

# Hydrocracking Lumped Kinetic Model with Catalyst Deactivation in Arak Refinery Hydrocracker Unit

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## Abstract

A kinetic model of a fixed bed tubular reactor incorporating catalyst deactivation was developed for the ISOMAX unit of Arak refinery. The kinetic parameters for the hydrocracking reactions over the commercial catalyst were determined using initial activity plant data i.e. when the catalyst is fresh. Catalyst deactivation was then taken into account by means of deactivation function based on plant data. The catalyst deactivation function is defined in terms of normalized time (BPP) of operation. Effect of catalyst deactivation on the product yield has been investigated. Steady state material and energy balances were then developed for an extended four lumped kinetic network. To determine the effect of reaction types on the rate, we calculate frequency factor for each individual bed with constant activation energy and heat of reaction. Furthermore, we calculate the frequency factor for individual beds, for the first one to estimate the rate of reactions in the different beds. The results show that the reactions in the first and second bed are faster than those in the 3<sup>rd</sup> and 4<sup>th</sup> beds. The comparison between model conversion and experimental conversion of the unit indicates that the model is capable of predicting product yield with an error of less than 5%.

**Key words:** Lumped Kinetic Model, Catalyst Deactivation Function, Normalized Time, Production Yield, Frequency Factor

## Introduction

Hydrocracking is one of the most versatile of all petroleum refining processes. It usually converts a heavy, low quality feedstock into lighter, valuable transportation fuels, contributing significantly to the overall profitability of the refinery.

Hydrocracking is usually carried out in two stages. The first stage decomposes sulfur and nitrogen containing compounds and hydrogenates the aromatics. The liquid fraction from the first stage is hydroisomerized and hydrocracked in the second stage.

For the purposes of reactor design, process optimization, and catalyst selection, it is necessary to develop kinetic models, which can accurately predict the product distributions under hydrocracking conditions. On the other hand, for hydrocarbon mixtures, the development of such kinetic models is a challenging task due to the presence of a great variety of structures. Therefore, it is difficult to study kinetics for every component in

this system. Catalytic hydrocracking is more complicated than non-catalytic hydrocracking. An alternative approach is to consider the mixture in terms of selected lumps, which can be specified in terms of such properties as boiling ranges, molecular weight ranges, carbon numbers, solubility class fractions, and other structural characteristics. Various discrete lumping schemes have been applied for kinetic modeling of complex reactions of hydrocarbon mixtures [1-7] involving series and parallel reactions. Axial dispersion model [7] and continuous lumping [8,9] have also been used for kinetic modeling of catalytic cracking and hydrocracking of hydrocarbon mixtures. In the discrete lumping approach, the individual components in the reaction mixture are divided into discrete pseudocompounds (lumps) based on the true boiling point (TBP), carbon number (CN), and/or molecular weight (MW). Instead of keeping track of individual molecules, the molecules with a similar CN, MW, or TBP group are treated as cracking with a

particular rate constant to give predefined lower lumps.

Since the catalyst activity decreases over the operation, it can affect the product yield distribution so the kinetic model must consist of the catalyst activity.

A good commercial catalyst is known through three characteristics namely activity, selectivity and life. The Catalysts have large concentrations of active sites and a layer of reactant material adsorbed on the active sites. The performance of catalysts decreases with time due to various reasons such as coke formation, sintering, pore plugging and poisoning. Thus, to maintain constant product yields, the catalytic activity must be kept constant.

In studies of mathematical models of chemical reactors with catalyst deactivation, much attention has been paid to question of how reactor performance varies with catalyst deactivation. Several kinds of reactor models have been derived incorporating a deactivation function [10,11]. For environmental friendliness, higher product yields and longer catalyst life industrial processes are increasingly required to operate under optimum conditions. For this purpose, process variables such as reactor temperature and feed composition under deactivating conditions are manipulated.

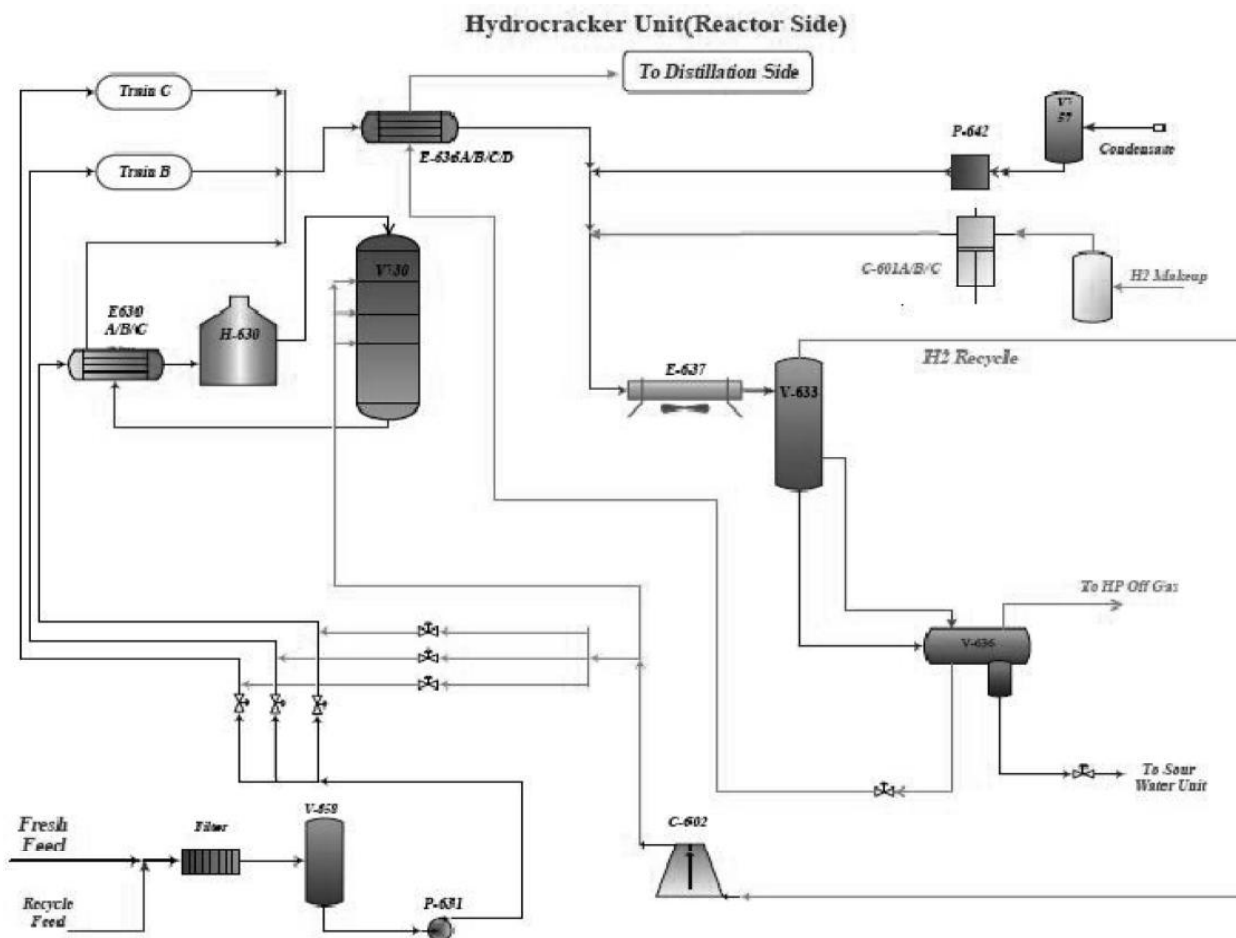
**Industrial Procedure**

A vacuum distillate fraction (B.R. 317-502 °C) was used as the Isofeed (table 1). The catalyst was a commercial

**Table 1-** Isofeed properties

Distillation range, °C	310-509
Specific Gravity	0.91
Total Fe, ppm	2.0
Total sulfure content, wt%	1.54
Total nitrogen content, ppm	935.0
Simulated distillation, °C	
IBP	311.0
5%	354.0
10%	372.0
30%	404.0
50%	426.0
70%	449.0
90%	478.0
95%	491.0
FBP	508.0

catalyst. The hydrocracker unit consisted of 3 parallels tubular fixed bed reactors of 2400 mm internal diameter, 2600 mm external diameter and 28.7 m height. Each reactor had four beds and as reactions are highly exothermic, there were 3 quench points in each reactor to cool the reaction mixtures. The schematic process flow diagram is shown in fig. 1.



**Figure 1-** Schematic representation of the Isomax unit

The flow of oil is once through and vertically downward. The main reactions in the first bed of each reactor are treating reactions in which sulfur, nitrogen and oxygen compounds are decomposed to hydrogen sulfide, ammonia, and water, while aromatics and olefins, if any, are hydrogenated. In other three beds, the hydroisomerization and hydrocracking are the main reactions.

### Catalyst deactivation model

During the process of hydrocracking, the activity of catalyst decreases as the reactions take place. The factors resulting in the catalyst deactivation include coking, poisoning, sintering and so forth. Among all these factors, coking is the most significant one.

Based on the activity function for the Arak refinery hydrocracker unit, catalyst deactivation affects the reaction conversion as follows [12]:

$$-r_A = K \cdot C_A^n \cdot a = K_0 e^{-E/RT} \cdot C_A^n \cdot a \quad (1)$$

$$a = e^{\left[ -E/R \left( \frac{1}{T_0} - \frac{1}{T} \right) \right]} \quad (2)$$

$$a = 0.76897246 + (-0.00424660)x + (1.59082020)/x^2 \quad (3)$$

Where  $a$  is the catalyst activity function,  $T_0$  is the weighted average bed temperature (WABT) when the catalyst is fresh ( $a = 1.0$ ), after the time of  $t$  temperature is  $T$  and  $x$  is the normalized time (BPP).

### Governing equations

The conventional hydrocracker is a tubular plug flow reactor that is a cylinder containing four fixed beds of catalyst through which a mixture of gas and liquid flows downward. The fluid pattern is plug flow. To simplify the model, the following assumptions are taken into account.

1. Concentration and temperature are uniform throughout a cross section so there are not any interphase and intraparticle concentrations or temperature gradients.
2. The heat capacities of liquid and gas and the heats of reactions are constant.
3. The pores of the catalyst pellets are filled with liquid so that reaction takes place at or near the surface of the pellets.
4. The liquid and vapor phases are in equilibrium and the compositions can be calculated using flash vaporization. The vapor behaves as an ideal gas.

With the above assumptions, the steady state mass and heat balances with catalyst deactivation function ( $a$ ) can be described as bellow [13].

Crackable hydrocarbons mass balance:

$$G_t \frac{\partial C_i}{\partial x} = -\rho_i k_i a C_i \quad (4)$$

Hydrogen mass balance:

$$G_t \frac{\partial C_H}{\partial x} = -\alpha \rho_i k_i a C_i \quad (5)$$

Heat and energy equation:

$$G_t (c_{p,l} C_H + c_p C_T) \frac{\partial T}{\partial x} = -(\Delta H) \rho_i k_i a C_i \quad (6)$$

Where  $G_t$  is the total mass velocity (liquid and gas),

$C_i$  and  $C_H$  are the weight fractions of the crackable hydrocarbons and hydrogen, respectively;  $C_T$  is the concentration of total hydrocarbons and  $c_{p,c}$  is the specific heat of hydrocarbons.  $\alpha$  is the hydrogen consumption coefficient that should be estimated.

Boundary conditions at the bed entrance:

$$\begin{aligned} C_i &= C_{ie}(t) \\ C_H &= C_{He}(t) \\ T &= T_e(t), x = 0, t > 0 \end{aligned} \quad (7)$$

For a fixed bed reactor with no axial mixing and with zero initial concentrations, no change in concentration and temperature will occur at any point before the entrance flow has had time to arrive that point. This time is equal to  $x/u$ , so the initial condition in the bed must be defined at  $t = x/u$ .

$$\begin{aligned} C_i &= 0.0 \\ C_H &= 0.0 \\ T &= T_i(x), t = x/u \end{aligned} \quad (8)$$

It is also necessary to define the conditions of fluid at the location of quenching:

$$\begin{aligned} G_{iq} &= G_t + G_{gq} + G_{lq} \\ C_i &= C_{iq}(t) \\ C_H &= C_{Hq}(t) \\ T &= T_q(t); x = x_q; t \geq t_q \end{aligned} \quad (9)$$

Where  $G_{gq}$  and  $G_{lq}$  are the amounts of gas and liquid quenching mixtures,  $G_{iq}$  is the total mass flow rate after the mixing and  $C_{iq}$ ,  $C_{Hq}$  and  $T_q$  are the concentrations of crackable hydrocarbons and hydrogen, and the temperature after the mixing, respectively.

### Kinetic model

The kinetic model should ideally take into account all reactions that the components in the feedstock undergo. However, in reality, it is difficult to do so due to the complex chemistry of hydrocarbons in the feed and reaction mixture, numerous components and reactions, and lack of kinetic data.

The result of present study confirms the finding of Qader et al. [14], that the overall rates of vacuum distillate hydrocracking, desulfurization and denitrogenation can be expressed by a simple first order kinetic equation [15].

$$\ln \frac{x_i}{x_f} = K \frac{1}{LHSV} \quad (7)$$

Where  $x_p$  is the initial concentration, wt%;  $x_f$  the final concentration, wt%;  $LHSV$ , liquid hourly space velocity, vol. of liquid feed per hour per vol. of catalyst; and  $K$ , reaction rate constant.

$$\frac{-d(\text{vacuum distillate})}{dt} = K_v(\text{vacuum distillate}) \quad (5)$$

$$\frac{-d(\text{sulfur})}{dt} = K_s(\text{sulfur}) \quad (6)$$

$$\frac{-d(\text{nitrogen})}{dt} = K_n(\text{nitrogen}) \quad (7)$$

Where  $K_v$ ,  $K_s$  and  $K_n$  are the rate constants for vacuum distillate hydrocracking, desulfurization and denitrogenation, respectively,  $t$  is the residence time. and  $k$  is expressed by the Arrhenius equation:

$$k = k_0 \exp(-E / RT) \quad (9)$$

Where  $k_0$  is the frequency factor ( $\text{hr}^{-1}$ ) and  $E$  is the activation energy (kJ/kmol).

The kinetic model parameters were determined utilizing an optimization code developed in Matlab version 7.8.0. The objective function used was to seek the minimum root of sum of the squared error between the model predictions and the measured values in the plant.

Objective function = Minimize

$$\sqrt{(\text{experimental conversion} - \text{theoretical conversion})^2 + (T_{\text{exp}} - T_{\text{model}})^2}$$

Where  $T_{\text{exp}}$  and  $T_{\text{model}}$  are experimental bed and model temperatures, respectively.

## Results and discussion

Our reactor has four catalytic beds in which many different reactions are taking place. To describe the effect of the types of reactions that take place in each bed on the rate of reactions, we calculate individual frequency factor for each catalytic bed for hydrocracking, desulfurization and denitrogenation reactions. With this assumption, the  $E/R$  and  $\Delta H$  are constant for every one of reactions in the hole of reactor.

For estimation of these 18 kinetic parameters ( $4 k_{0,v}$ ,  $4 k_{0,s}$ ,  $4 k_{0,n}$  in 4 beds and 6  $E/R$  and  $\Delta H$  for three kinds of reactions), we use an optimization code. The result of this calculation is shown in tables 2 and 3.

Table 2 shows that the reactions in the first bed are more rapid than those in the three other beds. Since approximately 90% of reactions in the first bed are hydrotreating reactions, the rate of these reactions is higher than those of other hydrocracking reactions. Table 3 shows the activation energy and heat of reaction for three classes of reactions.

**Table 2-** Kinetic parameters of model for each bed.

	Bed 1	Bed 2	Bed 3	Bed 4
$k_{0,v}$ ( $\text{hr}^{-1}$ )	$9.272 \times 10^{15}$	$5.53 \times 10^{15}$	$4.37 \times 10^{15}$	$4.3852 \times 10^{15}$
$k_{0,s}$ ( $\text{hr}^{-1}$ )	$1.719 \times 10^{10}$	$8.32 \times 10^9$	0.0001	0.0000
$k_{0,n}$ ( $\text{hr}^{-1}$ )	$1.982 \times 10^{12}$	$7.943 \times 10^{11}$	0.00045	0.0000

**Table 3-** Activation energy and heat of reaction for hydrocracking, desulphurization and denitrogenation

	Hydrocracking reactions	Desulphurization reactions	Denitrogenation reactions
$E/R$ (k)	23333.0	13410.0	16520.0
$\Delta H$ (kJ/kg)	130	60	70

Table 4 shows the model results in prediction of hydrogen consumption in every bed of reactor.

**Table 4-** Hydrogen consumption in every bed

Reactor	Hydrogen consumption (kg/m <sup>2</sup> .hr)
Bed 1	374.5191
Bed 2	121.4175
Bed 3	292.5986
Bed 4	262.5144
Total Hydrogen cons.	1051.05
Total input Hydrogen	1321.776

Fig. 2 shows the change of crackable hydrocarbon concentrations in the bed length based on model predictions. As it can be seen from fig. 2, the concentration change in the 1<sup>st</sup> bed is less than that in other beds because the main reactions in the 1<sup>st</sup> bed are hydrotreating and not hydrocracking.

Fig. 3 shows the frequency factor for hydrocracking reactions vs. reactor length. As we can observe from fig. 3, the hydrocracking reactions take place in all 4 beds, but the rate of hydrocracking reactions decrease through the reactor length with a low slope, and the reactions in the first and second beds are faster than those in the 3<sup>rd</sup> and 4<sup>th</sup> beds.

Fig. 4 shows the frequency factor for the desulfurization reactions in the bed length. As we can see from fig. 3, the main part of desulfurization reactions take place in the first bed and approximately no desulfurization takes place in the 3<sup>rd</sup> and 4<sup>th</sup> beds.

Fig. 5 shows the frequency factor of denitrogenation reactions in the bed length. Like desulfurization reactions, approximately all of denitrogenation reactions take place in the first bed, so we can say most reactions in the first beds are treating reactions. We can also see from figs. 4 and 5 that in the first bed the denitrogenation reactions are faster than desulfurization reactions.

Fig. 6 presented the Arrhenius plot of first order kinetic model for hydrocracking of heavy gas oil feed in the hole of reactor.

Fig. 7 shows Arrhenius plots for hydrocracking, desulfurization, and denitrogenation reactions in the first bed of reactor. The results indicate that denitrogenation and desulfurization take place faster than the hydrocracking in the first bed, and the activation energy for hydrocracking is much higher than desulfurization and denitrogenation. Also, the activation energy of desulfurization is higher than that of the denitrogenation.

This model can also predict the inlet and outlet temperatures of each catalytic bed. Figure 8 shows the model temperature predictions that are compared with industrial data. This figure shows the model ability to predict the temperature of catalytic beds.

Figure 9 is the final figure that shows the comparison between model predictions and plant data. This comparison shows an error of less than 5%, so the model is capable of predicting product yield distribution accurately in all of unit operation condition.

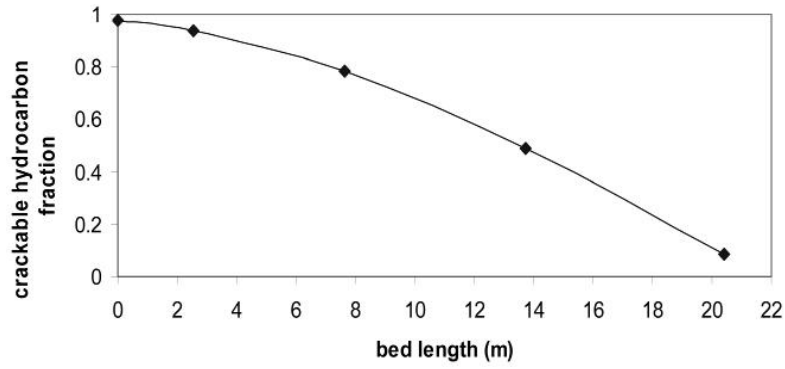


Figure 2- Concentration change of crackable hydrocarbons in the reactor length

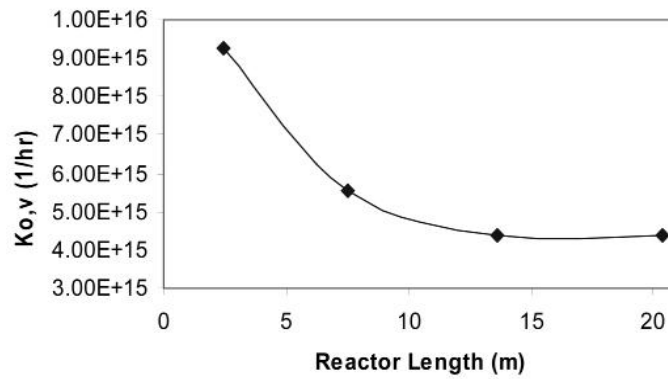


Figure 3- Frequency factor for hydrocracking reactions vs. reactor length

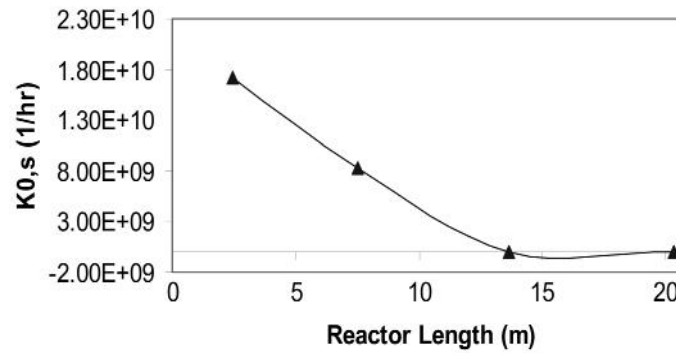


Figure 4- Frequency factor for desulfurization reactions vs. reactor length

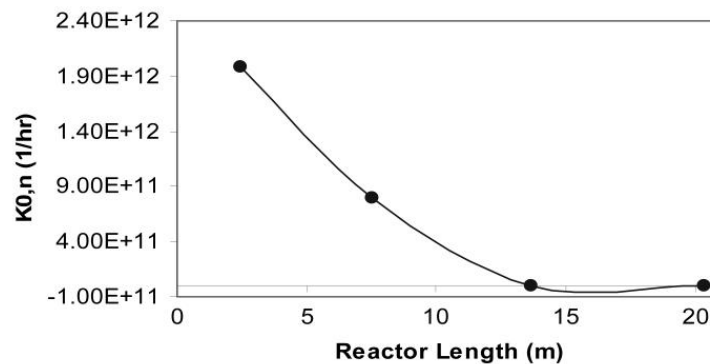


Figure 5- Frequency factor for denitrogenation reactions vs. reactor length

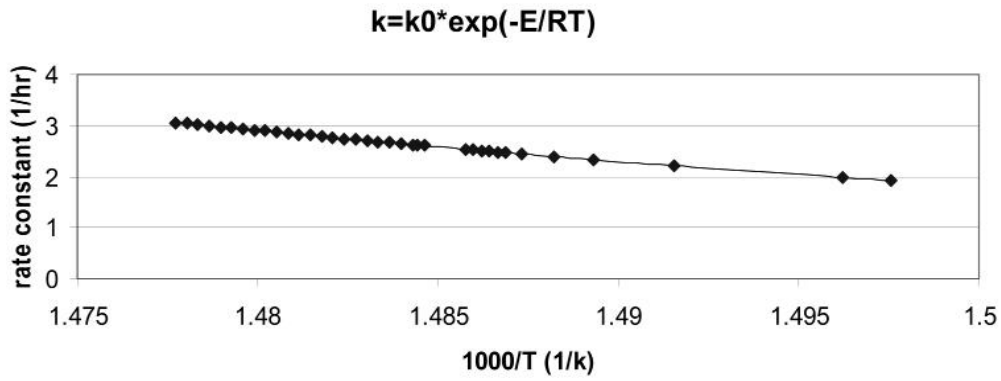


Figure 6- Arrhenius plot of kinetic hydrocracking (first order)

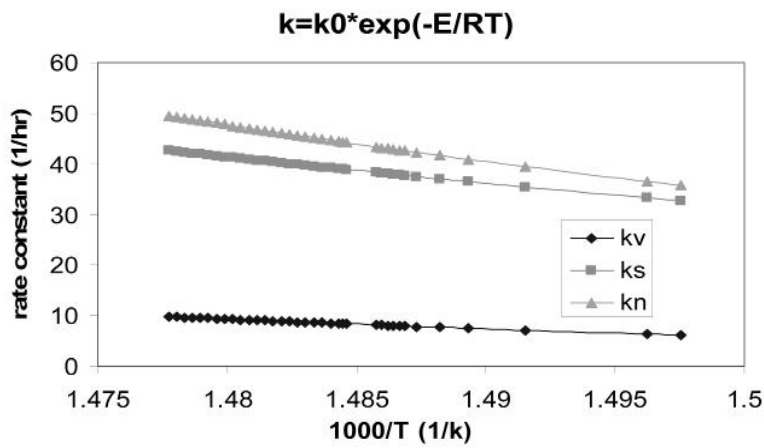


Figure 7- Arrhenius plots of kinetic hydrocracking for hydrocracking, desulphurization and denitrogenation reactions

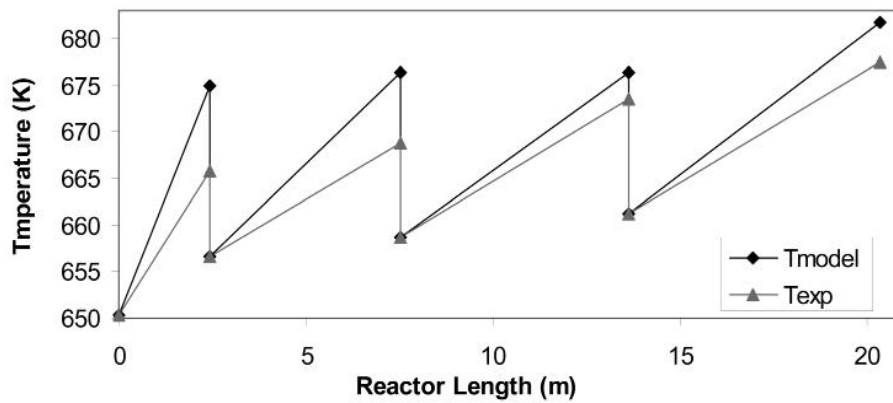


Figure 8- Model predictions and industrial data of inlet and outlet bed temperatures vs. reactor length

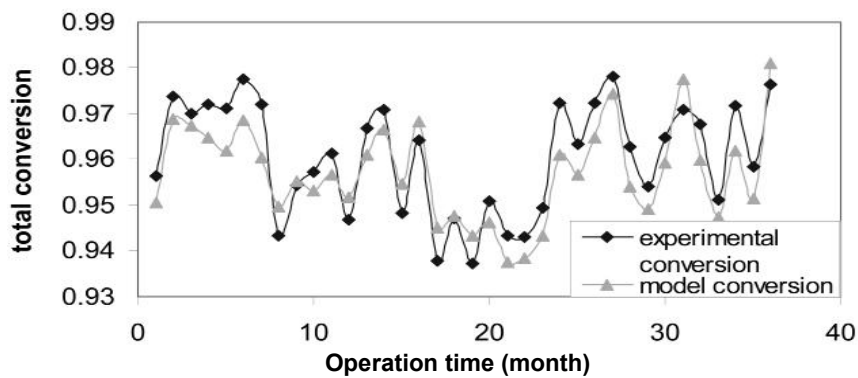


Figure 9- Comparison between model predictions with experimental data

## Conclusion

The main issues that hydrocracker units of refineries have to deal with in the daily operation of the plant are product yield and quality, reactor temperature, and the make up hydrogen requirement. Thus, a good kinetic model must be able to predict the product distribution and temperature accurately. The comparison between model predictions and plant data shows that this model is capable of predicting these quantities satisfactorily.

Since the kinetic parameters of this model are estimated when the catalyst is fresh, the conversion in the other month that the catalyst activity is less than one, should be calculated using activity function (equation 2). The kinetic parameters are then calculated for hydrocracking, desulfurization, and denitrogenation reactions in individual beds. The results show that most reactions in the first bed are hydrotreating (desulfurization and denitrogenation) (fig. 3-5). Also, in the first bed the rate of denitrogenation and desulfurization are more than hydrocracking reactions (fig. 7). Figure 6 shows the Arrhenius plot of first order kinetic model for hydrocracking. The model can also predict the change of concentration of crackable hydrocarbons, inlet and outlet temperatures of beds, and hydrogen consumption in the every catalytic bed, accurately (figures 2 and 8 and table 4). In addition, the final figure shows the accuracy of model predictions with an error of less than 5%.

## References

- [1] Weekman V.W.Jr., "Lumps, models and kinetics in practice", Chem. Eng. Prog. Monogr. Ser. 75, pp. 3-29, 1979.
- [2] Weekman V.W.Jr. and Nace D.M., "Kinetics of Catalytic Cracking Selectivity in Fixed, Moving and Fluid Bed Reactors", AIChE J., 16 (3), pp. 397-404, 1970.
- [3] Koseoglu R.O. and Philips C.R., "Kinetic model for the noncatalytic hydrocracking of Athabasca bitumen", Fuel, 67, pp. 906-915, 1988.
- [4] Ramdoss P.K. and Tarrer R.C., "High temperature liquification of waste water", Fue. 77, pp. 293-299, 1998.
- [5] Liguras D.K. and Allen D.T., "Structural models for catalytic cracking (2) Reactions of simulated oil mixtures", Ind. Eng. Chem. Res. 28, pp. 665-673, 1989.
- [6] Zarkesh J., Akbarnejad M., Badakhshan A. and Khorasheh F., "Kinetic study on Iranian paraffin hydrocracking", Petro. and Coal. 41, pp. 77, 1999.
- [7] Khorasheh F., Zainali H., Chan E.C. and Gray M.R., "Kinetic modeling of bitumen hydrocracking reactions", Petro. and Coal. 43, pp. 208-218, 2001.
- [8] Cicarelli P., Astarita G. and Gallifuoco A., "Continuous Kinetics Lumping of Catalytic Cracking Processes", AIChE J. 38, pp. 1038-1044, 1992.
- [9] Laxminarasimhan C.S., Verma R.P. and Ramachandran P.A., "Continuous Lumping Model for Simulation of Hydrocracking", AIChE J. 42, pp. 2645-2653, 1996.
- [10] Froment G.F. and Bischoff K.B., "Chemical Reactor analysis and Design", pp. 284, Willy, New York, 1979.
- [11] Hughes R., "Deactivation of Catalysts," 184, Academic Press, London, 1984.
- [12] Moghadassi A.R., Amini N., Fadavi O. and Bahmani M., "Investigation and parametric study of hydrocracker catalyst activity in Iran-Arak Shazand Refinery Company", in "The 6<sup>th</sup> Int. Chem. Eng. Cong. and exhibit.," Kish Island, Iran, November 16-20, 2009.
- [13] Yan T.Y., "Dynamics of a trickle bed hydrocracker with a quenching system", Can. J. Chem. Eng. 58, pp. 259, 1980.
- [14] Qader S.A. and Hill G.R., "Coal liquefaction in a slurry system", Ind. Eng. Chem. Process Des. DeV.8, pp. 98-105, 1969.
- [15] El-Kady F.Y., "Hydrocracking of Vacuum Distillate Fraction over Bifunctional Molybdenum Nickel/Silica-Alumina Catalyst", Ind. J. of Tech. 17, pp. 176-183, 1979.
- [16] Wojciechowski B.W., "A Theoretical treatment of catalyst decay", Can. J. Chem. Eng. 46, pp. 48-52, 1968.