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SIMULATION AND MODELING OF CATALYTIC REFORMING PROCESS

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Abstract

One of the most important processes in oil refineries is catalytic reforming unit in which high octane gasoline is produced. The catalytic reforming unit by using Hysys-refinery software was simulated. The results are validated by operating data, which is taken from the Esfahan oil refinery catalytic reforming unit. Usually, in oil refineries, flow instability in composition of feedstock can affect the product quality. The attention of this paper was focused on changes of the final product flow rate and product's octane number with respect to the changes in the feedstock composition. Also, the effects of temperature and pressure on the mentioned parameters was evaluated. Furthermore, in this study, Smith kinetic model was evaluated. The accuracy of this model was compared with the actual data and Hysys-refinery's results. The results showed that if the feed stream of catalytic reforming unit supplied with the Heavy Isomax Naphtha can be increased, more than 20% of the current value, the flow rate and octane number of the final product will be increased. Also, we found that the variations of temperature and pressure, under operating condition of the reactors of this unit, has no effect on octane number and final product flow rate.

Keywords: Catalytic reforming unit; Simulation; Modeling; Hysys-Refinery.

1. Introduction

Naphtha is transformed into reformate by catalytic reforming. This process involves the reconstruction of low-octane hydrocarbons in the naphtha into more valuable high-octane gasoline components without changing the boiling point range.Naphtha and reformate are complex mixtures of paraffins, naphthenes, and aromatics in the C_5 -C_{12} range, naphtha composition.

Paraffins or alkanes are saturated aliphatic hydrocarbons with the general formula C_nH_{2n+2}. They are either straight-chain (n-paraffins) or branched structures (i-paraffins). The boiling point increases by about 25-30^oC for each carbon atom in the molecule, and the boiling point of an n-paraffin is always higher than that of the i-paraffin with the same carbon number. The density increases with increasing carbon number as well. Olefins or alkenes are unsaturated aliphatic hydrocarbons. Like the paraffins, they are either straight chains or branched structures, but contain one or more double bonds. Mono-olefins have the general formula C_nH_{2n}. Naphthenes or cycloalkanes are saturated cyclichydrocarbons that contain at least one ring structure. The general formula for mononaphthenes is C_nH_{2n}.The most abundant naphthenes in petroleum have a ring of either five or six carbon atoms. The rings can have paraffinic side chains attached to them. The boiling point and the density is higher than for any paraffin with the same number of carbon atoms.

Aromatics have the general formula C_nH_{2n-6} and contain one or more polyunsaturated rings (conjugated double bonds). These benzene rings can have paraffinic side chains or be coupled with other naphthenic or aromatic rings. The boiling points and the densities of these polyunsaturated compounds are higher than that of both paraffins and naphthenes with the same carbon number. The reactivity of the unsaturated bonds make the C_6, C_7, and C_8 aromatics or BTX (benzene, toluene, xylenes) important building blocks for the petrochemical industry, Aromatics have high octane numbers.

The composition of a given naphtha depends on the type of crude oil, the boiling range of the naphtha, and whether it is obtained directly from crude oil distillation or produced by catalytic or thermal cracking of heavier oil fractions. A typical straight-run medium naphtha contains 40 - 70 wt % paraffins, 20 -50 wt % naphthenes, 5 - 20 wt % aromatics,

and only 0 - 2 wt % olefins. Naphtha produced by fluid catalytic cracking (FCC), coking, or visbreaking may contain 30 - 50 wt % olefins. Table1 shows the hydrocarbon composition for different naphtha streams [1].

Table 1 Typical compositions and characteristics of refinery naphtha streams originating from the same crude oil.

Stream	Parafins %wt.	Olefins %wt.	Naphtha %wt.	Aromatics %wt.	IBP-FBP ^{o}C
Light SR	55	0	40	5	C5-90
Medium SR	31	0	50	19	90-150
Heavy SR	30	0	44	26	150-180
FCC	34	23	11	32	C5-220
Light VB	64	10	25	1	C5-90
Heavy VB	46	30	16	8	90-150

SR- Straight-run; FCC- fluid catalytic cracker; VB-visbreaker ; IBP- initial boiling point; FBP-final boiling point

In this study, the feed composition oil refinery catalytic reforming unit has been investigated, and the effects of different feed composition on product properties is evaluated.

2. Description of the process, simulation and modeling

The semi-regenerative continuous catalytic reforming unit flow diagram is shown in Fig.1. The naphta, used as the catalytic reformer feedstock generally comprising more than 300 chemical compounds of naphthenes, aromatics, and paraffins in the carbon range of C_5 to C_{12}, is joined with a recycle gas stream including 70% to 90% (by mol) hydrogen. The feed flow rate of this unit is about 22500 bbl/day gasoline with octane number 45 and the final product rate 18200-16700 bbl/day gasoline with octane number 88-95.5.

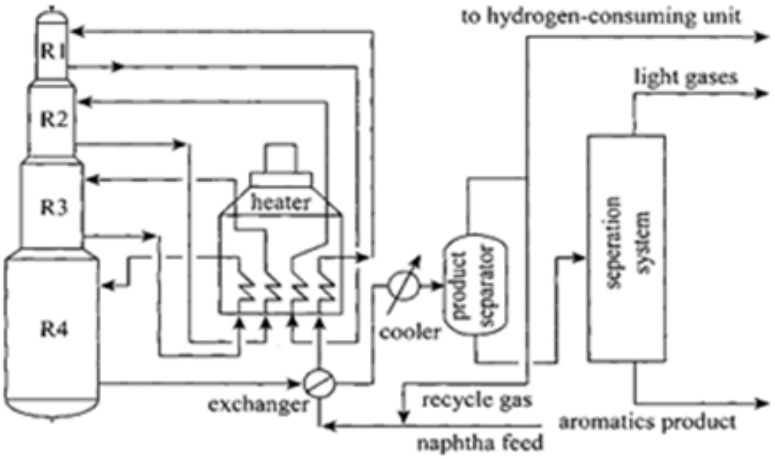

Fig. 1 Catalytic reforming flowsheet (semi-regenerative)

The entire reactors charge is heated and passed through the catalytic reformers, which are designed with 4 adiabatically operated reactors and 4 furnaces (heaters) between the reactors to keep the reaction temperature at design levels. The effluent from the fourth reactor is cooled, which then enters to the product separator (flash column).The flashed vapor circulates to combine the naphtha feedstock as recycle gas. Extra hydrogen from the separator is sent to other hydrogen consuming units. The separated liquid that mainly included the desired the aromatics together with heavy paraffins and light gases is sent to the separation system (distillation column) to achieve aromatics products (final product). The final products are obtained by the conversion of naphthenes and n-paraffins in naphtha to aromatics and iso paraffins over bifunctional catalysts such as Pt-Sn/Al_2O_3 in 4 reactors.
The actual operating data of catalytic reforming unit that is handled to simulate and validate the obtained results, is tabulated in Tab. 2-6.

Catalytic refoming unit is frequently modeled based on the following principles:
1- The kind of used kinetic model
2- The number of reactive species

Table 2 Reactor's operating data

Operating data	Reactor No.1	Reactor No.2	Reactor No.3	Reactor No.4
Inlet T,[^{o}C]	503.0	503.0	503.0	503.0
Inlet P ,[bar]	28.5	27.13	25.76	23.5
Measured delta T,[^{o}C]	60.00	35.00	14.00	6.00
Catalyst volume, [m^3]	7.76	11.64	19.4	38.8
Catalyst ages, [days]	700	700	700	700
Recycle rate, [MMSCFD]	151.5	-	-	-

Table 3. Flash Column's operation data

Operating data	Separator Data
Temperature, [oC]	38.00
Pressure, [bar]	20
H_2 purity	0.79

Table 4. Reactor's informations

Reactor's informations	Data
Catalyst density, [kg/m^3]	5.106
Preheater inlet T, [^{o}C]	413
Last reactor delta P, [bar]	1

Table 5 The feed composition of catalytic reforming unit

Naphtha composition	Volume [%]
Hydrogen	0.0
Methane	0.0
Ethane	0.0
Propane	0.0
Isobutane	0.0
N-Butane	0.0
C_5-Paraffins	0.0
C_6-C_7-C_8-C_9-C_{10}-C_{11} Paraffins	56.3
C_6-C_7-C_8-C_9-C_{10}-C_{11} Naphthenes	31.2
Benzene,Toluene,C_8-C_9-C_{10}-C_{11} Aromatics	12.5
Total	100.0

Table 6 Simulation parameters for separation system

Simulation parameters for distillation data column	
Number of stages	36
Feed tray	19
Feed temperature (oC)	147
Partial condenser temperature (^{o}C)	38
Tray 1 temperature (over head)(^{o}C)	125
Tray 36 temperature (Bottom)(^{o}C)	230
Distillate rate(light gases)(bbl/day)	1200
Partial condenser pressure (bar)	16.5
Reboiler pressure (bar)	27.5
Maximum number ofi	300
Equilibrium error tolerance	$1.00e^{-5}$
Heat/Spec erorr tolerance	$5.00e^{-5}$

Due to many components as reactants or intermediate products in the reactive mixture and new reactions as a result, it will exeedingly make a complicated situation for modeling the reactors. To reduce the complication, reactants in the mixture are classified in definite and restricted groups, defined Pseudo Components.The number of selected pseudo components in the feed is a typical factor, the key in offered models.

Langmuir-Hinshelwood and Arrhenius kinetics are used for reactions models. It must be noted that for all of the offered models, the reactions are considered as Pseudo homogen that some of them will be mentioned summarily:

In 1959, Smith suggested the first kinetic model for reactions [2]. In 1960, someone else was introduced by Krane and his colleagues [3]. Arrhenius kinetic model is used for Smith and Krane reactions. The other models are suggested by Zohrov, Heningsen, Marin, and Kmak [4,5,6,7]. In 1972, Kmak used Langmuir kinetic model for reactors as first time [6]. In 1983, Marin et.al. [7] developed that, as if it was included of Naphtha in the C_5-C_{10}

range, and reaction network comprises of 23 pseudo components. Froment model [8] was developed by Umesh Taskar so that it consisted of 35 pseudo components in the reaction network, and 36 reactions has been seen, in 1997 [9]. In 1997, As a result of using Arrhenius kinetic, a famous model has been suggested by Padmavathi [10] in which it included of 26 pseudo components in the reaction network.

In fact the reaction of cyclohexane formation from cyclopantane and paraffins isomeration are considered in modified Krane model-Ancheyta model.The new modified Ancheyta model varies from Krane model, as naphtha comprised 1:11 paraffinic,6:11 naphthenic and aromatic hydrocarbons [11]. More in recent times, Liang et.al developed a model to simulate a catalytic reformer process with four reactors in series [12].

In the current study, catalytic reforming unit using Hysys-refinery software was simulated [13], and the effects of the different feed composition as well as some proccessing variabels, temperature and pressure, on octane number and final product flow rate has been investigated. Using the obtained results one can estimate the processing interesting variables, product octan number and final flow rate, along the existing of the undesirable fluctuating of the feed composition. Furthermore, in this work, Smith model, was used to simulate catalytic reforming unit with 4 reactors in series. To evaluate the accuracy of this model, the actual data from Esfahan oil refinery catalytic reforming unit were used.

2.1. Smith model for catalytic reforming unit

Smith model feed will be classified in three general groups: paraffins, naphthenes and aromatics. moreover, hydrogen, methane, Propane, butane, and pentane are also considered. Smith model reactions are classified in four groups, they are as the following [14]:

1. Naphthenes to paraffins

$$\text{Naphthene} + H_2 \leftrightarrow Paraffin$$

Rate constants will be [2]:

$$k_{e1} = e^{(-7.12+\frac{8000}{T})}, atm^{-1} \quad (1)$$

$$k_{f1} = e^{(35.98-\frac{59600}{T})}, \frac{moles}{(hr)(lbcat)(atm)^2} \quad (2)$$

2. Naphthenes to aromatics

$$\text{Naphthenes} \leftrightarrow \text{aromatics} + 3H_2$$

Rate constant will be [2]:

$$K_{e2} = e^{(46.15-\frac{46045}{T})}, atm^3 \quad (3)$$

$$K_{f2} = e^{(23.21-\frac{34750}{T})}, \frac{moles}{(hr)(lbcat)(atm)^2} \quad (4)$$

3. Hydrocracking of naphthenes

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

Rate constants will be [2]:

$$-r_{naphthene-cracking} = \frac{k_{f3}}{P_t} P_p \quad (5)$$

$$K_{f3} = e^{(42.97-\frac{62300}{T})}, \frac{moles}{(hr)(lbcat)} \quad (6)$$

4. Hydrocracking of paraffins

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

Rate constants will be [2]:

$$-r_{paraffin-cracking} = \frac{k_{f4}}{P_t} P_p \quad (7)$$

$$K_{f4} = e^{(42.97-\frac{62300}{T})}, \frac{moles}{(hr)(lbcat)} \quad (8)$$

Where k, K, *T*, p and n is rate constant, equilibrium constant, temperature(^{o}R), partial pressure (atm) and number of carbon atoms, respectively.

3. Results and discussion

After Smith model reactions mention, due to analysis actual data of operation unit at the start of running, smith model reactions was defined in the 4 series plug reactors, and then catalytic reforming unit was simulated [15].

Table7. The results of simulation in comparing the actual results

Operating parameters	Hysys-Refinery	Actual	Smith model
Final product flow Rate (bbl/day)	17 870	17 900	18 830
Final product octane number	94.94	95.2	93.3

The feed flow rate of the catalytic reforming unit with 22500 bbl/day naphtha, are included of 80% volumetric from atmospheric distillation column product, straight run gasoline (SRG), and 20% volumetric from Heavy Isomax Naphtha. Unfortunately, the quality and quantity of the product can be significantly affected by the fluctuation of the feed composition such as the amount of paraffinic, naphthenic, aromatic compounds. The effects of these parameters as well as temperature and pressure are analyzed for the product's octane number and the final product flow rate. The results show that temperature and pressure have no effect on the products [Fig.2] but rather they affect on the deactivation rate of the reactor's catalysts.

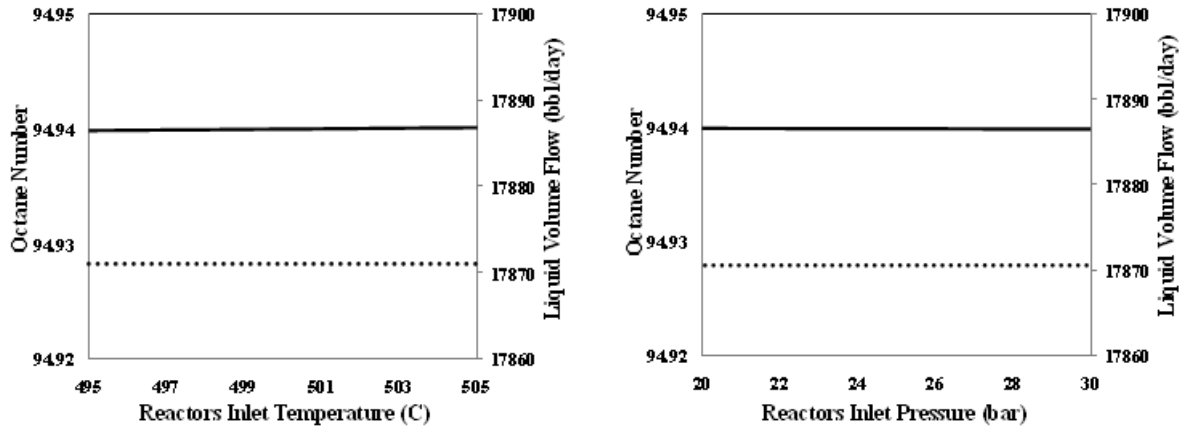

Figure2. The effects of reactor's inlet temperature and pressure on final product octane number (solid line) & liquid volume flow (doted line)

The effects of variation of feedstock composition for C_6-C_{11} (paraffinic, naphthenic and also aromatic), are shown in [Fig 3,4,5]. The feed flow rate of C_{10-11} naphthenic compounds are directly related to the final octane number and final product flow rate whilst for C_9, final product octane number has no change. The high amounts of aromatic C_{7-11} in feed flow cause to increase both octane number and final product flow rate. The flow rate of benzene in feed has unique behavior; the octane number remarkably increased by an decreasing the benzene flow rate. Although we thought that increasing the paraffinic compounds lead to increase the product octane number and an decreased in the product flow rate, it is not necessarily true. For example by increasing the flow rate of paraffinic C_8 and C_9 the octane number for both cases decreased, but, the flow rates for C_8 increased and for C_9 decreased. C_6, C_7 and C_8 naphthenic compounds have different manner in comparison to the others. For paraffinic C_7 compounds, even, the results are so different.

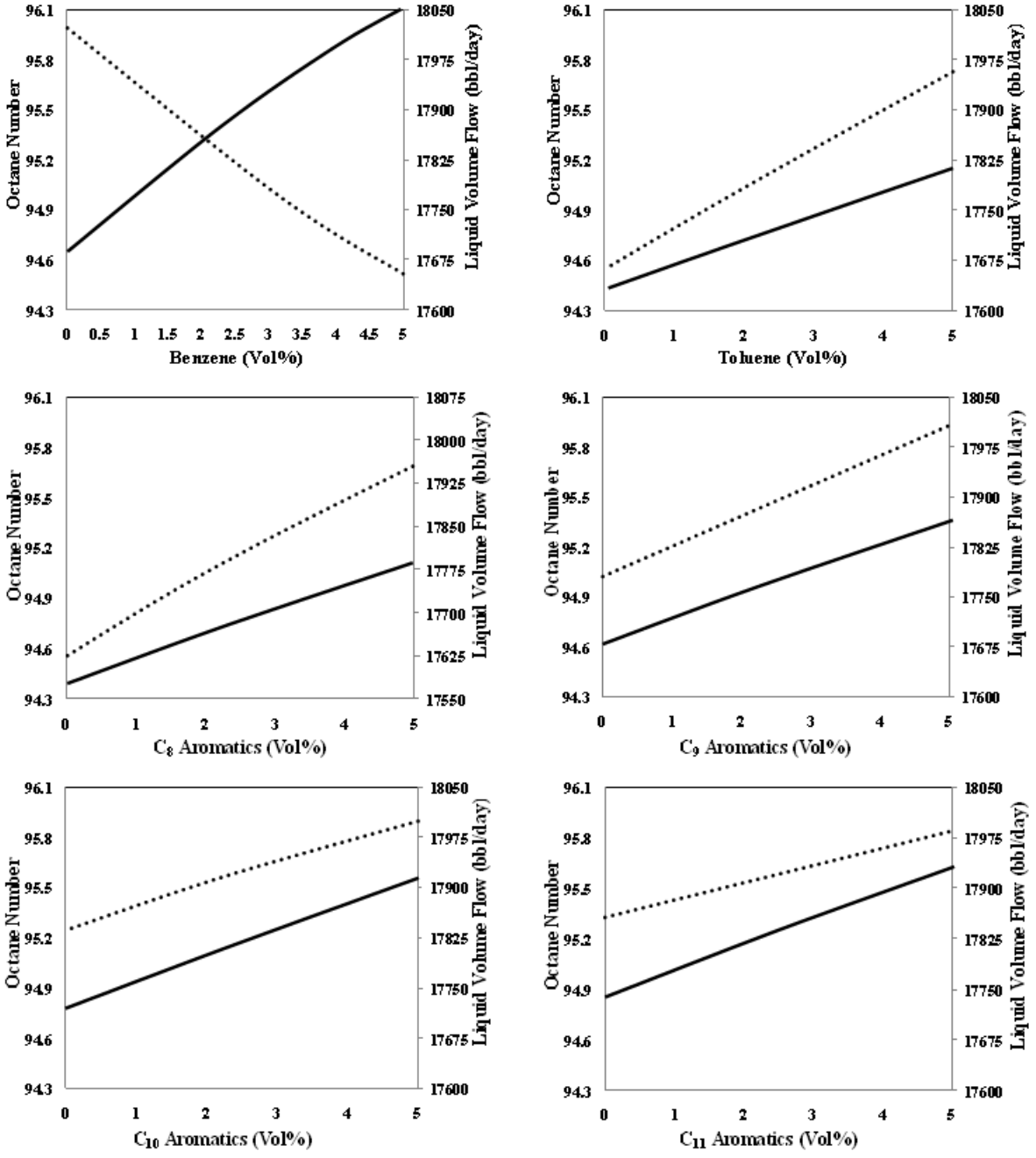

Fig. 3. The effects of aromatics feedstock composition on final product octane number, (solid line) & liquid volume flow (doted line).

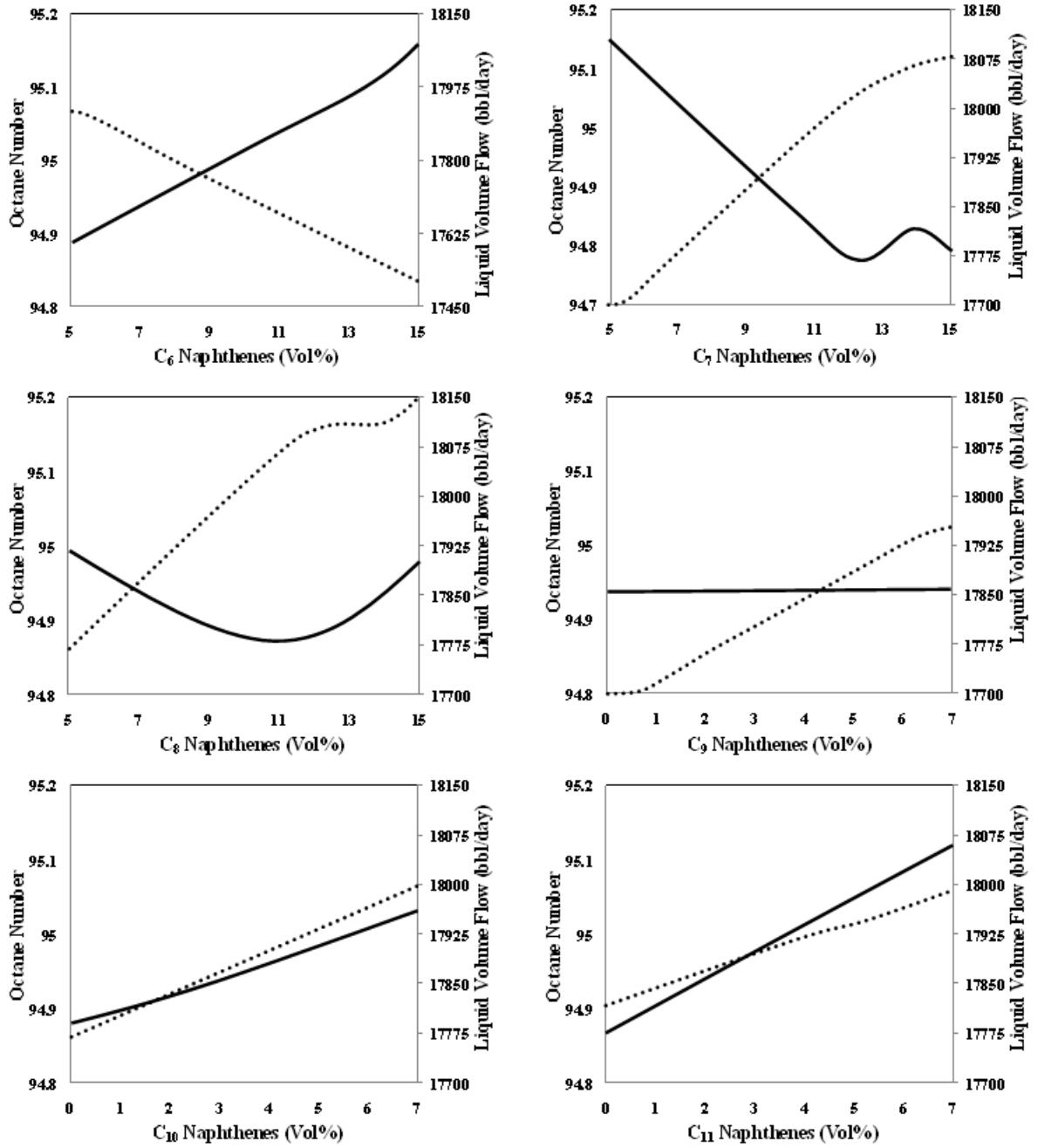

Fig. 4 The effects of naphthenes feedstock composition on final product octane number, (solid line) & liquid volume flow (doted line).

4. Conclusions

The comparison between simulation's results using Hysys-refinery software and actual results show that kinetic model used in Hysys-Refinery is in good agreement. The results of catalytic reforming unit by Smith model at the start of running is not consistent with actual results. In the conventional range, the temperature and pressure has no effect on octane number and final product flow rate.

In this simulation, the operating data for catalytic reforming unit has been measured at the given time of catalyst age (fresh catalysts). With the view point of stability of catalyst deactivation rate in the given time range, and because changes in different feed composition causes variation on octane number and final product Flow rate; in this study the effects of components of the feedstock on octane number and final product flow rate was evaluated and the results was observed.[fig 3,4,5]. Hence, because of the feed catalytic reforming unit comprising 20% volumetric from heavy isomax naphtha, so, it is suggested that if this amount is increased, consequently, octane number and final product flow rate will increase, too. But, its effect on catalyst deactivation rate must be investigated.

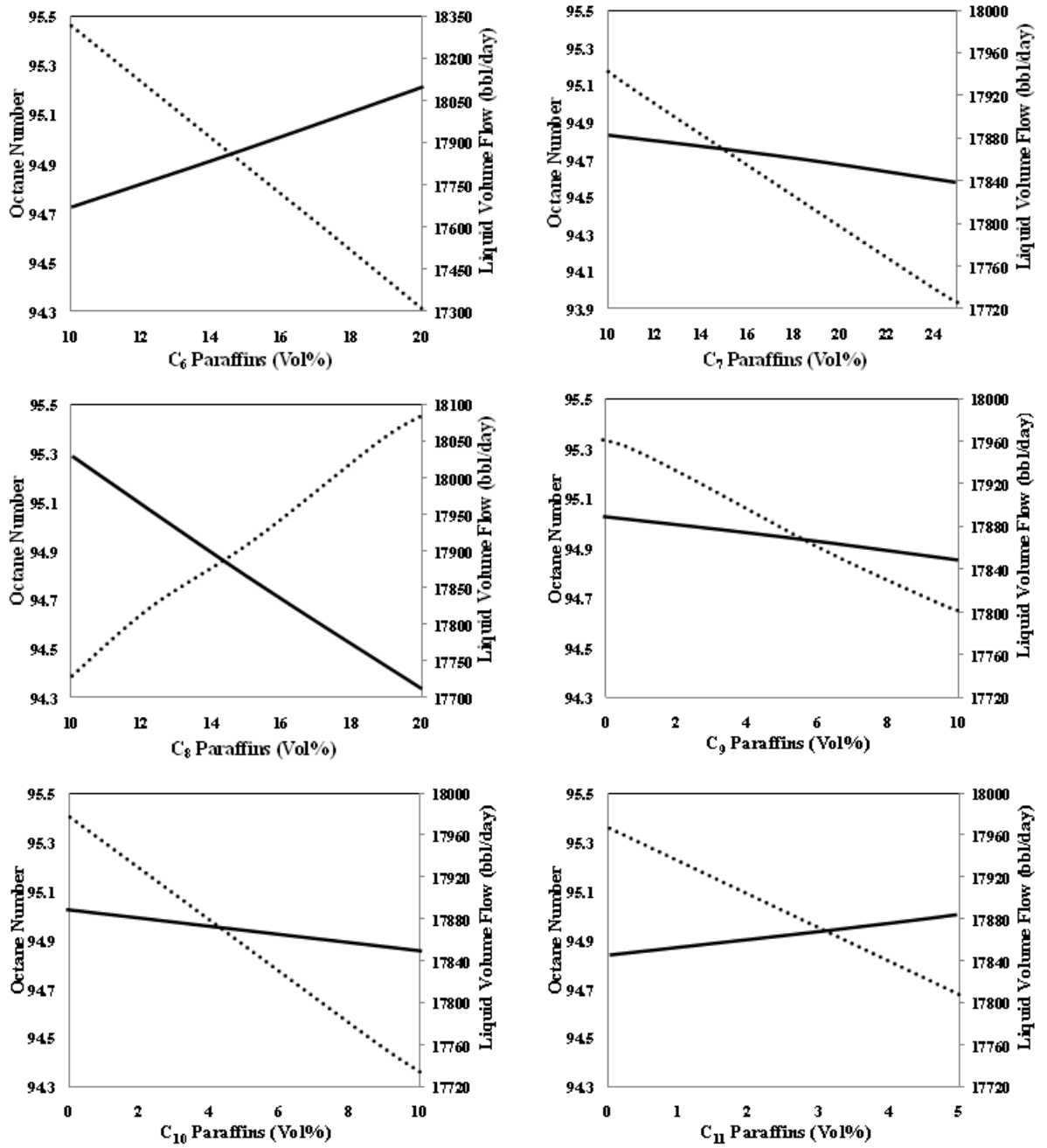

Fig. 5 The effects of paraffins feedstock composition on final product octane number, (solid line) & liquid volume flow (doted line)

By comparising between simulated and actual results of Hysys-refinery software, it could be said that this software is able to simulate the catalytic reforming unit at the start of running to end, and catalyst deactivation rate effect on octane number and flow rate of final product could be observed.

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