Al-Khwarizmi Engineering Journal

Al-Khwarizmi Engineering Journal, Vol. 10, No. 1, P.P. 47- 61(2014)

Prediction of Reaction Kinetic of Al- Doura Heavy Naphtha Reforming Process Using Genetic Algorithm

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(Received 31 October 2012; accepted 2 March 2014)

Abstract

In this study, genetic algorithm was used to predict the reaction kinetics of Iraqi heavy naphtha catalytic reforming process located in Al-Doura refinery in Baghdad. One-dimensional steady state model was derived to describe commercial catalytic reforming unit consisting of four catalytic reforming reactors in series process.

The experimental information (Reformate composition and output temperature) for each four reactors collected at different operating conditions was used to predict the parameters of the proposed kinetic model. The kinetic model involving 24 components, 1 to 11 carbon atoms for paraffins and 6 to 11 carbon atom for naphthenes and aromatics with 71 reactions. The pre-exponential Arrhenius constants and activation energies were determined after fine tuning of the model results with experimental data. The input to the optimization is the compositions for 21 components and the temperature for the effluent stream for each one of the four reactors within the reforming process while the output of optimization is 142 predicted kinetic parameters for 71 reactions within reforming process. The differential optimization technique using genetic algorithm to predict the parameters of the kinetic model.

To validate the kinetic model, the simulation results of the model based on proposed kinetic model was compared with the experimental results. The comparison between the predicted and commercially results shows a good agreement, while the percentage of absolute error for aromatics compositions are (7.5, 2, 8.3, and 6.1%) and the temperature absolute percentage error are (0.49, 0.5, 0.01, and 0.3%) for four reactors respectively.

Keywords: *Heavy Naphtha, Reforming, Genetic Algorithm, Optimization, Reaction Kinetic.*

1. Introduction

The catalytic reforming process is one of the most critical operations in petroleum refineries. This process involves the reconstruction of low-octane hydrocarbons in the naphtha into more valuable high-octane gasoline components without changing the boiling point range, production of aromatic feedstock for petrochemical industries also hydrogen and lighter hydrocarbons are obtained as side products [1, 2].

The catalytic reforming of naphtha involves reactions such as dehydrogenation, dehydrocyclization, hydrocracking, isomerization, and dehydroalkylation. The naphtha feed to reformer is very complex usually consisting of about three hundreds components with carbon number range from C5 – C12[3]. Recent environment legislation in the United States has banned the use of lead as an additive for boosting antiknock properties of motor fuel. Coupled with these stricter environmental regulations, there has been a consistent increase in the demand for higher octane number gasoline. This can be achieved by reforming the naphtha under more severe conditions, but this will also cause an increase in the rate of coke deposition, resulting in the reduction of cycle lengths of catalyst [4].

Concerning the kinetic modeling of the naphtha processes smith 1959 [5] firstly proposed four lumps model by considering naphtha as three group regents, paraffins, naphthenes, and aromatic hydrocarbons. Due to its simplicity, this model has been used in some recent reformer modeling work. Krane et al., 1960[6] recognized the presence of various carbon numbers from C6 - C10 as well as the difference between paraffins, naphthenes, and aromatics within each carbon number group. The model derived contained a reaction network of 20 different components.

Kmak 1972 [7] used Langmuir kinetic model for reactors as first time. Marin and coworkers 1982 [8] presented the reaction network for the whole naphtha, containing hydrocarbons in the carbon number fraction from C5-C10. The reaction network included 23 pseudo components and used Hougen-Watson type rate equations.

Ramage et al., 1987 [9] decided to develop a comprehensive kinetic model which (involving a reasonable number of group components and pathway) would capture the reactivity differences between particular raw materials. Their studies led to the construction of Mobil kinetic model of the reforming process (KINPtR start of cycle and deactivation kinetics).

Taskar 1997 [10] developed a detailed kinetic scheme involving 35 pseudo components connected by a network of 36 reactions in the C5 – C10 range. Deactivation of the catalyst was modeled by including the corresponding equations for coking kinetics.

Jorge 2000 [11] proposed a kinetic model for the naphtha catalytic reforming process (mathematical representation of the reaction that take place) and carbon number ranging from 1-11 atoms for paraffins , 6-11 for naphthenes, and aromatics. The kinetic parameters values were estimated using experimental information obtained in three fixed-bed pilot plant.

Weifeng 2003 [12] developed mathematical model for simulation and optimization of commercial naphtha catalytic reformers with four reactors in series. The model along with deactivation function of catalyst can monitor the reformer performance with time on stream.

Arani 2010 [13] simulated a dynamic model of the catalytic naphtha reformer process by MATLAB software. The kinetic parameters of model are based on the steady state condition and obtained from a commercial plant data furnished by a domestic petroleum refinery. Askari 2012 [1] developed model for simulating catalytic reforming unit with four reactors in series by using Hysys-refinery software. The results are validated by operating data, taken from the Esfahan oil refinery catalytic reforming unit.

In the industrial applications of reaction kinetics, the estimation of parameters in kinetic expressions from data series is essential for the design, optimization, and control of many chemical systems. The use of process models as a tool for simulation of commercial process has been growing rapidly. The advantage of utilizing rigorous mathematical models as compared to empirical approaches is related to the fact that the prediction accuracy of rigours models can be significantly superior over a wide operating range. To design new catalytic reforming process or to optimize the existing ones, an appropriate kinetic model to represent the reactions within the process is needed. Therefore the aim of this study is to determine the values of kinetic model parameters for Iraqi heavy naphtha reforming process by using differential optimization technique (genetic algorithm).

2. Process Description

The process flow diagram of the reforming process is shown in Figure 1. The commercial semi-regenerative catalytic naphtha reforming contains four fixed-bed adiabatically operated reactors in series. The naphtha used as feedstock which contains a mixture of paraffins, naphthenes, and aromatics in the carbon number range C_4-C_{11} was combined with a recycle gas stream containing 60 – 90 mol% hydrogen. The used catalyst is Pt-Re/Al_2O_3 which is bifunctional bimetallic catalyst providing the metal function and the acid function. Usual catalytic reforming consists of multiple reactors (three or four) with heaters between the reactors to maintain reaction temperature at operable levels, since the major reactions in the first reactor dehydrogenation of naphthenes, which are endothermic and very fast, causing a very sharp temperature drop in the first reactor. As the total reactor charge passes through the sequence of heating and reacting, the reactions become less and less endothermic and temperature differential across the reactors decreases.

The product from the fourth reactor is cooled and then enters to the product separator. The flashed vapor circulates to combine the naphtha feedstock as recycle gas. Extra hydrogen from the separator is sent to other hydrogen consuming units in the refinery. The separated liquid that mainly included the desired aromatics together with heavy paraffins and light gases is sent to the reformate stabilizer. Reformate off the bottom of the stabilizer is sent to storage for gasoline blending.

Table (1) shows the design parameters and operating conditions of the catalytic reformers of Al-Doura refinery in Baghdad. The operating conditions of this unit were: 470 °C inlet temperature, 27.5 bar reactor pressure, and the feedstock flow rate of 33.5 m^3/hr.

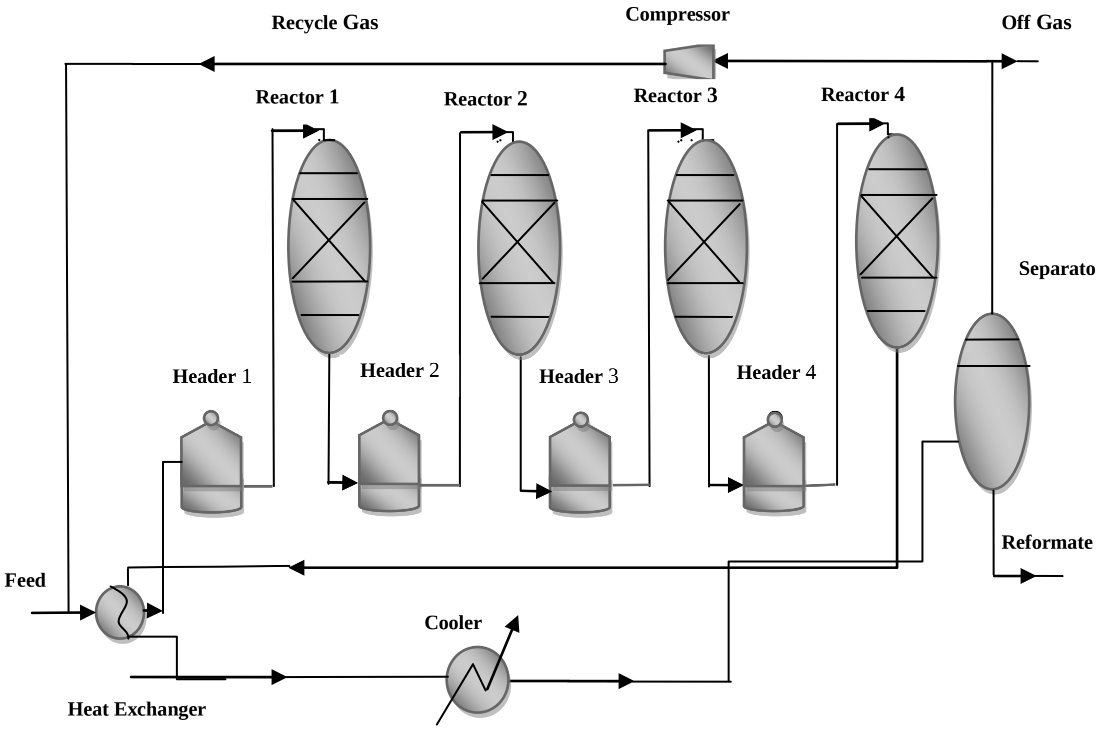


Fig. 1. Process flow of four reactors naphtha reforming process.

Table 1,
Operating conditions of heavy naphtha reforming process.

Reactor number	1	2	3	4
Catalyst weight kg	2700	4500	4750	5750
Inlet Temperature C	470	468	468	468
Reactor Length m	6	6	6	6
Reactor Diameter m	2.4	2.4	2.4	2.4

3. Mathematical Model

The following assumptions were considered in the present mathematical model:

1. The system was in a steady state.
2. The variation in the radial direction was negligible.
3. All reactions were in homogenous phase.
4. All reactions are pseudo first order with respect to hydrocarbon.

The equations of mathematical model results from application of material and energy balance principles in a differential volume [14].

$$-\frac{dC_i}{dZ} = \sum_{i=1}^{m} \frac{M.Wt}{z.WHSV}(r_i) \qquad \ldots(1)$$

$$\frac{dT}{dZ} = \frac{s\sum_{i=1}^{m}(r_i)(-\Delta H_{Ri})}{\sum_{i=1}^{m} F_i.C_{P_i}} \qquad \ldots(2)$$

The Ergun equation was used for computing total differential pressure drop in axial flow reactor [15]:

$$-\frac{dP_t}{dZ} = 1.75*10^{-5}\frac{1-e}{e^3\ell d_P}G^2 + 1.5*10^{-3}\frac{(1-e)^2 m}{e^3\ell d_P^2}G \quad \ldots(3)$$

In order to evaluate the heat capacity the following correlation was used [16];

$$Cp_i = A_i + B_iT + C_iT^2 + D_iT^3 \qquad \ldots(4)$$

The effect of temperature and pressure on the kinetic constants was expressed in equation (5), Jenkins et al. 1980 [17];

$$k_i = k_i^{\circ}\left[\frac{E_{Aj}}{R}\left(\frac{1}{T_{\circ}} - \frac{1}{T}\right)\right]\left(\frac{p_t}{p_{\circ}}\right)^{ak} \qquad \ldots(5)$$

The values of pressure effect factors on reaction rate are given in Table (2).

Table 2,
Values of pressure effect reaction rate [17].

Reactions	a_k
isomerization	0.37
dehydrocyclization	-0.7
hydrocracking	0.433
hydrodealkylation	0.5
dehydrogenation	0.0

4. Kinetic Model

In this study, 24 lump kinetic model which proposed by Ancheyta et al 2000 [11] was used. According to this model, the naphtha feed to reforming process contain paraffin's, naphthenes, and aromatics with carbon number from 1 to 11 carbon atoms for paraffin's (P_1-P_{11}) and from 6 to 11 carbon atoms for naphthenes (N_6-N_{11}) and aromatics (A_6-A_{11}). The extended kinetic model employs a lumped mathematical representation of the seventy-one chemical reactions for all 24 lumps that taken place can be shown in Table (3). All reaction steps are combined into twenty-four rate reaction equations (ri), one for each component. Each reaction rate equation is a function of the kinetic constant (ki) and the component partial pressure (Pi).

Table 3,
Reactions of the kinetic model (Ancheyta et al. (2001)).

Number of Reactions					
Paraffin's		**Naphthenes**		**Aromatics**	
$P_n \rightarrow N_n$	6	$N_n \rightarrow A_n$	6	$A_n \rightarrow A_{n-j} + P_j$	7
$P_n \rightarrow P_{n-j} + P_j$	26	$N_n \rightarrow N_{n-j} + P_j$	11	$A_n \rightarrow P_n$	5
subtotal	32	$N_n \rightarrow P_n$	7	$A_n \rightarrow N_n$	1
		subtotal	24	subtotal	13
Total			71		

n: Number of atoms of carbon ($1 \le i \le 5$)

5. Optimization

Optimization can be for minimization or maximization of the desired objective function with respect to decision variables subject to process constraints and bounds on the variables. An optimization problem can have a single optimum or multiple optima, one of which is the global optimum and the others are local optima. A global minimum has the lowest value of the objective function throughout the region of interest. Most of the traditional optimization algorithms based on gradient methods have the possibility of getting trapped at local optimum depending upon the degree of non-linearity and initial guess. Unfortunately, none of the traditional algorithms are guaranteed to find the global optimum solution. In the recent past, nontraditional search and optimization techniques (Evolutionary Computation) based in natural phenomenon such as Genetic Algorithms (GAs) has been developed to overcome these problems. Arx et al., 1998 [19] used genetic algorithm technique for finding a global minimum for the error function. Tongcheng et al., 2005 [20] combine Numeric Genetic Algorithm (NGA) and Tabu Search (TS) to optimize the estimated rate constants of a consecutive reaction. Zhao et al., 2006 [21] used a nonlinear least squares regression to fit the kinetic profiles.

Genetic Algorithms (GAs) are powerful and widely applicable stochastic search and optimization methods based on the concepts of natural selection and natural evaluation. Genetic Algorithm works on a population of individuals represents candidate solutions to the optimization problem. These individual consists of a strings (called chromosomes) of genes. The genes are a practical allele (gene could be a bit, an integer number, a real value or an alphabet character,…,etc depending on the nature of the problem). GAs applying the principles of survival of the fittest , selection , reproduction , crossover (recombining) , and mutation on these individuals to get , hopefully , a new butter individuals (new solutions). Genetic Algorithm generates new population of chromosomes by selecting the better fit solutions from existing population and applying genetic operators to produce new offspring of the solutions. The process is repeated successively to generate new population iteratively. This process is repeated until some criterion is met or a reasonably acceptable solution is found.

The Outline of the Genetic Algorithm is given below **[18]**.

1. **[Start]** Generate random population of n chromosomes (suitable solutions for the problem).
2. **[Fitness]** Evaluate the fitness f(x) of each chromosome x in the population.
3. **[New population]** Create a new population by repeating following steps until the new population is complete.
   I. **[Selection]** Select two parent chromosomes from a population according to their fitness (the better fitness, the bigger chance to be selected).
   II. **[Crossover]** with a crossover probability cross over the parents to form a new offspring (children). If no crossover was performed, offspring is an exact copy of parents.
   III. **[Mutation]** with a mutation probability mutate new offspring at each locus (position in chromosome).
   IV. **[Accepting]** Place new offspring in a new population
4. **[Replace]** Use new generated population for a further run of algorithm
5. **[Test]** if the end condition is satisfied, **stops**, and returns the best solution in current population
6. **[Loop]** Go to step **2** Proportional selection, ranking, and tournament selection are the most popular selection procedures.

Table 4,
Contains the parameters of genetic algorithm.

Population size	10
Maximum generation	3000
Crossover probability	0.8
Mutation probability	0.05
Neighborhood size	0.05

6. Numerical Computation

For each individual reactor within the process, numerical integration method was used to integrate the component mass balance, energy balance and pressure drop differential equations (1, 2 and 3) to obtain concentration, temperature and pressure profiles along the reactor as follows. The rate equations (system of simultaneous differential equations) of the reaction were solved to get the analytical concentration versus reactor length profiles.

Fourth order Runge-Kutta integration command named ode45 was used to integrate 24 stiff ordinary differential equations for mass balance and two other equations for heat balance and pressure drop.

Genetic Algorithm was used to predict the parameters of kinetic model by minimizing the objective function J in equation 6, which is the sum of squares of errors between the predicted and measured values for all of the state variables.

$$J = \frac{1}{n_{\exp}} \sum_{i=1}^{nr} \left(\sum_{j=1}^{nc} (y_{i,j}^{pred} - y_{i,j}^{\exp})^2 + (\frac{T_i^{pred} - T_i^{\exp}}{T_i^{\exp}})^2 \right) \qquad \ldots(6)$$

Where: $y_{i,j}^{\exp}$ is the composition of component j for the effluent stream of reactor No i.

Using the differential optimization algorithm to optimize the system through a sequence of optimization-evaluation, the objective function [Eq. (6)] was minimized and the global optimum set of kinetic parameters was found out. It is important to mention here that [Eq. (6)] was used in evaluation the fitness (objective function) for each chromosome x in the population. Values of the Frequency factors (A1, A2 to A71), Activation Energies (E1, E2 to E71) were found by minimization of the sum of the squares of the deviations between the plant and the calculated results of the key variables (the compositions and temperature of effluent from each one of the four reactors). The fitness for each generation of chromosomes was calculated and the minimum fitness represents the best chromosomes within the chromosomes and the average fitness was also calculated. Figure (2) shows a plot of the best and mean fitness (J) with respect to generation number. Genetic algorithm has one disadvantage which is a huge computation time in the case of complex systems. In the present case study a PC with 4.12 GHz and 4GB RAM. 5 runs take more than 120 hr to reach produced results. Finally the better chromosomes was selected which represent less objective function for all chromosomes and all generations. The kinetic parameters of obtained reaction rate with the genetic optimization procedure are presented in the Table 5.

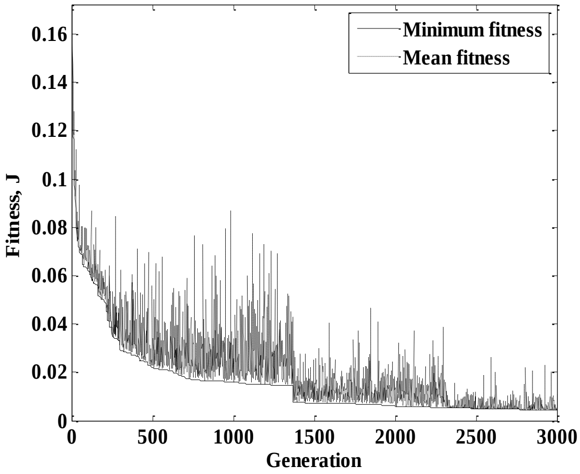


Fig. 2. Minimum and mean fitness with respect to generation number.

7. Results and Discussion

7.1. Validation of Reaction Kinetics

To validate the predicted kinetic model, the model results using the predictive kinetic model were compared with actual results collected from AL-Doura refinery (catalytic reforming process**)**. Figure 3 (a, and b) shows the comparison between the actual and simulated reformate composition (run 1 means the data collected in 1/12/2012, while run 2 in 1/1/2012). It can be observed that the calculated reformate compositions of all (paraffins , naphthenes, and aromatics) for the four reactors in catalytic reforming unit agree very well with experimental information with average deviation less than 2% as shown in table (6 and 7).

Table 5,
Kinetic constants of the kinetic model.

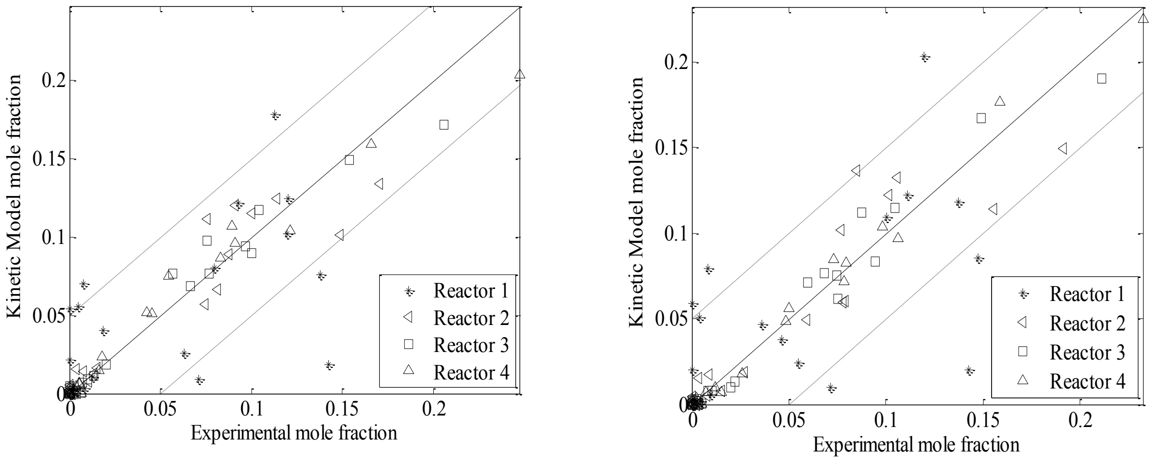
Reaction Step	**K_o**	**E_A (cal/mol)**	**Reaction Step**	**K_o**	**E_A (cal/mol)**	**Reaction Step**	**K_o**	**E_A (cal/mol)**
$P_{11} \rightarrow N_{11}$	0.073082	53553.8	$P_8 \rightarrow 2P_4$	0.001478	65074.0	$N_8 \rightarrow N_7+P_1$	0.000016	27622.9
$P_{10} \rightarrow N_{10}$	0.037751	37965.0	$P_7 \rightarrow P_6+P_1$	0.000704	58826.6	$N_{11} \rightarrow A_{11}$	1.146035	24527.0
$P_9 \rightarrow N_9$	0.055255	9439.8	$P_7 \rightarrow P_5+P_2$	0.003188	39451.4	$N_{10} \rightarrow A_{10}$	0.903828	23982.5
$P_8 \rightarrow N_8$	0.033905	53951.7	$P_7 \rightarrow P_4+P_3$	0.000376	65101.8	$N_9 \rightarrow A_9$	0.403788	6489.7
$P_7 \rightarrow N_7$	0.004895	39023.9	$P_6 \rightarrow P_5+P_1$	0.003237	19289.4	$N_8 \rightarrow A_8$	0.395175	29318.6
$P_6 \rightarrow N_6$	0.000004	41629.3	$P_6 \rightarrow P_4+P_2$	0.000070	64572.5	$N_7 \rightarrow A_7$	0.286847	31262.2
$P_{11} \rightarrow MCP$	0.009867	36845.6	$P_6 \rightarrow 2P_5$	0.007834	11940.1	$N_6 \rightarrow A_6$	0.090934	33819.9
$P_{11} \rightarrow P_{10}+P_1$	0.055585	33531.3	$P_5 \rightarrow P_4+P_1$	0.000668	60910.7	$A_{11} \rightarrow P_{11}$	0.014602	13735.3
$P_{11} \rightarrow P_9+P_2$	0.070800	29879.0	$P_8 \rightarrow P_3+P_2$	0.020922	14733.7	$A_{10} \rightarrow P_{10}$	0.014531	11859.7
$P_{11} \rightarrow P_8+P_3$	0.090772	22115.8	$N_{11} \rightarrow P_{11}$	0.033542	16723.6	$A_9 \rightarrow P_9$	0.015793	11816.5
$P_{11} \rightarrow P_7+P_4$	0.013195	58984.6	$N_{10} \rightarrow P_{10}$	0.047576	47431.2	$A_8 \rightarrow P_8$	0.010064	9059.9
$P_{11} \rightarrow P_6+P_5$	0.057271	63624.4	$N_9 \rightarrow P_9$	0.051031	35413.1	$A_7 \rightarrow P_7$	0.001665	27438.8
$P_{10} \rightarrow P_9+P_1$	0.003473	27543.6	$N_8 \rightarrow P_8$	0.024635	12039.8	$A_{11} \rightarrow A_{10}+P_1$	0.002544	21381.4
$P_{10} \rightarrow P_8+P_2$	0.000517	39959.3	$N_7 \rightarrow P_7$	0.009329	11474.4	$A_{11} \rightarrow A_9+P_2$	0.005768	37776.0
$P_{10} \rightarrow P_7+P_3$	0.001024	61173.5	$N_6 \rightarrow P_6$	0.195584	17660.9	$A_{10} \rightarrow A_9+P_1$	0.003530	43959.9
$P_{10} \rightarrow P_6+P_4$	0.000822	64218.0	$MCP \rightarrow P_6$	0.001872	35936.4	$A_{10} \rightarrow A_8+P_2$	0.000541	40180.9
$P_{10} \rightarrow 2P_5$	0.000389	62410.0	$N_{11} \rightarrow N_{10}+P_1$	0.082099	58751.5	$A_{10} \rightarrow A_7+P_3$	0.000005	40148.4
$P_9 \rightarrow P_8+P_1$	0.008461	16828.6	$N_{11} \rightarrow N_9+P_2$	0.114900	24140.5	$A_9 \rightarrow A_8+P_1$	0.001916	39779.4
$P_9 \rightarrow P_7+P_2$	0.000367	61631.1	$N_{11} \rightarrow N_8+P_3$	0.066425	18506.9	$A_9 \rightarrow A_7+P_2$	0.001371	42474.0
$P_9 \rightarrow P_6+P_3$	0.001029	61813.5	$N_{10} \rightarrow N_9+P_1$	0.131747	15698.4	$A_8 \rightarrow A_7+P_1$	0.000059	32571.2
$P_9 \rightarrow P_5+P_4$	0.000012	48938.2	$N_{10} \rightarrow N_8+P_2$	0.087315	46817.6	$A_6 \rightarrow N_6$	0.013302	24076.0
$P_8 \rightarrow P_7+P_1$	0.000228	60915.0	$N_{10} \rightarrow N_7+P_3$	0.001255	38799.8	$MCP \rightarrow N_6$	0.234651	36084.8
$P_8 \rightarrow P_6+P_2$	0.015421	64298.5	$N_9 \rightarrow N_8+P_1$	0.056925	64391.1	$N_6 \rightarrow MCP$	0.014943	24377.5
$P_8 \rightarrow P_5+P_3$	0.000375	29372.1	$N_9 \rightarrow N_7+P_2$	0.002137	61898.0			

Table 6,
Comparison between actual and simulated reformate compositions (run 1).

	Composition												
	Feed	**Reactor 1**			**Reactor 2**			**Reactor 3**			**Reactor 4**		
		Exp.	**Pred.**	**Abs. diff.**	**Exp.**	**Pred.**	**Abs. diff.**	**Exp.**	**Pred.**	**Abs. diff.**	**Exp.**	**Pred.**	**Abs. diff.**
n-P4	0.0036	0.0023	0.0000	0.0023	0.0014	0.0000	0.0014	0.0026	0.0000	0.0026	0.0014	0.0000	0.0014
n-P_5	0.0106	0.0128	0.0130	0.0002	0.0135	0.0192	0.0057	0.0200	0.0242	0.0042	0.0177	0.0278	0.0101
n-P_6	0.0802	0.0797	0.0890	0.0093	0.0879	0.0936	0.0057	0.0969	0.0962	0.0007	0.0908	0.0955	0.0047
n-P_7	0.1243	0.1201	0.1242	0.0041	0.1139	0.1162	0.0023	0.1040	0.1062	0.0022	0.0894	0.0945	0.0051
n-P_8	0.1023	0.1194	0.1156	0.0038	0.1003	0.0980	0.0023	0.0756	0.0748	0.0008	0.0548	0.0597	0.0049
n-P_9	0.1782	0.1130	0.1191	0.0061	0.0913	0.0682	0.0231	0.0666	0.0510	0.0156	0.0452	0.0432	0.0020
n-P_{10}	0.1214	0.0928	0.1107	0.0179	0.0754	0.0756	0.0002	0.0569	0.0513	0.0056	0.0424	0.0364	0.0060
n-P_{11}	0.0020	0.0040	0.0009	0.0031	0.0043	0.0001	0.0042	0.0064	0.0000	0.0064	0.0063	0.0000	0.0063
MCP	0.0033	0.0021	0.0047	0.0026	0.0005	0.0049	0.0044	0.0005	0.0050	0.0045	0.0036	0.0052	0.0016
N_6	0.0214	0.0000	0.0055	0.0055	0.0000	0.0034	0.0034	0.0000	0.0041	0.0041	0.0000	0.0047	0.0047
N_7	0.0554	0.0046	0.0160	0.0114	0.0035	0.0021	0.0014	0.0036	0.0019	0.0017	0.0032	0.0017	0.0015
N_8	0.0699	0.0078	0.0141	0.0063	0.0076	0.0070	0.0006	0.0072	0.0065	0.0007	0.0055	0.0056	0.0001
N_9	0.0406	0.0183	0.0169	0.0014	0.0152	0.0090	0.0062	0.0098	0.0063	0.0035	0.0055	0.0052	0.0003
N_{10}	0.0542	0.0000	0.0022	0.0022	0.0000	0.0022	0.0022	0.0000	0.0016	0.0016	0.0000	0.0012	0.0012
N_{11}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
A_6	0.0035	0.0080	0.0078	0.0002	0.0106	0.0114	0.0008	0.0135	0.0155	0.0020	0.0161	0.0215	0.0054
A_7	0.0255	0.0632	0.0664	0.0032	0.0812	0.0907	0.0095	0.1001	0.1053	0.0052	0.1215	0.1238	0.0023
A_8	0.0762	0.1379	0.1338	0.0041	0.1707	0.1705	0.0002	0.2059	0.2027	0.0032	0.2478	0.2305	0.0173
A_9	0.0182	0.1427	0.1030	0.0396	0.1485	0.1514	0.0029	0.1536	0.1611	0.0075	0.1659	0.1572	0.0087
A_{10}	0.0091	0.0713	0.0570	0.0143	0.0742	0.0763	0.0021	0.0768	0.0860	0.0092	0.0829	0.0861	0.0032
A_{11}	0.0000	0.0000	0.0002	0.0002	0.0000	0.0003	0.0003	0.0000	0.0003	0.0003	0.0000	0.0002	0.0002
Paraffins	0.623	0.544	0.574	0.030	0.488	0.476	0.012	0.429	0.413	0.016	0.348	0.371	0.023
Naphthenes	0.245	0.033	0.059	0.026	0.027	0.028	0.002	0.021	0.025	0.004	0.018	0.023	0.005
Aromatics	0.132	0.423	0.366	0.057	0.485	0.496	0.011	0.550	0.562	0.012	0.634	0.606	0.028
Temp. (K)	743.150	698.150	697.454	0.696	732.150	729.251	2.899	738.150	738.414	0.264	745.150	742.418	2.732

Table 7,
Comparison between actual and simulated reformate compositions (run 2).

	Composition												
	Feed	**Reactor 1**			**Reactor 2**			**Reactor 3**			**Reactor 4**		
		Exp.	**Pred.**	**Abs. diff.**	**Exp.**	**Pred.**	**Abs. diff.**	**Exp.**	**Pred.**	**Abs. diff.**	**Exp.**	**Pred.**	**Abs. diff.**
n-P4	0.0025	0.0021	0.0000	0.0021	0.0025	0.0000	0.0025	0.0033	0.0000	0.0033	0.0036	0.0000	0.0036
n-P_5	0.0059	0.0097	0.0080	0.0017	0.0150	0.0138	0.0012	0.0223	0.0189	0.0034	0.0257	0.0229	0.0028
n-P_6	0.0378	0.0462	0.0492	0.0030	0.0590	0.0618	0.0028	0.0753	0.0718	0.0035	0.0782	0.0778	0.0004
n-P_7	0.1225	0.1110	0.1219	0.0109	0.1016	0.1134	0.0118	0.1046	0.1030	0.0016	0.0983	0.0911	0.0072
n-P_8	0.1182	0.1375	0.1327	0.0048	0.1058	0.1121	0.0063	0.0877	0.0843	0.0034	0.0733	0.0661	0.0072
n-P_9	0.2035	0.1196	0.1357	0.0161	0.0851	0.0763	0.0088	0.0683	0.0562	0.0121	0.0500	0.0471	0.0029
n-P_{10}	0.1093	0.1004	0.1012	0.0008	0.0766	0.0704	0.0062	0.0596	0.0483	0.0113	0.0484	0.0343	0.0141
n-P_{11}	0.0016	0.0030	0.0007	0.0023	0.0034	0.0001	0.0033	0.0049	0.0000	0.0049	0.0053	0.0000	0.0053
MCP	0.0009	0.0009	0.0023	0.0014	0.0015	0.0031	0.0016	0.0023	0.0036	0.0013	0.0026	0.0042	0.0016
N_6	0.0199	0.0000	0.0046	0.0046	0.0000	0.0021	0.0021	0.0000	0.0029	0.0029	0.0000	0.0036	0.0036
N_7	0.0507	0.0042	0.0156	0.0114	0.0035	0.0021	0.0014	0.0037	0.0019	0.0018	0.0034	0.0017	0.0017
N_8	0.0793	0.0085	0.0168	0.0083	0.0088	0.0078	0.0010	0.0083	0.0072	0.0011	0.0072	0.0061	0.0011
N_9	0.0469	0.0363	0.0191	0.0172	0.0268	0.0100	0.0168	0.0201	0.0069	0.0132	0.0152	0.0056	0.0096
N_{10}	0.0588	0.0000	0.0020	0.0020	0.0000	0.0020	0.0020	0.0000	0.0015	0.0015	0.0000	0.0012	0.0012
N_{11}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
A_6	0.0017	0.0046	0.0054	0.0008	0.0075	0.0077	0.0002	0.0102	0.0103	0.0001	0.0119	0.0149	0.0030
A_7	0.0244	0.0547	0.0607	0.0060	0.0789	0.0842	0.0053	0.0946	0.0985	0.0039	0.1064	0.1165	0.0101
A_8	0.0858	0.1473	0.1487	0.0014	0.1911	0.1890	0.0021	0.2110	0.2238	0.0128	0.2323	0.2530	0.0207
A_9	0.0200	0.1427	0.1158	0.0269	0.1553	0.1691	0.0138	0.1492	0.1782	0.0290	0.1588	0.1720	0.0132
A_{10}	0.0100	0.0713	0.0594	0.0119	0.0776	0.0748	0.0028	0.0746	0.0824	0.0078	0.0794	0.0816	0.0022
A_{11}	0.0000	0.0000	0.0001	0.0001	0.0000	0.0003	0.0003	0.0000	0.0002	0.0002	0.0000	0.0002	0.0002
Para-ffins	0.601	0.530	0.551	0.022	0.449	0.453	0.004	0.426	0.391	0.035	0.383	0.353	0.029
Naph-thenes	0.257	0.050	0.060	0.010	0.041	0.027	0.014	0.034	0.024	0.011	0.028	0.022	0.006
Aro-atics	0.142	0.421	0.389	0.032	0.510	0.521	0.010	0.540	0.585	0.045	0.589	0.625	0.036
Temp. (K)	743.15	698.15	694.69	3.456	732.15	728.49	3.660	738.15	738.22	0.078	745.150	742.442	2.708



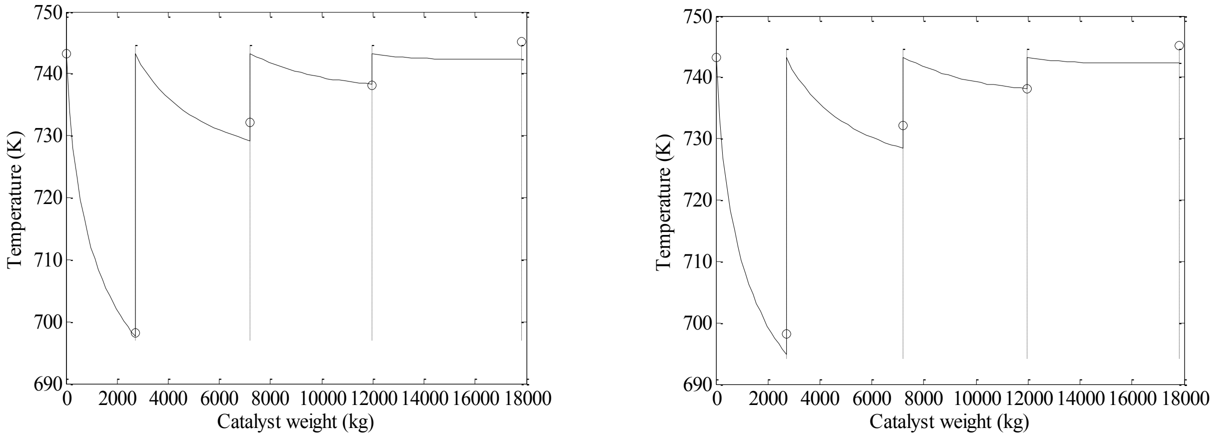
a (run 1) **b (run 2)**

Fig. 3. Comparison between actual and simulated reformate compositions (symbols actual ,lines predicted).

7.2. Reactor Temperature Simulation Results

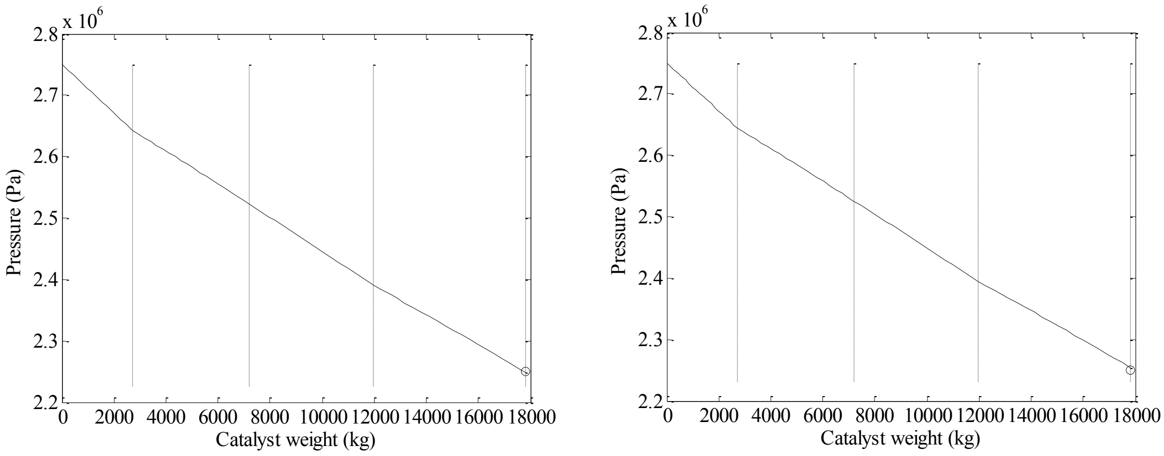
The temperature decreases along the catalyst bed in the reactors of reforming process, because the process reactions are, overall, endothermic. For this reason, commercial catalytic reformers are designed with multiple reactors and with heaters between the reactors to maintain reaction temperature at operable levels. The simulated temperature profile with the actual reactors temperature is plotted in Figure (4), it can be seen that in the first reactor the temperature decrease very sharp, since the major reactions are endothermic and very fast reaction, such as dehydrogenation of naphthenes components to aromatics and the temperature decreasing drop is less in other reactors especially in the last two reactors, which is due to the exothermic hydrocracking reaction. The comparison between the simulated temperature and the actual temperature of commercial reforming unit shown in table (6 and 7), which shows a good agreement results and the accumulated difference is 6.5 °C between the predicted and actual reactors temperature.

Figure (5) shows both the actual and the simulated pressure drop with respect to accumulative catalyst weight within the four reactors in commercial reforming process, it can be seen that a good agreement between these results.



a (run 1) **b (run 2)**

Fig. 4. Comparison between actual and simulated temperature profile (symbols actual, lines predicted).

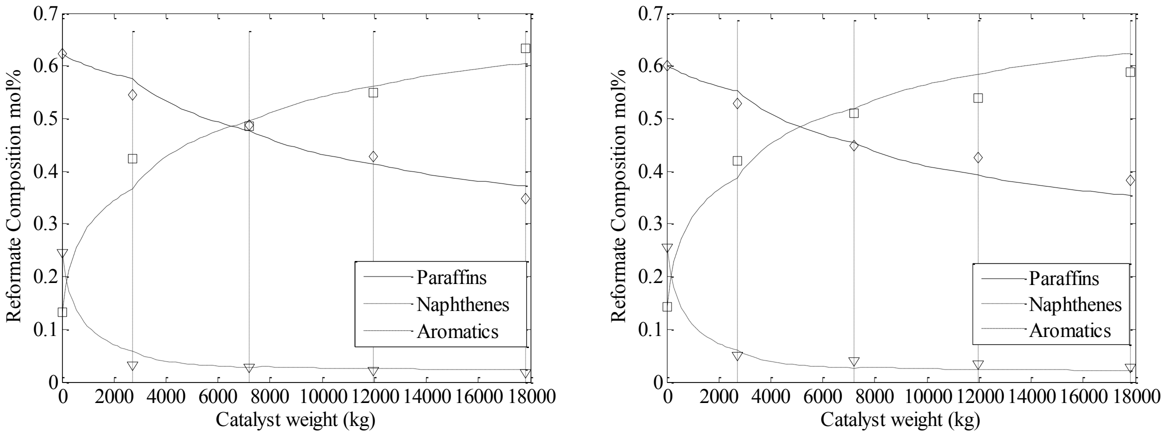


a (run 1) **b (run 2)**

Fig. 5.Comparison between Actual and Simulated Pressure Drop (symbols actual ,lines predicted)

7.3. Reformate Composition Simulation Results

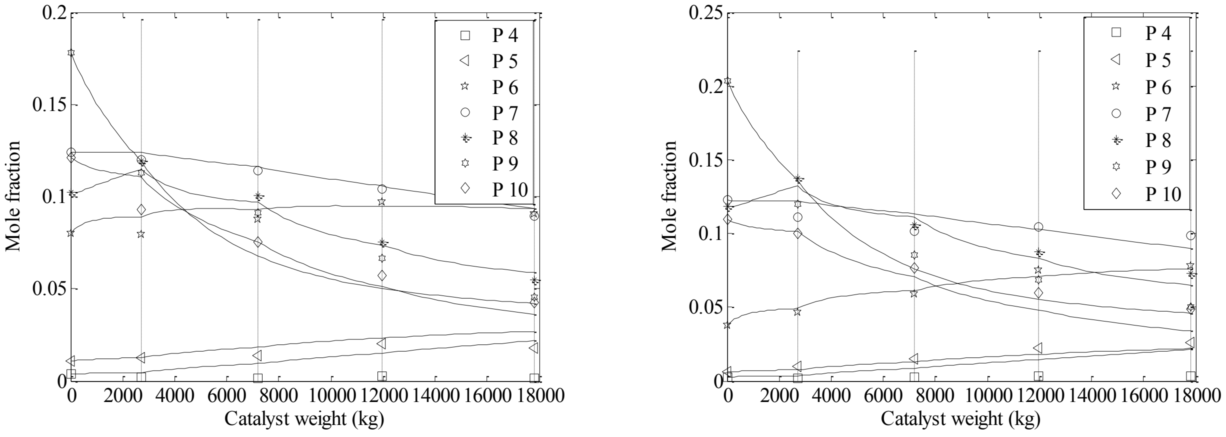
Reformate composition of total paraffins, naphthenes, and aromatics obtained from actual catalytic reforming unit with the proposed model are shown in Figure (6), the results show a good agreement between the actual and the simulated results. Tables (6 and 7) show comparison between the actual and the simulated reformate compassion of all paraffins components (4 – 11) carbon number, naphthenes and aromatics components from (6 – 11) carbon number through the four reactors in catalytic reforming process. It can be observed that total aromatics hydrocarbons yields are higher as goes from the first reactor to the last reactor, therefore the total amount of aromatics increase from 13.2 mol% to reach 42.3%, 48.5%, 55%, and 63.4% for feedstock of run 1. While for feedstock of run 2 increasing from 14.2 mol% to 42.1%, 51%, 54%, and 58.9%.



a (run 1) **b (run 2)**

Fig. 6. Comparison between actual and simulated total Paraffins, naphthenes, and aromatics in reforming process (symbols actual ,lines predicted).

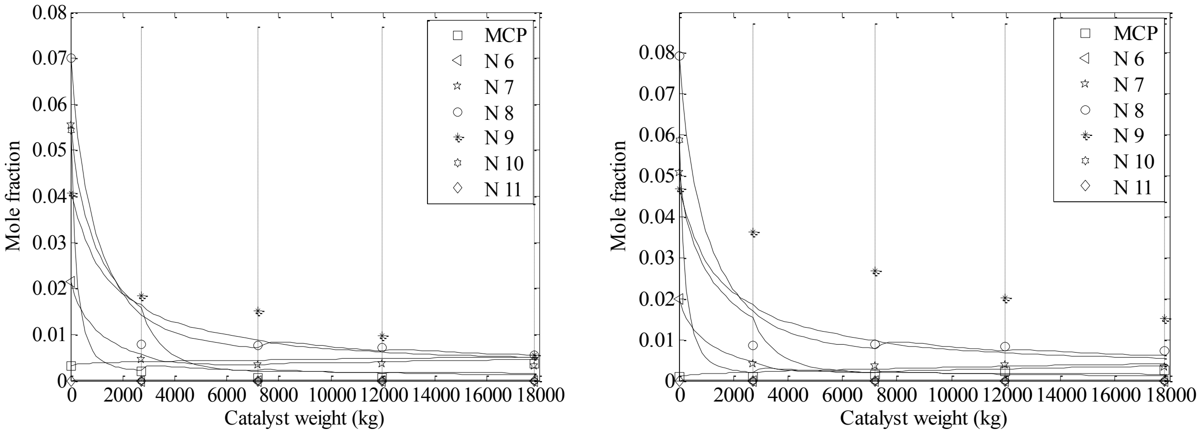
Figure (7) shows a comparison between the actual and the simulated results of the heavy and the light paraffins along the reactor as a function of catalyst weight. It can be seen that light paraffins increased because they are produced by hydrocracking reaction, while heavy paraffins decreasing because exhibited high levels of conversion this is because the increase in the probility of ring formation is high as the molecular weight of paraffins increases also in the last two reactors since dehydrocyclization and reaction take place.



a (run 1) **b (run 2)**

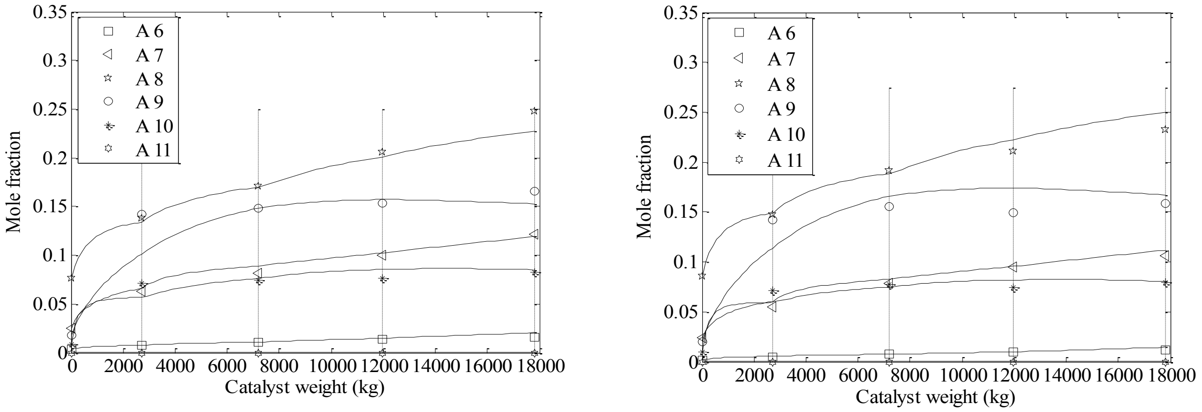
Fig. 7. Comparison between actual and simulated Paraffins composition (symbols actual, lines predicted).

The naphthenes and aromatics reformate comparison results shown in Figures (8, and 9). Naphthenes components which are the most desirable in reforming feed stocks react and converted to aromatics components through dehydrogenation reaction which take place in the first two reactors and these reactions goes to completion. Also it is important to mention her that all aromatics comparison in reformate are increased as feedstock passes through the catalytic reforming reactors especially lighter aromatics (A_6, A_7, A_8, and A_9), while heavy aromatics (A_{10}, and A_{11}) increasing very low or nearly remains unchanged.



a (run 1) **b (run 2)**

Fig. 8. Comparison between actual and simulated naphthenes composition (symbols actual, lines predicted).



a (run 1) **b (run 2)**

Fig. 9. Comparison between actual and simulated aromatics composition (symbols actual ,lines predicted).

8. Conclusions

The kinetic parameters of model are based on the steady state condition and are obtained from a commercial plant data furnished by a domestic petroleum refinery. In this work a mathematical model of semi-regenerative catalytic reforming unit with four reactors in series it has been developed. The model parameters were estimated on the basis of data obtained from industrial unit (Al-Dura refinery). The effects of different feed composition on product properties are evaluated, and simulation results were compared with the actual data, there for the absolute percentage error of aromatics compositions range between (2% to 8.3%) and the temperature absolute percentage error range between (0.01% to 0.5%) for four reactors respectively.

Nomenclature

A	Aromatics	(-)
N	Naphthene	(-)
P	Paraffin	(-)
MCP	Methylcyclopentane	(-)
n-P	Normal Paraffin	(-)
k_i	Reaction rate constant	hr^{-1}
k°_i	Pre-exponential factor	(-)
E_A	Activation energy	kcal/mole
R	Gas constant	J/mole.K
T	Reaction temperature	°C
$T^{\bullet}$	Initial temperature	°C
P_t	Total pressure	bar
$p_{\circ}$	Partial pressure	bar
αk	Pressure effect	(-)
C_i	Concentration of species i	$mole/cm^3$
C_P	Specific heat	J/mole.K
Z, z	Length of reactor	Cm
M.Wt	Molecular weight	g/gmole
WHSV	Weight hour space velocity	hr^{-1}
r_i	Reaction rate of species i	mole/gcat.hr
S	Cross sectional area of reactor	m^2
ΔH°_r	Heat of i th reaction	J/ mole
F_n	Molar flow rate of species n	mole/hr
Cp	Specific heat	J/mole.°C
d_p	Equivalent diameter of a catalyst particle	m
e	Void fraction of reactor bed	m^3/m^3
m	Viscosity	pa.s
G	total mass flux of fluid	$kg.s/m^2$
ℓ	density	kg/m^3

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استخدام النظرية الجينية لإيجاد حركية تفاعلات تهذيب النفثا الثقيلة لوحدة مصفى الدورة

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الخلاصة

في هذا البحث تم استخدام النظرية الجينية لإيجاد حركية تفاعلات وحدة تهذيب النفثا الموجودة في مصفى الدورة ببغداد. وحدة التهذيب تتكون من اربع مفاعلات على التوالي. تم تطوير موديل رياضي لمحاكاة عملية التهذيب ذاتية التنشيط للنفثا في الحالة المستقرة ولبعد واحد. الموديل الرياضي يصف تغير التراكيز والضغط ودرجة الحرارة على طول المفاعلات الاربعة المستخدمة لعملية التهذيب.

تم تجميع نتائج عملية بظروف مختلفة وتم استخدامها لوصف ثوابت حركية التفاعلات التي تتضمن وصف ٢٤ مادة وهي البرافينات (الايزو والنورمال) التي تحتوي من١ الى ١١ ذرة كاربون والنفثينات والمواد الاروماتية التي تحتوي من ٦-١١ ذرة كاربون بالاعتماد على حركية من ٧١ تفاعل. الداخل للاختيار الافضل هو التركيب ل ٢١ مادة وكذلك درجة الحرارة لتيار التدفق لكل مفاعل من المفاعلات الاربعة المستخدمة ضمن عملية التهذيب بينما الخارج هو ١٤٢ ثابت للموديل الرياضي المحسوبة المتكونة من ٧١ تفاعل ضمن عملية التهذيب, واستخدمت النظرية التفاضلية للاختيار الافضل لحساب ثوابت الموديل الرياضي.

تم مقارنة النتائج الرياضية المستحصلة من الموديل الرياضي المعتمد على حركية التفاعل المقترحة مع نتائج عملية ماخوذة بنفس الظروف حيث كان هناك انطباق جيدجدا بين نتائج الموديل الرياضي والنتائج العملية وهذا يدل على ان حركية التفاعل المقترحة تصف بشكل جيد التفاعلات في وحدة تهذيب النفثا وكانت النسبة المئوية المطلقة للخطأ للمواد العطرية (7.5, 2, 8.3, and 6.1%) والنسبة المئوية للخطأ لدرجة الحرارة هي (0.49, 0.5, 0.01, and 0.3%) للمفاعلات الاربعة على التوالي.