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REACTOR MODELING AND SIMULATION OF CATALYTIC 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. In view of the importance of this process for producing gasoline, simulation of catalytic reforming process and prediction of vital parameters such as octane number, Liquid Hour Space Velocity (LHSV), reactor inlet temperatures, yield and catalyst life aiming at process optimization is of prime importance. In this work, the oldest kinetic model mentioned for this unit is reconsidered. The accuracy of the model is compared with the collected data from Tehran refinery and results of Petro-Sim simulator, one of the newest for simulation of petroleum refinery processes. The results show that this model has relatively acceptable ability to predict octane number, outlet temperature of reactors and yield.

Keywords: Catalytic Naphtha Reforming, Petro-Sim, Modeling, Simulation

1. Introduction

The catalytic reforming process is one of the most critical operations in petroleum refineries to produce gasoline with high octane number. This process uses naphtha or cracking oil as feedstock to produce rich aromatic compounds and high octane value liquid products through reactions such as aromatization, cyclization and hydrocracking. At the same time, it produces hydrogen (H) and liquefied petroleum gas (LPG) as its by-products. In this process, products with different octane number are produced unlike the production of certain octane number in others such as catalytic cracking, alkylation and isomerization.

Industrial catalysts used in recent catalytic reforming units are consisted of Gama Alumina support, metals such as Platinum, Rhenium, Germanium, and Iridium, less than one weight percent, and additives such as chlorine to increase isomerization reactions. Usually, feed of catalytic reformers 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 from 5 to 10. The design or simulation of the catalytic reforming reactor is very difficult because of intricacy of catalytic reforming feedstock, high operating temperature of reactors, and the complex reactions in the reactor.

In the catalytic reforming process, seven types of reactions are taken place as the following:

1-Dehydrogenation 2-Isomerization 3-Hydrocracking 4-Cyclization
5-Hydrogenolysis 6-Aromatization 7-Coke Formation

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

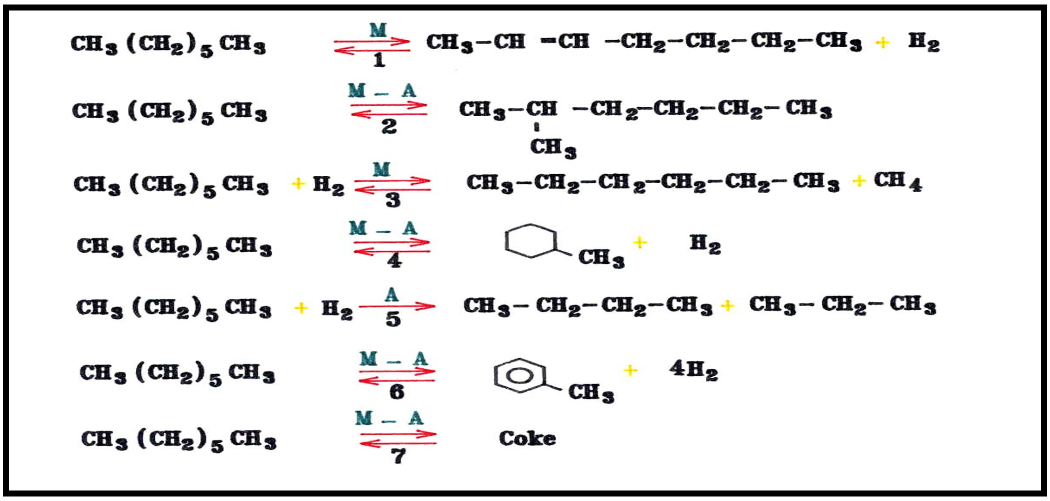

Figure 1. A typical of reactions in the Catalytic Reforming Process

Some of these reactions such as cyclization and aromatization are desirable because of increasing octane number. On the other hand, coke formation and coke deposition, causing the deactivation of the catalyst, are undesired reactions.

The catalytic reforming process discussed in this paper is the Semi-Regenerative type (figure 2) including of 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.

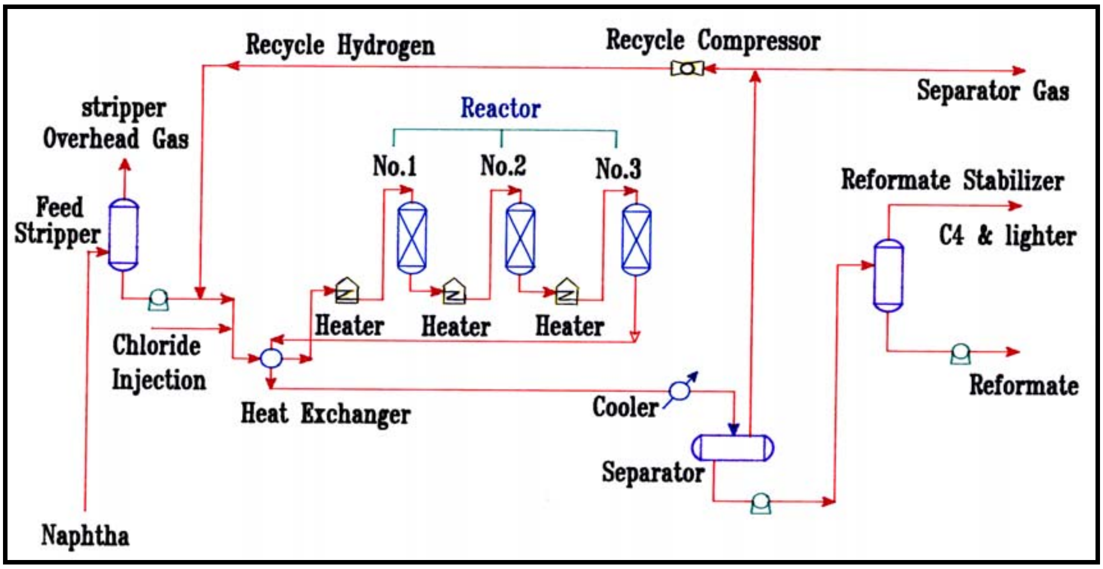

Figure 2. Catalytic Reforming Flowchart (Semi-Regenerative)

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 to improve vapor pressure (RVP) of gasoline. After that, bottom of the tower, called reformate, will be sent to the gasoline pool.

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 the present work, Smith model for catalytic reforming reactors will be developed entirely. Then resulted data from the model will be compared to the ones from Tehran refinery catalytic reformer and Petro-Sim simulator to evaluate the accuracy of the model.

2. Catalytic Reforming Process Modeling

Catalytic reforming process is often modeled based on the following factors:
1-The number of reactive species
2-The type of used kinetic model

Because of many components as reactants or intermediate products in the reactive mixture and new reactions as a consequence, it will extremely make a sophisticated situation for modeling the process. To mitigate the complication, reactants in the mixture are classified in certain and limited groups, called Pseudo Components. The number of selected pseudo components in the feed is a characteristic factor, the key in presented models.

Arrhenius and Langmuir–Hinshelwood kinetics are used for catalytic reforming models. It should be noted that for all of the presented models, the reactions are considered as Pseudo 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 he assumed that naphtha includes of three fundamental groups: paraffins, naphthens, 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. Reactions according to Smith model are as the following:
1- Naphthenes to aromatics
2- Naphthenes to paraffins
3- Hydrocracking of paraffins
4- Hydrocracking of naphthenes

One year later in 1960, the other one was introduced by Krane and his colleagues [2]. In this model, feed was consisted of 20 pseudo components and hydrocarbons from 6 to 10 carbon atoms. Moreover, reaction network was contained of 53 reactions. Arrhenius kinetic model is used for mentioned models.

The other models are proposed by Zohrov, Heningsen, Kmak, and Marin [3], [4], [5], [6]. Kmak used Langmuir kinetic model for catalytic reforming process for the first time in 1972 [5]. Marin and his colleagues developed that in 1983, as if it was consisted of naphtha from 5 to 10 carbon atoms and reaction network includes of 23 pseudo components [6]. In 1997, Froment model [7] was developed by Umesh Taskar so that it included of 35 pseudo components in the reaction network, and 36 reactions has been observed [8]. As a consequence of using Arrhenius kinetic, a well-known model has been proposed by Padmavathi [9] in 1997 in which 26 pseudo components in reaction mixture were used. In this model, the following pseudo components are considered:
1- Alkyl Cyclohexane (ACH)
2-Alkyl cyclopentane (ACP)
3- Normal Paraffins (NP)
4-Isoparaffins (IP)
5-Aromatics (A)
6-Hydrogen (H_2)
7-Light Hydrocarbons (C1 to C5)

Krane model was modified by Ancheyta[10] in which naphtha contained 1:11 paraffinic, 6:11 naphthenic and aromatic hydrocarbons. Indeed the reaction of cyclohexane formation from cyclopantane and paraffins isomeration are considered in this model unlike Krane model. More recently, Liang et. al. [11] developed a physical model to simulate a catalytic reformer unit with 4 reactors in series. kinetics and thermodynamic equations were selected to describe the naphtha catalytic reforming reactions characterized based on idealizing the complex naphtha mixture by representing the paraffin, naphthene and aromatic groups by single compounds.

In this paper, one of the presented models, Smith model, was used for simulation of a Semi-Regenerative process with 3 reactors in series. To evaluate the accuracy of the model, the actual data from Tehran refinery catalytic reforming unit were used. Furthermore, simulation results were compared with Petro-Sim software.

3. Development of Smith Model for Catalytic Reforming Process

To simulate catalytic reforming unit, the simplest model, Smith model, is preferentially used. As mentioned previously, for this model feed will be classified in three general groups: aromatics, naphthens 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, they are as the following:

1- Naphthenes to aromatics

$$naphthenes \leftrightarrow aromatics + 3H_2$$

Rate constants concerning this reaction will be [1]:

$$K_{e1} = e^{(46.15 - \frac{46045}{T})}, \qquad atm.^3 \tag{1}$$

$$k_{f1} = e^{(23.21 - \frac{34750}{T})}, \qquad \frac{moles}{(hr.)(lb.cat.)(atm.)^2} \tag{2}$$

2- Naphthenes to paraffins

$$naphthene + H_2 \leftrightarrow paraffin$$

Rate constants concerning this reaction will be [1]:

$$K_{e2} = e^{(-7.12 + \frac{8000}{T})}, \qquad atm.^{-1} \tag{3}$$

$$k_{f2} = e^{(35.98 - \frac{59600}{T})}, \qquad \frac{moles}{(hr.)(lb.cat.)(atm.)^2} \tag{4}$$

3- Hydrocracking of paraffins

$$C_nH_{2n+2}(paraffin) + \frac{n-1}{3}H_2 \longrightarrow \frac{n}{15}\sum_{i=1}^{5} C_iH_{2i+2}$$

Rate constants concerning this reaction will be[1]:

$$-r_{naphthene\_cracking} = \frac{k_{f3}}{P_t} p_p \tag{5}$$

$$k_{f3} = e^{(42.97 - \frac{62300}{T})}, \qquad \frac{moles}{(hr.)(lb.cat.)} \tag{6}$$

4 – Hydrocracking of naphthenes

$$C_nH_{2n}(naphthene) + \frac{n}{3}H_2 \longrightarrow \frac{n}{15}\sum_{i=1}^{5} C_iH_{2i+2}$$

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

$$-r_{naphthene\_cracking} = \frac{k_{f4}}{P_t} p_N \tag{7}$$

$$k_{f4} = e^{(42.97 - \frac{62300}{T})}, \qquad \frac{moles}{(hr.)(lb.cat.)} \tag{8}$$

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

$$\frac{dN_A}{dV_R} = \frac{k_{f1}}{K_{e1}} P_N (K_{e1} - \frac{P_A P_{H_2}^{\ 3}}{P_N}) \tag{9}$$

$$\frac{dN_N}{dV_R} = -\frac{k_{f1}}{K_{e1}} P_N (K_{e1} - \frac{P_A P_{H_2}^{\ 3}}{P_N}) - \frac{k_{f2}}{K_{e2}} P_N (K_{e2} - \frac{P_A}{P_N P_{H_2}}) - \frac{k_{f4}}{P_t} P_N \tag{10}$$

$$\frac{dN_P}{dV_R} = \frac{k_{f2}}{K_{e2}} P_N (K_{e2} - \frac{P_A}{P_N P_{H_2}}) - \frac{k_{f3}}{P_t} P_P \tag{11}$$

$$\frac{dT}{dV_R}=-\frac{k_{f1}}{K_{e1}}P_N\left(K_{e1}-\frac{P_A P_{H_2}{}^3}{P_N}\right)\left(\frac{\Delta H_{f1}}{N_t C_P}\right)-\frac{k_{f2}}{K_{e2}}P_N\left(K_{e2}-\frac{P_A}{P_N P_{H_2}}\right)\left(\frac{\Delta H_{f2}}{N_t C_P}\right)-\frac{k_{f3}}{P_t}P_N\left(\frac{\Delta H_{f3}}{N_t C_P}\right)\left(\frac{n}{3}\right)$$
$$-\frac{k_{f4}}{P_t}P_P\left(\frac{n-3}{3}\right) \quad (12)$$

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

4. 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 subroutin, Levenburg-Marquardt optimization algorithm is used and the following target function is optimized:

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

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

Table 1. Reaction Constants calculated

Reaction Number	Reaction Name	k0	$\frac{E}{R}(Rankin)$
1	Aromatic Production	18.59	34807
2	Paraffins production from aromatics	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, resulted data from the model are compared to the ones from Petro-Sim simulator and actual data. The comparison between outlet temperatures obtained by the model, Petro-Sim and the actual data for three reactors are presented in figures 3 to 5.

Another significant operating parameter in catalytic reforming process is yield which is defined the ratio of reformate volume flow rate to the feed volume flow rate. In figure 6 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. This parameter has been calculated by the Octane Index method [12]. The comparison among octane number of the unit and the model has been shown in figure 7.

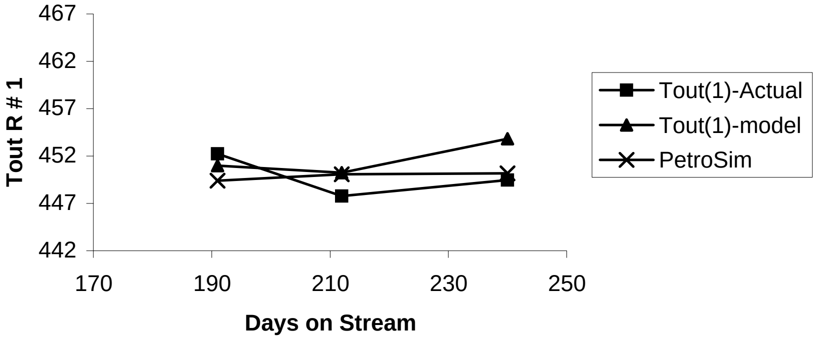

Figure 3. Comparison of Outlet Temperature (^{0}C) in the First reactor

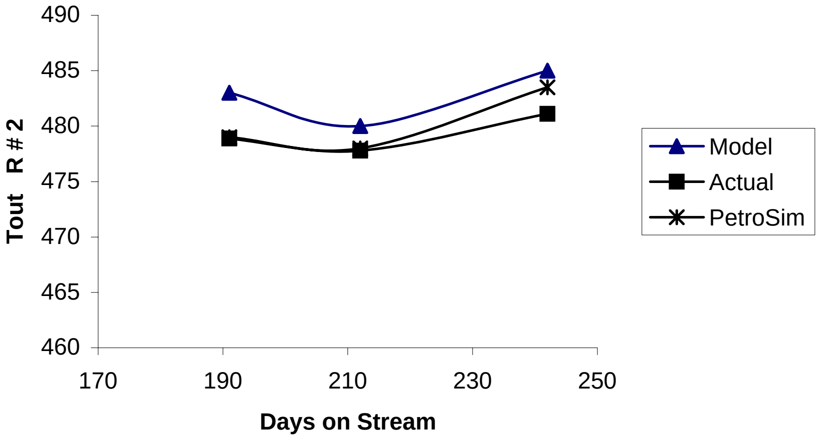

Figure 4. Comparison of Outlet Temperature (^{0}C) in the Second reactor

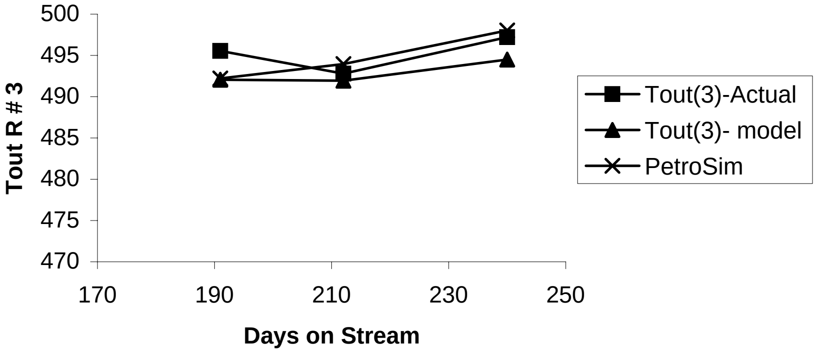

Figure 5. Comparison of Outlet Temperature (^{0}C) in the Third reactor

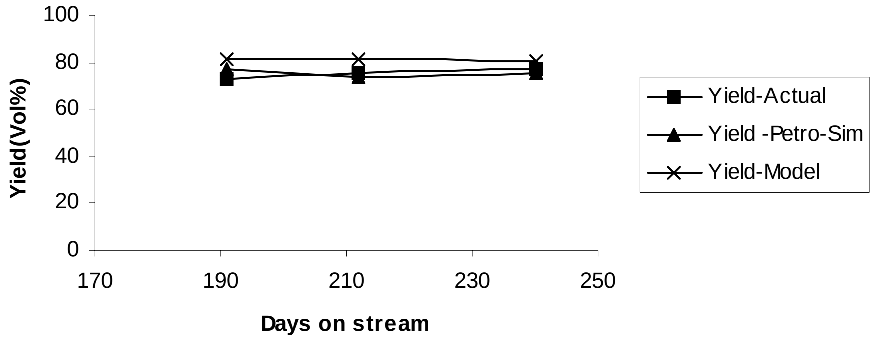

Figure 6. Comparison of Total Yield

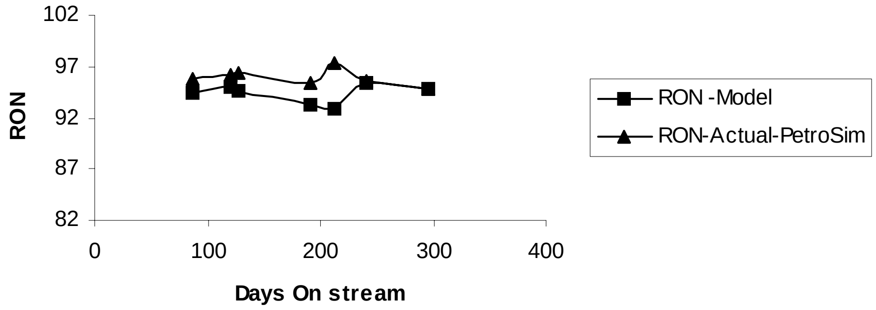

Figure 7. Comparison of RON Product

5. Conclusions

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

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

3- It was a consistency between Smith model and Petro-Sim in estimating operating parameters.

4- 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 Petro-Sim results and actual data showed the appreciated ability of this software to simulate catalytic reforming unit.

Notation

C - concentration, moles per unit volume
k - rate constant for forward reactions (variable dimension)
k_0*- frequency factor of forward reactions*
K - equilibrium constant (variable dimension)
n- number of carbon atoms
N - mole number
P - partial pressure (atm.)
R- ideal gas constants
T - temperature (R)
V_R*- volume of reactor*
Δ H - heat of reaction (Btu./ mol)
C_P *- heat Capacity (Btu./mol F.)*

Subscripts

A- aromatic
exp - experimental
i - reaction number
predict - predicted
N - naphthenes
P - paraffins
t - total

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