FULL LENGTH ARTICLE

Optimization of the reaction parameters of heavy naphtha reforming process using Pt-Re/Al₂O₃ catalyst system

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Abstract One of the most significant procedures in oil refineries is naphtha catalytic reforming unit in which high octane gasoline is gained. Normally, in oil refineries, flow instability in the composition of feedstock can affect the product quality. The aim of the present work was focused on modifications of the final product flow rate and product's octane number with respect to the modifications of the feedstock composition. The main three reforming reactions investigated, namely; dehydrogenation, dehydrocyclization, and hydrocracking were conducted employing silica supported bimetallic (Pt-Re) patented catalyst. Optimization of the catalytic process reaction conditions, i.e.; temperature, hydrogen pressure and liquid hourly space velocity (LHSV) was carried out with regard to conversion and selectivity. The optimization results indicated that heavy naphtha component conversion (paraffin’s and naphthenes) increases with an increasing in reaction temperature and pressure while decreases with an increase in LHSV. The kinetic study of catalytic reforming reactions reported helped establishing the reaction model explicitly.

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1. Introduction

Naphtha is transformed into reformates through catalytic reforming process which requires the reconstruction of low-octane hydrocarbons in the petroleum naphtha into more valuable high octane gasoline components. Naphtha and reformate are complex mixtures of paraffin’s, naphthenes, and aromatic in the C5–C12 range of naphtha compositions. Paraffin’s or alkanes are saturated aliphatic hydrocarbon of either straight-chain (n-paraffin’s) or branched structures (isoparaffins). Olefins or alkenes are unsaturated aliphatic hydrocarbons, are either straight chains or branched structures, but contain one or more double bonds. Also, in the naphtha range, naphthenes or cycloalkanes are saturated cyclodihydrocarbons that contain at least one ring structure. The most abundant

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naphthenes found in fossil fuel acquire ring structures of either five or six carbon atoms. The composition of any naphtha depends on the type of crude oil, boiling range, 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% paraffin’s, 20–50 wt% naphthenes, 5–20 wt% aromatic, and only 0–2 wt% olefins. Naphtha produced by fluid catalytic cracking (FCC), coking, or visbreaking may contain 30–50 wt% olefins. Naphtha produced by fluid catalytic cracking (FCC), coking, or visbreaking may contain 30–50 wt% olefins. Naphtha produced by fluid catalytic cracking (FCC), coking, or visbreaking may contain 30–50 wt% olefins.

Several principle reactions take place during the catalytic reforming operation, including dehydrocyclization, dehydrogenation, isomerization and hydrocracking of the hydrocarbon molecules [3]. These reactions occur catalytically through the acid and/or metal sites; hence, the use of bifunctional catalysts is favored. The acid function with a certain acid strength is typically provided by a solid support such as alumina promoted by fluorine or chlorine and is mainly responsible for isomerization and cracking reactions; whereas the metal function, usually a noble metal, acts as active sites for hydrocarbon–dehydrogenation reactions [4,5]. Many different types of reforming catalysts were developed such as bi-metals and tri-metals supported catalysts.

The major chemical reactions that occur during the catalytic reforming which are required for the octane number increase and decrease of coke formation are noted as follows [6]:

1. Dehydrocyclization of paraffins into aromatic.
2. Isomerization of alkylcyclopentanes into cyclohexanes.
3. Dehydrogenation of cyclohexanes into aromatics.
4. Isomerization of linear paraffins into iso-paraffins.
5. Hydrocracking of naphthenes and paraffins.
6. Hydrodealkylation of aromatic.
7. Coke formation.

Pt-Re bimetallic catalysts are favorable for their lower coking rate and higher resistance to deactivation. These factors enable the process to be operated with smaller regeneration frequencies leading to a subsequent reduction of operating costs [7]. The main two challenges that are accounted for Pt-Re bimetallic catalytic during the catalytic process are the carbon deposition on the catalyst surfaces that enhances its deactivation and bed blockage [8] in addition to the increasing demand for high octane gasoline [9]. Such challenges could be overcome basically using fluidized bed reactor at strict operational conditions that would include catalyst reaction procedure in-situ in addition to the selection of an adjustable reaction conditions as will be concluded hereafter.

1.1. Reaction kinetics

A mathematical kinetic model has been developed to describe the main catalytic reforming reaction and reaction rate [10]. Scheme 1 shows the reaction used in the kinetic model reporting the constant to be dependent on the feed composition and the catalyst properties. Heterogeneous catalytic reaction mechanism of heavy naphtha has been identified to include the following proposed steps [11–13]:

1. Adsorption of n-paraffin molecule on catalyst surface followed by dehydrogenation–hydrogenation to n-olefins.
2. Desorption of n-olefin and diffusion to a skeletal rearranged site, which converts n-olefin into iso-olefin.
3. Hydrogenation of iso-olefin into iso-paraffin molecule.

In general, the hydroisomerization of n-paraffin occurs through the bifunctional scheme as represented herein n-paraffin → n-olefin → i-olefin → i-paraffin

The hydroisomerization process of heavy naphtha is regarded as one of the complex chemical reaction networks, where such types of reactions take place on the metal and acid sites of catalysts [14–17].

Thus, three groups of compounds are recognized, namely; paraffin’s (normal and ISO), naphthenes (N), and aromatics (A). Therefore, it was prospective to anticipate the content of the defined reagents in the course of the process for an arbitrary temperature within the investigated range.

\[
P \leftrightarrow N + H_2 \quad (1)
\]

\[
N \rightarrow A + 3H_2 \quad (2)
\]

\[
P + H_2 \rightarrow 2G \quad (3)
\]

The kinetic reaction rate is believed to follow simple power law kinetic expression for the above reactions [17]:

\[
r_1 = k_1 C_p - k_3 C_N P_{H_2} \quad (4)
\]

\[
r_2 = k_2 C_N \quad (5)
\]

\[
r_3 = k_4 C_p \quad (6)
\]

In general form

\[
r_i = k_i C_i, \quad \text{where} \quad (7)
\]

Ki = Ao exp\left(-\frac{Ea}{RT}\right) \quad [18]

The reaction rate constant ki confirms the Arrhenius expression:

\[
Ln ki = Ln Ao - \frac{Ea}{RT} \quad [19]
\]

The kinetic expression is linear (first order with respect to reactants) under the present reactions.

2. Experimental

2.1. Feedstock

Hydrotreated heavy straight-run naphtha, provided by Middle East Oil Refinery (MIDOR) Company, Borg Al-Arab–Alexandria, was used as the feed stock characterized as detailed in Table 1. The feed stock is a fraction that is characterized by boiling in the range of 80.9–205.5 °C and consists of mainly C5–C12 hydrocarbons in addition to minimum quantities of C2–C4.

2.2. Catalyst

The catalyst used in all experiments (in extradite form) is commercially available platforming catalyst, R64 (UOP) (Pt-Re/AI2O3)
The catalyst beds were diluted with an ceramic beads inert material both with the same particle size in order to have a better distribution of heat losses over the reactor and an axial thermocouple was used all over the experiments for temperature indications.

2.3 Reactor setup

A high pressure micro fixed bed reactor unit – down flow (catalyst unit) that consists of a stainless steel reactor (internal diameter 19 mm, external diameter 27 mm, and length 50 cm) was employed (Fig. 1). It is divided into three zones, each is heated and separately temperature controlled. 50 cc of the catalyst is charged in the middle zone of the reactor. The hydroconversion reactions of the feed stock were carried out at reaction temperature ranges of 375–490 °C, hydrogen pressure ranges of 15–25 bar and liquid hourly space velocity (LHSV) at ranges of 1.5–3.0 h⁻¹ at constant H₂/oil ratio (vol./vol.). After reaction runs are completed the reaction products of liquid and gases are collected and subjected to gas chromatographic analysis using Varian GC-450 (Fast DHA) GC chromatograph. The catalyst was activated prior runs at 450 °C for 4 h. in a stream of hydrogen.

3. Results and discussion

3.1 Effect of the reaction temperatures on reforming catalyst

Fig. 2. illustrates the influence of reaction temperatures at 375, 400, 425, 450 and 490 °C, LHSV at 1.5 h⁻¹ and hydrogen pressure, 15 bars on the naphtha reforming conversion and selectivity. The results indicate that isomerization of n-paraffins to iso-paraffins at high values indicating in turn product of high octane number. Catalytic isomerization is reported to be a fast reaction catalyzed by acid sites and it accomplishes the catalytic reforming conditions [20,21]. Fig. 2 reveals the relationship between the temperature increase and the profile of paraffins concentration produced. As the temperature increases from 375 to 490 °C an increase in the concentrations of the components in light paraffin’s (n and ISO) P5, P6 P7 was observed, while decrease of the heavier component concentration is recorded. This behavior is mainly due to the dehydrocyclization process which is stimulated at high reaction temperature and high molecular weight to the number of carbon. The paraffin’s isomerization reaction is important due to the reactions of isomerization of n-paraffins to i-paraffins which are highly desired during catalytic reforming of naphtha, since the produced i-paraffins contribute to the increase in octane number of the reformate. The naphtha used in the present work is characterized by high paraffin content at 24.78 wt% and 36.22 wt.% iso-paraffin. Fig. 3, also shows that ring formation possibly leads to the formation of heavy n-paraffin’s (n-C9–n-C11) at higher conversion ratio while lighter paraffins exhibited lower values. This is explained as due to an increased possibility of molecular weight increase of the paraffins. Similar to naphthenes dehydrogenation reaction, paraffin’s dehydrocyclization is noticeably favored at high reaction temperature, Fig. 4. Isomerization reactions promoted by the acid catalyst functionality seems to have elevate as the temperature is increased being important as a source of branched hydrocarbon; that are characterized by higher octane value than those of linear hydrocarbons recognized basically as an endothermic reaction [22]. Fig. 4, illustrates increased values of the octane number from 57.7 to 94.1 with temperature increase from 375 to 490 °C. In addition, it is observed that the total amount of aromatic increases from 18.99 to 23.09, 25.52, 29.00, 36.57 and 49.00 wt.% at 375, 400, 425, 450, 490 °C, respectively. As shown in Fig. 5, higher production of aromatic was observed following the increase in the high octane gasoline where the octane number increased from 57.7 to 94.1 as the temperature increased from 375 to 490 °C. Fig. 6, indicates that naphthenes decreased from 19...
to 6.9 wt.% by increasing the reaction temperature, from 375 to 490 °C, which indicates that the reactivity of dehydrogenation reactions increases with naphthene increase in carbon number (9), i.e. increase of aromatic components, Fig. 7, exhibits naphthenes’ profile augmentation by temperature increase which is known to be highly selective to aromatic compounds via dehydrogenation. It is also confirmed that naphthenes’ dehydrogenation is favored by high reaction temperature as they were almost completely converted at higher temperatures 490 °C. This is the main reason why naphthenes are the most desirable components in the reforming products [23], where, catalytic reforming usually utilizes a feedstock naphtha that contains non-aromatic hydrocarbons with 6 to 11 or 12 carbon atoms that typically produce a reformate product containing C6 to C8 aromatics (benzene, toluene, xylenes) as well as paraffins and heavier aromatics containing 9–11 or 12 carbon atoms as the reaction temperature increases. Reforming serves the dual purpose of producing

**Figure 1** Schematic diagram of the reactor design: (PI) pressure indicator; (PCV) pressure cont. valve; (PSV) pressure safety valve; (TI) temperature indicator; (TR) temperature recorder; (TC) temperature control; (FI) flow indicator; (LI) level indicator; (1) calibrated feed tank; (2) feeder buret; (3) three way valve; (4) feed pump; (5) stop cock; (6) non return valve; (7) filter; (8) reactor; (9) 3-shell furnace; (10) water condenser; (11) separator; (12) adjust cock; (13) calibrated receiving tank; (14) nasal tank and (15) gas sample tube.

**Figure 2** Effect of reaction temperature on saturate components at LHSV (1.5 h⁻¹) and pressure 15 bar.

**Figure 3** Effect of reaction temperature on of n-paraffin components at LHSV (1.5 h⁻¹) and pressure, 15 bar.
both high octane number gasoline and aromatics for chemical industry use. The octane rating of reformed naphtha is a function of the proportion of different hydrocarbons within the product reformate and their respective octane numbers.

3.2. Assessment of the catalytic reaction kinetic parameters

The classical reaction mechanism, as revealed by scheme 1, proceeds via an olefin intermediate that is formed through a dehydrogenation step on the metal site. As the olefin concentration under hydroisomerization conditions is rather low; due to the equilibrium position of the strongly endothermic dehydrogenation step; it has to be guaranteed that a sufficient number of olefin molecules are present to assure conversion formation of carbon on the acid sites of catalyst. It was observed that the rate of the isomerization reaction strongly depends on the chain length of the involved alkanes. The longer the chain length, the more stabilized the associated carbonium ion and the faster the isomerization reaction [24].

The activation energies of the isomerization reaction were determined over the temperature range of 375, 400, 425, 450 and 490 °C at hydrogen pressure of 15 bar and LHSV of 1.5 h⁻¹. The apparent activation energy (Eₐ) is established from the Arrhenius equation as given in Eqs. (8) and (9). The plot of Ln k vs. 1/T is shown in Figs. 8–10 for functioned for the employed catalyst R64. The slope is represented by −Eₐ/RT and the intercept is represented by Ln k which indicates the value of pre-exponential factor. The apparent activation energies for the different procedure were found in the range of 22–57 kJ/mol and are given in Table 2, calculated from the Arrhenius equation. It is noted, that there is a simple difference among its values. In general, the small values of the apparent activation energies could favor increased selectivity toward paraffin's hydroisomerization.

3.3. Effect of liquid hourly space velocity

Variations of LHSV in the range of 1.5, 2, 2.5, 3 h⁻¹ were studied at 490 °C, and a pressure of 15 bar, results of which are demonstrated in Figs. 11–13. The reaction profile at the stated condition reveals that the light component paraffins; normal and iso; of carbon number P5 and P6 had decreased as the LHSV was increased, which causes a decrease in the contact
time as reported by Rahimpour et al. [25]. Also the heavier paraffin’s (n and iso) reactivity decreases as LHSV increases, which leads to a decrease in the aromatic yield, dehydrocyclization reactions of paraffins (n and iso), are the slowest reaction and are affected by the increase in LHSV [26], as shown in Figs. 13 and 14. Naphthenes’ component conversion shows a slight increase with increasing LHSV and this can be attributed to dehydrogenation reaction which is the fastest reaction in all heavy naphtha reforming reactions as shown in Fig. 15.

3.4. Effect of pressure

Fig. 16 demonstrates the pressure variation on the concentration of light and heavier paraffin component conversion. The concentration of light and heavier paraffin components was observed to increase as the pressure increases which then
decreases at higher pressure probably due to the dehydrocyclization reaction that is favored at higher reaction pressure and higher molecular weight of carbon number [27] with the same pattern followed for iso-paraffin’s, Fig. 17. Naphthenes mole % formation pattern was found to decrease as the reaction pressure increases and then increases at 15 bar hydrogen pressure; since the conversion of naphthenes to aromatics is the primary naphthene reaction and is regarded as the most favorable among all other reactions in catalytic reforming, Fig. 18. It is important to mention here that the reactivity of dehydrogenation reactions increases with an increase in naphthenes’ carbon number [28]. Fig. 19, shows that the mole percentage of aromatic components (toluene and xylene) increases as the reaction pressure was increased. This conduct can be explained on the basis of faster dehydrogenation of naphthenes and dehydrocyclization of paraffin’s is accompanied by the increase in pressure and carbon number [29].

4. Effect of time on stream in the activity of catalyst

The processing of hydrocarbons is basically accompanied by the formation of carbonaceous deposits upon the catalyst surface, which is referred to as coking that is considered as the most rapid cause of catalyst deactivation. Deactivation is a very important drawback with most catalytic process not only due to carbon deposits but also due to many inflected causes that are based on: catalyst active sites reactivity to foreign...
molecules; such as sulfur and nitrogen compounds; adjustment of reaction parameters, sintering (decrease in metallic active surface area), and heavy metal deposition which is determined at the end the catalyst life duration. Among the processes of petroleum refining and the petrochemical industries, catalytic reforming of naphtha has been regarded as one of the most complicated processes that face catalyst ambiguous deactivation elements. Due to the continuous coking and deactivation of the reforming catalysts during operation, the conversion process temperature had to be constantly increased with time to overcome deactivation causes and hence, to maintain a rather acceptable product of high octane number of the reformed product stream, Fig. 20. Under the adjusted reaction parameters adopted, herein, the reforming operation process had to be ended after 130 h due to complete exhaustion of the catalyst and its deactivation.

5. Conclusion

Improving conversion of heavy naphtha reactants (paraffin’s and naphthenes) to desired high octane number product, selectivity and catalyst function toward aromatization reactions especially light aromatics (A6, and A7), were studied under controlled reaction parameters using Pt/Re-alumina supported catalyst.

The major conclusions drawn from the present study are as follow:

1. Adjustable reaction parameters adopted accomplished higher conversion and selectivity toward the course of hydroisomerization of heavy naphtha toward isomerization and octane number rating. Three reforming process variables were studied along with their effects on the reformate composition and the results of which are summarized as follows:
   a. Increasing the reaction temperature of the feedstock will increase aromatic yields, at a maximum value of 490 °C.
   b. Increasing the total hydrogen pressure had a little effect on the increase in the aromatic composition in the reformate products.
   c. Decreasing the LHSV ratio had immense effect on increasing the aromatic composition in the reformate products.

2. The results show that the best operating temperature for the hydroisomerization process (with high selectivity toward isomerization) is 490 °C.

3. The total conversion of heavy naphtha achieved was 91.4% at 375 °C, 15 bar and LHSV = 1.5 h⁻¹. The conversion of heavy naphtha and selectivity of hydroisomerization reaction increased with a decrease in LHSV at a minimum of (1.5 h⁻¹) that gave the best rate of isomers.

4. The values of apparent activation energy for hydroisomerization of heavy naphtha over the commercial catalyst helped understanding the possible routes of reformate products along the specific catalyst used.

5. The reforming products of benzene, toluene, and xylene are considered as critical feedstocks for the petrochemical industry, which was considered as an aim for the present study which could be envisaged positively from the present study.

Rather, adjusting the reaction parameters had improved the currently available commercial reforming catalyst with regard to conversion and selectivity, further studies on the catalyst microstructure along the reforming process regarding the
support influence; structure, nature and type, in addition, to
the investigation of the influence of pressure variation on the
activity and selectivity of the process will be considered for fur-
ther work.

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