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The Effect of Feed Characterization on Naphtha Reformer Modeling

Isam A.B Salem*
Chemical Engineering Department, University of Benghazi, Benghazi, Libya

Original Research Article

***Corresponding author**
Isam A.B Salem

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Abstract: In this paper naphtha feed characterization and reactor modeling are thoroughly investigated. Naphtha feed characterization method is based on the work of proposing candidate components which have the potential to provide behavior similar to the behavior of the original naphtha feed. HYSYS software is used to provide the thermodynamic properties for the different true boiling points distillation cuts of the naphtha feed. Physical and thermodynamic properties of the selected components which represent each volume fraction (cut) are related to the properties obtained from HYSYS. The results which are the predicted molar composition of the lumped chemical species of the feed are compared to the paraffin-naphthene-aromatic (P,N and A) analysis of the studied commercial data. The relative errors of the feed stream are around 5%. The kinetic model and reaction network are based on the major reforming reaction such as dehydrgenation of naphthenes, dehydrocyclization of paraffin, cracking of paraffins and hydrocracking of cycloalkanes. The characterized data and model were bench marked against the real production data of a Libyan local refinery and the final results of the reformer such as outlet temperatures and reformate octane number have shown deviations with the actual operating data which considered in direct relation with weak points inherited to characterization method.

Keywords: Naphtha, Feed characterization, Reforming reactions, Reformer modeling, Lumping, Component profile.

INTRODUCTION

The importance of catalytic reforming processes is that they are used to convert petroleum straight run naphtha which is considered low octane number gasoline to a one with high - octane gasoline known as reformate. One of the main advantages of reformate is that it is used to increase the octane number of gasoline pool in the refinery [1] and also it is an important source of aromatics used in the petrochemical industry such as benzene, toluene, xylenes and ethylbenzene (BTXE).The first platinum-based reforming process is UOP's Platforming process, which started in 1949.

There are two main types of napththa catalytic reforming processes [1].

Semi regenerative reactor

The first catalytic reforming reactors were designed as semi regenerative (SR), or fixedbed reactors, using Platinum on alumina support catalysts. Semi regenerative reforming reactors are periodically shut down for catalyst reactivation.

Continuous regeneration process

The second catalytic reforming process with continuous catalyst regeneration (or the CCR Platforming process) was introduced by UOP in 1971.

There is a great amount of previous work done by researchers on the naphtha catalytic reforming process especially with the reaction kinetic, reaction network, and catalyst selection which lays the basis for naphtha reformer simulation and modeling. The work on reaction modeling started with Smith 1959 in which he simplified the large number of components present in naphtha to a smaller set of lumps [2]. In his work he classified the naphtha composition to paraffins, naphthenes and aromatic undergo four reactions. After his model other researchers such as Umesh Tasker, Padmavath and Ancheyta presented more complicate models with more lumps and reaction networks [3]. Normally the data regarding the naphtha feed composition is reported in terms of ASTM distillation analysis or API. Such data is not suitable as input to the mentioned models. The deal with such models requires providing the naphtha feed composition in molar basis. The procedure to infer the molar feed composition from the ASTM distillation analysis is called feed characterization. The accuracy of the reformer simulation depends on the method of naphtha feed characterization.

Because less information is available on this aspect, this paper will check the effect of feed characterization method on the naphtha reformer simulation.

Process description

The reforming process modeled in this paper starts with the feed which is straight run naphtha passes through hydrotreater. Because the major reforming reactions are endothermic, temperature reduction of the feed stream causes reaction rate to decrease, and to avoid such a problem, the catalyst is distributed over two reactors. The hydrotreatd straight run naphtha feed is mixed with recycled hydrogen stream and preheated to desired temperature before entering the first reactor. The product from the first reactor after heating enters the second reactor, the outlet from the second reactor enters a separator in which hydrogen rich gas is separated and recycled back and mixed with fresh feed to the first reactor.

Table-1: catalyst distribution in the studied reactors

Catalyst	First Reactor	Second Reactor
Weight (kg)	690	1685
Distribution (wt %)	0.29	0.71

The catalyst used in the reactors is Pt/Re on alumina also in Table 2 some operational conditions of the studied reforming unit.

Table-2: process variables

Process variable	Value
Inlet temperature ^{o}C	510 ~535
Hydrogen /hydrocarbon ratio (mol/mol)	4 ~ 9
LHSV(h^{-1})	1.5~ 2
Yield (vol%)	80 ~ 90

Reformer dynamic model

As discussed above an essential start in the modeling procedure is to provide the input data to the model as molar ratios which is called feed characterization. The feed to the studied platforming unit is a hydrotreated straight run naphtha which is condidered as complex mixture. The feed will be considered to consist of naphthenes which are (alkyl cyclohexane (ACH) and alkyl cyclo pentane (ACP)), paraffins which are (normal and isoparaffins (NP, IP) respectively) and aromatic (A) in the range from C_6 to C_9 [4].

Feed characterization

The Naphtha feed composition information used in this work is reported in terms of ASTM D86 distillation. The problem with such information is that it cannot be used directly as an input to the mathematical models, because most of the modeling approaches require the molar composition of the lumped chemical species of the feed. The idea of the feed characterization is to develop a method that will provide a set of (lumped) mainly from the given ASTM or TBP distillation data. The method used in this paper utilizes the approach of candidate components which will behave in a way similar to the naphtha feed [5]. The procedure illustrated below presents the sequence of steps which deals with the data obtained from a refinery in Libya.

- Conversion of ASTM D86 distillation data as in table 3 obtained from the refinery, which represents the straight run naphtha to the form of the true boiling point (TBP) distillation data by using HYSYS software.

Table-3: feed distillation analysis

Volume %	IBP	10	50	90	FBP
ASTM TEMP C	89	102	117	144	164

- The overall temperature range is divided (cut) into a system of non-overlapping temperature intervals continuously covering the volume range.

- Each true boiling point (TBP) volume fraction would actually consist of a mixture of chemical species whose boiling points would fall within the TBP range (cut) of the corresponding volume. Small and limited database developed for this purpose which contains hydrocarbon components and their physical properties and the values of these properties obtained from the available literature. The purpose of this database is to provide candidate components as in table 4. On the other hand HYSYS software used to predict the properties of each cut as shown in table 5.

- The physical and thermodynamic properties of these chemical compounds are obtained from the database.
  If the mole fractions of these chemical species in each fraction are known then the average property of the fraction can be estimated by a simple mixing rule as

$$\Omega = \sum x_i \Omega_i \qquad (1)$$

  Where Ω means the property and x is the mole fraction of component (i).

Table-4: Candidate components

Temp. interval ^{o}C	Components	Category	Boiling point (^{o}C)	Mol. weight kg/kmol.	Molar volume m3/kmol.	Heat of vaporization j/kmol.
60-80	Cyclo Hexane	ACH6	80	84	0.108	33059
	benzene	A6	80	78	0.1	33833
	normal hexane	NP6		86	0.132	30560
81 -99	2-Methylhexane(iso heptane)	IP7	91	100	0.147	34702
	1-1 dimethy cyclo pentane	ACP7	88	98	0.1225	31400
	normal heptane	NP7	98.4	100	0.147	36570
99 -105	Methyl cyclo hexane	ACH7	101	98	0.128	31270
	ethyl cyclo pentane	ACP 7	103	98	0.126	32000
	iso octne	IP8	99	114	0.165	35100
105- 113	1,1,3 tri methyl cyclo pentane	ACP8	105	112	0.14	36000
	2,2 dimethyl hexane	IP 6	105	114	0.165	37000
	Toluene	A7	110	92	0.11	38000
113- 123	3 ethyl hexane	IP6	119	114	0.163	56500
	2 methyl heptane	IP7	119	114	0.163	39500
	1,1,2 tri methyl cyclo pentane	ACP8	114	112	0.147	39360
123- 137	ethylcyclo hexane	ACH8	132	112	0.145	40200
	1-ethyl,2-methyl cyclo pentane	ACP9	128	112	0.145	40000
	normal octane	NP8	125	114	0.162	41400
137-150	Iso nonane	IP9	143	128	0.177	36480
	meta xylene	A8	139	106	0.123	42650
	ortho xylene	A8	144	106	0.121	45000
151-170	normal nonane	NP9	151	128	0.178	46400
	Propyl cyclo hexane	ACH 9	155	126	0.159	45100

Table-5: data obtained by HYSYS software

TBP Cut fraction	Molecular weight	Molar volume	Heat of vaporization
0-7%	83.89	0.1217	31160
7-31%	92.67	0.1301	33840
31-39%	101.2	0.1386	35000
39-49%	104.9	0.1424	36500
49-60%	110	0.1473	38490
60-75%	116	0.1541	40580
75-88%	123.4	0.1612	42610
88-100%	134	0.17	45870

- It is possible to solve for the mole fraction of the species that would minimize the difference between the properties predicted from the HYSYS software and the mixture according to equation 1. Linear multi objective optimizing function was generated, normalized, and then solved with built in Excel solver. The results are shown in table 6.

The results obtained from the characterization method of the feed showed that the predicted paraffin-naphthene-aromatic analysis is 56.6, 38.8 and 4.6% in comparison to the actual analysis which is 55.5, 41.6 and 2.9%. These data will be used as input data for the developed dynamic model.

Table-6: catalyst specification

Component	Mole Fraction
ACH6	0.0049
ACH7	0.0118
ACH8	0.0018
ACH9	0.1026
ACP6	0.0049
ACP7	0.0642
ACP8	0.1454
ACP9	0.0524
NP6	0.0478
NP7	0.141
NP8	0.0977
NP9	0.0114
IP6	0.037
IP7	0.0487
IP8	0.0506
IP9	0.132
A6	0.0139
A7	0.0317
A8	0.005
A9	0

Model development

To check the effect of the feed characterization method, Smith model [2] which simplifies the calculations was selected. Smith proposed a model based on the following assumptions. Pseudo components or lumps are used to simplify the naphtha feed complexity, all reactions are homogenous, the kinetic and the reaction network of the catalytic reforming process are described only with four reactions and hydrocracking produces nearly the same amount of moles.

The following two reactions (A, B) reach thermodynamic equilibrium.

Cycloalkanes → Aromatic +H2 (A)

Cycloalkenes +H2 → Alkanes (B)

Smith's model represented the hydrocracking of alkanes and cycloalkanes by the following reaction equations (C,D) is totally irreversible and kinetically controlled.

- Hydrocracking of cycloalkanes.

$$C_2\ H_2 + \left(\frac{n}{3}\right) H_2 \rightarrow \left(\frac{n}{15}\right) \textstyle\sum_{i=1}^{5} C_i \qquad \text{(C)}$$

- Hydrocraking of alkanes

$$C_2\ H_{2+2} + \left(\frac{n-3}{3}\right) H_2 \rightarrow \left(\frac{n}{15}\right) \sum_{i=1}^{5} C_i \qquad (D)$$

Where n is the carbon number and is given by equation (2)

$n = (M_{wt\ f} + 2x_p + 6x_A)/14$ (2)

Where x_p, x_A are mole fractions of parafins and aromatics in the feed respectively. The kinetic equations and their initial parameter estimation were taken from literature [6]. The following four rate expressions used to describe the lumping kinetic are as follows.

1- The dehydrogenation is the principal reforming reaction because it produces aromatics which are the main reason for the increase in octane number. This reaction is very fast and reaches equilibrium very quickly. It is also considered as the main endothermic reaction and causes the transformation of cycloalkane to aromatic, which is represented with the reaction rate given by equation (3).

$$r1 = k_{p1}(P_E - P_A\, P_H^3/K_{P1}) \qquad (3)$$

E, A, and H represent naphthenic, aromatic and hydrogen respectively. k_{p1} represents the rate constant of equation (3) with units of (kmol/(h.kgcat.MPa) and is given in equation (4).

$$\mathrm{k_{p1}} = 9.87\exp(23.21 - \frac{34750}{1.8\mathrm{T}}) \qquad (4)$$

The equilibrium constant with units $(MPa)^3$ is given by equation (5).

$$\mathbf{K_{p1} = 1.04 \times 10^{-3}\exp(46.15 - \frac{46045}{1.8T}}) \qquad (5)$$

2- The transformation of cycloalkane to alkane in the presence of hydrogen gas which is exothermic reaction and considered as rapid reaction and reaches equilibrium fast. It represented by the chemical reaction rate given by equation (6)

$$r2 = k_{p2}(P_E P_H - P_P\, /K_{P2}) \qquad (6)$$

P represent paraffin and k_{p2} represent the rate constant with units of $(kmol/(h.kgcat.MPa^2)$ and is given by equation (7)

$$\mathrm{k_{p2}} = 9.87\exp(35.98 - \frac{59600}{1.8\mathrm{T}}) \qquad (7)$$

The equilibrium constant with units $(MPa)^3$ and is given by equation (8)

$$K_{p2} = 9.87\ \exp(\frac{8000}{1.8T} - 7.12) \qquad (8)$$

3- Hydrocracking of paraffin and cycloalkane molecules in the presence of hydrogen into lower molecular weight molecules. This reaction is exothermic and the only source of producing light gases, like, methane, ethane, propane, etc., which are outside the gasoline boiling range and can be classified into two types, which are the hydrocracking of alkanes and cycloalkanes. Both represented by the chemical reaction rates given by equation (9, 11) respectively.

$$r3 = k_{p3} P_P\, /P \qquad (9)$$

$$k_{p3} = \exp(42.97 - \ 62300/1.8T) \qquad (10)$$

P represent total pressure and the reaction rate constant kp3 for the rate of alkane cracking with units of kmol/(h.kgcat.)

$$r4 = k_{p4} P_E\, /P \qquad (11)$$

The reaction rate constant kp4 for the rate of cycloalkane cracking with units of kmol/(h.kgcat.). And is given in equation(12).

$$k_{p4} = \exp(42.97 - \ 62300/1.8T) \qquad (12)$$

The reaction network considered here in this paper and other previous works [4-7] consists of 26 components and 47 reactions. The following equation represents the mass balance for each component in the model.

$$\frac{dF_i}{dw} = \sum_{k=1}^{m}(r_k \times \nu_{k,i}) \qquad (13)$$

Where F_i is the molar flow rate of the i th component (kmol./hr), w is the catalyst weight in kg , r_k is the k th reaction rate and $v_{k,i}$ is the stochiometriy coefficient of the i th component in the k th reaction. The partial pressure of the individual component P_i in the rate equation is given by the following equation

$$P_i = \left(\frac{Fi}{\sum_{i=1}^{26} Fi}\right) \times P_t \qquad (14)$$

The change in napthene concentration is represented by equation (15).

$\frac{dF_E}{dw} = \sum_{i=1}^{8}(- r_1 - r_2 - r_4)$; i =1, 2, 3, 8 (15)

Where components from 1 to 4 represent alkycyclohexane (ACH) while components from 5 to 8 represents alkycyclopentane (ACP).

The change in paraffins concentration is represented by equation (16).

$\frac{dF_P}{dw} = \sum_{i=9}^{16}(r_2 - r_3)$; i = 9,10,11,….,16 (16)

Where components from 9 to 12 represent normal parraffins (NP) while components from 13 to 16 represents isoparaffins (IP).

The change in aromatic concentration is represented by equation (17).

$\frac{dF_A}{dw} = \sum_{i=17}^{20}(r_1)$; i=17, 18,…., 20 (17)

Components from 17 to 20 represent aromatic (A).

The change in hydrogen gas concentration is represented by equation (18).

$\frac{dF_H}{dw} = (-3r_1 - r_2 - \left(\frac{n-3}{3}\right) r_3 - \left(\frac{n}{3}\right) r_4)$ (18)

The energy balance on the adiabatic reactor of the reformer is given by equation (19). The energy balance was carried out based on the enthalpy and the number of moles of hydrogen reacted in the above four reactions.

$$\frac{dT}{dw} = \left(\frac{1}{\sum Fi \times CPi}\right)\left(3r_1\Delta h_1 + r_2\Delta h_2 + \left(\frac{n-3}{3}\right) r_3\Delta h_3 + \left(\frac{n}{3}\right) r_4\Delta h_4\right)$$

Reactions enthalpy used in this model which obtained from literature [6] are as follows

Δh_1= 71038 k J/kmol.H_2

Δh_2= - 36953 k J/kmol.H_2

Δh_1= -56597 k J/kmol.H_2

Δh_1= 51939 k J/kmol.H_2

The above ordinary differential equations of mole and energy balances were solved with built in solver (ode 23) in MATLAB software. Feed characterization data where used as initial conditions to the first reactor and the outlet data was used as input to the second reactor except of temperature which is changed due to the presence of heater.

RESULTS AND DISCUSSIONS

In the feed characterization method the selection of the candidate components is affected by the quality of the available database .by other words the increase in the size of data will increase the probability of finding suitable components in the characterization procedure. Our limited database failed to find suitable components in the 8th cut to match the component A9.

Inspite the fact that the method of characterization provided results in good proximity with the PNA, but the deviations especially in the aromatic concentration expected to propagate through the model which will be clear in the component profiles obtained.

The model provided temperature profile in addition to all profiles of the component concentration. Figure 1 shows high temperature drop in first reactor, which is an indication that the dominant reaction is the aromization of cycloalkane this reaction is very fast and reaches equilibrium very quickly .on the other hand the reaction of hydrocracking provided good amount of heat which caused restriction on temperature drop and even showing some temperature increase in the second reactor. The predicted outlet temperatures of the first and second reactor are 445 and 490 K that slightly deviate from the actual data which are 433 and 481 K.

Figures 2 shows the Aromization reaction profiles of alkylcyclo pentane and also it is clear that the reaction is very fast and reaches equilibrium quickly. In spite the fact that all the naphthenes are consumed and converted to aromatics which can be observed in other literature [7].

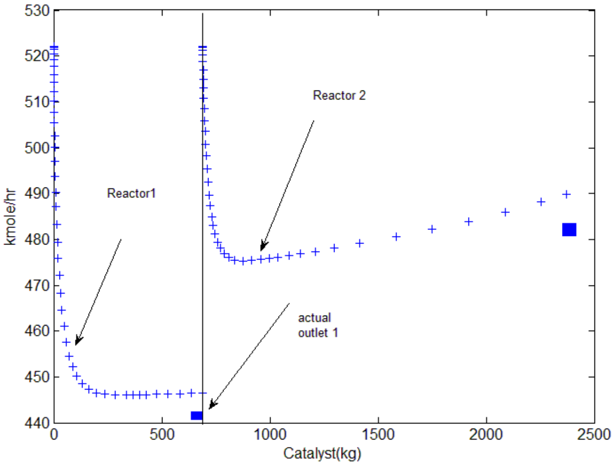

Fig-1: temperature profiles in the reforming reactors

But component ACP6 provided unusual behavior and increased in the first reactor. This can be explained by the presence of the predicted ACP6 component in very small concentration less than the corresponding aromatic component A6 as will be seen in figure 6. According to aromization reaction equation (A), this reaction will proceed in the reverse direction which means A6 will be converted to ACP6.This reaction will continue till the complete consumption of A6. The direct result of this behavior is that, this reaction became exothermic and will cause restriction on the temperature decrease. Also will reduce the reformate octane number.

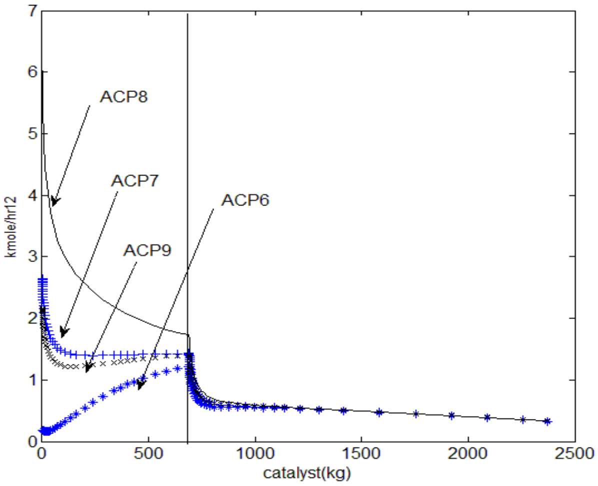

Fig-2: alkylcyclo pentane molar flow rate

On the other hand the dehydrocyclization reaction in figure 3 shows unusual behavior of component ACH8.this trend is normally associated with the zero initially predicted components. The component ACH8 will be formed as a result of A8 formation which will affect the temperature and octane number as mentioned before. Also observed that A8 showed normal trend of increase because of ACP8 is available in high concentration.

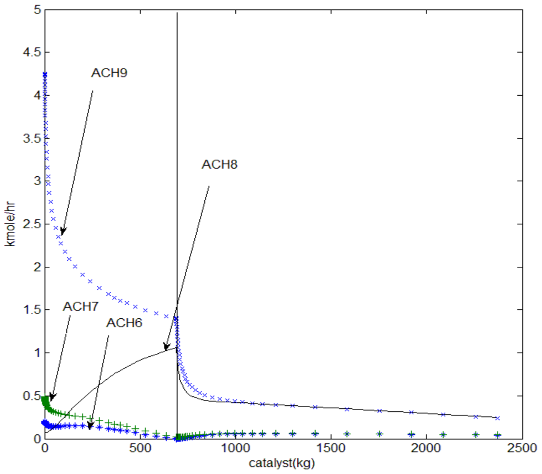

Fig-3: alkylcyclo pentane molar flow rate

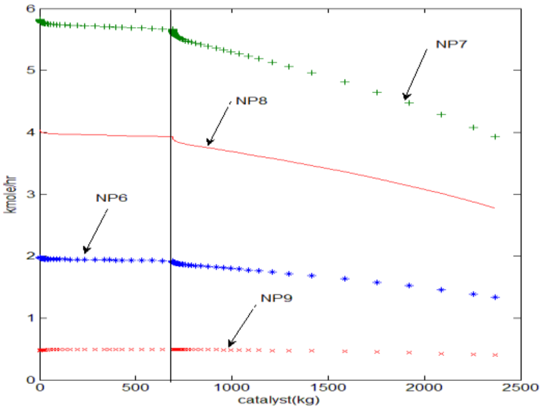

Fig-4: normal paraffins molar flow rate

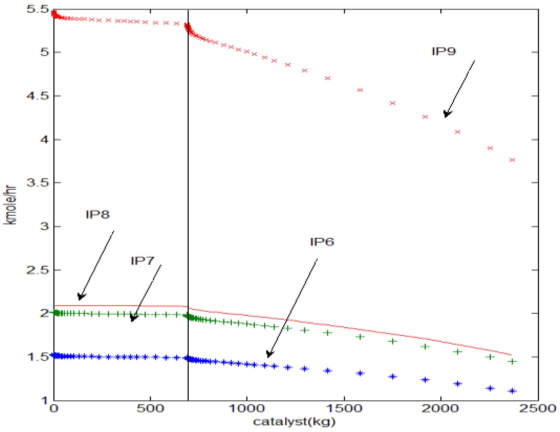

Fig-5: isoparaffins molar flow rate

Figures 4, 5 are the profiles of hydrocracking reaction of normal and isoparaffins which slow that, the decline in components concentration is higher in the second reactor. Figure 7 shows higher rate of hydrogen consumption in the second reactor which indicates that significant increase in hydrocracking reaction.

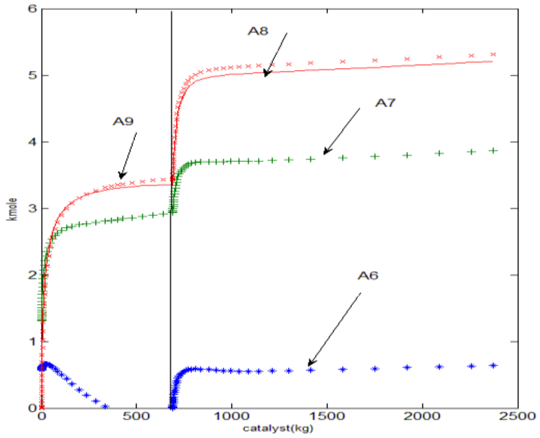

Fig-6: aromatics molar flow rate

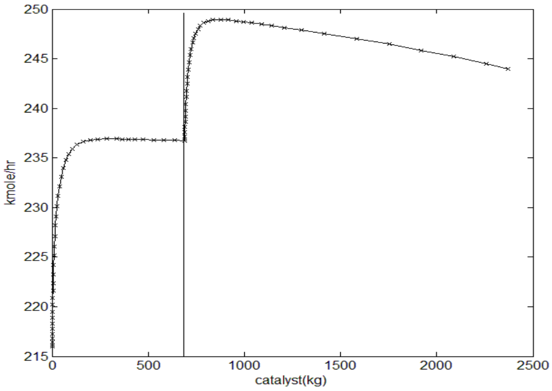

Fig-7: hydrogen molar flow rate

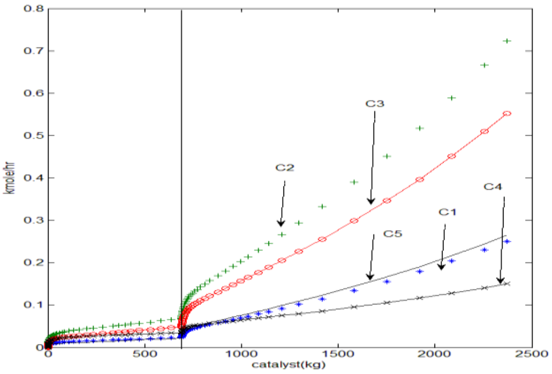

Fig-8: light gases molar flow rate

Figure 8 shows that the second reactor provide higher yield of lighter hydrocarbon such as methane, ethane, propane and butane .the production of such lighter hydrocarbon causes significant gasoline loss.

CONCLUSION

Although the results obtained from the characterization method of the feed showed good consistency with actual P, N and A analysis, But preliminary analysis of the characterization method showed inherited weak points which can affect any selected model outcomes.

The characterization method should depend on big size databases, because Size of the database used can affect the quality of the candidate components, this means limited databases will fail of obtain suitable candidate components in some cuts or can provide one component only.

The method should provide the aromatic components in concentration lower than their corresponding naphthene components (alkylcyclo pentane and hexane) to avoid the reversal of the aromization reaction which is highly exothermic and can affect the reformer outlet temperature.

Predicted component with zero value especially with naphthenes can favor the consumption of aromatic components and cause restriction on the reformer outlet temperature and the reformate octane number.

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