Kinetic Modeling of Hydrocracking Process

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***Abstract*— An investigation for achieving the kinetic of hydrocracking process with HC-201 catalyst, that is used in isomax unit of Tehran refinery, was carried out in a tubular reactor at temperatures of 380 and 420°C, pressures of 115 and 150 bar and space velocity of 1.5 hr-1 . In order to design and optimize hydrocracking process, a model is needed to express the effect of key features on the overall reaction rate. In this paper, based on the experimental results, a suitable kinetic model for the catalytic hydrocracking process was achieved in operating condition. There is a good agreement between theoretical results and experimental data.**

Keywords—Modeling; Hydrocracking; Orthogonal Collocation; Kinetic;

I. INTRODUCTION

In non-homogeneous multi-phase reactors, the overall reaction rate is affected by different parameters including flow pattern, the parameters of mixing, heat and mass transfer, catalytic properties and intrinsic speed of reaction. The design of a new reactor requires a lot of laboratory works and experimental investigations required to design a new reactor. Firstly, the reactor performance is reviewed in pilot-plant and then the data will be used to develop the industrial units. The study in the field of reactors was made by some researchers such as Satterfield (1988), Crine (1980), Holub (1992) and Lopes (2009) [1-4]. They presented relations for hydrodynamic, mass transfer and heat transfer of those reactors.From the point of importance, hydrocracking is the second process in the petroleum industry. The feed of this unit is usually in the range of vacuum gas oil (VGO) to residue.

The process includes cracking of heavy petroleum fractions in presence of hydrogen. This unit is mostly used for increasing productions in the middle of distillate, gas and gasoline. According to the importance of this process in the petroleum industries, software and mathematical model is needed to examine the effect of operating parameters on the efficiency of this process [5]. The process is used for converting heavy components such as vacuum gas oil into lighter products such as gasoline, diesel and natural gas. The aim of most of hydrocracking units is to produce more gasoline. Isomax unit of Tehran refinery was launched by Shervon Company about 44 years ago. Reactions of isomax unit take place under temperatures between 380 ° C and 440° C and pressure up to 2668 psia. The reactions are done in a trickle bed reactor, which also includes hydrodynamic effects. When the percentage of nitrogen composition of the feed is high, using a two-step system is preferred. The catalysts of hydrocracking process basically involve metal compounds precipitated on the support. These catalysts are used for two purposes, one for reinforcement of cracking reactions (silica, alumina) and the other for reinforcement of hydrogenation reactions (noble metals, non-noble metals Vlb and Vlll groups).

Cracking of petroleum fractions include complex chemical reactions such as hydrogenation, dehydrogenation, isomerization, hydrogen transfer, disproportionate molecular share, saturation of loops, de-looping and de-alkylation.

Non-isothermal treatment of trickle-bed reactors leads to the evaporation of the liquid phase and formation of hot and dry areas on the catalyst which will result in a complex behavior and could be very important in the modeling of these reactors.

Complexity of hydrodynamic and wettability of the catalyst depends on the geometry, the kind of fluid and the catalyst. So, even if the intrinsic rate of reaction, thermal and mass properties of all phases is well established, it may not be successful to predict the behavior of the bed [6,7]. In addition, the scale-up of reactor can also be unreliable because the change in geometric specification of the bed is inevitable. In addition to the above issues, when pores of the particles are considered symmetrical and the film thickness around it is assumed steady, it is not true in practice.

Modeling of complex kinetic of hydrocracking in terms of its importance in the petroleum industry seems necessary. Predicting the efficiency of desirable and undesirable products in various operating conditions is needed to optimize process and select the type of catalyst. The ideal kinetic model includes different reactions and different kinetics for all components of the reaction. Therefore, such a model is difficult to find in practice. In this study, it is attempted to model the effect of the kinetic parameters on the hydrocracking process in order to overcome these problems. Various problems can be solved by the methods of [10] and [11].

II. HYDROCRACKING PROCESS

To model hydrocracking process, a pseudo component model is provided which in this model mixture of petroleum fractions is considered as a single component. Hydrocracking process can be assumed to be adiabatic, because the produced heat is more to compare with the wasted heat. Hydrocracking involves exothermic reactions that the heat of reaction depends on the type of feed and reaction products.

Catalysts of hydrocracking process are bi-functional, so there are two active sites (acidic and metallic). Pore structure, the location of the active sites of the catalyst and the size of the metal crystals are parameters which play an important role in the quality and efficiency of the products [8,9].

Due to the sensitivity of hydrocracking catalysts to the compounds such as nitrogen, sulfur and some metals, first the feed enters into the filtering stage. In this section, nitrogenated, sulfurated and oxygenated compounds are reduced as much as possible. Also, because water is harmful to the catalyst, first the feed passes through a silica gel. Several parameters and functions are effective on the hydrocracking reactions and its industrial design. Perhaps the most important parameter is the gas-liquid ratio which has major impact on system efficiency and catalyst properties. Several parameters affected by the ratio of gas to liquid are given as follows:

Catalyst life-time; partial pressure of hydrogen; the product distribution; flow regime; liquid accumulation; catalyst wetting efficiency; gas and liquid film resistance. In general, the reactions that are carried out in the isomax reactor can be categorized as follows:

A) cracking and isomerization in the presence of catalyst; B) denitrogenation; C) desulfurization; D) olefins hydrogenation; E) aromatics saturation.

Hydrocracking is a mixture of complex reactions and kinetics of these reactions are strongly dependent on the type of feedstock, catalyst and operating conditions. In addition, the kinetic data related to hydrocracking reactor with a specific feed cannot be generalized to other reactors and feeds. A good model should have sufficient parameters to satisfy the intricacies of kinetic.

III. EXPERIMENTS

Used tubular reactor in the pilot scale is with inner diameter of 0.75 inches and a height of 40 inches and has a temperature, pressure, gas and liquid flow rate control system. 10 centimeters of the beginning of the reactor is filled with the ceramic spherical beads and then up to 100 cc of catalyst. The feed is heated and then is pumped to the beginning of the reactor. All feed transport paths are insulated. The body of the reactor, fitted with heat exchangers and thermocouples are for stabilizing the temperature. Used hydrogen with maximum pressure of 2300 pounds per square inch is provided from cylinders. The maximum pressure created by the compressor is about 180 bars. A schematic diagram of the pilot is shown in figure 1.

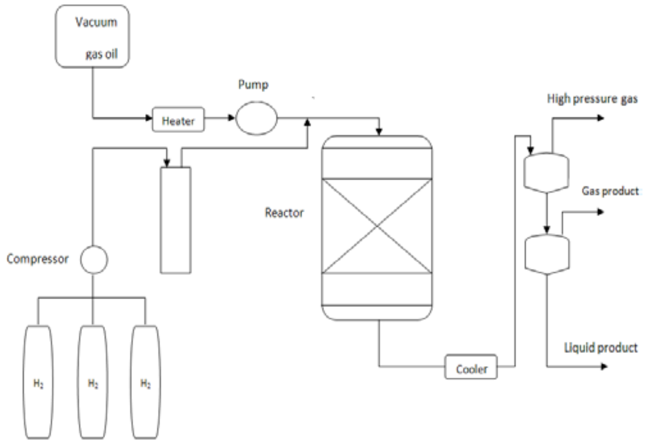

Fig. 1. A schematic diagram of the pilot

IV. RESULTS AND DISCUSSION

Since the process productions are classified according to the boiling point, the following petroleum fractions used in isomax unit are assumed (table 1).

Table 1. Petroleum fractions used in isomax unit

Type of fraction	Number of Carbon	Boiling point (^{o}C)
light gas	C_1-C_5	-----
naphtha	C_6-C_9	IBP-141
kerosene	C_9-C_{15}	141-260
diesel	C_{15}-C_{23}	260-360
Residue	C_{23}^{+}	360^{+}

TBP feed curve shows that it is almost possible to consider feed as a residue. On the other hand, the boiling point temperature of the recycled liquid of isomax unit is at the boiling point temperature range of the residue. To make the use of the model easier, the reaction rate constant and the liquid flow rate are calculated in standard conditions. To select the appropriate model, first it should be assumed that the feed converts into diesel, kerosene, naphtha and gas in one stage. The data obtained from the pilot reactor is fitted for this model.

$$F \rightarrow V_1 D + V_2 K + V_3 N + V_4 G \qquad (1)$$

Where

F: feed; D:diesel: N: naphtha; K: kerosene; G: gas.

Increasing the residence time, it is observed that the stoichiometric coefficient of V_1 decreases and stoichiometric coefficients of V_2 and V_3 increase. This indicates that in addition to diesel production, the consumption of it also occurs and kerosene and naphtha can be obtained from other reaction. By analyzing the feed and products concentration data, the following model was achieved that by comparing with industrial data, its results are acceptable.

$$F \xrightarrow{K_1} V_1 D + V_2 K + V_3 N + V_4 G \qquad (2)$$

$$D \xrightarrow{K_2} V_5 K + V_6 N \qquad (3)$$

The initial conditions of the above model are as follows:

$F = 1,\ D = 0,\ K = 0,\ N = 0,\ G = 0$ (4)

Products analysis shows that residue fraction is not completely intact. Thus the residue conversion does not follow the first order kinetic. By analyzing the data obtained from the pilot reactor, the second order kinetic was considered for the residue. Differential equations of the above model are as follows:

$dF/dt = - K_1 \cdot F^2$ (5)

$dD/dt = K_1.V_1.F^2 - K_2.D$ (6)

$dK/dt = K_1.F^2.V_2 + K_2.V_5.D$ (7)

$dN/dt = K_1.V_3.F^2 + K_2.V_6.D$ (8)

$dG/dt=K_1.V_4.F^2$ (9)

By drawing the function of 1/F-1 versus $LHSV^{-1}$, the reaction rate constant of K_1 is obtained. The relation between reaction rate constant with temperature is obtained according to Arrhenius equation.

$K = K_0 \ EXP(-E/RT)$ (10)

For two temperatures 400 and 430 ° C, the reaction rate constant of K_1 was calculated according to the equation 5. Then, by using equation 10, the relationship between the reaction rate constant of K_1 and temperature is obtained as follows:

$K_1 = 5.10^{17} \ . \ EXP(-27261/T) \quad [hr^{-1}]$ (11)

T:temperature

The values of K_2, V_1 are obtained according to the above results as follows:

$V_1 = 0.495$; $K_2 = 1.996.10^{22}. EXP[-36332/T]$ (12)

By analyzing the efficiency of kerosene and naphtha, it is observed that the ratio of these two products is almost constant.

Efficiency of kerosene / efficiency of naphtha = 0.536. By drawing the efficiency of gas versus the residue consumed gas, the stoichiometric coefficient of V_4 is obtained. According to the conversion of the residue and stoichiometric coefficient of V_1, the total amount of diesel produced. The stoichiometric coefficients are available in Table 2.

Table 2. Stoichiometric coefficients based on two-step model

V_1	V_2	V_3	V_4	V_5	V_6
0.495	0.273	0.147	0.086	0.651	0.349

The efficiencies obtained from pilot reactor are available in the following figures:

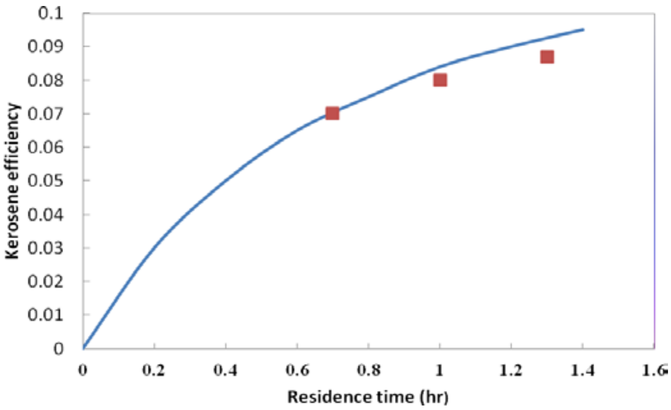

Fig. 2. Experimental data(points) versus theoretical model(curve)for kerosene at temperature of 400 ºC.

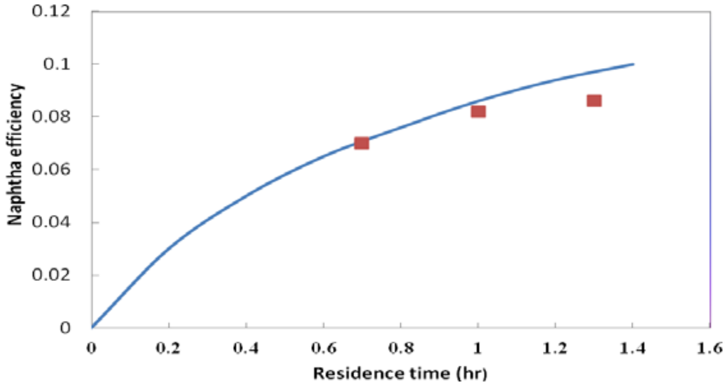

Fig. 3. Experimental data(points) versus theoretical model(curve) for naphtha at temperature of 400 ºC.

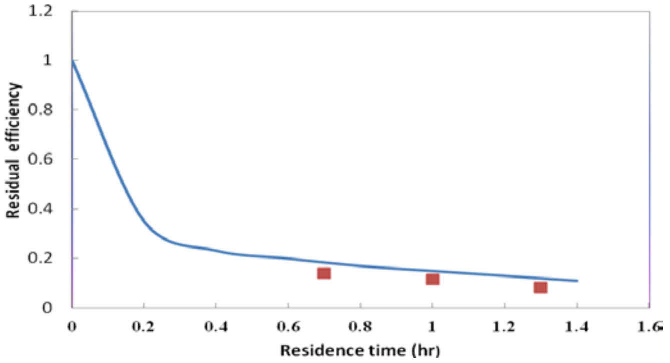

Fig. 4. Experimental data(points) versus theoretical model (line)for un-reacted feed at temperature of 430 ºC.

V. CONCLUSION

The primary study of operating parameter’s effect on hydrocracking process should be analyzed in pilot-scale reactor, due to high risk of industrial hydrocracker reactors. Also, modeling will reduce the operating costs. It was shown that under operating conditions, model estimates matched the plant data closely. The increase in reactor temperature will increase the percentage of light products, but the life of the catalyst will decrease dramatically. Moreover, temperature sensitivity was introduced to the model by estimating the parameters using operating data at two different temperatures. For converting the pilot data to industrial one, correction factor should be used that is obtained by comparing results of pilot and industrial data. According to the catalyst used and the operating conditions, feed conversion is of the second order reaction and diesel conversion is of the first order reaction. The effect of pressure on the conversion rate at the pressure of higher than 100 bar is negligible, but in less than 100 bar, the amount of feed conversion rate increases.

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