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Lumping kinetic model and simulation of catalytic naphtha reforming process

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ABSTRACT

One of the most important and critical processes in petroleum refineries is Catalytic Reforming in which high octane gasoline and valuable aromatics, such as Benzene, Toluene and Xylene (B.T.X.) are produced. According to the importance of this process for producing gasoline, simulation of catalytic reforming process to optimize and predict of operational parameters, such as octane number, Liquid Hour Space Velocity (LHSV), Input temperature to reactors, yield and catalyst life are vital. In this paper, one of the famous kinetic models mentioned for this unit is reconsidered. The accuracy of the model is compared with the actual data from catalytic naphtha reforming process of Tehran refinery. The results show that this model has relatively acceptable ability to predict octane number, output temperature of reactors and yield.

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KEYWORDS

Catalytic Naphtha Reforming;
Modeling;
Simulation.

INTRODUCTION

The Catalytic Reforming Process is one of the most operations in each of petroleum refinery for producing gasoline with high octane number.

In this process, products with different octane number are produced unlike the production of certain octane number in other processes, such as catalytic cracking, alkylation and isomerization.

Antiknock property of gasoline depends on the nature of hydrocarbons involved in fuel. This property can be improved by increasing the octane number of fuel in catalytic reforming process.

Industrial catalysts used in recent catalytic reforming units are consisted of Gama Alumina support and some metals, such as Platinum, Rhenium, Germanium, and Iridium, less than one weight percent, and additive,

such as chlorine to increase isomerization reactions.

Usually, catalytic reforming process feed is Heavy Straight Run Naphtha (H.S.R.G) including four hydrocarbon groups: Paraffins, Olefins, Naphthenes, and Aromatics (P.O.N.A) with carbon number between 5 to 10.

The main reactions are taken place in the catalytic reforming process as the following:

1- Dehydrocyclization, 2- Hydrocracking, 3- Paraffin isomerization, 4- Naphthene isomerization 5- Dehydrogenation (Aromatization)

A typical of these group reactions is shown in Figure 1.

Some of these reactions are desired because of increasing octane number of gasoline and some of them are undesired because of decreasing it. For paraffins, increment of octane number is the result of increasing

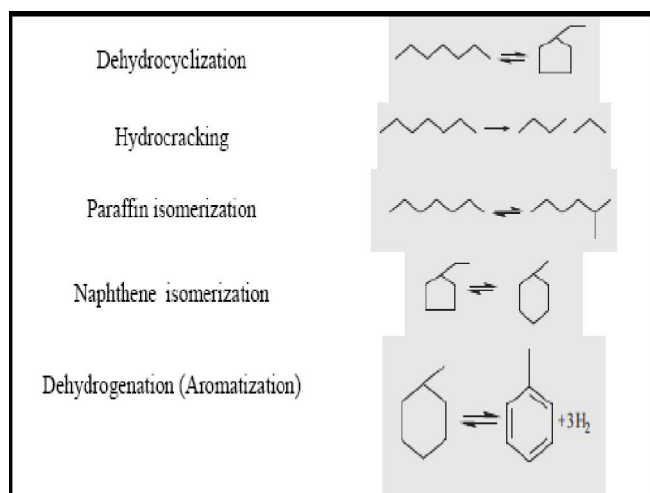


Figure 1 : Main reactions in the Catalytic Reforming Process

the number of branches, such as cyclization and aromatization. Therefore, normal paraffins conversion to isoparaffins, naphthenes, and aromatics result in increasing octane number.

The catalytic reforming process discussed in this paper, the Semi-Regenerative type (Figure 2) includes three reactors. Due to the endothermic nature of most catalytic reforming reactions, there is a furnace (heater) at the inlet of each reactor to heat up the feed to the required temperature.

A separator after the reactors recirculates light gases, such as hydrogen and methane to the beginning of the process by a recycle compressor. Liquid product from the separator enters the stabilizer tower for stabilizing vapor pressure (RVP) of gasoline and bottom product of the tower will be sent to gasoline pool.

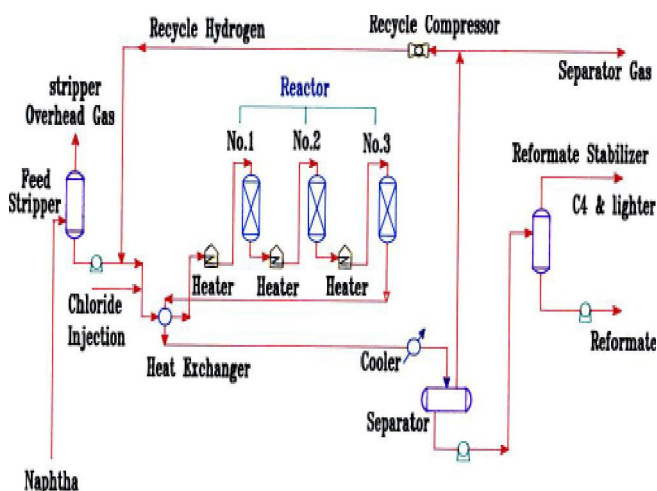


Figure 2 : Catalytic Reforming Flowchart (Semi-Regenerative)

Normally, catalytic reforming process includes of three or four adiabatic reactors with a furnace before each of them. Initially, the feed will be mixed with the recycle stream and heated, then entered the first reactor at a definite temperature.

In this paper, Smith model as one of the famous kinetic model for catalytic reforming reactors will be developed entirely. Then data resulted from the model will be compared to the results from catalytic reforming unit of the Tehran Refinery to evaluate the accuracy of the model.

KINETIC MODEL OF CATALYTIC REFORMING PROCESS

Catalytic reforming process is often modeled based on the two following factors:

- 1- The number of reactive species
- 2- The type of used kinetic model

Presence of many components as reactants or Intermediate products in the reactive mixture and presence of new reactions as a consequence, will extremely make a sophisticated situation for modeling the process. To decrease these complications, reactants in the mixture are classified in certain and limited groups, called Pseudo Components or lumps. The number of selected lumps in the mixture is a determinant factor resulted in designed models.

Obviously, the more the number of specified lumps are, the higher the accuracy and management of the model will be.

Arrhenius and Langmuir–Hinshelwood kinetics are used for catalytic reforming models. It should be noted that for all of the given models, the reactions are considered lump homogen that some of them will be noted briefly:

Smith proposed the first kinetic model for catalytic reforming process in 1959^[1]. In this model the first model given for petroleum processes, the reactants mixture has been classified in 10 groups. Smith assumed that naphtha includes of three fundamental groups: paraffins, naphthenes, and aromatics. Moreover, he introduced hydrogen, Ethane, propane, and butane into the system in addition to these groups. Based on these assumptions, he could give a simple and accurate kinetic for catalytic reforming process.

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Reactions according to Smith model are as the following:

- 1- Naphthenes to aromatics
- 2- Naphthenes to paraffins
- 3- Paraffins hydrocracking
- 4- Naphthenes hydrocracking

Based on Smith model, reaction network is shown in Figure 3.

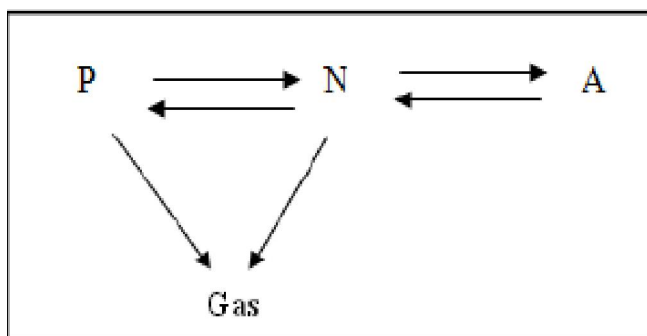


Figure 3 : Network reaction based on Smith model

One year later in 1960, the other model was given by Krane and his colleagues^[2]. In this model the feed was consisted of 20 lumps and reaction network includes of 53 reactions. Therefore, it is included of 53 first order rate equations. In this model the feed contains hydrocarbons with 6 to 10 carbon atoms for paraffinic, naphthenic, and aromatic groups. Arrhenius kinetics is used in two models. Dependence of rate constants on temperature and pressure is not reported. Indeed, reaction rate for hydrocarbons with 11 carbon atoms is not considered.

Some other models are proposed by Zohrov, Heningsen, Kmak, and Marin model that reactions network of these model have been shown in Figures 4 and 5^[3-6]. There are some pseudo components and lumps such as A, N₅, ACH, LP, P and Gas in these model.

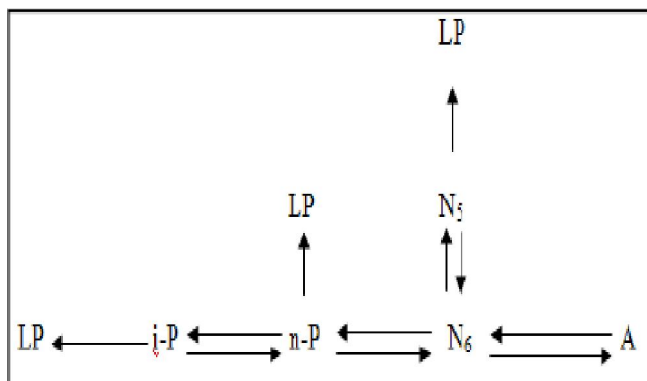


Figure 4 : Network reaction based on Zohrov model

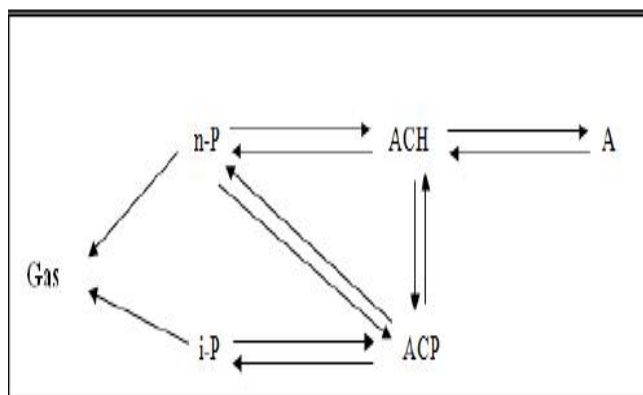


Figure 5 : Network reaction based on Heningsen model

Kmak model used Langmuir kinetic for catalytic reforming process for the

first time in 1972^[5]. Marin and his colleagues developed this model in 1983 so that it is consisted of naphtha with 5 to 10 carbon atoms and reaction network includes 23 pseudo components^[6].

In 1997 Froment model^[7] was developed by Umesh Taskar so that it contains 35 pseudo components in the reaction network and 36 reactions has been observed^[8].

As a consequence of using Arrhenius kinetics, a well-known model has been proposed by Padmavathi^[9] in 1997 in which 26 pseudo components in reaction mixture are used. In this kinetic model given by Padmavathi, the following lumps are considered:

- 1- Alkyl Cyclohexane (ACH)
- 2- Alkyl cyclopentane (ACP)
- 3- Normal Paraffins (NP)
- 4- Isoparaffins (IP)
- 5- Aromatics (A)
- 6- Hydrogen (H₂)
- 7- Light Hydrocarbons (C1 to C5)

Krane model was modified by Ancheyta^[10] in 2000 in which naphtha contains 1:11 carbon paraffinic hydrocarbons and 6:11 carbon naphthenic and aromatic hydrocarbons. Indeed, the reaction of cyclohexane formation from cyclopentane and paraffins isomeration is considered in this model unlike Krane model.

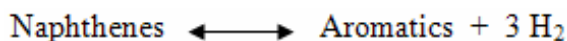
Now we develop the first model of catalytic reforming process for Semi-Regenerative process. To evaluate the accuracy of the model, data given from one of the catalytic reforming units (Tehran Refinery) has been used.

DEVELOPMENT OF SMITH KINETIC MODEL [1] FOR CATALYTIC REFORMING PROCESS

To simulate catalytic reforming unit, Smith model is preferentially used. As mentioned previously, for this model inlet feed will be classified in three general groups: aromatics, naphthenes and paraffins. In addition, hydrogen, methane, propane, butane, and pentane are also considered.

Reactions within the model are classified in four groups. In order of significance, these four groups are:

Naphthenes to Aromatics



Rate constants concerning this reaction will be^[1]:

$$K_{eq1} = e^{(46.15 - \frac{46045}{T})} \quad (1)$$

$$k_{C1} = e^{(23.21 - \frac{34750}{T})} \quad (2)$$

Naphthenes to Paraffins

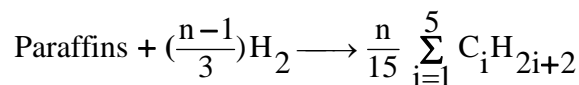


Rate constants concerning this reaction will be^[1]:

$$K_{eq2} = e^{(-7.12 + \frac{8000}{T})} \quad (3)$$

$$k_{c2} = e^{(35.98 - \frac{59600}{T})} \quad (4)$$

Paraffins hydrocracking

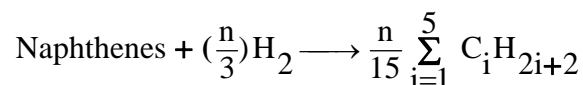


Rate constants concerning this reaction will be^[1]:

$$-r_{\text{Paraffines_Cracking}} = \frac{k_{C3}}{P_t} P_p \quad (5)$$

$$k_{C3} = e^{(42.97 - \frac{62300}{T})} \quad (6)$$

Naphthenes hydrocracking



In this case rate constants concerning this reaction will be^[1]:

$$-r_{\text{Naphthene_Cracking}} = \frac{k_{C4}}{P_t} P_N \quad (7)$$

$$k_{C4} = e^{(42.97 - \frac{62300}{T})} \quad (8)$$

Due to the developed rate equations, mass and energy balance have been resulted in the following relations:

$$\frac{dN_A}{dV_R} = \frac{k_{C1}}{K_{eq1}} P_N \left(K_{eq1} - \frac{P_A P_{H_2}^3}{P_N} \right) \quad (9)$$

$$\frac{dN_N}{dV_R} = -\frac{k_{C1}}{K_{eq1}} P_N \left(K_{eq1} - \frac{P_A P_{H_2}^3}{P_N} \right) - \frac{k_{C2}}{K_{eq2}} P_N \left(K_{eq2} - \frac{P_A}{P_N P_{H_2}} \right) - \frac{k_{C4}}{P_t} P_N \quad (10)$$

$$\frac{dN_P}{dV_R} = \frac{k_{C2}}{K_{eq2}} P_N \left(K_{eq2} - \frac{P_A}{P_N P_{H_2}} \right) - \frac{k_{C3}}{P_t} P_P \quad (11)$$

$$\frac{dT}{dV_R} = -\frac{k_{C1}}{K_{eq1}} P_N \left(K_{eq1} - \frac{P_A P_{H_2}^3}{P_N} \right) \left(\frac{\Delta H_1}{N_T C_P} \right) - \frac{k_{C2}}{K_{eq2}} P_N \left(K_{eq2} - \frac{P_A}{P_N P_{H_2}} \right) \left(\frac{\Delta H_2}{N_T C_P} \right) - \frac{k_{C3}}{P_t} P_P \left(\frac{\Delta H_3}{N_T C_P} \right) - \frac{k_{C4}}{P_t} P_P \left(\frac{\Delta H_4}{N_T C_P} \right) \left(\frac{n-3}{3} \right) \quad (12)$$

Where n is the number of each presumed carbons of pseudo components^[1] which is $\frac{7}{6}$ for the feed in the model.

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RESULTS AND DISCUSSION

After developing the model, it should be scaled up to the industrial unit. An optimization subroutine has been used to determine the coefficients so that a suitable consistency between the unit and the model can be achieved. In this subroutine, Levenburg-Marquardt optimization algorithm is used and the following target function is optimized:

$$f = \sum_{i=1}^n (0.5(C_{i \text{ exp}} - C_{i \text{ model}})^2 + 0.5(T_{i \text{ exp}} - T_{i \text{ model}})^2) \quad (13)$$

The magnitudes of constants are presented in TABLE 1 for Tehran refinery.

TABLE 1 : Reaction Constants calculated

Reaction Number	Reaction Name	k_0	$\frac{E}{R}$ ($^{\circ}\text{R}$)
1	Aromatic Production	18.59	34807
2	Paraffins production	26.74	58591
3	Paraffins Hydrocracking	42.97	62857
4	Naphthenes Hydrocracking	42.97	61224

In a catalytic reforming process, major operating parameters are:

- 1- Inlet and outlet temperature of reactors
- 2- Total Yield
- 3- Octane Number

To measure the accuracy of the model, data resulted from the model are compared with actual (industrial) data. A comparison between outlet tempera-

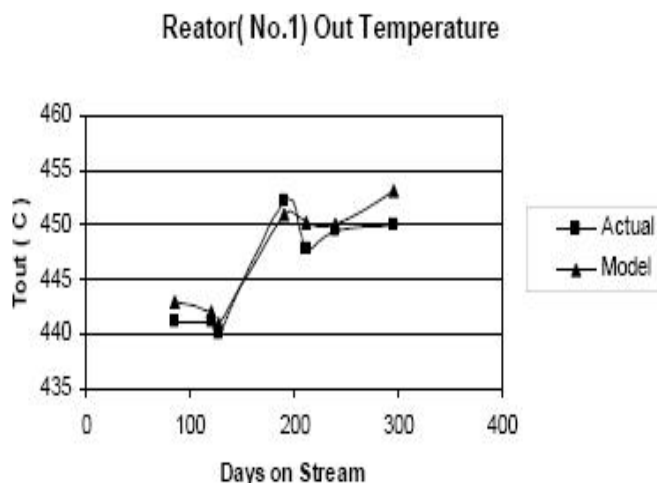


Figure 6 : Comparison of Outlet Temperature in the First reactor

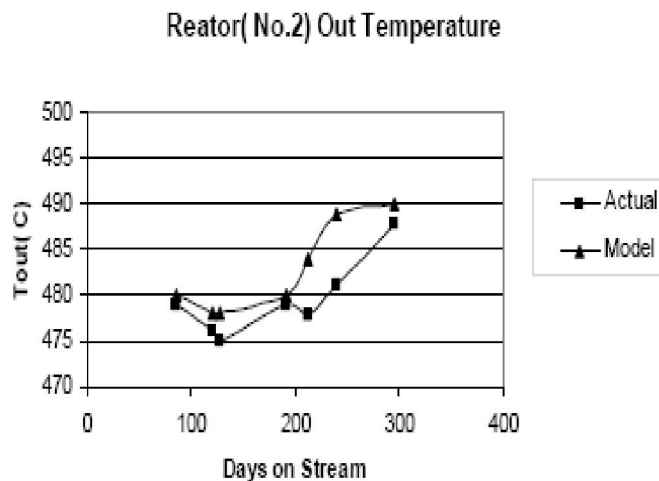


Figure 7 : Comparison of Outlet Temperature in the Second reactor

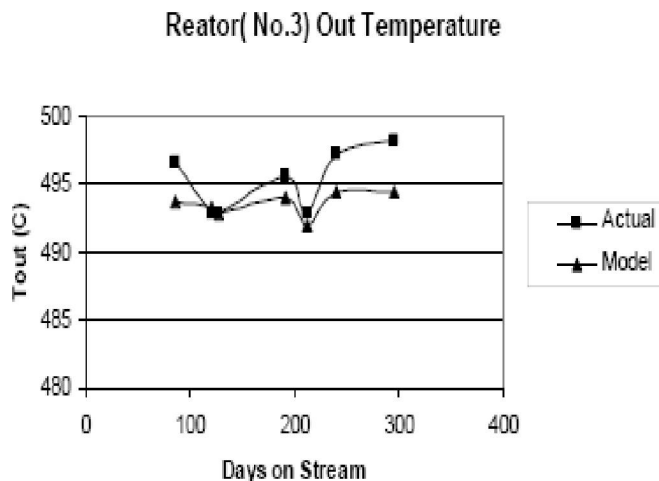


Figure 8 : Comparison of Outlet Temperature in the Third reactor

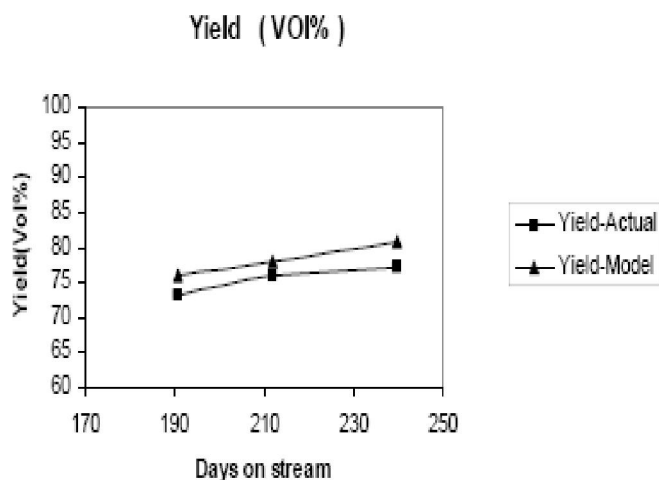


Figure 9 : Comparison of Total Yield

tures obtained by the model and the actual data for three reactors are presented in Figures 6 to 8.

Another significant operating parameter in catalytic

reforming process is yield of the process. In Figure 9 the comparison between the yield of the unit, the model and Petro-Sim has been shown.

Octane number is one of the other important parameters in catalytic reforming process. The comparison among octane number of the unit and the model has been shown in Figure 10.

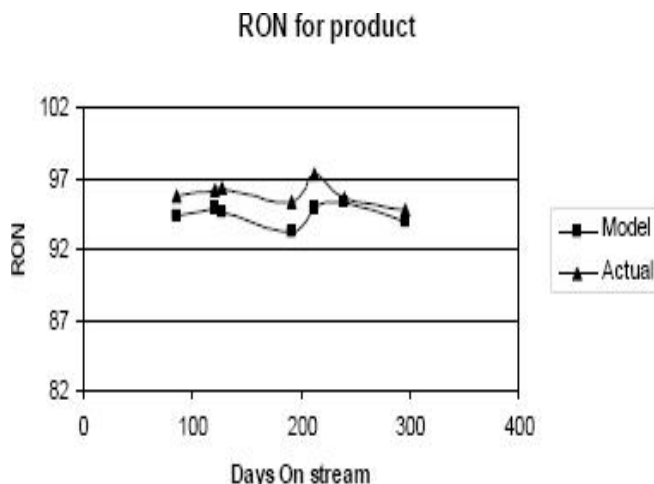


Figure 10 : Comparison of RON Product

CONCLUSIONS

From the presented Figures, it can be perceived that:

1- Smith model, can result the acceptable estimation of operating conditions, such as outlet temperature of the reactors, octane number, Total yield and PONA.

2- With Consideration of suitable deactivation number, effect of time on the process can be discussed.

3- Due to the necessity of controlling the amount of benzene and aromatics in Gasoline, a model for determining concentration of Benzene and aromatic should be developed.

5- Comparison between model results and operational data shows the appreciated ability of this model for simulating catalytic reforming unit.

NOMENCLATURE

P = Paraffins
 N = Naphthenes
 A = Aromatics
 Gas = Light gas (methane, ethane, propane, i-butane, n-butane)

n-P = Normal Paraffins
 i-P = Iso Paraffins
 N_6 = Naphthenes with 6 carbon ring
 N_5 = Naphthenes with 5 carbon ring
 LP = Light Paraffins (Light gas)
 ACP = Alkyl Cyclo Pentane
 ACH = Alkyl Cyclo Hexane
 k_c = Rate constant (variable dimension)
 K_{eq} = Equilibrium constant (variable dimension)
 i = Reaction number
 T = Temperature ($^{\circ}$ R)
 P_P = Partial Pressure of Paraffins (atm)
 P_N = Partial Pressure of Naphthenes (atm)
 P_t = Total Pressure (atm)
 N_P = Mole number of Paraffine produced
 N_N = Mole number of Naphthene produced
 N_A = Mole number of Aromatic produced
 N_T = Total Mole number of produced
 ΔH = Heat of Reaction (kJ / mol)
 C_p = Heat Capacity (kJ/mol $^{\circ}$ C)

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