Improving the Quality of Gasoline Production in Catalytic reforming Processes for Basrah Refinery

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Abstract

The catalytic reforming process is one of the most significant systems in petroleum refineries .It converts heavy naphtha with low octane number to a light naphtha (reformate) with high octane number through a group of catalytic reactions such as dehydrogenation , isomerization , dehydro-cyclization and hydro- cracking . At the same time, it produces hydrogen gas(H_2) and liquefied petroleum gas (LPG) as by-products.

The proposed model assumes three adiabatic catalytic reactors with a central furnace relative to Basrah refinery plant in Basrah city, one of the largest industrial cities in the southern part of Iraq. The catalytic reforming units are operated at relatively high operation conditions where the temperature is in the range of **(470 -500)◦C**, pressure is in the range of **(30-35 atm)** and hydrogen to hydrocarbon molar ratio is about 5.9. The reactors have been provided with platinum- alumina as a catalyst and the density of feedstock is **(732.8 -766.7 Kg/m^3**).

In the present work, a mathematical model was adopted to determine the **product** moles and temperature distributions as a function of the reactor bed radius **for** the Basrah refinery catalytic reforming system where both feed and products streams are assumed as ideal gasses, and all of the catalytic reforming reactions occur at the same time in each reactor with first order reaction with respect to reactants . The axial dispersions are neglected and only radial direction variables are considered.

The results of the prediction model were compared with experimental data log book from Basrah Refinery catalytic reforming system and with the **Ke-min** et.al model **2004** and a good agreement was shown. The results of Examination of the effect of operation conditions such **as** feed temperature and feed pressure show that the quality of the produced gasoline can be improved by adjusting the system's operation conditions. Also, for the existing plant, the results of the prediction program have established the ability of reducing the feed stock temperature to about 430°C and the **operation pressure at (35 atm)** for achieving improvement in the quality of gasoline production.

Introduction

Catalytic reforming of naphtha is a very important process in hydrocarbon processing industry for octane improvement or as sources of aromatics and hydrogen. The catalytic reforming process is designed to transform the low octane number constituents in the gasoline composition into very high octane rating aromatics in the range of 6 to 10 carbon atoms. This number is the percentage of iso-octane in a blend with n-heptane that produces the same amount of knocking produced by the tested gasoline.

The process is carried out either thermally or catalytically. The nature of the final product is of course influenced by the source (and composition) of the feedstock. The demand of today's automobiles for high-octane gasoline has stimulated the use of catalytic reforming. Catalytic cracking is the most important and widely used refinery process for converting heavy **oils** into

more valuable gasoline and lighter products. Originally **cracking** was accomplished thermally but the catalytic process has almost completely replaced thermal cracking because more gasoline having a higher octane and less heavy fuel oils and light gases are produced [1]. The light gases produced by catalytic cracking contain more olefins than those produced by thermal cracking. The cracking process produces carbon (coke) which remains on the catalyst particle and rapidly lowers its activity. To maintain the catalyst activity at a useful level, it is necessary to regenerate the catalyst by burning off this coke with air. As a result, the catalyst is continuously moved from reactor to regenerator and back to reactor or may be the regeneration processes can be carried through the same reactor. Sometime this drop is very rapid in the order of seconds, and sometimes it is so slow that regeneration or replacement is needed only after years of use. In any case with deactivated catalysts regeneration or replacement is necessary from time to time [3]. Many reasons **are** contribute**d** to catalyst deactivation such as;

1-operating time

2-carbon precipitation on the catalyst surface **so, only the surface reaction will participate in the cracking reaction and some of side reactions occur**

3-sudden**ly** plant shutdown may participate to catalyst deactivation.

Various kinetic models to represent catalytic reforming have been proposed by many researchers. A successful kinetic analysis proposed in **1959**, **Smith [3]**, was based on idealizing the complex naphtha mixture by representing the paraffin, naphthene, and aromatic groups by single compounds.

In 2005 , Ke- min et. al. [4]. proposed a physical model to describe the catalytic reforming unit with four fixed bed reactors in series with radial flow under adiabatic operating conditions. **In 2006 , Mohaddecy et. al. [5]** , studied simulation of catalytic reforming process and prediction of vital parameters such as octane number, Liquid Hour Space Velocity, reactor inlet temperatures , yield and catalyst life aiming at process optimization was of prime importance. **In 2006, Weifeng et. al. [6]** , developed a model as a user module by Aspen pulse system , this model developed to discusses 18 kinetic model for naphtha catalytic reforming reactions then simulated a whole industrial continuous catalytic reforming process. **In 2010 , Mahdavian et. al. [7]** , developed a mathematical model of a (CCR) with catalyst recirculation for simulation and optimization of the industrial continuous reformers . The process model used an extended version of the kinetic model reported by Padmavathi , with some modifications on kinetic constants. Also, it considered the deactivation rate of the catalyst and pressure drop with in reactor , the process model was based on 12 kinetics reaction network .The naphtha was based on 25 pseudo components including (C_6- C_{10}) hydrocarbons in three categories PNA . The model is taken into account the light hydrocarbons (C_1-C_5) as the products of hydrocracking reaction.

Plant Description of Basrah Refinery

Basrah refinery plant is considered as one of the industrial plants in Basrah city , one of the industrial cities in the southern part of Iraq. This plant consists of many sub- plants such as wax , Benzen and reforming plants . Basrah refinery plant was built before more than four decades ago by one of the BP Trading Limited companies. Reforming plant is considered one of the important plant in this project . It's responsible for improvement the quality of heavy Naphtha with low octane number (about of 65) to light naphtha with high octane number (about of 95). This system is capable of producing about 8000 brail / day of light Naphtha . However this plant **has** subjected to many Military attacks through the Iraq . Iran war and first and second Arab Gulf war .

The reforming system consists of three main fixed bed catalytic reactors . Each one has provided with Pt/γ Al_2O_3 as a catalyst. The volume of catalyst in the first , second and third reactor is about 4.7, 9.5 and **18.9** m^3 catalyst respectively. Also , the height of these reactors are 3 , 4 and 6.1 m.

However, reformer feed is first pretreated with hydrogen in first section of the furnace which contains 14 flares for heating the feed mixture to the desired value of temperature (about of 505 -530 °C) and then enters the first catalytic reactor. The most desirable reactions are carried out inside the reactor such as dehydrogenation and Isomerization reactions. The product stream from the first reactor after preheating in the second part of the furnace , which contains 8 flairs, enters the second reactor and similarly the product stream from the second reactor after preheating enters the third reactor. Anyway, the overall reforming reactions occurring in the reactors are endothermic and therefore there is a pre-heater installed before each reactor.

Figure (1) shows the catalytic reformer distribution in the Basrah refinery plant while the plant characteristics have summarized in table (1).

Recently, the Basrah refinery is suffered from many technical problem in most plants. The reforming plant unable to produce gasoline with high octane number. Now, another new refinery will be constructed beside the old one for covering the requirement of gasoline with high octane number in Basrah city.

Figure (1) shows the external shape of high pressure unit in Basrah Refinery .

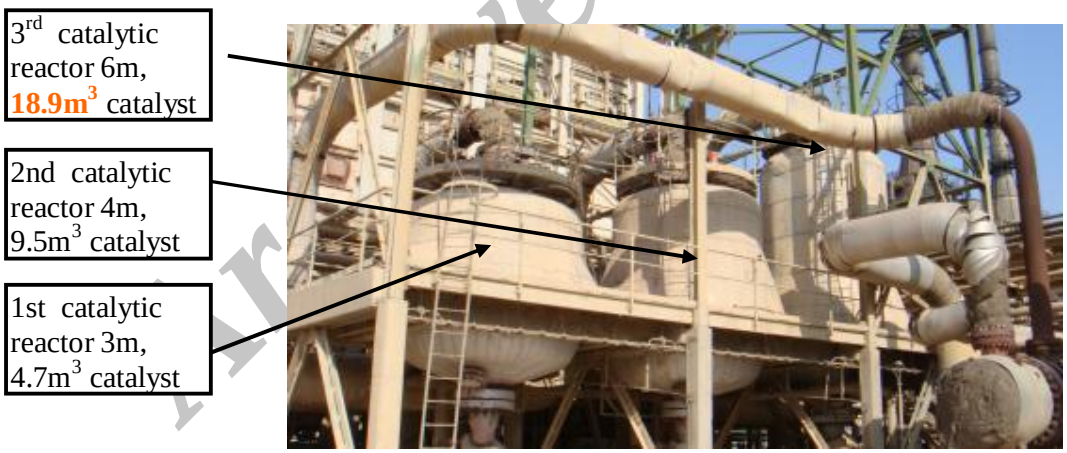

Table (1)shows the designing description of three fixed bed reactors which are used in Basrah refinery

Reactor	Inlet temp. (°C)	Outlet temp. (°C)	Length (mm)	Radius (mm)	Catalyst volume (m^3cat)	Height of catalyst (mm)
1st	**(505-530)**	**(465-480)**	**3**	**2.7**	**4.7**	**1050**

2nd	**(505-530)**	**(485-500)**	**4**	**2.7**	**9.5**	**2100**
3rd	**(500-525)**	**(495-515)**	**6.1**	**2.7**	**18.9**	**4200**

Model Description And Assumptions

In the present work , the kinetics of catalytic reforming process will be analyzed relative to Smith Model 1959 and the effect of reaction temperature, pressure and feedstock compositions , which contains three groups of compounds Paraffins P, Naphthenes N, and Aromatics A, will be studied.

For simplification the analysis of the theoretical model, the following assumptions are assumed;

1- Steady state operation and plug flow adiabatic operation.
2- Both reactants (feed) and products as **ideal gasses.**
3- All of catalytic reforming reactions occur at the **same time** in each reactor and first order reaction with respect to reactants.
4- The mole and temperature distributions along the axial direction can be neglected and only radial direction variables are considered.
5- Each three compounds which contain in **feedstock** (paraffins , Naphthenes and aromatics) have the same number of carbon atoms.
6- Neglected the calculation of **mole flow rates** distributions of light gasses(C_1- C_5) which are produced from hydrocracking reactions of paraffins and Naphthenes because these distributions relatively small.
7- The effectiveness factor of the catalyst (η) taken as equal for each four reactions and it is equal to **one**.

In the present work, several types of reactions are assumed as follows:

Cycloalkane (Naphthene) $\rightleftharpoons$ Arene (Aromatic)+ $3H_2$ ---- (1)
C_nH_{2n} (E) C_nH_{2n-6} (A) + $3H_2$ (H)

Cycloalkane (Naphthene) + H_2 $\rightleftharpoons$ Alkane (Paraffin) ---- (2)
C_nH_{2n}(E) + H_2 (H) C_nH_{2n+2} (P)

Hydrocracking of alkane ---- (3)

$$C_nH_{2n+2} + \left(\frac{n-3}{3}\right)H_2 \longrightarrow \left(\frac{n}{15}\right)C_1 + \left(\frac{n}{15}\right)C_2 + \left(\frac{n}{15}\right)C_3 + \left(\frac{n}{15}\right)C_4 + \left(\frac{n}{15}\right)C_5$$

Hydrocracking of cycloalkane ---- (4)

$$C_nH_{2n} + \left(\frac{n}{3}\right)H_2 \longrightarrow \left(\frac{n}{15}\right)C_1 + \left(\frac{n}{15}\right)C_2 + \left(\frac{n}{15}\right)C_3 + \left(\frac{n}{15}\right)C_4 + \left(\frac{n}{15}\right)C_5$$

The table below (2) shows the equations of reactions rate, reaction rate constant and equilibrium constants relative to reactions model:

$r_1 = \eta\, k_{f1} (p_E - p_A . p^3_H / K_{eq1})$	$k_{f1} = \exp (28.68 - 34750/T)$	$K_{eq1} = P_A P^3_H / P_E = \exp(46.15 - 46045/T)$
$r_2 = \eta\, k_{f2} (P_E . P_H - P_P / K_{eq2})$	$k_{f2} = \exp (35.98 - 59600/T)$	$K_{eq2} = P_P/(P_E . P_H) = \exp(8000/T - 7.12)$

$r_3=\eta\, k_{f3} * P_P/P$	$k_{f3}= \exp(42.97–62300/T)$	
$r_4=\eta\, k_{f4} * P_E/P$	$k_{f4} = \exp(42.97–62300/T)$	

The reaction rate equations can be developed for each component (Paraffins, Naphthenes and Aromatics) and Recycle Hydrogen as follows:-

$$\frac{dN_P}{dV}=-r_P r_b \quad \frac{dN_E}{dV}=-r_E r_b \quad \frac{dN_A}{dV}=-r_A r_b \quad \frac{dN_H}{dV}=-r_A r_b \qquad \text{-----(5-a,b,c,d)}$$

The above equations can be modified as follows:

$$\left[\begin{array}{ll} \frac{dN_P}{dV}=(r_2-r_3)\,r_b & \frac{dN_N}{dV}=(-r_1-r_2-r_4)\,r_b \\ \frac{dN_A}{dV}=(r_1)\,r_b & \frac{dN_H}{dV}=(3r_1-r_2-\left(\frac{n-3}{3}\right)r_3-\left(\frac{n}{3}\right)r_4)\,r_b \end{array}\right]$$

----(6-a,b,c,d)

The equation used to estimate the temperature profile along the reactor is obtained from an energy balance over the differential reactor control volume as follows:

$$F\,\rho\,C_p\,dT= r_{N\leftrightarrow A}\,\Delta H_r^*{}_{N\leftrightarrow A}\,dV + r_{N\leftrightarrow P}\,\Delta H_r^*{}_{N\leftrightarrow P}\,dV + r_{P\rightarrow G}\,\Delta H_r^*{}_{P\rightarrow G}\,dV + r_{N\rightarrow G}\,\Delta H_r^*{}_{N\rightarrow G}\,dV \qquad \text{---- (7)}$$

the above equation can be re-written as follows [4]:

$$\frac{dT}{dR}=\frac{2pRL\,r_b}{\sum F_i c_p}\{3r_1(-\Delta H_1)+r_2(-\Delta H_2)+\left(\frac{n-3}{3}\right)r_3(-\Delta H_3)+\left(\frac{n}{3}\right)r_4(-\Delta H_4)\} \qquad \text{---(8)}$$

A mathematical model was developed by assembling the mass and energy balances on the system of reactions, equations (5-a,b,c&d) and 8. The mass balance equations provided the variation of concentration of the components selected along the reactors radius, and the energy balance equation gives the variation of temperature. **Mole** and energy balances were carried out on one element of radial section of the reactor and then integrated over the whole reactor by using the

numerical calculation for finding the reactant compositions and temperature profile as a function reactor radius.

Results and Discussion:

The modeling and simulating of catalytic reforming processes are considered the first step to find the best operation conditions then ensuring the production of gasoline with high quality. The aim of controlling and monitoring of the operation conditions is connected with the ability of increasing the aromatic compounds in the production of catalytic reformer which it's improved the quality of gasoline production, high octane number.

The modeling of naphtha catalytic reforming processes have been carried out by solving the ordinary differential equations of mole flow rates and temperature as a function of reactor **bed** radius and relative to smith model assumptions(equations 6 a,b,c & d and 8). The need for looking into the simple model was due to the complexity of other models that accompany multi-component reactions. Also, the component data for specific rate constant, pressure exponent and equilibrium constant for several of these reforming reactions are not easily available in literature. The Smith kinetic scheme as compared to the other complex models described in literature provides a shortcut approach for estimating the product yield of the catalytic reforming process.

The first step is performed for checking the accuracy of predicting program relative to initial data as published in Ke-min model [4] and the results show a good agreement between them. Table (2) shows the results of the first catalytic reactor for Ke-min and predicting program.

	Ke- min et al model (N_i Kmol/hr)					Prediction model (N_i Kmol/hr)				
R(mm)	T(°c)	NA	NE	NP	NH	T(°c)	NA	NE	NP	NH
460	496.88	32.979	71.642	76.65	1300.845	484.5	*35.323*	*70.891*	*76.6305*	1315.257
410	486.04	39.943	64.052	76.603	1320.133	476.535	*39.356*	*66.857*	*76.63044*	1327.351
360	479.48	44.096	59.601	76.565	1331.804	471.451	*41.912*	*64.3*	*76.63041*	1335.016
310	475.03	46.879	56.644	76.535	1339.686	467.865	*43.706*	*62.505*	*76.63038*	1340.40
260	471.88	48.843	54.569	76.513	1345.276	465.226	*45.023*	*61.189*	*76.63035*	1344.347
210	469.6	50.254	53.084	76.496	1349.304	463.26	*46.001*	*60.209*	*76.63033*	1347.283
170	468.26	51.084	52.213	76.486	1351.676	462.097	*46.579*	*59.631*	*76.63032*	1349.016

Table (2) shows the comparison results between literature [4] and prediction model

After the accuracy of predicting program has established, the process model was applied on the one of the existing plant, Basrah Refinery catalytic reforming plant, where the details of this plant was described in the previous section. Table(3) shows the feed operation conditions for the Basrah Refinery plant and table (4) depicts the plant comparison results between prediction model and exact plant for the value of outlet stream temperature on the third catalytic reactor, **PNA** compositions and RON.

Table (3) shows the exact operation conditions for Basrah Refinery plant

Feed pressure atm	30
Feed flow rate Kmol/hr	353.0618

Mole% Naphthenes	21.26
Mole% Aromatics	13.56
Mole% Paraffins	65.7
RON	65

From practical point of view, the results of prediction model was more acceptable than exact plant and this is due to the effect of effectiveness factor on the reaction kinetics. The performance of catalyst activity has change between time to time so, the impurities compounds have a large effect on the catalyst activity also, unsteady state operation, continues plant turn off due to electrical sources, catalyst characteristics delivering from different manufacturer sources and central furnace efficiency, all of them have participated to reduce the quality of gasoline production. The theoretical value of RON gives a very acceptable value comparative with the exact plant results also, the deviation between them have approved the incorrect in the actual plant operation conditions or catalyst activity. For this reason, the catalysts regeneration or replacement was necessary from time to time.

For the exact catalytic reforming system the effect of operation temperature and pressure have been tested and the best operation conditions have been specified by evaluating the octane number values where it's correlation derived by another authors [8]. The effect of operation feed stock temperature for different range between (430-490^{o}C) and operation pressure (25-35 atm) on the quality of gasoline production have been examined and tabulated in table (5).

Table(4) shows the plant test results compared to prediction model

variable	**Exact plant results**	**Model results**
Inlet temperature reactor ^{o}C	470	470
Outlet temperature reactor ^{o}C	465	445.52
Mole% Naphthenes	7.18	7.56
Mole% Aromatics	20.38	27.3
Mole% Paraffins	72.44	65.18
RON	**87**	113.24

These results should be included in the table of the conclusions to show the RON improvement from 87 to 113
4

The results have **been** ensured the ability of reducing the actual hard operation conditions by controlling on the other process operation conditions. The paraffinic properties of the Basra refinery oil feed relative to any **other naphthenic base oils**, have a large effect on the reaction mechanism and reaction temperature. This is due to the high conversion reaction temperature of **naphthenic** compounds in comparison with the conversion temperature of paraffinic base oils nature. Table (5) shows the PNA composition as a function of feed stock temperature and operation pressure where the effectiveness factors for three reactors have assumed to be equal to one. The results depicted the ability of improvement the quality of gasoline production by selecting the operation conditions which have ensured the requirement of gasoline production. On another side, the results indicated the significance of feed stock temperature, operation pressure and catalyst activity on the quality of gasoline production.

For the existing plant, the results of predicting program have established the ability of reducing the feed stock temperature to about of 430 °C under the operation pressure (35atm) by reducing the number of flairs inside the thermal furnace for improvement the quality of gasoline production.

Consequently, the burned fuel requirements for the thermal furnace will be reduced. Also, the results indicated the ability of reducing the operation pressure from 35 to 25 atm, because the ratio of improvement in the quality of gasoline production was very limited also, from the industrial point of view, it is better to operate the existing plant under moderate conditions.

Conclusions:

The results show the capability of using Smith model for **paraffinic or naphthenic base oil** nature. The predicting program can be used to estimate the efficiency of Basrah refinery, gasoline plant, and can be applied to any other plant by changing the initial data. The quality of gasoline production from catalytic reforming system can be improved by monitoring the feed stock operation conditions. For the existing plant, the results of predicting program have established the ability of reducing the feed stock temperature to about of 430 °C under **the** an operation pressure of (35atm) by reducing the number of flairs inside the thermal furnace for improvement the quality of gasoline production. Consequently, the burned fuel requirements for the thermal furnace will be reduced. Also, the results indicated the ability of reducing the operation pressure from 35 to 25bar because the ratio of improvement in the quality of gasoline production was very limited also, from industrial point of view, it is better to operate the existing plant under moderate conditions.

Table(5) shows the effect of operation conditions on the quality of gasoline production

Feed pressure (atm)	Feed stock temperature	y_N Mol %	y_A Mol %	y_P Mol %	RON
25	460	7.83	27.0	65.18	113.33
	470	5.46	29.4	65.17	112.55
	480	3.5	31.3	65.166	111.91
	490	2.057	32.8	65.15	111.46
27.5	450	11.7	23.14	65.177	114.6
	460	8.97	25.85	65.176	113.7
	470	6.48	28.35	65.17	112.89
	480	4.353	30.58	65.07	112.31
30	440	15.8	19.0	65.18	115.95
	450	12.9	21.89	65.18	115
	460	10.2	24.66	65.18	114.1
	470	7.56	27.3	65.18	113.24
35	430	21.13	13.7	65.17	117.71
	440	18.3	16.5	65.18	116.77
	450	15.44	19.38	65.18	115.83
	460	12.54	22.28	65.18	114.87

You should include the current refinery conditions and produced gasoline quality to show the improvement achieved in the proposed conditions.Also include in the Nomenclatures definitions of Yn,Ya and Yp. A graphical representation of the data should be given

Nomenclatures

A= Arene (Aromatic).

B.R.R.P= Basrah Refinery Reforming Plant.
$Cp_{=}$ Heat capacity constant (KJ/ $Kmol_{H2.}$ °C).
F=Feedstock flow rate(Kmol/hr).
F_i= Feed flow rate for each compound (Kmol/hr).
H= Hydrogen.
$Hr°_{, T (1,2,3\&4) =}$ Heat of reaction at any temperature for reaction 1,2,3&4 respectively (KJ/ Kmol).
k_{f1}= Reaction rate constant corresponding to r_1 (kmol/ kg_{cat} .hr .mpa).
k_{f2} = Reaction rate constant corresponding to r_2 (kmol/kg_{cat}.hr.mpa^2).
k_{f3} , k_{f4} = Reaction rate constant corresponding to r_3 and r_4 respectively (kmol/kg_{cat}.hr).
K_{eq1}= Equilibrium constant of cycloalkane transformed into arene (mpa^3) .
K_{eq2}= Equilibrium constant of cycloalkane transformed into alkane(mpa^{-1}).
L=height of catalyst bed in reactor(mm).
M_f = Average molecular weight of feedstock (Kg/Kmol).
M_A= molecular weight of Arene (Kg/Kmol).
M_E= molecular weight of Cycloalkane (Kg/Kmol).
$M_{P=}$ molecular weight of Alkane (Kg/Kmol).
n= Number of carbon atoms.
N= Cycloalkane (Naphthene).

Ni= Mole flow rate for each compound (Kmol/ hr).
P= Alkane (Paraffin).
p_i = Partial pressure of each compound (Mpa).
p =Total inlet pressure (Mpa).
R_i= Inlet reactor radius.
R_o= Outlet reactor radius.
r_1=Reaction rate of cycloalkane transformed into arene (kmol/kg_{cat}.hr).
r_2=Reaction rate of cycloalkane transformed into alkane (kmol/kg_{cat}.hr).
r_3=Reaction rate of hydrocracking of alkane (kmol/kg_{cat}.hr).
r_4=Reaction rate of hydrocracking of cycloalkane (kmol/kg_{cat}.hr).
T= Inlet temperature(^oC).
To= Outlet temperature(^oC).
V= Reactor volume (mm^3) .
y_i= Mole fraction for each compound.
ρ_b= Catalyst bulk density (Kg_{cat} / mm^3).
η = Catalyst effectiveness factor

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