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Applying Modern Optimization Techniques for Prediction Reaction Kinetics of Iraqi Heavy Naphtha Hydrodesulferization

Abstract- *In this study, a powerful modern optimization techniques such as Genetic Algorithm (GA), Particle Swarm Optimization (PSO) and Artificial neural network (ANN) were applied to estimate the optimal reaction kinetic parameters for Heavy naphtha Hydrodesulferization (HDS), the hydrodesulferization unit located in AL-Daura refinery-Baghdad/Iraq. The reactions was carried out in a fixed-bed reactor packed with Co-Mo/γ-Al_2O_3 catalyst and the operating was 315-400 °C temperature 35 bar Pressure and 0.5-2.1 hr^{-1} liquid hourly space velocity. The result showed that hydrodesulferization of heavy naphtha follows the pseudo-first order reaction kinetics. This study signifies that the reaction kinetic parameters calculated by Genetic Algorithm was found to be more accurate and gives the highest correlation coefficient (R^2= 0.9507) than the other two methods. ANN technology by using the topology of (3-3-1-1) provides an effective tool to simulate and understand the non-linear behavior of the process. The model result showed very good agreement with the experimental data with less than 5%. mean absolute error.*

Keywords- *Hydrodesulferization, Reaction Kinetics, Genetic Algorithm, Particle Swarm Optimization, Artificial neural network.*

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1. Introduction

The quality of liquid fuels is playing the major role of consumer conviction and the refineries performance [1]. Many capital investments are inclined to produce cleaner middle distillates to meet the environmental standards in refining industries. On the other hand, poisoning and deactivation of valuable metal catalysts in refinery units as a result of their contact with such harmful compounds are the main reasons that oblige the hydrotreating of fuels; Furthermore, the stringent trend of environmental regulations and standards in most countries causes a drawback in the export of highly pollutant fuels [2]. Many scientists studied the removal of sulfur, nitrogen and metal compounds to predict the petroleum fractions with acceptable impurities. Hydrotreating (HDT) is one of processes in the petroleum refinery used to achieve petroleum products with acceptable quality. In general, sulfur impurities are the major concern because sulfur compounds are poisons and inhibitors of secondary upgrading catalytic processes. Sulfur combustion products cause serious environmental pollution such as acid rain. Thus, the Hydrodesulphurization (HDS) reactions which taken place within the hydrotreating reactor is the most important enhancement process in petroleum refinery [3,4].

Simulation and optimization of catalytic reactors in petroleum refinery is important to operate them within the product specifications at high productivity and without causing environmental hazards. Reaction kinetics is a system of equations that used to correlate data of the reaction rate [5]. Optimization is usually used for choosing the best reaction rate parameters among the full parameters ranges and selects the best by effective quantitative ways [6]. There is no general optimization method that could be applied to optimize all engineering problems. In recent years, many of optimization methods have been modified. These modern optimization methods such as genetic algorithms GA, particle swarm optimization PSO and artificial neural networks ANN are powerful and popular for optimizing different engineering problems [7]. Genetic algorithm (GA) is an intelligent optimization technique that based on the mechanics of natural selection and natural genetics, which combines an artificial survival of the fittest with genetic operators abstracted from nature. GA is used to solve difficult search and optimization problems that have resisted the analytical solutions [8]. The Particle Swarm Optimization (PSO) is a global optimization method based on swarm intelligence. It comes from the research on the bird and fish flock movement behavior. PSO method uses only primitive mathematical

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operators and does not require any gradient information of the optimized function [9]. Artificial neural network (ANN) is a computational model based on the structure and functions of biological neural networks. ANN is developed and derived to have a function similar to the human brain by memorizing and learning various tasks and behaving consequently [10].

2. Mathematical Kinetic Model

Developing kinetic of heavy naphtha HDS is not a simple task due to the complexities concerned with sulfur components reactions and analysis. In detailed reaction kinetics sulfur compounds such as mercaptanes, sulfides, thiophenes, benzothiophenes, dibenzothiophenes must be describe by its own reactivity and its reaction pathways. Therefore, each group of reactions is usually lumped into one general reaction and represented with power-law kinetics [11]. The mechanism of the P-L model is described by the equilibrium reaction in equation (1).

$$A + xH_2 \underset{K_r}{\overset{K_f}{\rightleftharpoons}} AH \quad \ldots (1)$$

By assuming, the HDS reaction is irreversible and $k_f >> k_r$. Sulfur content in reaction products is evaluated by the following differential equation:

$$\frac{dC}{dt} = -kC^n \quad \ldots (2)$$

Under plug flow conditions, the solutions of equation (2) are:

$$C_f - C_p = \frac{k_i}{LHSV} \quad \text{for } n = 0 \quad \ldots (3)$$

$$\ln\left(\frac{C_p}{C_f}\right) = \frac{-k_i}{LHSV} \quad \text{for } n = 1 \quad \ldots (4)$$

$$\left[\frac{1}{C_p^{n-1}} - \frac{1}{C_f^{n-1}}\right] = (n-1)\frac{k_i}{LHSV} \quad \text{for } n \neq 0,1 \quad \ldots (5)$$

Equation (6) is generally used for calculating the sulfur concentration change within a fixed bed reactor.

$$\frac{dC_s}{d\frac{1}{LHSV}} = -K_S C^n \quad \ldots (6)$$

Three types of equations (zero, 1st and 2nd) would be used to simplify the prediction of reactions order. Table 1 illustrates characteristics of each reaction order.

Table 1: Characteristics of reaction order

Reaction Order	Rate	Integrated Rate Equation
Zero	K_S	$C_f - C_p = \frac{k_S}{LHSV}$
First	$K_S C$	$\ln\left(\frac{C_p}{C_f}\right) = \frac{-k_S}{LHSV}$
Second	$K_S C^2$	$\frac{1}{C_p} - \frac{1}{C_f} = \frac{k_s}{LHSV}$

The reaction rate constant k_i can be determined using the Arrhenius equation

$$k_i(T) = A_o e^{\frac{-E_A}{RT}} \quad \ldots (7)$$

A nonlinear stochastic optimization method was used to calculate n: reaction orders, E_A: activation energy and A_o: pre-exponential factor.

The mean absolute relative error (MARE) which is a mean relative error between the actual and predicted sulfur content in product was used to evaluate the error.

$$MARE = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{C_{s(act)} - C_{s(pred.)}}{C_{s(act)}}\right| \quad \ldots (8)$$

The correlation coefficient, R^2 was used to justify the model with the predicted data.

$$R^2 = \frac{1 - SSE}{SST} \quad \ldots (9)$$

Where; SSE = Total sum of squares, and SST = Error sum of squares. R^2 ($0 \leq R^2 \leq 1$) is coefficient of determination. A value R^2 close to 1 signifies a perfect fit.

3. Optimization

The optimization steps were represented as follows:

- Given: Feed composition, product composition, temperature, LHSV.
- Optimize n reaction rate order, A^o pre-exponential factor and E_A activation energy.
- Fitness function: The sum of the mean absolute relative error (MARE).

4. Results

A series of real data for HDS of heavy naphtha in Al-Duara refinery was taken within the operating conditions (315-400 ^oC temperature, 35 bar pressure and 1.86-2.13 hr^{-1} LHSV). The values of reaction constant and order were determined using the best fit of real data. Different values of reaction order; n, thus different forms of solutions (Eq. 3, 4 and 5) were tested and one that yielded the highest correlation coefficient value (R^2 close to 1) was considered as appropriate reaction order. Linearization of reaction equation was taken to determine the Arrhenius equation constants. The Arrhenius-based dependence of the reaction rate constants with respect to temperature ($\ln K = -Ea/RT + \ln A$) was plotted in Figures 1, 2 and 3 for zero, first and second reaction order, respectively. The plot of ($\ln k$) versus ($1/T$) establishes a straight line with slope ($-Ea/R$) and intercept ($\ln A$).

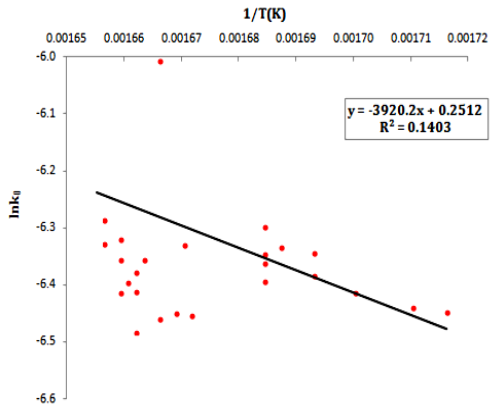

Figure 1: Arrhenius plot of zero order reaction equation

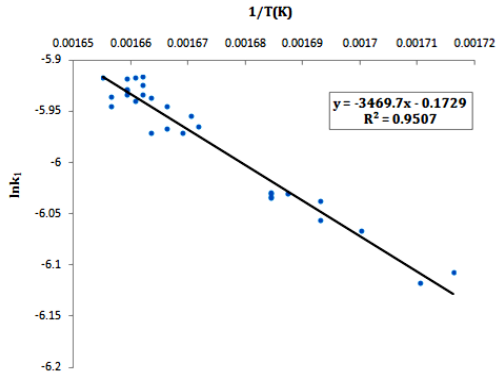

Figure 2: Arrhenius plot of first order reaction equation

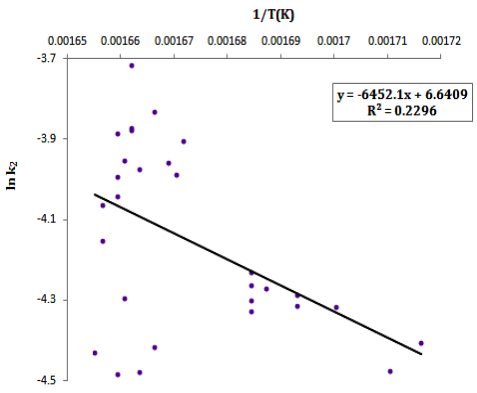

Figure 3: Arrhenius plot of second order reaction equation

It was observed that the first order reaction gives the highest value of R^2 and the smallest sum of squared errors (MARE) than the other two orders. Therefore, the hydrodesulphurization reaction is represented very well by first order reaction kinetic. The generated kinetic parameters for HDS process are presented in Table.

Table 2: Kinetic parameters for HDS process.

Zero Order n=0			
A_o (hr^{-1})	E_A (J/mole)	MARE	R^2
1.2842	3.2588e+004	11.6915	0.1403
First Order n=1			
A_o(hr^{-1})	E_A (J/mole)	MARE	R^2
0.8404	2.8842e+004	0.0513	0.9507
Second Order n=2			
A_o (hr^{-1})	E_A (J/mole)	MARE	R^2
765.0266	5.3638e+004	0.1480	0.2296

In addition, two least square optimization method, three different non-linear optimization methods (GA, PSO and ANN) were applied to calculate optimum reaction parameters. The optimum kinetic parameters were obtained by GA optimizer under MATLAB R2010b software. Genetic algorithm was considered with a population of 30 individuals, which evolved for 100 maximum number of generations, 0.8 crossover probability and 0.01 uniform mutation probability. The experimental and predicted sulfur concentration established by first order equation is plotted as shown in Figure 4, the maximum deviation less than 10%, indicating very good agreement between the actual and predicted results. Figure 5 show the value of objective function with respect to generation number achieved by GA.

Figure 5 demonstrates the best fitness value against the number of generations for the first order kinetic model. In fact, this figure shows that GA gradually converges to the global optimal point with evolutions of generations. It indicates that for this case study, after 100 generations, the optimal result can be obtained.

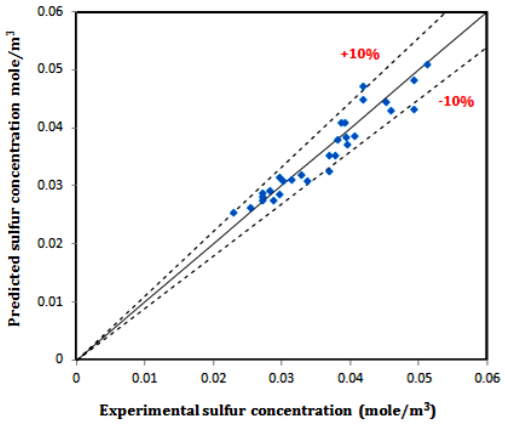

Figure 4: Comparison between experimental and predicted results by GA.

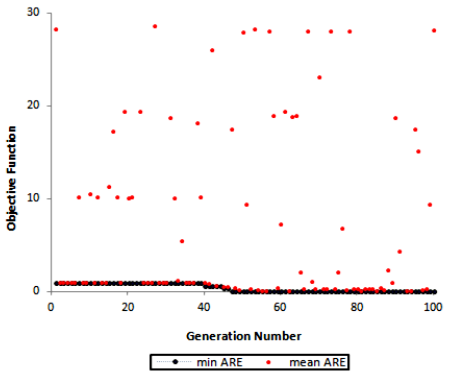

Figure 5: Fitness function vs. generation number of the first order kinetic model.

PSO optimization algorithm has been written using MATLAB R2010b software. The population of particles (N = 30) was initialized with the number of iterations of 100 for each particle to control parameters that give the minimum mean absolute error (MARE). The experimental and predicted sulfur concentration established by first order equation is plotted as shown in Figure 6. As similar to GA, PSO optimization results also shows maximum deviation less than 10%, indicating very good agreement between the actual and predicted results. Figure 7 demonstrates the best fitness value with respect to the iterations number achieved by PSO optimization maethod.

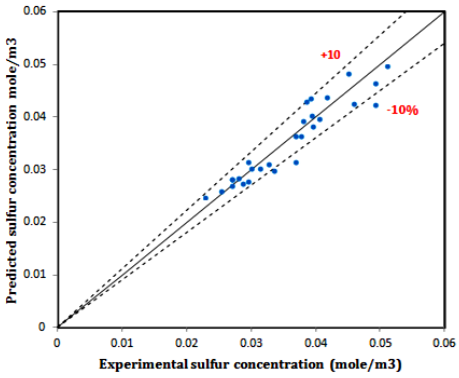

Figure 6: Comparison between experimental and predicted results by PSO

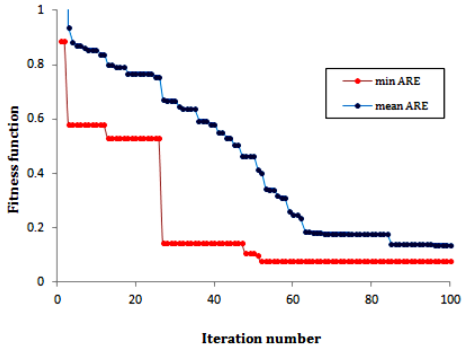

Figure 7: PSO objective function convergence of the first order kinetic model.

To select the optimal ANN topology that represents the output variables depending on the values of input variables, several structures of multi-layer feedforward BP neural networks have been tested. The input to the ANN network was: input concentration of sulfur (S_{in}), liquid hourly space velocity (LHSV) and temperature (T); and the output from the network was the output concentration of sulfur from the process (S_{out}).
The results of different network arrangements having either one or two hidden layer(s) were compared as shown in Table 3.

Table 3: The (MARE) and R^2 results for different ANN models.

Topology	Train data set		
	R^2	MARE	Computation prediction time (sec)
3-3-1	0.3420	0.1593	13.3881
3-3-1-1	0.9277	0.0436	11.1546
3-4-1	0.3612	0.1560	10.1980
3-4-2-1	0.8050	0.0851	10.7092
3-5-1	0.3778	0.1508	10.0161
3-5-3-1	0.9220	0.0482	10.6657
3-6-1	0.3774	0.1521	10.0434
3-6-4-1	0.8608	0.0667	11.1563
3-7-1	0.3579	0.1552	9.9803
3-7-5-1	0.9117	0.0522	10.7728
3-8-1	0.3759	0.1538	9.9500
3-8-6-1	0.9189	0.0455	10.9551
3-9-1	0.3699	0.1543	10.7833
3-9-7-1	0.8941	0.0541	10.8006
3-10-1	0.3717	0.1536	9.8553
3-10-8-1	0.8812	0.0565	10.8694

As can be seen in Table 3, ANN topology of (3-3-1-1) had the best performance among all other networks giving minimum MARE and highest correlation coefficient R^2. Therefore, in this study the optimum network configuration consist of an input layer with three neurons, first hidden layer of three neurons, second hidden layer of one neuron, and the output layer with one neuron. Network outputs of Predicted sulfur concentration and the corresponding actual data of Experimental sulfur concentration is shown in Figure 8.

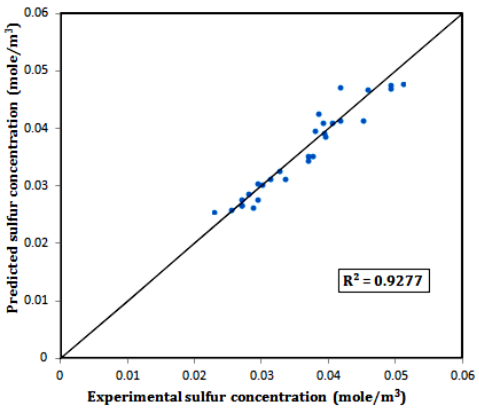

Figure 8: ANN regressions between predicted and experimental results.

5. Conclusions

Heavy naphtha HDS of the AL-Daura refinery was kinetically modeled and the following points can be concluded:

1. The pseudo-first order model can fit the kinetic data under real operating conditions. The values of the pre-exponential factor and activation energy were 0.8404 hr^{-1} and 28.8 kJ/mol, respectively.
2. It can be noticed that the least square approximation method (deterministic method) gives the highest correlation coefficient (R^2=0.9507) than the other methods. It indicates that this method has strong statistical properties when the system includes a single reaction equation.
3. The artificial neural network by using the topology of (3-3-1-1) gave the minimum mean absolute relative error (MARE=0.0436) as compared with the other two stochastic methods. But, this method has a drawback that it estimates the reaction rate without giving any kinetic model equation and without the estimation of kinetic constants.
4. Despite of their flexibility and robustness, genetic algorithm and particle swarm optimization gave almost the lowest correlation coefficient and the highest mean absolute relative error.

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