



Improving of gasoline quality via hydroisomerization process under different operating parameters in petroleum refineries: A review

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Abstract

The hydroisomerization process of light naphtha is the chief process to produce high-octane gasoline in petroleum refineries. The reaction mechanism is designed to produce branched hydrocarbons with high octane numbers.

The hydroisomerization reaction mechanism over bifunctional catalysts is influenced by both acid and metallic sites on the catalyst surface. Moreover, it was found that the product quality and distribution in this process are highly dependent on the catalyst type and operating conditions in the fixed-bed reactor. The feed quality (light naphtha) is the major challenge in this process due to its direct effect on the catalyst activity, selectivity, and deactivation mechanism (catalyst lifetime). According to the results of many authors, it has been observed that the pre-treatment processes usually carried out on the light naphtha feedstock provided high performance for the applied bifunctional catalysts.

Finally, the economic feasibility of this process is a function of the catalyst type and its resistance to the contaminants present in the light naphtha.

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1. Introduction

In the petroleum refining industry, the hydroisomerization process gains a significant position in providing high-quality gasoline with high octane numbers. The environmental restrictions that prevent the use of leaded gasoline in many countries, make hydroisomerization technology the chief source of enhanced gasoline. Accordingly, the produced gasoline from this unit is characterized by a reduced impact on the environment [1-3]. Also, the limited concentration of benzene, olefin, and aromatics in hydroisomerization gasoline is regarded as the main improvement in fuel quality and then human health due to the carcinogenic effects of these compounds [4,5].

From an industrial point of view, the production of branched hydrocarbons in the hydroisomerization process makes this technology an important source of efficient gasoline with high octane values. The light naphtha usually included a high content of n-pentane and n-hexane with low octane values. Accordingly, the hydroisomerization

technology produces isomers such as 2,2-Dimethylbutane, 2,3-Dimethylbutane, 2-Methylpentane and 3-Methylpentane which have high octane ratios. Then, the hydroisomerization process of light naphtha produce gasoline with enhanced research octane number by values from 10 to 20 units [6-8]. Table (1) summarizes the general octane number of various hydrocarbons.

The hydroisomerization reactions are usually carried out using different kinds of bifunctional catalysts. These catalysts included an active metal side such as Pt and an acid side such as SiO₂, Al₂O₃, mordinte, and zirconia. The bifunctional catalysts are characterized by efficient hydroisomerization activity to produce branched isomers. The hydrogenation and dehydrogenation reactions are usually carried out on the metal side (platinum), while, the aromatization and cracking reactions occur on the support side.

Table 1: Octane number of various hydrocarbons [4].

Type of isomer	Research Octane Number (RON)
n-pentane	61
n-hexane	31
Iso-pentane	93.5
Methylpentanes	75
Di-methylbutanes	94-105
Cyclohexane	84
Benzene	120

To achieve high hydroisomerization selectivity, an accurate balance between the active metal side of the catalyst and acid functions is required. Accordingly, in order to increase the reaction rate of isomerization processes to produce more branched hydrocarbons, a deep evaluation is needed to select the appropriate operating conditions for the synthesized catalyst. Moreover, the catalyst selectivity toward the desired products (branched isomers) and catalyst stability with time are the main criteria that determine the quality of applied catalyst long life [9-11].

The careful management of the catalyst preparation process will prevent the catalyst deactivation problem with reaction time. Usually, coke formation or poisoning of active sites are is the most general types of loss catalyst activity in hydroisomerization processes. It is important to mention that the catalyst deactivation by sintering does not highly influence the catalyst deactivation rate in the isomerization reaction due to the moderate reaction temperature of the process. Therefore, a high-purity light naphtha without any impurities and sulfur content must be used in the hydroisomerization process to prevent catalyst deactivation from occurring with reaction time [12-14].

The hydroisomerization reactions of light naphtha are highly based on the chlorinated Pt/Al₂O₃ catalysts which operate at a low reaction temperature. Also, many catalysts were developed with time based on zeolites as an acid function which is favorite to operate at a high reaction temperature. The zeolite-based catalysts is operating at higher temperature undergoing a clear reduction to the final conversion to the desired products. Accordingly, high-performance catalysts are needed to operate at a lower reaction temperature with a high conversion rate of light naphtha. Moreover, different petroleum refining companies designed and constructed hydroisomerization technology commercially, such as GTC, Axen, and UOP isomerization processes [15]. The Penex hydroisomerization process was initiated by UOP. This process is achieved in a fixed bed catalytic reactor to convert n-C₅ and n-C₆ in light naphtha to produce gasoline with high octane ratings. The process applies the I-82 catalyst which is a platinum on chlorinated alumina (Pt/Al₂O₃-Cl) [16]. This catalyst has proven to be active at lower temperatures in the range of 120 to 180°C [17]. The goal of this paper is improving the gasoline quality via hydroisomerization process under different operating parameters in petroleum refineries Figure (1) shows the scheme of the Penex process of UOP.

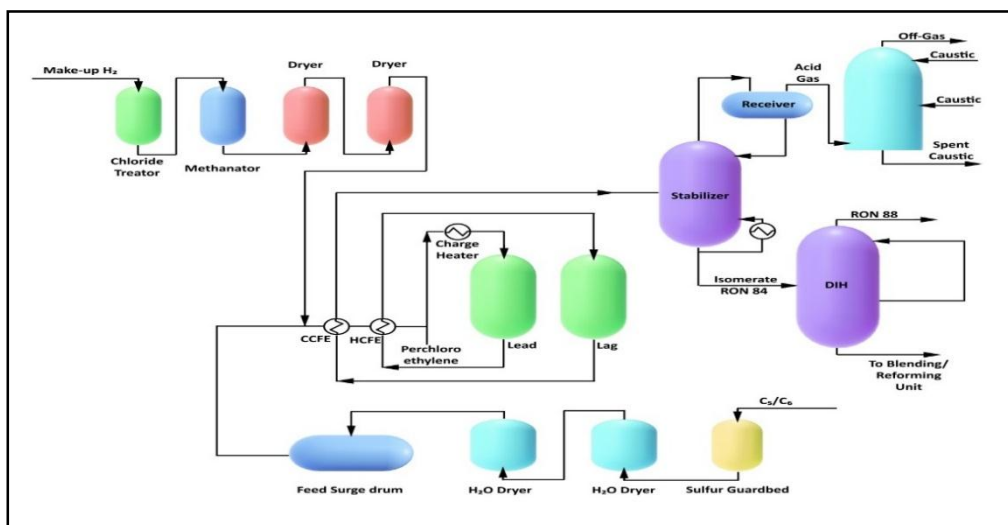


Figure 1: Process flow Diagram of Penex technology at Al-Dora Refinery-Baghdad [12].

Many papers have been published in the literature to improve the hydroisomerization process. All of these studies focused on enhancing the catalyst performance such as:

Nemati et al. [1] investigated the deactivation of a chlorinated alumina catalyst if the light naphtha feed was contaminated in the hydroisomerization process. They found that if the catalyst was deactivated with oxygenated compounds such as methanol it would not be able to restore the catalyst's initial activity due to its effect on the acidic functional groups. But if the deactivation occurs through mercaptans such as dimethyl disulfide, it is possible to complete the recovery of the catalyst since it affects the metal sites of the catalyst.

Faskhutdinov et al. [18] developed a detailed kinetic model used to describe the catalytic isomerization of the hydrotreated gasoline cuts with boiling points in the range (62-70°C) as a feedstock and a bifunctional catalyst SI-2 (Izomalk-2 technology) was used in the process. The result was very accurate compared to the data obtained from industrial plants for hydroisomerization of the pentane and hexane and the model was used to retrofit the reactor configuration of the existing plants and finding the optimal amount of catalyst and reactor size.

Aboul-Gheit et al. [19] prepared modified sulfated zirconia catalysts with different loading of Platinum metal (0.15, 0.30, 0.45, and 0.60 wt%) with and without Rhenium metal. They found that by increasing Pt loading in the monometallic catalysts the activity would increase and the addition of Re metal has a significant effect on the activities of the catalysts. The best combination of these two metals was (0.45wt%) Pt and (0.15wt%)Re which gave the highest selectivity of n-pentane isomerization.

Bayati et al. [20] investigated the hydroisomerization of n-pentane and a mixture of n-pentane and isopentane using Pt loaded on H-mordenite as a supported catalyst in a fixed-bed reactor. They studied the reaction parameters such as temperature, pressure, and WHSV, and the H₂/HC. They found that a maximum conversion of 77% is achieved at 220 °C.

Ejtemaei et al. [21] prepared a catalyst of sulfated zirconia with bohemite to provide aluminum and then impregnated it with platinum to produce (Pt-SZ/Al) for isomerization of n-pentane at atmospheric pressure and temperatures ranging from (180-240°C) in a flow reactor. They concluded that with increasing temperature the conversion of n-pentane will increase but the selectivity will decrease. They found that the optimal temperature of the reaction is 220°C with about 94% selectivity for isopentane and 70% n-pentane conversion.

Mohamed et al. [22] studied the light naphtha isomerization unit in the Alexandria-Egypt that recycles the unconverted hexane (C₆) which uses Chloride-alumina as a catalyst. Different scenarios were suggested, adding fractionators for iso-pentane separation in the feed, recycling the unconverted pentane, hexane, and the combinations of these two fractionators. The results showed that the using of de-iso-pentanizer– de-pentanizer and

de-hexane can result in gasoline with a 92.3 octane number, competing with a once-through process without fractionators give a lower octane number of 81.

Samimi et al. [23] studied the problems that arise with the increasing the capacity of naphtha hydrotreating unit such as the increase of pressure downfall, reduction of output pressure of circulating gas compressor, the increase of the eventuality of coke formation on the catalyst, increasing the thermal load of the reboiler furnaces of unit towers and eventually reducing the catalyst life span.

Shakor et al. [24] developed a sophisticated accurate kinetic model to describe light naphtha hydroisomerisation complicated reactions, with 52 components and 207 reactions and comparing the predicted data with experimental for six different temp. in a three catalysts. The comparison of the predicted experimental data showed a very good agreement.

Hamied et al. [25] proposed a kinetic model using a universal mathematical Algorithm which is newly developed and applied in MATLAB to describe the light naphtha hydroisomerization on a (Pt/Al₂O₃-Cl) catalyst for Penex process reactions in Al-Dura Oil Refinery. These calculation including (207) hydroisomerization reactions of (52) light naphtha components to calculate the optimal kinetic parameters. The mean absolute error for this model was to be (0.00360).

Jarullah et al. [26] prepared Pt/HY-H-Mordenite, from Iraqi sand for hydroisomerization of Iraqi light naphtha from Baiji North Refinery and tested in a fixed bed reactor under different operating conditions: temperature 150-250 °C, LHSV 2.46-4.7 hr⁻¹, at 6 bar, and H/C =3.7 mol/mol. They concluded that Iraqi sand is an excellent economical source for preparing zeolite materials with good characteristics. The conversion and yield of hydroisomerization of light naphtha were found to be 89.38% and 76.36%, respectively.

Al-Zaidi et al. [27] studied upgrading the octane number of n-heptane using a mixture of commercial zeolite as a catalyst (75% HY and 25% HZSM-5) loaded with pt range (0.25 to 1 wt.%) and with a temperature range of (300–400 °C). They examined theoretically and experimentally the hydroisomerization and hydrocracking processes in various operating conditions and simulated them using artificial neural network. They found that the best reaction conditions were Pt loading (0.85 wt.%), temperature (359.36 °C), H₂/C (6.562), and WHSV (3.409 h⁻¹), with boost octane number reach to (106.84).

2. The Industrial Hydroisomerization Processes

The hydroisomerization process is a chemical reaction that rearranges the molecule by breaking and making the molecule bonds. This process changes the molecule's orientation within the molecule to become branched without changing the molecular formula [28,29]. Hydroisomerizing of light paraffin to the corresponding branched chain isomers to upgrade the gasoline composition and enhance the octane numbers, and making it an eco-friendly fuel, which has a huge impact on increasing the efficiency of the motor engine [30,31]. Light-naphtha hydroisomerization is an essential process in the oil refinery to meet the octane up-grading demands in the gasoline pool, which leads to increasing the production of premium grades gasoline [32].

From a chemical reaction point of view, the hydroisomerization reaction means that the transformation of the molecular structure of normal paraffins to a branched paraffins with the same number of carbon atoms [4]. However, due to the nature of the reaction, hydroisomerization affects the naphthene components and hydrogenates the aromatics. In fact, hydroisomerization is considered the most economical process for decreasing the concentration content of benzene in gasoline [34]. There are numerous industrial processes for the hydroisomerization of n-Hexane and light naphtha commercially available. A brief description of some of these processes in the following sections. The first commercial hydro isomerization process was built in 1953 by UOP, and it was a lead and dominant in this field now using various techniques. UOP has many isomerization processes which can summarize below. The Penex process usually uses (I-82,1-84) which are Pt/Al₂O₃ as a bi-functional catalyst for converting pentanes, hexanes, or mixtures of them which is presenting in the light straight run naphtha to its isomers for the octane number to be improved as an economical and environmental substitute for the presenting of benzene which is consider carcinogenic [33]. The feedstock to the Penex process must contain no more than 5 vol% benzene in its stream. And also there is the Penex plus process which is used if the benzene content in the feedstock is more than

5 vol% . UOP has developed new types of catalyst for the isomerization of light paraffin and offers extra flexibility for the Butmar process and in the Penex applications. The I-82 has a highly actively used by UOP since 2003. This catalyst has a long working life of about 10 years with a high yield near 99% per unit vol. and is considered economical with less reactor cost.

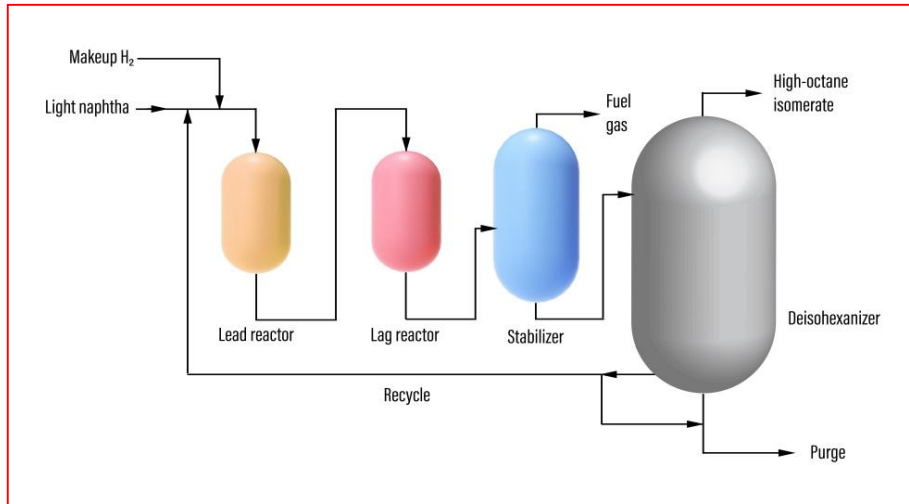


Figure 2: Process flow diagram of Penex hydroisomerization unit.

Hamadi and Kadhim [35] derived a mathematical model for the prediction rate constants and activation energy E_a at operating temperatures range 120-180°C for Penex hydroisomerization process in Daura Refinery and predict the rate constants K_1 and K_2 and activation energy E_a at operating temperatures range 120-180°C. According to their model, the results show that increasing temperature leads to increased K_1 directly. **Fazlali et al. [36]** studied the problem that the isomerization process faces in the Shazand refinery in Iran. The process was dynamically simulated by Aspen Hysys and then nine steps of the plant-wide process control theory has been implemented on his model to achieve an acceptable control system.

Moreover, the Par-Isom process uses non-chlorinated alumina (PI-242) as a catalyst for light naphtha isomerization. This catalyst has the feature of tolerant water and it can be regenerated in this process is regenerable and water tolerant. Another process which is Butamer process using a catalyst (I-122, I-124) for converting n-butane into isobutene was first commercialized in 1959. After that, Axens company provided many isomerization techniques using advanced technologies (Ipsorb and Hexorb) and the conventional method which include using two reactors with chlorinated alumina as a catalyst flowed by deisohexanizer. In an Ipsorb process used with chlorinated alumina as a catalyst, the process starts with a deisopentanizer to remove isopentanes and reduce dehydration requirements. The deisopentanizer column bottom sent to the isomerization reactor. After the reaction, the isomerates are stabilized and passed to the molecular sieve for separating unconverted n-paraffins and recycling them. The yield from the Ipsorb unit has with an octane number of 89 [12]. Figure (3) shows the flow sheet of the industrial IPSORB process.

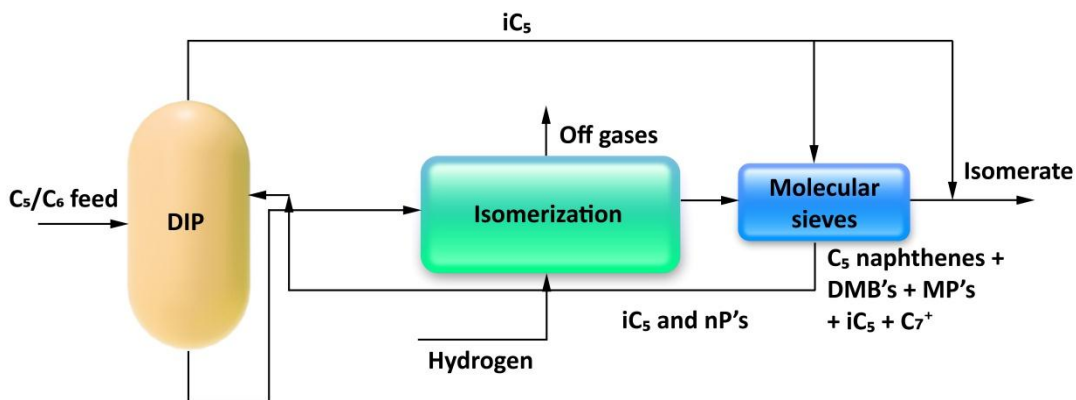


Figure 3: Flow diagram representing the industrial IPSORB technique.

Furthermore, the Hexorb isomerization technique used the zeolite and deisohexanizer column for the separation of methyl pentanes which is recycled the isomerate. This technique can upgrade the RON up to 92 since the n-paraffin fully converted to isomers in the products. Also, British Petroleum company initiated new isomerization method for upgrading C₄, C₅ and C₆ using a flexible Pt on chlorinated alumina catalyst [37]. On the other hand, Shell Company suggested Hysomer Process to improve the octane of light naphtha by 10-12 units using the metal-zeolite catalyst which has the ability of resist water and sulphur in the feedstock. Additionally, TIP technology generated isomerization process with enhanced octane number by 20 points [38]. Also, there're another hydroisomerization processes such as GTC Isomerization Technology and Ducreux and Jolimaitre which provided high octane number with high selectivity to branched hydrocarbons [18,39,40].

3. Applied Catalysts in the Hydroisomerization Technology

The modern industrial light naphtha hydroisomerization catalysts is mostly a bifunctional catalysts (a noble metal supported by solid acids). Platinum is preferred as the promoter metal used with the acid support. Generally there are three types of support that are commonly available zeolites, chlorinated alumina, and sulphated Zirconia [41]. The chlorinated alumina is one of the first bi-functional catalyst used in hydroisomerization reaction containing of (8-15 W%Cl₂) which is responsible for the catalyst acidic function. And about (0.3-0.5 wt%) of platinum metal which is deposited on the alumina [29]. One of the main features of this reaction is that it carried out at low temperature normally at about (130-180)°C and since the hydroisomerization reaction is an exothermic reaction working at low temperature has a great effect on the improving the equilibrium yield and has an effect on the reduction of chlorine elution [42].

One of the down side of using chlorinated alumina it is very sensitive catalyst to impurities such as water and sulphur compounds, therefore hydrotreating of the feed is necessary, these compounds affect the catalyst activity causing to poison it. Another point is that the presence of the hydrogen stream in the reactor will remove the chlorine in the catalyst producing hydrogen chloride therefore the addition of carbon tetrachloride with the feed is necessary to maintain the activity of the catalyst [1]. Mansour et al. [43] tested a prepared chlorinated alumina catalyst Pt/γ-Al₂O₃ with (0.25 wt. % Pt by impregnation method) ;for the C₆ alkane hydroisomerization. They noted that the maximum conversion from light naphtha, 80.06 wt. % was achieved for the catalyst at 160 °C and the highest octane number was observed at the low space velocity (1.2 h⁻¹) & (H₂/HC = 1.2). Fekri et al. [44] investigated the production of isomers with high octane numbers and reduce the content of benzene for the light naphtha in Al Kartoum Refinery in Sudan. They prepared type Gamma Alumina Improved Pt./H-γ Al₂O₃, with (0.5wt% Pt) by impregnation method and found that the best operating temperature for the hydroisomerization process (with high selectivity toward isomerization) is 160°C and noted that, the Research Octane Number increased to (95.55).

The zeolites catalysts regard the main type of catalysts that has the ability to operate at high temperature up to 300°C. Zeolite is a crystalline porous aluminosilicates which mainly consist of aluminum, silicon and oxygen. They consist of tetrahedra (TO₄) as building blocks having a Si⁴⁺ or Al³⁺ cation (T atoms) at the center and four oxygen atoms at the sides. Each side has two TO₄ units forming tridimensional framework cavities, tunnels and spaces generally denoted as “micropores”. The porosity of the zeolite crystal lattice easily allowing the mass to transfer from the external to the internal part of the zeolite particle and help the intracrystalline diffusion for the molecules that are smaller than the dimensions of the micropore [45]. Li et al. [46] evaluated NaOH treatment modifies the acidity of ZSM-22 and ZSM-48 diversely. The n-hexane hydroisomerization performances of Pt supported protonic form ZSM-22 and ZSM-48 (Pt/HZSM-22 and Pt/HZSM-48) as a bifunctional catalysts in a fixed bed reactor. The authors observed that the catalytic activity and selectivity depend on both pore structure and acidity of zeolites. Also, they concluded that a better n-hexane hydroisomerization performance at relatively low temperature (<300 °C), meanwhile, at relatively high temperature (>300 °C) Pt/HZSM-48 exhibits better catalytic performance. Moreover, alkali treated Pt/HZSM-48 could produce more di-branched isomer compared with alkali treated Pt/HZSM-22. The conversion for the two kinds of catalyst is almost the same at higher temperature (360 °C), which reaches close to 90%.

Moreover, Zirconia supported catalysts consider promising catalysts for alkanes hydroisomerization at higher rates. Due to its super acidity (H₀= -15.9) and can be used for n-alkanes hydroisomerization at ambient temperature [47]. Due to the high activity of Sulfated zirconia as a catalyst it goes to a fast deactivation as a result of coke deposition, this can be avoided at super-critical conditions. Deactivation can also be reduced by adding of the transition metals as promoters, such as manganese, iron, platinum, and other metals [48]. Naqvi et al. [12] summarized the role of

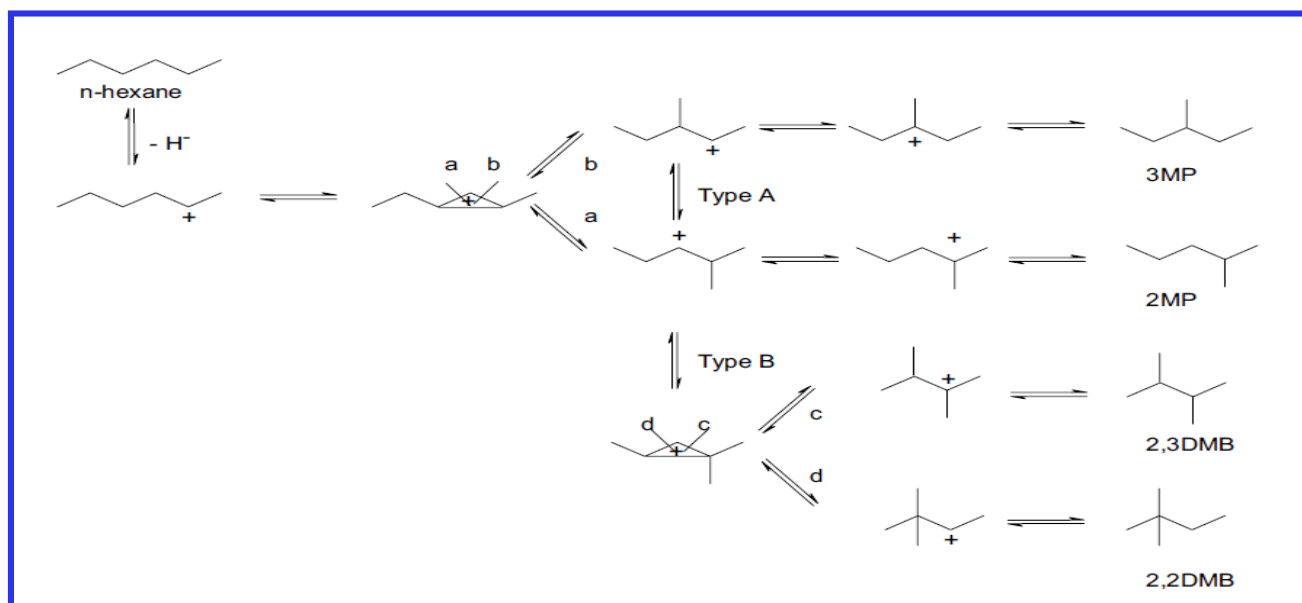


Figure 6: The monomolecular mechanism of *n*-hexane hydroisomerization over an acid catalyst [54].

It is important to mention here that the bifunctional catalysis is catalysis with two functions at the same time. Generally, consist from two part a base part which consist of alumina or zeolite loaded with one or more of the transition metals [7, 56, 57]. The bifunctional catalysts is has a two types of functions an acidic function which drive isomerization reaction. And the metallic function, which is responsible for the hydrogenation and dehydrogenation action [58]. The hydroisomerization of an alkanes is started with the dehydrogenatreaction on the metal site to form alkene. The produced alkene is protonated on the acid site to form carbenium ion, which isomerized to a branched carbenium ion. The branched carbenium ion return the proton to the acid site, the result is branched alkene which is hydrogenated in the present of hydrogen on the metallic site. The alkane isomer is formed, and easily desorb from the surface of the catalyst [59]. There are two factors support this mechanism: The first one is the high activity of the catalytic achieved only when both a metallic hydrogen part is present while the second reason is the reaction order with respect to hydrogen is negative.

5. Catalysts Deactivation

The deactivation problem in hydroisomerization catalysts regards the main challenge in petroleum refineries [60, 63]. Then, the prepared catalysts usually must have the ability to resist the deactivation factors. Accordingly, catalyst deactivation can be defined as the change in the structure of catalyst by severe conditions. Continuing to work for a long time without activation and may be by high temperatures leads to a loss of the activity of active sites, thus decreasing in the performance of catalysts as the catalysts are subject to old age as a function of time [64,65]. Table (3) shows the general types of the catalyst decay. Moreover, the deactivation process on the catalyst surface included many cases that affect the catalyst performance:

- 1- The active sites are marked with nutrient and impurity ingredients.
- 2- Blocking active sites (adsorption in pores).
- 3- A change in the shape of the structures.
- 4- Sintering of the supported minerals (bi-function catalysts).

The type of the catalyst that used in the hydroisomerization proces has a major role factor in the catalyst deactivation. By using catalyst that work at low temperature such as chlorinated alumina the problem of sintering greatly reduced also purification steps for the feed in the industrial hydroisomerization process including desulfurization and drying steps will eliminate the deactivation through poisoning [1, 66]. The main cause of catalyst deactivation in the hydroisomerization process is the coke deposition on the surface of the catalyst which can cause a blockage in the catalyst pour affecting the activity and selectivity of the catalyst [64,67].

Table 3: Catalyst deactivation mechanisms [60-62].

Mechanisms	Type	Brief definition/description
Poisoning with contaminants or sulfur	Chemical deactivation	Strong chemisorption of species on catalytic sites, thereby blocking sites for catalytic reaction (e.g., pb)
Fouling due to coke formation	Mechanical deactivation	Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores (c & soot-deposition or mechanical wear)
Sintering or Thermal degradation	Thermal deactivation	Thermally induced loss of catalytic surface area, support area, and active phase-support reactions (sintering)
Vapor formation	Chemical deactivation	Reaction of gas with catalyst phase to produce volatile compound (pd is volatile at temperatures around 850 C and above)
Vapor-solid and solid-solid reaction	Chemical deactivation	Reaction of fluid, support, or promoter with reaction catalytic phase to produce inactive phase (alumina dissolve in acidic and chelating medium)
Attrition/crushing mechanical	Mechanical deactivation	Loss of internal surface area due to mechanical-induced crushing of the catalyst particle

6. The Main Operating Conditions

There are many factors that affect the selectivity and conversion of catalytic hydroisomerization as follows:

6.1 Effect of Operating Pressure

An isomerization reaction is carried out at an elevated pressure in the presence of hydrogen atmosphere to suppress coke deposition which favored at low pressures of hydrogen and to prevent polymerization and not too high to avoid Hydrocracking and loss of product yield which is balancing the reaction pressure at minimum, but not too low for coke deposition [68].

6.2 Effect of Operating Temperature

The hydroisomerization reaction of straight alkanes to branched isomers is an exothermic reaction. Thus the reaction yield of branched alkanes is favored by low temperature. Thermodynamically among n-hexane isomers 2,2-dimethylbutane is favored by low temp. while 2,3-dimethylbutane is an affected by the whole temperature range. Methyl pentanes are formed at higher temperature since the dibranched isomers having a higher octane numbers, a low reaction temperature is desired and thus a highly active catalyst is needed [69, 70].

6.3 Hydrogen to Hydrocarbon ratio

The hydrogen-to- hydrocarbon ratio is an important industrial operational factor, due to its impact on sizing of the equipment and processes economics. Economically, it prefers to operate at a minimum hydrogen-to-hydrocarbon ratio, but reducing this factor will increase catalyst deactivation and the formation of unwanted side product. For high activity catalyst the rapid hydrogenation leads to hydrogen starvation, and formation of coke eventually causes a catalyst deactivation [71].

Also, the diluting effect of hydrogen, decreases the dimerization reactions, and the higher hydrogen partial pressure will suppress monomolecular side reactions, such as cracking [73].

6.4 Space Velocity (Contact Time)

The space velocity is considered one of the most important process parameters along with temperature. It is calculated as the residence time of reactants in the reaction space at reaction conditions for the unit volume of the reactor [73]. High space velocity has great economic benefits for the operating process due to the increase in process yield per unit time, but this requires an active and highly selective catalyst for the feed and requires less Contact time to complete the reaction [74].

7. Conclusions

The isomerization process is classified based on catalyst, configuration, and feedstock. This review will benefit the oil refineries using suitable technology for their processes.

this paper reviewed the isomerization process, catalysts that are used for isomerization, the main reactions that occur during the isomerization process in the reactor, the reaction mechanism, reaction conditions for the various reactions, the main contaminants that are present in the feedstock. The octane enhancement of light straight-run naphtha (LSRN) is one of the significant processes in today's oil refineries due to the limitations of benzene, aromatics, and olefin content in gasoline. Therefore, the isomerization process has become important in oil refineries as it produces compounds with fewer alkenes and aromatics.

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