Studying of Catalyst Deactivation in a Commercial Hydrocracking Process (ISOMAX)

M. Rashidzadeh[*1], A. Ahmad[2] and S. Sadighi[1,2]
1- Catalysis Research Center, Research Institute of Petroleum Industry, Tehran, Iran
2- Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia,
UTM Skudai, Johor Bahru, 81310 Malaysia
Rashidzadehm@ripi.ir

Abstract

Catalyst deactivation is usually indispensable, although the rate at which it occurs varies greatly. At first, this article discusses the causes of deactivation in a commercial hydrocracking unit called Isomax. Then, a 5-lump kinetic model including catalyst decay function for hydrocracking of vacuum gas oil in a commercial plant is proposed. The model considers vacuum gas oil (VGO) having boiling point higher than 380°C (380^+°C), diesel (260-380°C), kerosene (150-260°C), naphtha (IBP:150°C), and gas as products. By using selective catalyst decay function in the kinetic model, the effect of the catalyst deactivation on the yield of products over time is studied. The prediction of the model during 1.5 years is in good agreement with the actual commercial data. The average absolute deviation (*AAD%*) of the model for the strategic products like naphtha, kerosene and diesel are about 1.784%, 1.983% and 1.971%, respectively. Also it is observed that the estimated parameters are consistent with the reported characteristics of amorphous catalysts.

Key words: Catalyst deactivation, Life model, Hydrocracking, Isomax

Introduction

Hydrocracking is one of the most important processes in a modern refinery to produce low sulfur diesel. The versatility and flexibility of the process makes it economically attractive to convert different types of feedstocks into various yields including gas, LPG, naphtha, kerosene and diesel, leading to its widespread applications. Typical of industrial processes, optimal operation is required to guarantee profitability and such a task necessitates the use of process models. These models are used to predict the product yields and qualities so that the effect of operating parameters such as reactor temperature, pressure, space velocity, as well as others on product yields and qualities can be understood. The models can also be used for process optimization and control, design of new units and selection of suitable hydrocracking catalysts [1]. However, the complexity of hydrocracking feed makes it extremely difficult to characterize and describe its kinetics at a molecular level. One way of simplifying the problem is to consider the partition of the species into a few equivalent classes, the so-called lumps or lumping technique, and then assume each class is an independent entity. This approach is attractive for kinetic modeling of complex mixtures because of its simplicity.

Mosby reported a model, which describes the performance of a residue hydrotreater using first order lumped kinetics [5]. The proposed model divides residue into lumps that are "easy" and "hard" crack. This scheme was used to determine the kinetic parameters of vacuum gas oil (VGO) hydrocracking. The first 3 lump model was presented by Yui and Sandford for gas oil hydrocracking, performed in a trickle bed reactor at various different operating conditions [6]. Then, Callejas and Martinez studied the kinetics of Maya residue in a perfectly mixed reactor in the presence of a hydrotreating commercial catalyst [7]. They used a first order kinetic model with a 3 lump configuration. Another 3 lump model with four kinetic constants was presented by Aoyagi et al., who studied the kinetics of hydrotreating and hydrocracking of conventional gas oil, coker gas oil and the gas oil derived from Athabasca bitumen [8]. Another 4-lump model was proposed by Aboul-Gheit to determine the kinetic parameters of VGO hydrocracking, expressing composition in molar concentration [9]. In this kinetic model, VGO was converted to gas, gasoline

and middle distillates. The model had eight kinetic constants estimated by experiments performed in a fixed bed plug flow micro reactor. Anchyeta et al. proposed a 5 lump kinetic model for catalytic cracking of gas oil in which the deactivation of catalyst was considered as an exponential law with one decay parameter depending on the time on stream [2]. Almeida et al. presented a 5 lump kinetic model for hydroconversion of Marlim vacuum residue in which by utilizing fourteen experiments in the batch reactor, 26 coefficients were estimated for the kinetic model [10]. Sanchez et al. proposed a five lump kinetic model with 10 kinetic parameters for moderate hydrocracking of heavy oils [11]. Singh et al. also adopted a five lump modeling strategy in predicting the yield of mild thermal cracking of vacuum residue [12]. The most advanced work in this field was proposed by Sadighi, in which an industrial scale VGO hydrocracking unit was simulated according to a 6 lump kinetic network [13].

Although many research outcomes on hydrocracking have been published, kinetic aspects with real feed and industrial scale and deactivation model of the catalyst have not received much attention. In line with this issue, this paper proposes a practical kinetic model with 5 lumps that includes VGO, diesel, kerosene, naphtha and gases, which calculates the yield of all products in an industrial hydrocracking unit, taking into account catalyst deactivation.

The advantage of the presented approach is lumping of middle distillate to two discriminated groups, which are diesel and kerosene (as middle distillate). Therefore, the evaluation of the catalyst from operating and economical aspects can be performed more accurately because each of the intended products have different worth, usage and finishing process. Moreover, in this model, decay parameters are considered for all reaction paths to simulate the effect of poisoning agents like coke and metals.

Catalyst deactivation
Deactivation is a complex phenomenon. Feed molecules might poison active sites; catalyst might produce intermediates and products that are lethal poisons for the catalyst. The deactivation time varies greatly for the different processes. At lower end, we found the FCC process with a deactivation time of seconds, or deactivation of hydrocracking process, which is much slower, depend on the feed, in order of months or a year [14]. It is essential that the catalyst deactivation be considered in the modeling of the process to have a lower deviation between the measured and the predicted values.

The five main causes of the catalyst deactivation are poisoning, fouling, thermal degradation initiated by often high temperature, mechanical damage and corrosion/ leaching by the reaction mixture. In a VGO hydrocracking reactor, poisoning by metals such as Ni and V, and coke deposition have major roles in the catalyst deactivation [14]. However, because of the low speed of that effect, modeling the catalyst deactivation in the pilot hydrocracking units is encountered with problems such as high operating charges. In the next sections, a mathematical model will be developed to simulate the effect of these phenomena.

Hydrocracking kinetic model
This work considers five lumps, i.e., VGO (or unconverted oil), diesel, kerosene, naphtha and gas to match main products in the refineries. Fig.1 illustrates the process pathways associated with the strategy. Note that if all reactions pathways are considered, the model would include twenty kinetic parameters and ten decay constants for the catalyst deactivation. All parameters should be estimated using experimental data and this is laborious. Some judgments are normally welcome to reduce the model complexity without sacrificing the accuracy.

Upon close scrutiny of the system under consideration, the model can be reduced to that in Fig.2, where only sixteen kinetic parameters and eight constants for catalyst deactivation, totally twenty four parameters are estimated. The reduction of parameters is done according to the order of magnitude of rate constants in comparison to the highest one in the average process temperature, which will be discussed later.
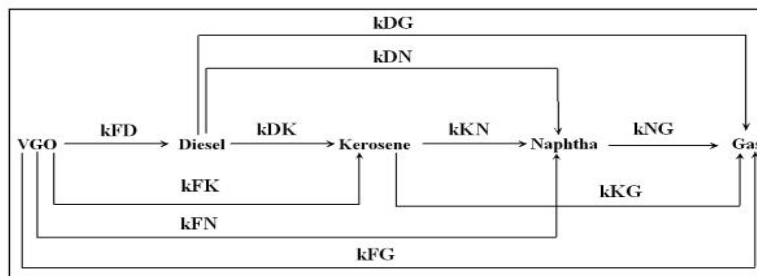

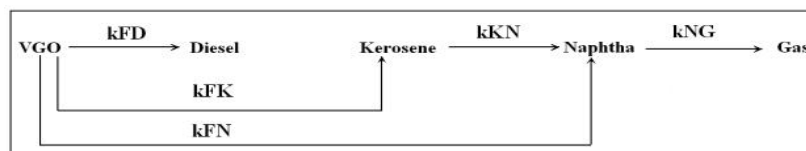**Figure 1-** The complete 5-lump kinetic model
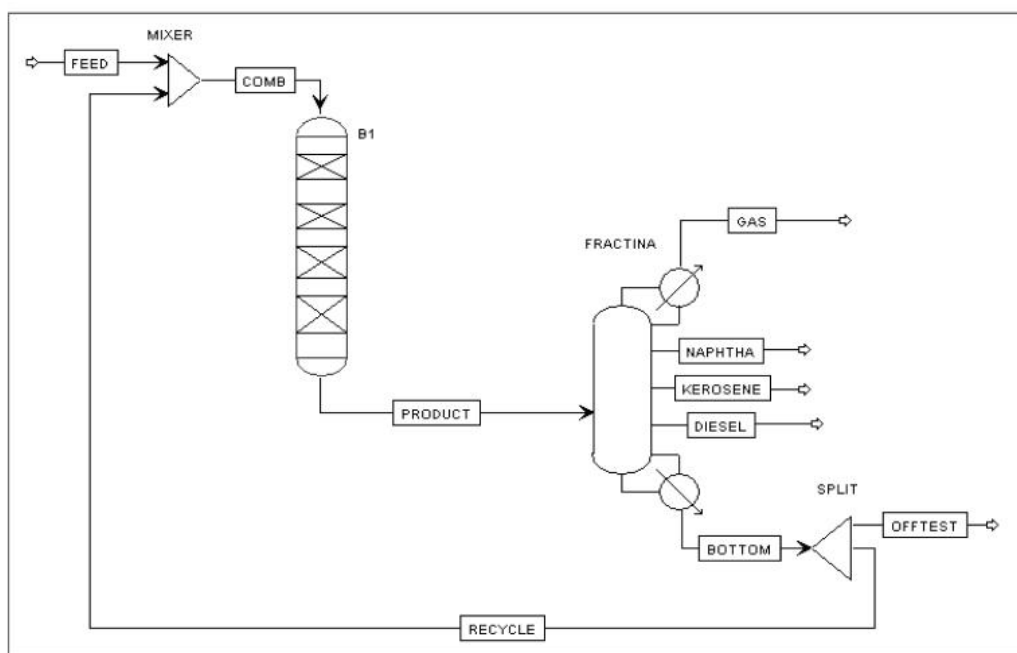

Figure 2- The reduced 5 lump kinetic model

Figure 3- A simplified scheme of hydrocracking process

Data gathering
Hydrocracking process
A commercial first stage hydrocracking unit, with the commercial name of Isomax licensed by UOP Company, was chosen as a case study. The feed of the hydrocracking reactor was a mixture of fresh vacuum gas oil (Table 1) and unconverted oil, recycled from the separation section at the end of the process (Fig.3).

Table 1- Properties of fresh vacuum gas oil

Density at 15°C	g /cm³	0.91
Density at 50°C	g /cm³	0.89
Sulfur	wt%	1.9
Total Nitrogen	ppm	1018
Conradson Carbon	wt%	0.04
Refractive index at 20°C	-	1.51
Ultimate analysis		
C	wt%	85.9
H	wt%	12.1
Distillation analysis (ASTM D1160)		
IBP	° C	333
10%	° C	381.1
30%	° C	411.7
50%	° C	431.7
70%	° C	453.3
90%	° C	480.0
FBP	° C	505.0

The combined feed (with combined feed ratio or CFR about to 1.5) was mixed with hydrogen and heated before entering the reactor. Since the strategy for modeling is lumping of feed and products, hydrogen is neglected in the mass balance. The hydrocracking reactor had 4 beds of a total amount of loaded catalyst in the reactor of about 69000 kg. The hydrocracking catalyst was an amorphous type with specifications given in Table 2.

Table 2- Catalyst Specifications of hydrocracking process

Shape	-	Extrude
Diameter	mm	2.5
Length	mm	6.1
Surface Area	m²/g	176
Pore Volume	m²/g	0.51
Bulk Density	g/cm³	0.75
Chemical Properties		
MoO_3	wt %	10.5
NiO	wt %	2.35
P	wt %	1.35
Na_2O	wt %	0.05

The product and feed samples were analyzed according to the ASTM standard procedures.
Operating conditions
From the start of run (SOR) to the middle of run (MOR), fourteen sets of data comprising of flow rates, pressure and temperature were gathered from the target commercial hydrocracking process (see Table 3). The main products of the process were gases, LPG, naphtha (N), kerosene, diesel and unconverted oil (offtest). Performing mass balance around the unit showed that the error for all selected experiments was mainly related to the consumed hydrogen for hydrocracking (HDC) and hydrodearomatization (HDA) reactions. This error was normalized on all lumps.

The average density and boiling point range of these products from the SOR to the MOR are presented in Table 4. Based on the gathered data, it was noted that properties of the offtest or unconverted oil were close to those of VGO feedstock. Therefore, considering them as one lump was a reasonable assumption.

Table 3- Feed flow rate and reactor operating condition

Day	Fresh Feed (kg/hr)	Recycle Feed (kg/hr)	WABT (°C)	P_{H2} (Mpa)
0	48545.5	32364.3	397.4	15
31	48515.4	32344.2	397.7	15
60	48515.4	32344.2	397.7	15
61	48515.4	32344.2	397.9	15
92	49445.8	32965.2	397.7	15
122	39245.2	26162.8	378.0	15
184	48567.6	32378.4	398.3	15
213	48567.6	32378.4	398.3	15
244	51139.9	34092.6	399.1	15
305	50038.6	33359.1	399.5	15
336	49841.7	33226.5	399.7	15
395	48722.3	32480.9	399.8	15
425	49940.2	33294.8	399.9	15
456	49867.8	33244.5	399.5	15

Table 4- Average properties of hydrocracking product

	Sp.gr	IBP-FBP Actual (°C)	IBP-FBP Model (°C)
Gas	0.35	40-	40
Naphtha	0.71	37-146	40-150
Kerosene	0.796	148-267	150-260
Diesel	0.823	266-378	260-380
Offtest	0.910	313-484	380+

Industrial fixed bed hydrocracking reactor model

Mathematical models for a trickle-bed catalytic reactor can be complex due to the many microscopic and macroscopic effects occurring inside the reactor; flow patterns of both phases, size and shape of a catalyst particles, wetting of the catalyst pores with liquid phase, pressure drop, intraparticle gradients, thermal effects, and, of course kinetics on the catalyst surface [15]. In pilot or laboratory fixed bed reactors, these non-idealities made researchers obey from some rules to assume the reactor in a plug flow regime [16,17]. However, a commercial hydrocracking can be virtually plug flow, which increases the accuracy of the yield prediction and reliability of the estimated kinetic parameters [18]. Therefore, all phenomena, which create non idealities, can be neglected.

Kinetic expression

For each reaction, a kinetic expression (R) is formulated as the function of mass concentration (C), deactivation function (φ) and kinetic parameters (k_0 and E). It is well known that the deactivation of a catalyst is caused by its surface coke. Thus, it is assumed that catalyst deactivation is a time function. The exponential law is assumed for catalyst decay (φ), which depends on deactivation constant (α) and time on stream (t_c). The previous re-

searchers used one or two decay parameters to simplify the overall kinetic model and parameter estimation [2,19]. This assumption was also used in other works in the modeling of catalytic reformers and fluid catalytic crackers [20,21]. In these works, a non-selective deactivation model, based on the hypothesis that (φ) was the same for all reactions was used to simplify the overall kinetic model and parameter estimation. However, in this research, a selective deactivation is applied in which different decay parameters are used for all possible reaction paths. This kind of selective models can approximate more the reality and would give better results [22].

According to above assumptions, kinetic constants of the model are expressed as:

Vacuum gas oil or Feed (F):

$$k_{Fj} = \varphi_{Fj} k_{0Fj} \exp(\frac{-E_{Fj}}{RT}) \qquad (1)$$

Note that j in Eq.1 represents diesel (D), kerosene (K), naphtha and gas (G) lumps.

Diesel (D): $k_{Dj'} = \varphi_{Dj'} k_{0Dj'} \exp(\frac{-E_{Dj'}}{RT}) \qquad (2)$

j' in Eq.2 represents kerosene (K), naphtha (N) and gas (G) lumps.

Kerosene (K): $k_{Kj''} = \varphi_{Kj''} k_{0Kj''} \exp(\frac{-E_{Kj''}}{RT}) \qquad (3)$

j'' in Eq.3 are naphtha (N) and gas (G) lumps.

Naphtha (N): $k_{Nj'''} = \varphi_{Nj'''} k_{0Nj'''} \exp(\frac{-E_{Nj'''}}{RT}) \qquad (4)$

In equations 1 to 4, T and R are the absolute values of weight average bed temperature (WABT) and ideal gas constant, respectively. The decay function (φ) in these equations is formulated as follows [14]:

Decay function (φ): $\varphi_{ij} = \exp(-\alpha_{ij} \times Life) \qquad (5)$

In Eq.5, α_{ij} shows the deactivation constant for converting i lump to j one in hydrocracking process. They are estimated from actual data as model parameters

to simulate the effect of coke deposition on the rate of hydrocracking reactions. Also, note that *Life* value in this equation can be expressed in days on stream (t_c).

Thus, the reaction rates (R) can be formulated as the following:

Vacuum gas oil reaction (R_F):

$$R_F = (\sum_{j=D}^{G} \varphi_{Fj} k_{Fj}) C_F^{\;2} \qquad (6)$$

C_F in Eq. 6 is the mass concentration of VGO. The VGO hydrocracking reaction is assumed to be second order [13].

Diesel (R_D): $R_D = \varphi_{FD} k_{FD} C_F^{\;2} - \sum_{j'=K}^{G} \varphi_{Dj'} k_{Dj'} C_D \qquad (7)$

Kerosene (R_K):

$$R_K = \varphi_{FK} k_{FK} C_F^{\;2} + \varphi_{DK} k_{DK} C_D - \sum_{j''=N}^{G} \varphi_{Kj'} k_{Kj'} C_K \qquad (8)$$

Naphtha (R_N):

$$R_N = \varphi_{FN} k_{FN} C_F^{\;2} + \varphi_{DN} k_{DN} C_D + \varphi_{KN} k_{KN} C_K - \varphi_{NG} k_{NG} C_{NG} \quad (9)$$

Gas (R_G):

$$R_G = \varphi_{FG} k_{FG} C_F^{\;2} + \varphi_{DG} k_{DG} C_D + \varphi_{KG} k_{KG} C_K + \varphi_{NG} k_{NG} C_N \quad (10)$$

Mass balance

In the interest of improving the accuracy of the developed model, the volumetric flow rate in the reactor (v) is considered variable; that is, it is calculated according to the density of the output stream (Eq.15). Thus, equations 11 to 16 should be solved simultaneously for the catalyst bed.

$$\frac{\partial(\upsilon C_j)}{\partial \omega} \pm R_j = 0 \qquad (11)$$

In Eq. 11, j, feed lump (F) to gas (G); C, mass concentration of lump; ω, weight of catalyst and "-" sign is for reactant (feed or VGO), as well as "+" sign is for products.

$$\frac{\partial(\rho v)}{\partial \omega} = 0 \qquad (12)$$

$$F_m = \sum_{j=F}^{G} C_j \upsilon \qquad (13)$$

$$X_j = \frac{C_j v}{F} \qquad (14)$$

$$\frac{1}{\rho} = \sum_{j=G}^{F} \frac{X_j}{\rho_j} \qquad (15)$$

In equations 12 to 15, ρ and v are density of stream and volume flow rate through reactor, respectively; F_m is the mass flow rate of stream passing through the bed; X and ρ_j are mass fraction and density of lumps (Table 4), respectively.

After calculating the mass concentration and volume flow rate of each lump in the effluent stream of the reactor, the product yields can be found as the following:

$$Y_j = \frac{C_j \upsilon.(1 - R_{sj})}{F_f} \qquad (16)$$

In equation 16, R_s and F_f are recycle fraction and mass flow rate of fresh VGO, respectively. It is obvious that the former parameter for all lumps, except for uncon-

verted oil, is zero.

Finally, for parameter estimation, sum of squared error, *SQE*, as given below, is minimized [2]:

$$SQE = \sum_{k=1}^{N_t} \sum_{j=F}^{G} (Y_{jk}^{\;meas} - Y_{jk}^{\;pred})^2 \qquad (17)$$

In Eq.17, N_t, Y_j^{meas} and Y_j^{pred} are the number of test runs, measured product yield and the predicted by model, respectively.

The hydrocracking reaction model according to equations 1 to 16 is coded and solved in Aspen Custom Modeler (Aspen Tech, 2006) programming environment. In order to estimate kinetic parameters, the objective function presented in Eq.17 is minimized by Nelder-Mead method.

To compare the simulated and measured product values, absolute average deviations (*AAD*) were calculated by the following equations [23]:

$$AAD\% = 100 \frac{\sum_{k=1}^{N_t} \sqrt{\dfrac{(Y_k^{\;meas} - Y_k^{\;pred})^2}{Y_k^{\;meas2}}}}{N_t} \% \qquad (18)$$

Results and discussions
Model without Decay Function

The twenty kinetic parameters for the assumed model (Fig.1), without decay functions, were estimated using measured industrial data, presented in Table 5. In this table, the ratio of magnitude of all rate constants to the highest one (k_{KN} or kerosene to naphtha) were calculated.

After parameter estimation and simulation, the *AAD%* for the first strategy, called complete model, were 8.044% in comparison to measured data.

Estimated parameters in Table 5 show that the rate constant of reactions in the average *WABT* (397.18°C) for k_{FG}, k_{DN}, k_{DG}, k_{DK} and k_{KG} are significantly lower compared to the highest value (k_{KN}). This means that these reactions, which are related to conversion of feed to gas (k_{FG}), diesel to lights (k_{DN}, k_{DG} and k_{DK}), and kerosene to gas (k_{KG}) have much lower selectivites so that they can be omitted. This phenomenon is consistent with the literature in that reported amorphous catalysts have the tendency to produce higher amounts of middle distillates, especially diesel, and lower amounts of naphtha fractions [24,25]. Also, we suppose that low rate constants for converting VGO to gas are rational because lighter products have more tendencies to be cracked to gas in hydrocracking unit. After eliminating the mentioned pathways, the final reaction network for the process under study, called reduced network, is presented in Fig. 2.

Model with Decay Function

Attempting to make the model closer to actual industrial scenario, a catalyst decay function (φ) was introduced (Eq.5). This function is multiplied by rate constants

Table 5- Kinetic parameters for the complete model

Frequency factor	(hr^{-1})	Activation energy	(kcal/mol)	Rate Constant	Order
k_{0DG}	2.37E-3	E_{DG}	35.14	8.181E-15	1.05E-11
k_{0DN}	0.0023	E_{DN}	24.73	2.029E-11	2.60E-8
k_{0DK}	0.1202	E_{DK}	28.09	8.244E-11	1.06E-7
k_{0FD}	0.0116	E_{FD}	12.48	9.853E-7	1.26E-3
k_{0FG}	0.00245	E_{FG}	58.62	1.851E-22	2.38E-19
k_{0FN}	30.307	E_{FN}	25.31	1.682E-7	2.16E-4
k_{0FK}	0.1062	E_{FK}	15.32	1.069E-06	1.37E-3
k_{0NG}	0.1933	E_{NG}	8.65	2.912E-4	3.74E-1
k_{0KG}	5.00E-4	E_{KG}	18.91	3.387E-10	4.35E-7
k_{0KN}	0.0771	E_{KN}	6.12	7.792E-4	1

(Eqs.1 to 4) to show decreasing of hydrocracking capability with time. The deactivation parameters (α_{ij}) were estimated like kinetic parameters to minimize the sum of square errors. The estimated deactivation and kinetic parameters are presented in Table 6. After implementing the deactivation model, the *AAD%* of the model reduced to 7.966%.

Decay constants in Table 6 show that all reactions were affected by the deactivation of the catalyst, which was unfavorable to yield main products. It can be concluded that decay constants for converting feed and kerosene to naphtha (α_{FN} and α_{KN}) was higher than those for middle distillates (α_{FD} and α_{FK}). Thus, the former were the most impressed desirable reactions. These phenomena can justify the necessity for increasing the bed temperature by the time in Isomax process from SOR to EOR (end of run) to maintain the ability of the catalyst to yield main products, especially naphtha.

From Table 6, it is obvious that apparent activation energy of VGO hydrocracking to middle distillate and naphtha are about 13 kcal/mol and 26 kcal/mol, respectively. The reported ones by Aboul-Ghiet for hydrocracking of VGO to middle distillate and naphtha were about 13-17.5 kcal/mol and 22-24 kcal/mol, respectively, not

far from this research [9]. Furthermore, the activation energy of catalytic cracking of naphtha to gas, reported by Ancheyta et al. was 9-9.92 kcal/mol, close to the reported one in this work [2]. All estimated activation energies in this paper are lower than reported values by Sanchez et al. for a 5 lump model [11]. It seems because VGO feed in Sanchez work was the product of heavy residue, its cracking to lighter lumps needs higher activation energy than the lighter VGO used in this current work. The average values of activation energy presented by Singh for mild thermal cracking of VGO to distillate and naphtha as well as distillate to naphtha were 25 kcal/mol and 30.88 kcal/mol, respectively [12]. It is obvious that the value presented in this work is lower than that in thermal cracking process because of existing catalyst and hydrogen.

The final reaction scheme for 5 lump VGO hydrocracking is shown in the Figure 2 with the title of reduced model. Figures 4 to 7 show comparisons between measured product yields from industrial hydrocracking reactor and the model predictions. It can be concluded that the predicted yields by model are in good agreement with the measured values from Isomax unit.

Table 6- Kinetic and deactivation parameter for the model with decay function

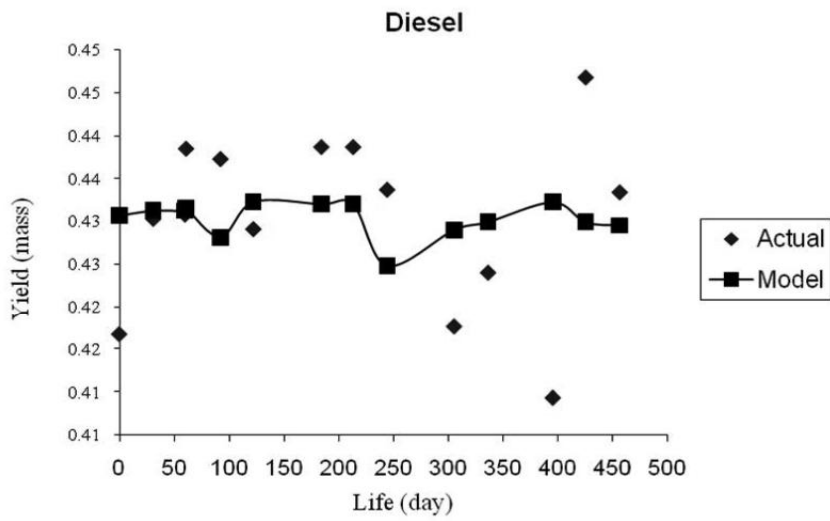| Frequency factor	hr^{-1}	Activation energy	kcal/mol	Decay coeff.	hr^{-1}
k_{0DN}	-	E_{DN}	-	α_{DG}	-
k_{0DK}	-	E_{DK}	-	α_{DN}	-
k_{0FD}	0.0156	E_{FD}	12.86	α_{DK}	4.13E-05
k_{0FG}	-	E_{FG}	-	α_{FD}	-
k_{0FN}	55.60	E_{FN}	25.86	α_{FG}	8.43E-05
k_{0FK}	0.1556	E_{FK}	15.84	α_{FN}	8.28E-05
k_{0NG}	0.2624	E_{NG}	9.07	α_{NG}	9.12E-05
k_{0KG}	-	E_{KG}	-	α_{KG}	-
k_{0KN}	0.0769	E_{KN}	6.19	α_{KN}	1.59E-04

Figure 4- Comparison of predicted diesel yield of model with measured data
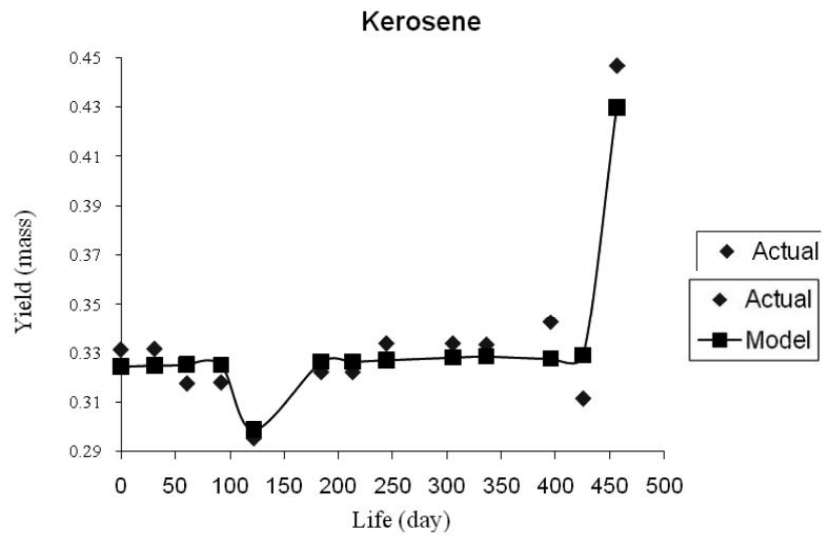

Figure 5- Comparison of predicted kerosene yield of model with measured data
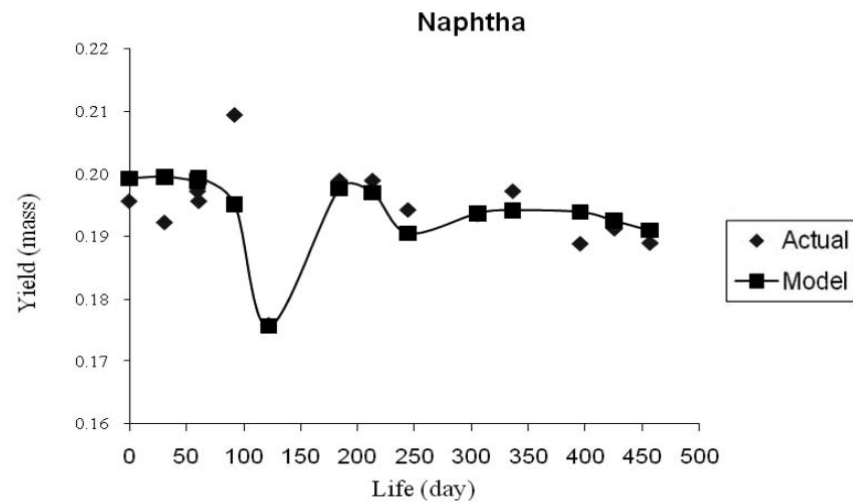

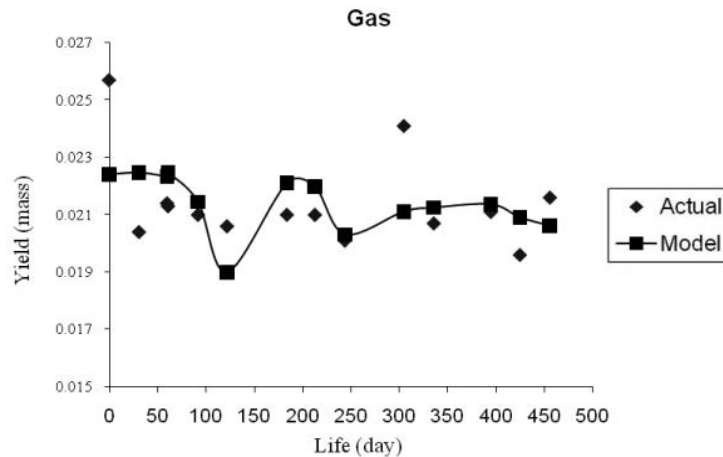**Figure 6-**Comparison of predicted naphtha yield of model with measured data

Figure 7- Comparison of predicted Gas yield of model with measured data

The *AAD%* of residue, diesel, kerosene, naphtha and gas are presented in Table 7. The prediction of final modeling approach including ten rate parameters and five deactivation constants, estimated from seventy observations, for all products, except residue, was acceptable. The average *AAD%* of model prediction in comparison with measured data for all main products (Gas, Naphtha, Kerosene and Diesel) is less than 3%, supposadly acceptable for a lumping strategy according to similar researches [2,4,12,23]. We thought that the flagrant error for the residue is because of its swinging with diesel, concluded from Table 4, as if their initial cuts cannot be completely separated in the separation unit of Isomax. Therefore, it tremendously impressed the accuracy of the model for prediction of offtest or residue. Since this is not the main product of Isomax and its yield is quite low, it cannot affect the application of the model to predict the yield of precious and strategic products such as naphtha, kerosene and diesel.

Table 7- *AAD%* of model prediction in comparison to measured data

AAD%	
Residue	28.30
Diesel	1.971
Kerosene	1.983
Naphthaa	1.784
Gas	5.784
Ave%	7.966

Conclusions

In this research, a 5 lump kinetic model for hydrocracking of vacuum gas oil (VGO) was proposed. The model includes gas, naphtha, kerosene, diesel and unconverted VGO or off test as lumps and ten kinetic parameters as well as five decay constants for the catalyst deactivation. The advantage of this model over the previous works was its capability to predict the diesel and kerosene separately from other lumps, which is important for better economic evaluation of the hydrocracking process. Fourteen test runs were gathered during 1.5 years from

a commercial hydrocracking unit and they were used to tune the model constants. The estimated parameters showed that the tendency of the catalyst to crack VGO and diesel to gas and naphtha was negligible and compatible with the nature of amorphous catalysts. After omitting these reactions and using a selective decay function to consider the life of the catalyst in the model, the absolute average deviation of the model decreased from 8.044% to 7.966%. Also, the error for main products including gas, naphtha, kerosene and diesel was less than 2%, supposed to be acceptable for a commercial hydrocracking model.

References

[1] Valavarasu G., Bhaskar M. & Sairam B., *"A Four Lump Kinetic Model for the Simulation of the Hydrocracking Process"*, Petroleum Science and Technology, Vol. 23, No. 11-12, pp. 1323-1332, 2005.

[2] Ancheyta J., Lopez F. & Aguilar E., *"5- Lump kinetic model for gas oil catalytic cracking"*, Applied Catalysis A: General, Vol.177, No.2, pp. 227-235, 1999.

[3] Astarita G. & Sandler, S. I., *"Kinetics and thermodynamics lumping of multicomponent mixtures"*, Elsevier: Amsterdam, pp. 111-129, 1991.

[4] Ancheyta J., Sanchez S. & Rodriguez M.A., *"Kinetic modeling of hydrocracking of heavy oil fractions: A review"*, Catalysis Today, Vol. 109, No. 1-4, pp. 76-92, 2005.

[5] Mosby F., Buttke R.D., Cox J.A. & Nikolaids C., *"Process Characterization of Expanded-Bed Reactors in Series"*, Chem. Eng. Sci., Vol. 41, No. 4, pp. 989-995, 1986.

[6] Yui S.M. & Sanford E.C.,*"Mild hydrocracking of bitumen-drived coker and hydrocracker heavy gas oils: kinetic product yield and product properties"*, Ind. Eng. Chem. Res., Vol. 28, pp. 319-320, 1989.

[7] Callejas M.A. & Martinez M.T., *"Hydrocracking of a Maya Residue. Kineic and Product Yield Distributions"*, Ind. Eng. Chem. Res., Vol. 38, pp. 98-105, 1999.

[8] Aoyagi K., McCaffrey W.C. & Gray M.R., *"Kinetics of Hydrocracking and Hydrotreating of Coker and Oil-*

sands Gas Oils", Petroleum Science Technology, Vol. 21, No. 5, pp. 997-1015, 2003.

[9] Aboul-Gheit K., *"Hydrocracking of Vacuum Gas Oil (VGO) for Fuels Production-Reaction Kinetics"*, Erdol Erdgas Kohle, Vol. 105, No. 7-8, pp. 319-320, 1989.

[10] Almeida R.M. & Guirardello R., *"Hydroconversion kinetics of Marlim vacuum residue"*, Catalysis Today, Vol. 109, No. 1-4, pp. 104-111, 2005.

[11] Sanchez S., Rodriguez M.A. & Ancheyta J., *"Kinetic model for moderate hydrocracking of heavy oils"*, Ind. Eng. Chem. Res., Vol. 44, No. 25, pp. 9409-9413, 2005.

[12] Singh J., Kumar M.M., Saxena A.K. & Kumar S., *"Reaction pathways and product yields in mild thermal cracking of vacuum residues: A multi-lump kinetic model"*, Chem. Eng. J., Vol. 108, No. 3, pp. 239-248, 2005.

[13] Sadighi S., Arshad A. & Mohaddecy S.R., *"6-Lump Kinetic Model for a Commercial Vacuum Gas Oil Hydrocracker"*, International J. of Chemical Reactor Engineering, Vol. 8, Article A1, pp. 1-24, 2010.

[14] Moulijin J.A., Van Diepen A.E. & Kapteijn F., *"Catalyst Deactivation; is it predictable? What to do?"* Applied Catalysis A: general, Vol. 212, No. 1-2, pp. 3-16, 2001.

[15] Sertic-Bionda K., Gomzi Z. & Saric T., *"Testing of Hydrosulfurization process in small trickle-bed reactor"*, Chem. Eng. J., Vol. 106, No. 2, pp. 105-110, 2005.

[16] Klinken J. & Dongen R., *"Catalyst dilution for improved performance of laboratory trickle-flow reactors"*, Chem. Eng. Sci., Vol. 35, pp. 59-66, 1980.

[17] Bej S., Dabrel R., Gupta P., Mittal K., Sen S. & Kapoor V., *"Studies on the performance of a microscale trickle bed reactor using different sized of diluents"*, Energy & Fuel, Vol. 14, No. 3, pp. 701-705, 2000.

[18] Mederos F.S., Ancheyta J. & Chen J., *"Review on criteria to ensure ideal behaviors in trickle-bed reactors"*, Applied Catalysis A: General, Vol. 355, No. 1-2, pp. 1-19, 2009.

[19] Forissier M. & Bernard J.R., *"Deactivation of Cracking Catalysts with Vacuum Gas Oil"*, Studies in Surface Science and Catalysis, Vol. 68, pp. 359-366, 1991.

[20] Padmavathi G. & Chaudhuri K., *"Modeling and Simulation of Commercial Naphtha Reformers"*, The Can. J. of Chem. Eng., Vol. 75, No. 10, pp. 930-937, 1997.

[21] Hongjun Y., Chunming X., Jinsen G., Zhichang L. & Pinxiang Y., *"Nine lumped kinetic models of FCC gasoline under the aromatization reaction conditions"*, Catalysis Communication, Vol. 7, No. 8, pp. 554-558, 2006.

[22] Corella J., Morales F.G., Provost M. & Espinosa A., *"Recent Advances in Chemical Engineering"*, McGraw-Hill, pp. 192-210, 1988.

[23] Marafi A., Kam E. & Stanislaus A., *"A kinetic study on non-catalytic reactions in hydroprocessing Boscan crude oil"*, Fuel, Vol. 87, pp. 2131-2140, 2008.

[24] Scherzer J. & Gruia A.J., *Hydrocracking Science and Technology*, 1st Ed. Marcel Dekker, Inc., New York, 1996.

[25] Ali M.A., Tatsumi T. & Masuda T., *"Development of heavy oil hydrocracking catalyst using amorphous silica-alumina and zeolites as catalyst supports"*, Applied Catalysis A: General, Vol. 233, No. 1-2, pp. 77-90, 2002.