+(aP_{H_2O}/P_{H_2}^{1/2}))^2}$
WGS-IV	$\dfrac{k(P_{CO}P_{H_2O}-(P_{CO_2}P_{H_2})/K_p)}{P_{CO}P_{H_2}+aP_{H_2O}}$
WGS-V	$\dfrac{k(P_{CO}P_{H_2O}-(P_{CO_2}P_{H_2})/K_p)}{P_{CO}+aP_{H_2O}+bP_{CO_2}}$

Table 3
Kinetic models of overall syngas consumption [1,2]

Model	Kinetic equation
OVL-I	$r_{OVL}=KP_{H_2}^{\alpha}$
OVL-II	$r_{OVL}=KP_{H_2}^{\alpha}P_{CO}^{\beta}$
OVL-III	$r_{OVL}=\dfrac{KP_{H_2}P_{CO}}{P_{CO}+aP_{H_2O}}$
OVL-IV	$r_{OVL}=\dfrac{KP_{H_2}^2P_{CO}}{P_{CO}P_{H_2}+aP_{H_2O}}$
OVL-V	$r_{OVL}=\dfrac{KP_{H_2}^2P_{CO}}{1+aP_{CO}P_{H_2}^2}$
OVL-VI	$r_{OVL}=\dfrac{KP_{H_2}P_{CO}}{P_{CO}+aP_{CO_2}}$
OVL-VII	$r_{OVL}=\dfrac{KP_{H_2}P_{CO}}{P_{CO}+aP_{H_2O}+bP_{CO_2}^{\varphi}}$
OVL-VIII	$r_{OVL}=\dfrac{KP_{H_2}^{1/2}P_{CO}^{1/2}}{(1+aP_{CO}^{1/2}+bP_{H_2}^{1/2})^2}$
OVL-IX	$r_{OVL}=\dfrac{KP_{H_2}^{1/2}P_{CO}}{(1+aP_{CO}+bP_{H_2}^{1/2})^2}$
OVL-X	$r_{OVL}=\dfrac{KP_{H_2}P_{CO}}{(1+aP_{CO})^2}$

The Fischer–Tropsch synthesis is a set of complicated parallel and series reactions involving different extents and determining altogether the overall catalyst performance. The whole synthesis reaction can be simplified as the combination of the FTS reactions and the Water–Gas-shift (WGS) reaction [1–3].

$$\mathrm{CO} + 2\mathrm{H_2} \rightarrow -(\mathrm{CH_2})- + \mathrm{H_2O} + 165\,\mathrm{kJ} \quad \text{paraffin} \tag{6}$$

$$y\mathrm{C} + x\mathrm{M} \rightarrow \mathrm{M}_x\mathrm{C}_y, \quad \text{bulk carbide formation} \tag{7}$$

$$2\mathrm{CO} \rightarrow \mathrm{C} + \mathrm{CO_2}, \quad \text{Bouduard reaction} \tag{8}$$

$$(2n+1)\mathrm{H_2} + n\mathrm{CO} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H_2O}, \quad \text{olefins} \tag{9}$$

$$(2n)\mathrm{H_2} + n\mathrm{CO} \rightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{H_2O}, \quad \text{WGS reaction} \tag{10}$$

$$\begin{array}{l} \mathrm{M}_x\mathrm{O}_y + y\mathrm{H_2} \rightarrow x\mathrm{M} + y\mathrm{H_2O}, \quad \text{catalyst ox}/red \\ \mathrm{M}_x\mathrm{O}_y + y\mathrm{CO} \rightarrow x\mathrm{M} + y\mathrm{CO_2} \end{array} \tag{11}$$

Table 4
Valid range and resolution of model parameters for Eqs. (18) and (18*)

Parameter	Lower limit	Upper limit	Precision or acceptable values
K	0.0001	5	0.0001
α	0.5	1	0.5
β	0.5	2	0.5, 0.75, 1, 2
a	0	1	0.01
χ	0.5	1	0.5
δ	0	0.25	0.25
b	0	35	0.01
ε	1	2	1

Table 5
Unknown parameters of the model with boundaries and resolution for Eqs. (19) and (19*)

Parameter	Lower limit	Upper limit	Precision or acceptable values
K	0	300	0.01
α	0	0.5	0.5
β	0.5	1	0.5
K_p	0	400	0.1
χ	0	1	1
a	0	400	0.01
δ	0	0.5	0.5
b	0	100	0.01
ε	0	1	1
c	0	200	0.01
Φ	0	1	1
φ	0	2	1

Table 6
Unknown parameters of the model with boundaries and resolution for Eqs. (20) and (20*)

Parameter	Lower limit	Upper limit	Precision or acceptable values
K	0	1000	0.01
α	0.5	2	0.5, 1, 2
β	0	1	0.5
χ	0	1	1
a	0	5	0.01
δ	0.5	1	0.5
ε	0	2	1
b	0	200	0.01
Φ	0	1	1
c	0	200	0.01
φ	0	2	0, 0.5, 1, 2
d	0	300	0.01
γ	0	2	1

Table 7
Selected GA parameters

Population size	50
Crossover rate	1
Mutation rate	0.15
Crossover type	Single point

$$CO + \left(1 + \frac{m}{2n}\right) H_2 \rightarrow \frac{1}{n} C_n H_m + H_2O, \quad \text{Fischer-Tropsch} \tag{12}$$

$$H_2O + CO \leftrightarrow CO_2 + H_2 \quad \text{Water–Gas-shift} \tag{13}$$

The experimental data used in comparison are those reported by van der Laan [1,2]. These data were derived at constant temperature 503 K and pressure range of 0.8–4.0 MPa in a differential reactor with different concentrations of reactants.

A general kinetic model is selected based on reasonable reaction mechanisms found in literature. These models are all based on Langmuir–Hinshelwood–Hougen–Watson model which can cover most type of FT, WGS and overall syngas rate equations. Tables 1–3 show various equations representing the rate of FT, WGS and overall syngas reactions.

Comparing the equations presented in Tables 1–3 one can come up with three general models with at least eight unknown parameters (Eqs. (12)–(14)) that can be used in a more general and accurate manner. These equations have been used to model the rates of FT, WGS and overall reactions. In fact, these models can be considered as the superset of different types of kinetic models observed in literatures [1–3].

$$r_{FT} = \frac{K P_{CO}^{\alpha} P_{H_2}^{\beta}}{(1 + (a P_{CO}^{\chi} / P_{H_2}^{\delta}) + b P_{H_2O})^{\varepsilon}} \tag{14}$$

$$r_{WGS} = \frac{K((P_{CO} P_{H_2O} / P_{H_2}^{\alpha}) - (P_{CO_2} P_{H_2}^{\beta} / K_p))}{(\chi + (a P_{H_2O} / P_{H_2}^{\delta}) + b P_{CO}^{\varepsilon} + c P_{CO_2}^{\phi})^{\varphi}} \tag{15}$$

$$r_{OVL} = \frac{K P_{H_2}^{\alpha} P_{CO}^{\beta}}{(\chi + a P_{CO}^{\delta} P_{H_2}^{\varepsilon} + b P_{H_2O}^{\phi} + c P_{H_2}^{\varphi} + d P_{CO_2})^{\gamma}} \tag{16}$$

The optimum values of unknown parameters are obtained such the overall error in the prediction of the rate of reactions is minimized using Genetic Algorithm. The overall error defined as average absolute relative deviation (AARD) is calculated through the following equation:

$$\text{AARD} = \frac{1}{m} \sum_{i=1}^{i=m} \frac{r_{\text{exp},i} - r_{\text{cal},i}}{r_{\text{exp},i}} \tag{17}$$

4. Results of kinetic modeling

Decision variables used in this study with their corresponding valid intervals are shown in Tables 4–6. It should be noted that in mechanisms proposed for FT and WGS reactions, the powers of the species concentration are usually integer numbers, although sometimes some of them may take value of 0.5 (if there is a 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 Tables 4–6 to be able to adapt to the mechanism of the reaction.

Table 8
Results of this study and comparison with other results

Model	Average percent relative error	Model	Average percent relative error	Model	Average percent relative error
(18)	27.059	(19)	26.55797	(20)	22.80169
(18*)	27.06461	(19*)	27.83614	(20*)	22.80169
FT-III2	42.89747	WGS-I5	86.82425		
FT-IV2	54.49429	WGS-II6	84.88095		
FT-III3	54.93696				

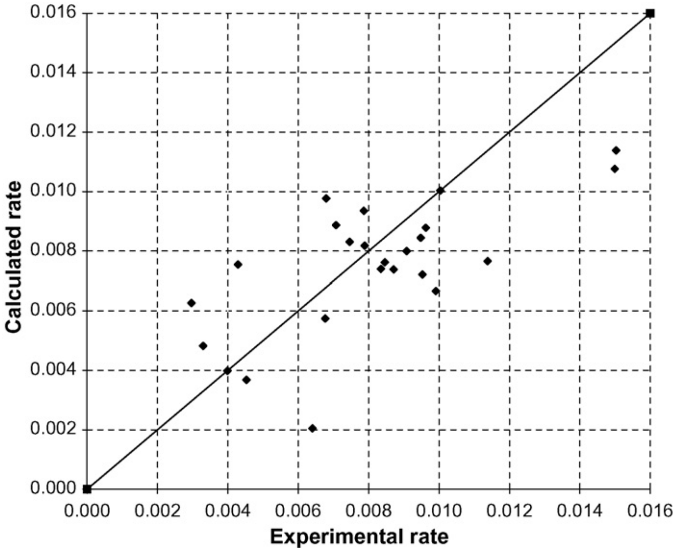

Fig. 2. Experimental rate of FT reaction vs. calculated rate, model no. (18).

In order to obtain the optimum values of the parameters of the reaction rate equations by Genetic Algorithm negative AARD is used as the fitness function of the Genetic Algorithm. A population size of 50 chromosomes (*N = 50*) was selected in this study. Because of the uncertainty in model parameters, large intervals are selected for frequency factors and activation parameters.

The convergence criterion used in the GA is to get to 100% similarity between chromosomes in the population. Table 7 shows the values of the parameters used in the implemented GA [17]. The optimum kinetic model obtained through Binary and Decimal encoded GA are shown in Eqs. (18)–(20) and (18*)–(20*), respectively. Percent relative errors of theses models and selected models from literature are summarized in Table 8.

$$r_{\mathrm{FT}} = \frac{0.07784 P_{\mathrm{CO}} P_{\mathrm{H_2}}^{1/2}}{1 + 1.3 P_{\mathrm{CO}}^{1/2}} \tag{18}$$

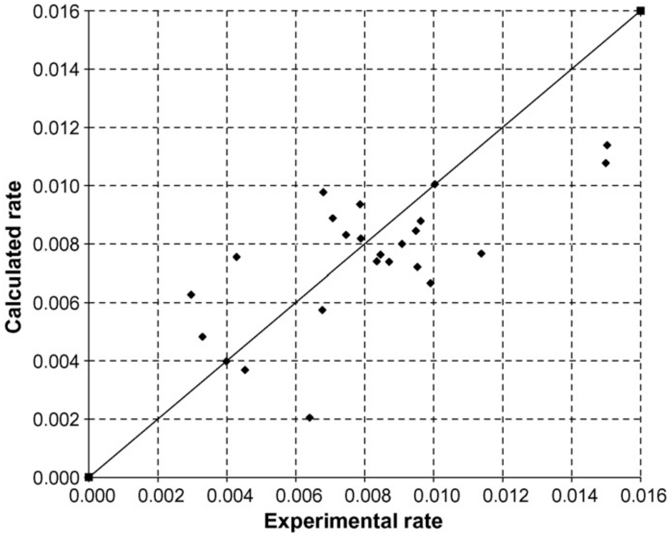

Fig. 3. Experimental rate of FT reaction vs. calculated rate, model no. (18*).

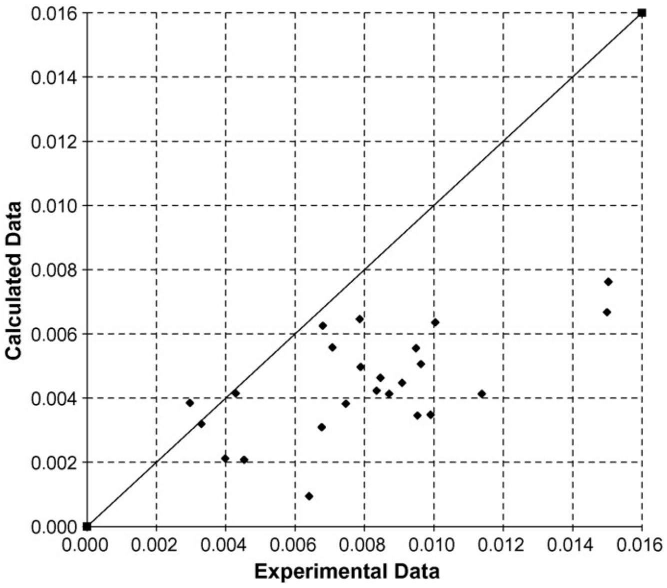

Fig. 4. Experimental rate of FT reaction vs. calculated rate, model no. (FT-III2).

$$r_{\mathrm{FT}} = \frac{0.0779 P_{\mathrm{CO}} P_{\mathrm{H_2}}^{1/2}}{1 + 1.3 P_{\mathrm{CO}}^{1/2}} \tag{18*}$$

$$r_{\mathrm{WGS}} = \frac{27.4058(P_{\mathrm{CO}} P_{\mathrm{H_2O}} - (P_{\mathrm{CO_2}} P_{\mathrm{H_2}}/327.68))}{(301.5 P_{\mathrm{H_2O}}/P_{\mathrm{H_2}}^{1/2}) + 31.85 P_{\mathrm{CO}} + 74.07 P_{\mathrm{CO_2}}} \tag{19}$$

$$r_{\mathrm{WGS}} = \frac{21.90470(P_{\mathrm{CO}} P_{\mathrm{H_2O}} - (P_{\mathrm{CO_2}} P_{\mathrm{H_2}}^{1/2}/202.76))}{1 + (263.68 P_{\mathrm{H_2O}}/P_{\mathrm{H_2}}^{1/2}) + 10.54 P_{\mathrm{CO}} + 79.75 P_{\mathrm{CO_2}}} \tag{19*}$$

$$r_{\mathrm{OVL}} = \frac{639.04 P_{\mathrm{H_2}} P_{\mathrm{CO}}^{1/2}}{(3.93 P_{\mathrm{CO}}^{1/2} + 165.47 P_{\mathrm{H_2}} + 295.67 P_{\mathrm{CO_2}})^2} \tag{20}$$

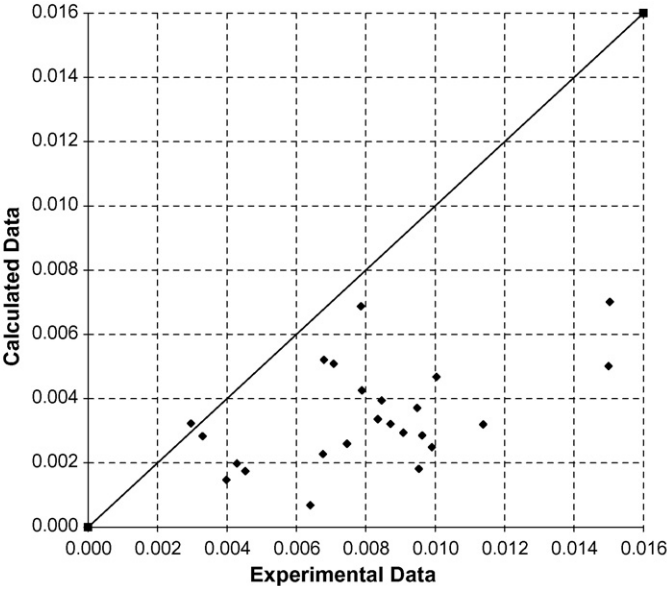

Fig. 5. Experimental rate of FT reaction vs. calculated rate, model no. (FT-IV2).

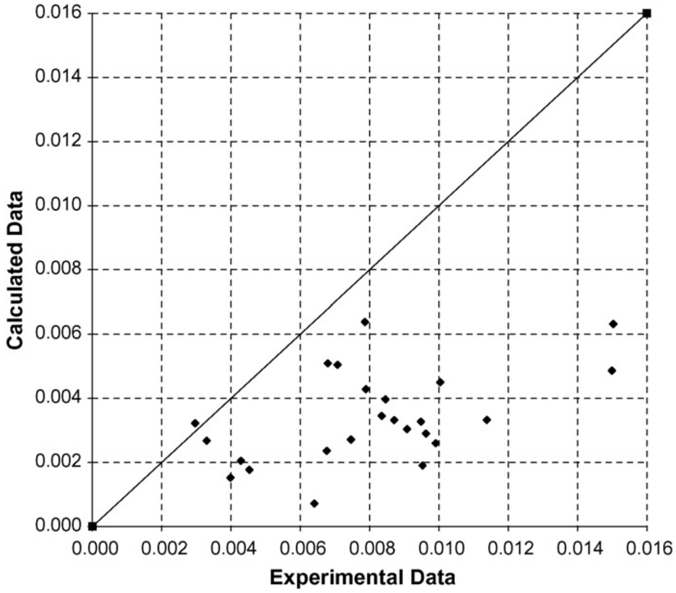

Fig. 6. Experimental rate of FT reaction vs. calculated rate, model no. (FT-III3).

$$r_{\mathrm{OVL}} = \frac{639.04 P_{\mathrm{H_2}} P_{\mathrm{CO}}^{1/2}}{(3.93 P_{\mathrm{CO}}^{1/2} + 165.47 P_{\mathrm{H_2}} + 295.67 P_{\mathrm{CO_2}})^2} \quad (20^*)$$

5. Kinetic model validation

Figs. 2–12 show the performance of various models for FT, WGS and overall reactions. These figures show that the proposed models along with their optimum parameters are more accurate than those models published in the literature. It should also be noted that the proposed model satisfies all physical criteria considered in the models proposed by other researchers and the higher accuracy is due to the more general form of the kinetic model and the fact that the obtained optimum values is either the global optimum or its closest possible point.

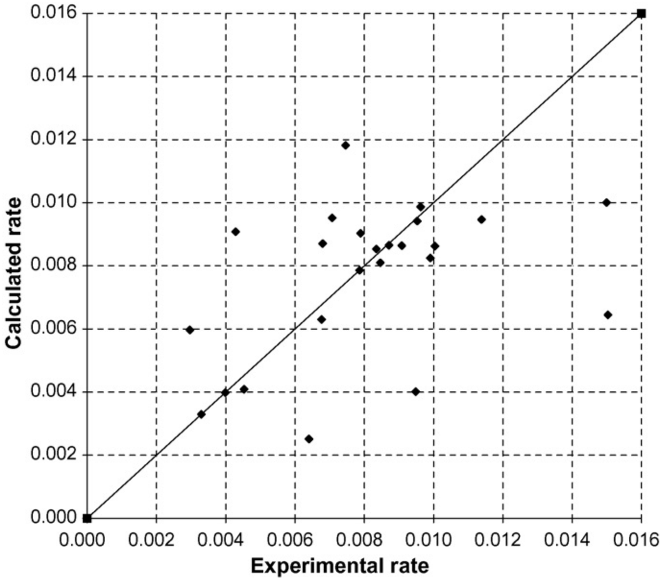

Fig. 7. Experimental rate of WGS reaction vs. calculated rate, model no. (19).

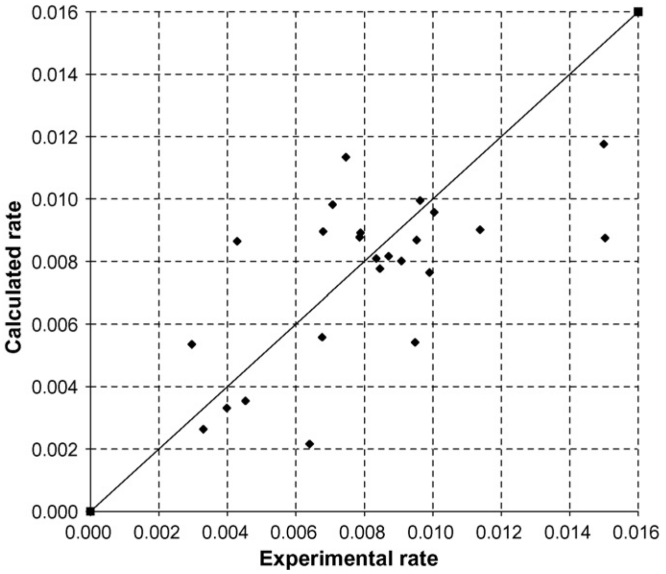

Fig. 8. Experimental rate of WGS reaction vs. calculated rate, model no. (19*).

6. Comparing Binary and Decimal encoded GA performance

Despite the fact that Decimal encoded GA has been used by many researchers to solve optimization problems in both scientific and engineering problems, it cannot be considered as an appropriate descendant of original GA. This is the fact that has been mentioned by various researchers studying the performance of various flavors of Genetic Algorithms including Goldberg [18] and Hertz and Kobler [19]. Although Decimal encoded GA can be tuned and designed to results in better performance for a specific problem, this better performance is usually obtained at the expense of its generality. In other word, as Gold-

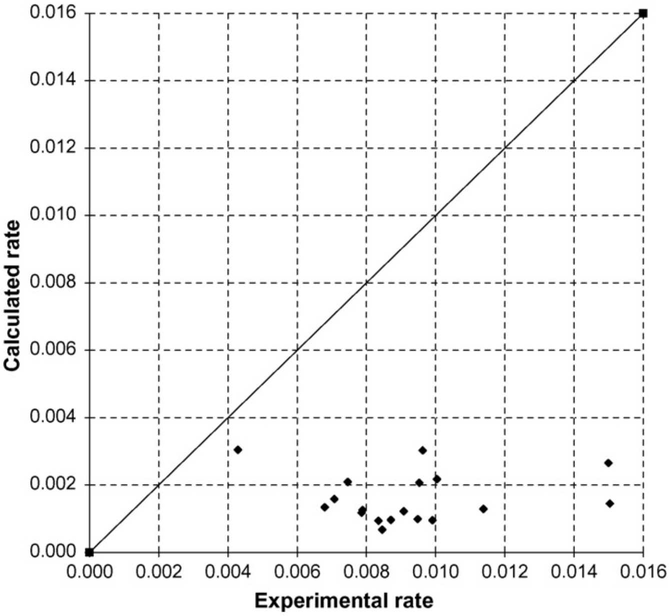

Fig. 9. Experimental rate of WGS reaction vs. calculated rate, model no. (WGS-I5).

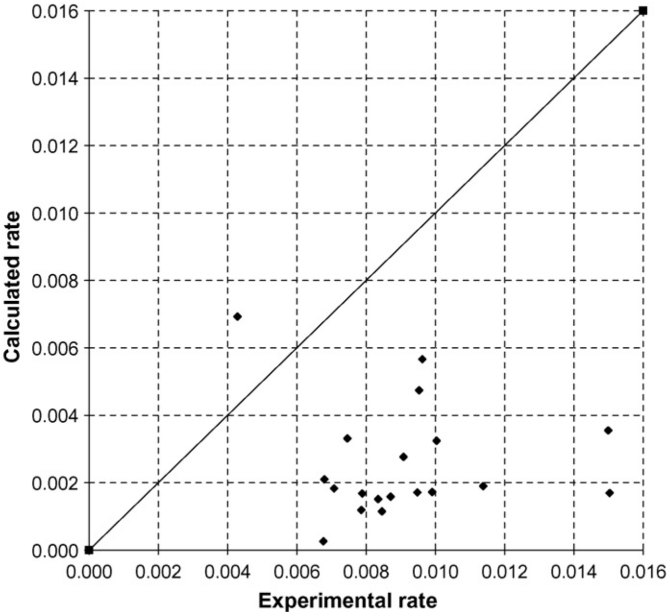

Fig. 10. Experimental rate of WGS reaction vs. calculated rate, model no. (WGS-II6).

berg has mentioned one of the pivotal benefits of the original Genetic Algorithm (i.e., Binary GA) is its generality and independence of the type of problem being solved [18]. Although one might tune the algorithm to perform better (i.e., converge faster) for a specific class of problem, it degrades the generality of the GA and its resemblance to what happens in nature.

In this paper, we have studied the performance of Binary GA and Decimal encoded GA for kinetic modeling. Figs. 13–15 show the performance of these two approaches of GA for the kinetic modeling bench mark of this study. According to these figures, in spite of what has been claimed by researchers using Decimal encoded GA, Binary GA outperforms the Decimal encoded GA both in speed and the possibility to get to the global optimum. Therefore, one can conclude, Binary GA performs better than Decimal encoded GA in the field of kinetic modeling, although according to Schemata theorem [20] this superiority has been proved in a general manner along with the robustness of Binary GA. In other words, considering the generality and robustness of Binary GA it seems that, it would get to the global optimum of various problems including kinetic modeling in a more general manner and with less tuning parameters. This makes the implementation of Binary GA in kinetic modeling almost independent of the reactions taking place in the system.

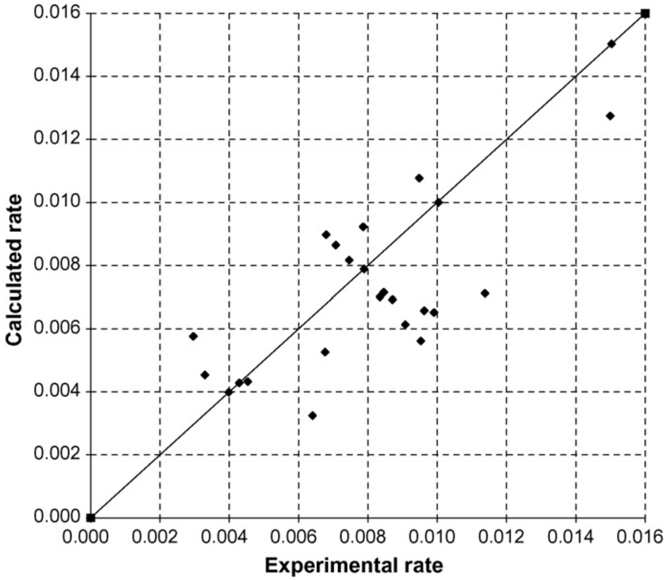

Fig. 11. Experimental rate of overall syngas consumption vs. calculated rate, model no. (20).

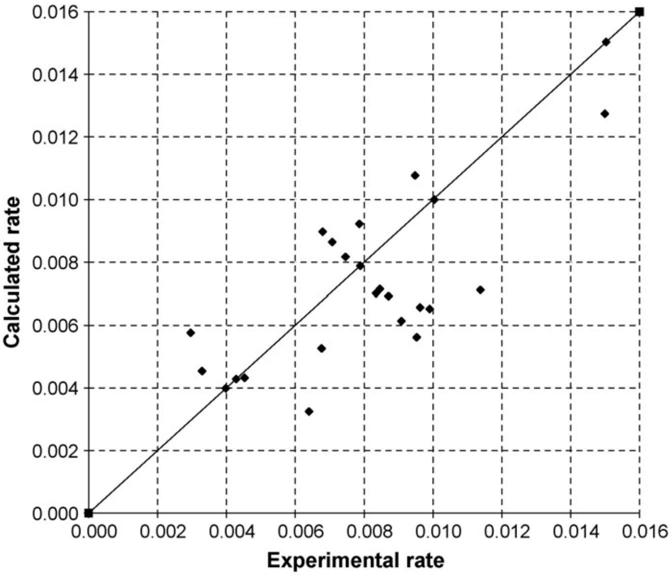

Fig. 12. Experimental rate of overall syngas consumption vs. calculated rate, model no. (20*).

It should be noted that we have used the original versions of both Decimal encoded and Binary GA and have not tuned them in order to keep them in their most general forms appropriate to solve various problems. Otherwise, one can tune both of the

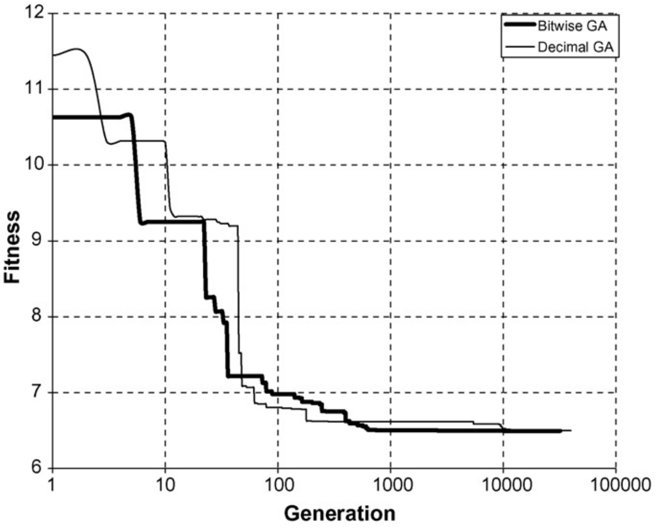

Fig. 13. Comparison of Decimal GA and bitwise GA for FT reaction.

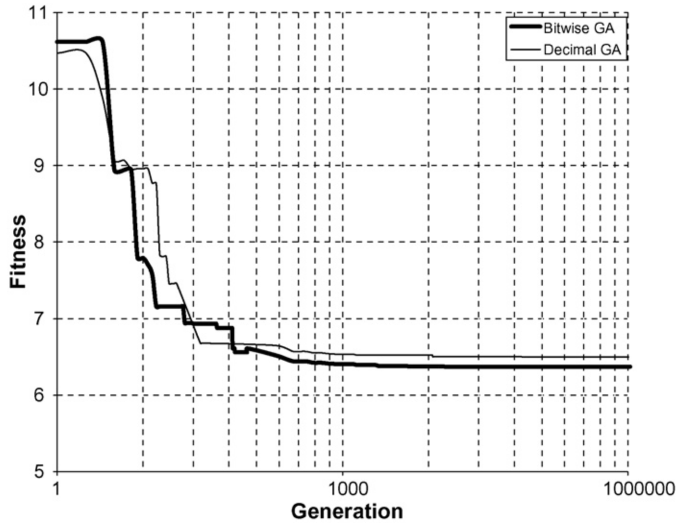

Fig. 14. Comparison of Decimal GA and bitwise GA for WGS reaction.

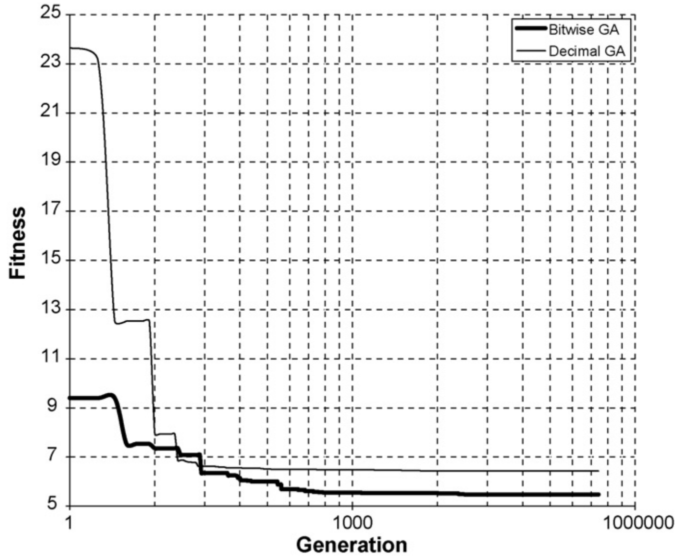

Fig. 15. Experimental comparison of Decimal GA and bitwise GA for overall reaction.

approaches in GA to make them perform better for this specific problem. However, this would lead to biased and unfair results.

7. Conclusion

Genetic Algorithms have been used in kinetic modeling, due to their ability to get the global optimum or its closest point. Fischer–Tropsch reactions have been selected as the kinetic modeling bench mark, due to their recent impacts on chemical industries particularly to produce more environmental friendly fuels. The proposed kinetic models outperform their alternatives in both accuracy and generality. Furthermore, the performance of Binary and Decimal encoded GA have been compared. It has been shown that the original version of Binary GA outperforms the Decimal encoded GA in both the convergence speed and possibility to get the closer point to the global optimum in a more general and less problem dependant manner. This is the same result obtained by other researchers working on other types of optimization problems.

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

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References

[1] G.P. van der Laan, A.C.M. Beenackers, Intrinsic kinetics of the gas–solid Fischer–Tropsch and water–gas-shift reactions over a precipitated iron catalyst, Appl. Catal. 193 (2000) 39–53.

[2] G.P. van der Laan, Kinetics, selectivity and scale up of the Fischer–Tropsch synthesis, Ph.D. Thesis. University of Groningen, 1999.

[3] M. Masoori, R. Boozarjomehry, J.M. Sarnavi, N. Reshadi, Application of Genetic Algorithm in kinetic modeling of Fischer–Tropsch synthesis, Iran. J. Chem. Chem. Eng., Submitted for publication, 2006.

[4] A. Brunette, A fast and precise Genetic Algorithm for a non-linear fitting problem, Comput. Phys. Commun. 124 (2000) 204–211.

[5] Y. Wang, et al., Heterogeneous modeling for fixed-bed Fischer–Tropsch synthesis: reactor model and its application, Chem. Eng. Sci. 58 (2003) 867–875.

[6] R. Zennaro, M. Tagliabue, C.H. Bartholomew, Kinetics of Fischer–Tropsch synthesis on titania-supported Cobalt, Catal. Today 58 (2000) 309–319.

[7] D.E. Goldberg, Genetic Algorithms in search, optimization and machine learning, Addison-Wesley Publication, 1989.

[8] R. Dawkins, Evolutionary Design by Computers, Morgan Kaufmann Publication, San Francisco, 1999.

[9] L. Balland, L. Estel, J.M. Cosmao, N. Mouhab, A Genetic Algorithm with decimal coding for the estimation of kinetic and energetic parameters, Chemom. Intell. Lab. Syst. 50 (2000) 121–135.

[10] L. Elliot, D.B. Inghen, A.G. Kyne, N.S. Mera, M. Pourkashanian, C.W. Wilson, Genetic Algorithms for optimization of chemical kinetic mechanisms, Prog. Energy Combust. Sci. 30 (2004) 297–328.

[11] R. Moros, H. Kalies, H.G. Rex, S. Schaffarczyk, A Genetic Algorithm from generating initial parameter estimations for kinetic models of catalytic processes, Comput. Chem. Eng. 20 (1995) 1257–1270.

[12] G.F. Froment, T.Y. Park, A hybrid Genetic Algorithm for the estimation of parameters in detailed kinetic models, Comput. Chem. Eng. 22 (1998) 103–110.

[13] Z. Michalewicz, Genetic Algorithms + Data Structures = Evolution Programs, Springer, 1996.

[14] D.E. Goldberg, The Design of Innovation: Lessons from and for Competent Genetic Algorithms, Kluwer Academic Publishers, Boston, MA, 2002.

[15] W.B. Langdon, R. Poli, Foundations of Genetic Programming, Springer-Verlag Publication, 2001.

[16] L.M. Schmitt, Fundamental study theory of genetic algorithms, Theor. Comput. Sci. 259 (2001) 1–61.

[17] M. Masoori, S. Fatemi, R. Boozarjomehry, Application of Genetic Algorithm in kinetic modeling and reaction mechanism studies, Iran. J. Chem. Chem. Eng. 24 (2005) 37–46.

[18] D.E. Goldberg, Zen and art of Genetic Algorithms, in: International Conference on Genetic Algorithms and Their Applications, France, 1989.

[19] A. Hertz, D. Kobler, A framework for the description of evolutionary algorithms, Eur. J. Operational Res. 126 (2000) 1–12.

[20] J.H. Holland, Adaptation in Natural and Artificial Systems, The University of Michigan Press, Ann Arbor, Michigan, 1975.