Sudan Journal of Science and Technology (2017) **18**(1): 90 - 100

عمـــادة البحـــث العلمـــي
DEANSHIP OF SCIENTIFIC RESEARCH

Sudan Journal of Science and Technology
Journal homepage: http://jst.sustech.edu/

Utilization of Improved (Pt/H-γ-Al_2O_3) Zeolite in the Production of High Octane Number Gasoline from Light Sudanese Naphtha

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ARTICLE INFO

ARTICLE HISTORY
Received: 18/07/2016
Accepted: 28/12/ 2016
Available online: August 2017

KEYWORDS:
hydroisomerization; light naphtha; impregnation; Gamma Alumina; zeolites

ABSTRACT

The hydroisomerization of light paraffins is an important industrial process to obtain branched alkanes, which are used as octane boosters in gasoline. The Sudanese light naphtha (Produced in kartoum Refinery) was chosen as the case study in this paper. The aims of this study were investigate the production of isomers with high octane numbers and reduce the content of benzene. Type Gamma Alumina Improved Pt./H-γ Al_2O_3, of catalysts was prepared, with 0.5wt% ($H_2PtCl_6.6H_2O$) by impregnation method. The hydroisomerization unit was constructed from copper blossom and designed to carry out the hydroisomerization process. The fixed bed reactor dimensions were O.D 3.5cm, I.D 1cm, reactor total volume 22.765 cm^3 and 30cm length. All experiments were made at atmospheric pressure and a reaction temperature of 160°C. The results show that the conversion of the main light naphtha components to (Isobutane, n-C_4, Neopentane, Isopentane, n-C_5, 2,2DMC_4, 2MC_5, 3MC_5, CC_6), at 160°C has increased. Also, it was noted that the selectivity to isomers increased at a temperature of 160°C and the aromatic component was converted to cyclohexane. The original light naphtha gives a Research Octane Number (RON 67.49) and light naphtha over Pt/H-γ Al_2O_3 catalyst give a Research Octane

Number (RON 95.55) which is a very good result.

INTRODUCTION

The hydroisomerization of light naphtha (C_5-C_6 fractions) is an important process in oil refineries oil and is used in the production of high octane gasoline blend stocks. The process involves the transformation (with minimal cracking) of the low octane normal (and less branched) paraffin components into the high octane isomers with greater branching of the carbon chain (**Al-Kandari, et al**. **2015; Andreas, 2003**; **Annemieke, et al**; **1997 Carsten, 2006)**. The metal–acid bifunctional catalysts, such as alumina or zeolites supported Pt catalysts, are used in hydroisomerization of light paraffins (n-pentane and n-hexane). It shows high efficiency in the isomerization of alkanes. The isomerization of pentane and hexane is successfully carried out using noble metals such as Pt-or Pd-supported on Al_2O_3, mordent, beta zeolite, and silicon catalyst. However, difficulties were countered with hydrocarbons larger than heptanes because the cracking reaction becomes more significant over these isomerization catalysts as the chain length increases. Therefore, some modification and pretreatment processes are required to increase the catalyst activity, selectivity and life time. (**Takeshi, 2003**, **Ping, 2009**, **Ravishankar, 1996**). The literature covers many studies which focused on the investigation of to investigate the hydroisomerization of n-paraffins (**Liu, 1996**, **Toshio, 2004**, **Yunqi . et al 2004**, **Runstraat, 1997**). Few investigations have used light naphtha as a feedstock for the process. On the other hand, many authors made kinetic studies on the hydroisomerization unit for n-hexane and n-heptane (**Chica, 1999**, **Rachid, et al 2006**, **Franciscus, 2002**, **Runstraat, et al, 1997**, **Matthew, 2008**). However few studies dealing with the hydroisomerization of light naphtha were published (**Holló, 2002**, **Yunqi, et al 2004**). The main objective of this investigation is to study the hydroisomerization of Sudanese light naphtha over bifunctional zeolite catalysts to produce high octane gasoline and reduce content of benzene.

Materials and Experimental Methods

Materials

Sudanese-Light-Naphtha was used as a feedstock in the present investigation. It was supplied by Khartoum Refinery. Table (1) and Table (2) shows impurity and chemical composition of Sudanese-light naphtha**.** On the other hand, other materials used such as bifunctional zeolite catalysts Gamma Alumina **(**$Pt/H\text{-}\gamma\text{-}Al_2O_3$). Table (3) shows the Chemical composition of Gamma Alumina support ($\gamma\text{-}Al_2O_3$). Figure (1) shows X-ray Diffraction (XRD) patterns of $\gamma\text{-}Al_2O_3$. Figure (2) and (3) show Scanning Electronic Microscopy (SEM) monograph and Energy Dispersive X-ray (EDAX) of $Pt/H\text{-}\gamma\text{-}Al_2O_3$, Hydrogen and Nitrogen.

Table (1): Impurities of Sudanese-Light Naphtha [Khartoum Refinery, 2016]

Impurity	By wt.
Total Sulfur	0.5ppm max.
Total Nitrogen compounds	0.1 ppm max.
Water + Oxygenates	0.1 ppm max.

Matels	5 ppb max.
Arsenic	1.0 ppb max.
Chloride	1 ppm max.
Olefins	1 % max.

Table (2): Chemical Composition of Sudanese-Light Naphtha [Khartoum Refinery, 2016]

Component	Composition (wt%)
C3	1.21
n-C_4	2.30
Isopentane	19.10
n-C_5	73.78
3MC5	1.43
BENZENE	2.18
Total	100
Research Octane Number (RON)	65
Sp Gr at 15˚C	0.671

Table (3): Chemical Composition of Alumina Support (γ-Al_2O_3)

Composition	Al_2O_3	SiO_2	Fe_2O_3	MgO_2	NiO	PtO_2	WO	TiO_2	SnO_2	L.O.I
γ-Al_2O_3	93.041	0.528	0.406	…	…	0.532	…	0.426	0.617	4.450

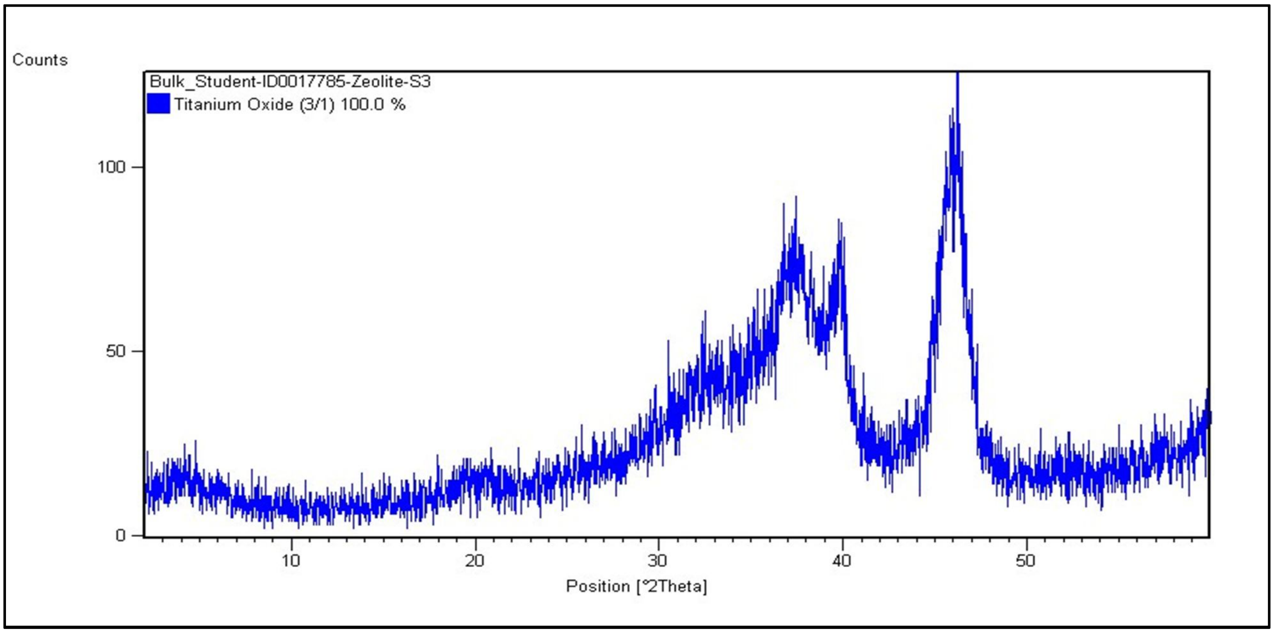
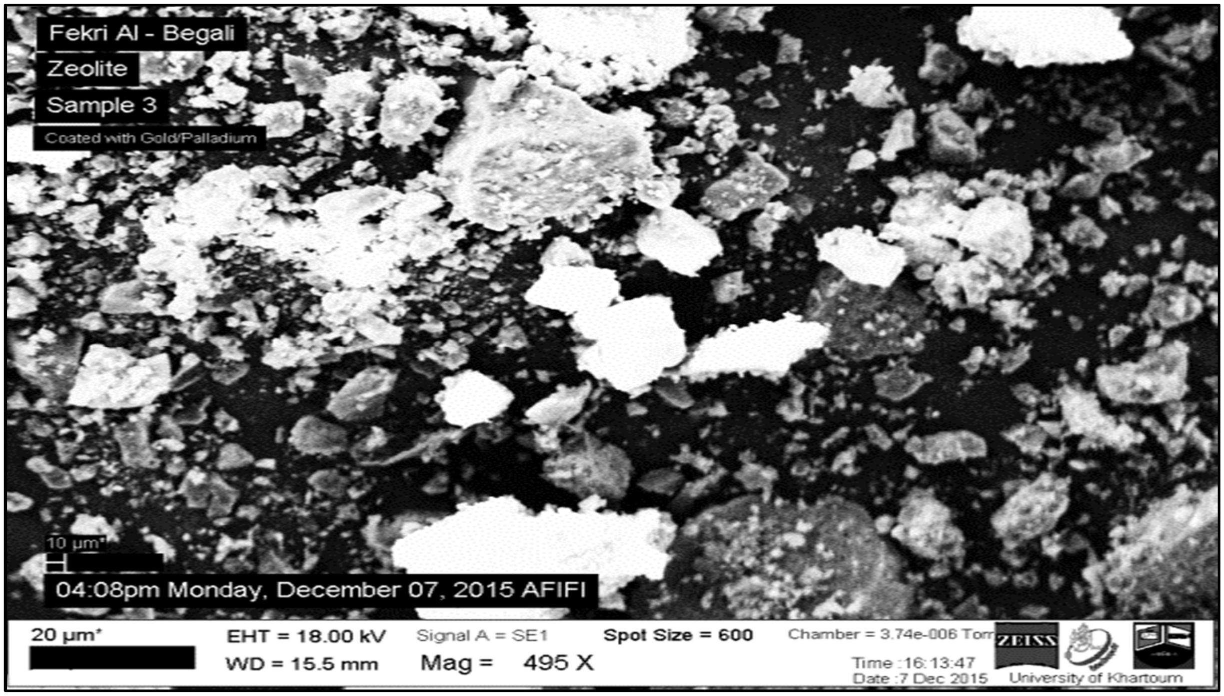


Figure (1): XRD Patterns of Gamma Alumina γ-Al_2O_3



Figuge (2): SEM Monograph of Gamma Alumina Pt/H-γ-Al_2O_3

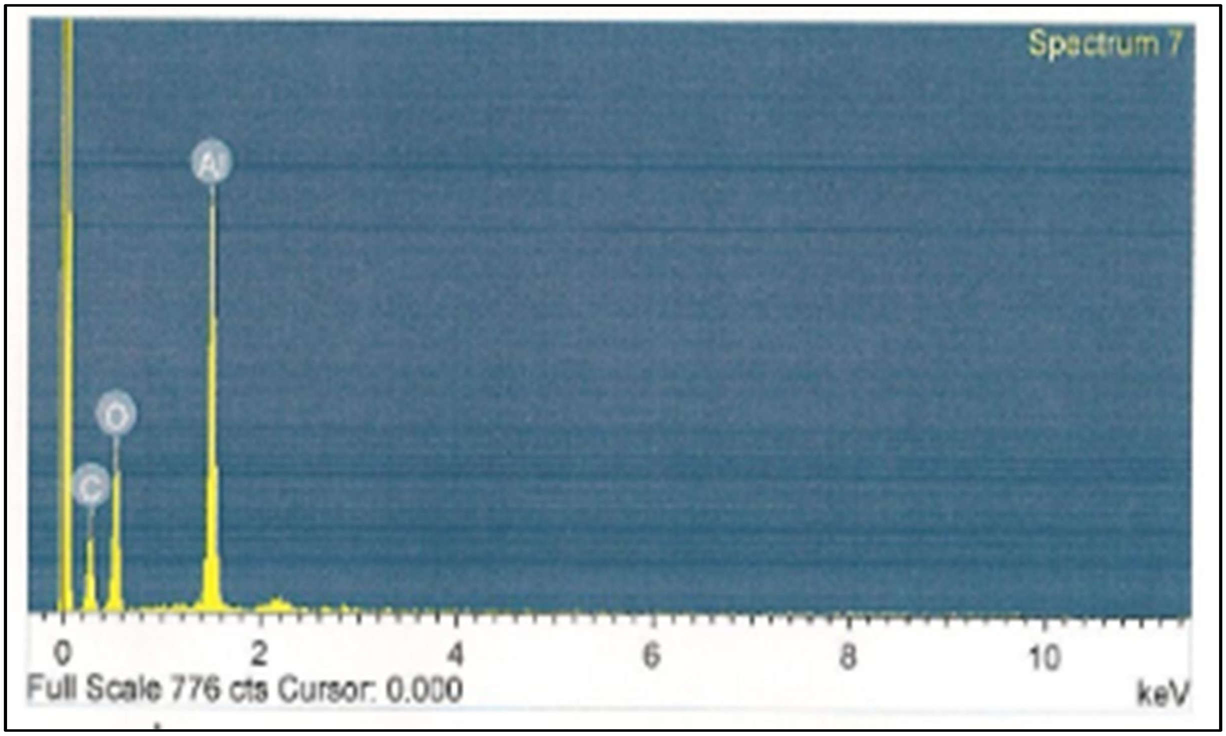


Figure (3): (EDAX) Gamma Alumina Pt/H-γ-Al_2O_3

EXPERIMENTAL METHODS

Design Experimental of Atmospheric Hydroisomerization Unit

The experiments were carried out by a semi batch catalytic unit. Figure (4) Shows the general view of a pilot plant for light naphtha hydroisomerization process, and a schematic diagram of the apparatus. Table (4) shows design specifications for the atmospheric hydroisomerization unit. The reaction was carried out in a catalytic fixed bed tubular reactor Table (5) shows the specifications of the atmospheric reactor and Figure (5) shows the design of the hydroisomerization atmospheric reactor, which is made of copper blossom. The reactor dimensions were 1cm internal diameter, 3.5cm external diameter and 30cm length (reactor volume 22.765 cm^3). The reactor was charged in each experiment with 5g of catalyst located in the middle zone, while the upper and lower zones were filled with glass beads. The reactor was heated to 160C° and controlled using oil, paraffin heated on mantle plate with a maximum temperature of 300°C. It was possible to measure the temperature of oil, paraffin which considered being the same temperature as that of the catalyst bed using a calibrated thermometer at 360°C in order to measure the control reaction temperature. The reactor was fitted with an accurate means for control of pressure gas and liquid flow rate. The liquid (light naphtha) was injected with a especial inject ampule.

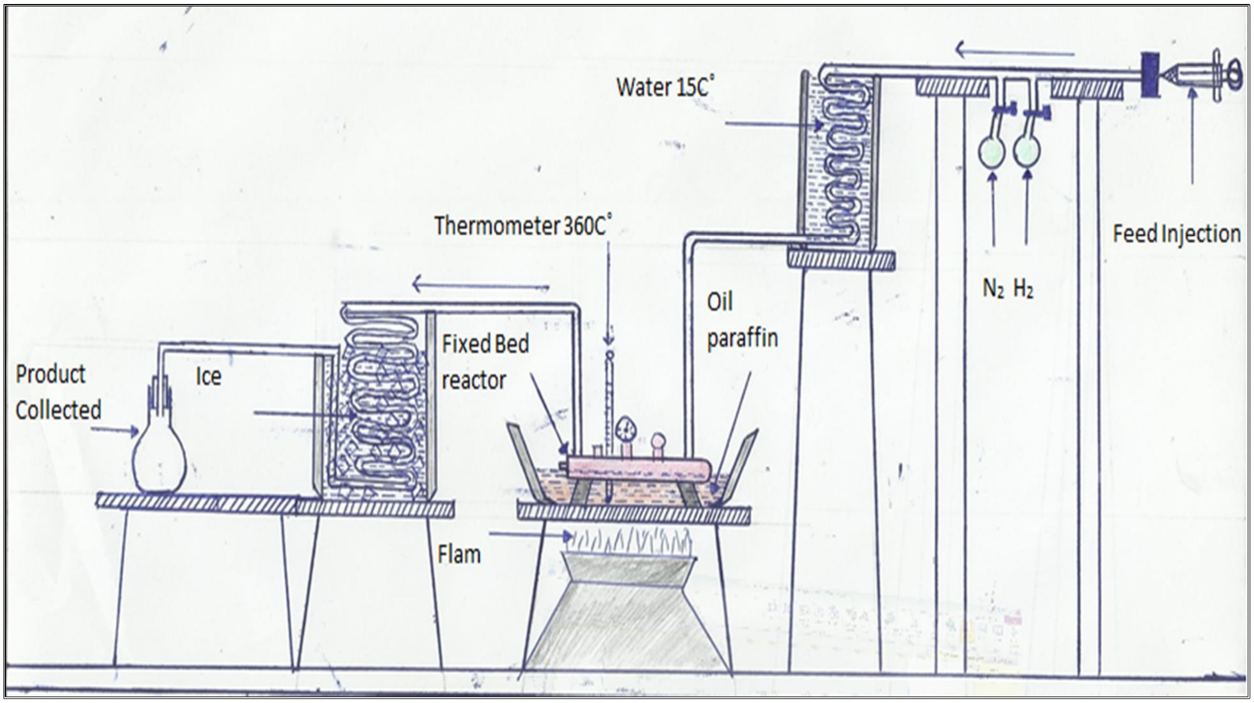


Figure (4): A Schematic diagram of the Hydroisomerization Experimental Unit Apparatus.

Table (4): Design Specifications for the Atmospheric Experimental Hydroisomerization Unit.

Design Parameter	Specification
Design/Operating Pressure	10 - 20 bar
Design Temperature	350°C
Operating Temperature	160°C
Light-naphtha Flow Rate	0.5-1ml/min
H_2 Flow Rate	100 – 1000 ml/min

Table (5): Specifications of the Atmospheric Reactor

Description	Specification
Material	Copper blossom
Reactor, Total Length	30 cm
External Diameter	3.5 cm
Internal Diameter	1 cm
Oil paraffin bed Length	35 cm
Oil paraffin bed thickness	2 cm
Operating Temperature	160°C
Thermometer Maximum range measuring	350°C
Reactor, Total Volume	22.765 cm^3
Maximum Operating Temperature	350°C
Acceptable Working Pressure at 350°C	9.29 psi

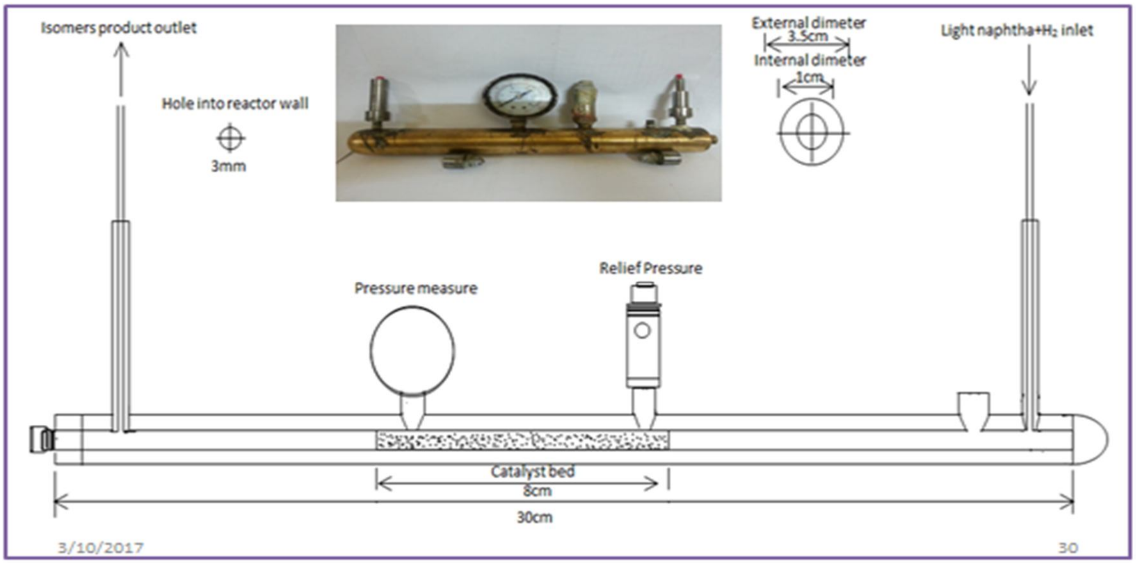


Figure (5): Design of the Hydroisomerization Atmospheric Reactor.

Procedures

Five grams of fresh prepared catalyst were charged into the middle zone of the reactor. The feed, (15ml of Sudanese light-naphtha) was injected into the reactor at atmospheric pressure. The feed sample was first passed through the molecular sieve filter HPLC 0.22µm type to remove any impurities. The hydrogen gas flow to the unit was set at about 10–1000 ml/min. The Sudanese light-naphtha was mixed with hydrogen gas at the reactor inlet. The mixture temperature was 15°C in reactor feed, and then passed through the catalyst bed. The performance of the catalysts was tested under constant operating temperature of 160°C and hydrocarbons flow rate 1ml/min. The hydrogen to hydrocarbon molar ratio was kept constant at 0.42. A pre-test period of one hour was used before each run to adjust the design specifications conditions to the desired values. The reaction products were cooled by cooling system and collected in the separator in order to separate the non-condensed gases from the top of the separator and the condensed liquid hydrocarbons from the bottom of the separator. Then the product samples were analyzed using Gas Chromatograph type Variant module CP_3800 using front detector type a flame ionization detector (FID) temperature equal 300°C. Injector front injector type 1177 with temperature 275°C and split ratio shown in Table (6). The column dimensions are 0.2mm internal diameter and length 50m and film thickness 0.5µm. The column oven specifications are shown in Table (7). The retention times for the hydrocarbons are shown in Table (8). The pressure of carrier gas Helium and its was 64.0 psi hold time was 140 minutes. It is important to mention here that, the calibration of gas chromatography was carried by injecting the same amount of a standard into the Gas Chromatography.

Table (6): Injector Split Ratio

Time	Split State	Split Ratio
Initial	On	20
0.01	On	20
1.00	On	100
5.00	On	20

Table (7): Column Oven Specifications

Temp (C)	Rate (C/min)	Hold (min)	Total (mint)
35	----	15.00	15.00
60	1.0	20.00	60.00
200	2.0	10.00	140.00

Table (8): Retention Times of Hydrocarbons in the Catalytic Isomerization of Light Naphtha Reaction

Components	Retention times (min)
Isobutene	5.215
n-C4	5.464
isopentane	6.6378
n-C5	6.875
2,2DMC4	7.295
3MC5	8.802

RESULTS AND DISCUSSION

The results of the experimental work are explained of the Characterization of Catalysts prepared, and produced a high octane number by converting Sudanese light naphtha over Improved Gamma Ammonia (Pt/H-γ-Al_2O_3) zeolite catalysts and reduce contain of benzene are displayed and discussion.

Characterization of Catalysts

In order to know the Characterization of Catalysts prepared sample Gamma Alumina Pt./H-(γ-Al_2O_3), It has been well-established that the specific surface area of support has important effects on the final properties of the supported catalysts. (**Fekri, et al , 2016**) Compositions shown in Table (3) The X-ray diffraction analysis (XRD) show in figures (1), was used to determine the crystalline structure of γ-Al_2O_3 on 2θ scale, from the results obtained, this step of characterization will give a real identification that used zeolite specification and its crystalline structure were γ-Al_2O_3 amorphous Aluminum Oxide with Titanium Oxide crystallite. Figure (2) shown the specific surface area of the supports Pt/H-γ-Al_2O_3 by Scanning Electronic Microscopy (SEM) were examined, and the results shown, Platinum particles were seen homogeneously distributed, where the white spots represent a platinum particle and black zone represent the support, with the average diameter 15μm. These results are in accordance with that the faujasite crystallite size range (10-20) μm. SEM is used to ensure good impregnation of active components. Also, from Figure (3) it is clear that the Aluminum main components. The Brunauer-Emmett-Teller (BET). Results of Surface Area equals 288.86 m2/mg and Pore Volume cm^3/gm equals 0.3199 were clear seen that high surface area and large pore volume.

Effect of Operating Conditions

The performance of catalysts was tested under a constant operating temperature of 160°C and hydrocarbons flow rate 1ml/min, 15ml of light-naphtha at constant time 15min. The product samples were analyzed using Gas Chromatograph. Table (10) and Table (11) shown components listed and Research Octane Number result.

Table (5.8): Components Listed in Chromatographic Order

Min.	Index	Component	Area	Wt %	Vol %	Mol %	Shift
5.218	382.65	Isobutane	14755	0.239	0.270	0.296	0.372
5.467	400.00	n-C_4	261424	4.242	4.554	5.237	0.000
5.593	408.76	Neopentane	6096	0.098	0.101	0.098	-0.063
6.390	464.26	Isopentane	2095665	33.769	33.911	33.570	0.000
6.903	500.00	n-C_5	3638466	58.633	58.290	58.287	0.000
7.300	527.64	2,2DMC_4	111633	1.791	1.730	1.490	2.214
7.813	563.31	2MC_5	5876	0.094	0.090	0.078	4.994
8.807	632.52	3MC_5	67399	1.081	1.014	0.900	-4.367
9.019	647.30	CC_6	3310	0.052	0.044	0.044	-0.988
			6204624	100.00	100.00	100.00	

Table (11) Gas Chromatograph Results of Light-Naphtha over Pt/H-γ-Al_2O_3

RON, MON, RVP, Wt%H, Wt%O, C/H Ratio	
Research Octane Number	95.55
Motor Octane Number	N/A
Reid Vapor Pressure (PSI)	21.70
Reid Vapor Pressure (kPa)	149.60
Weight% Hydrogen	16.78
Weight% Oxygen	0.00
Carbon/Hydrogen Mole Ratio	0.42
Temperature @ V/L=20 (deg C)	14.18

According to the results of Gas Chromatograph (G.C), analysis, the isomerization of light naphtha leads to the formation of mainly mono-branched and dibranched molecules. the selectivity to isomers is increased with no aromatics production. It was noted that, the Research Octane Number increased to (95.55) and benzene was converted to cyclohexane (CC_6). This is in agreement with the investigation of Falco, Canavese, Comelli and Fıgoli (**Falco, et al 2000**, and **María, et al, 2008**). Also RON in the limit of Gasoline Fuel Specifications (92 to 100).

Conclusions

The Hydroisomerization of Sudanese Light Naphtha over Pt/H-γ-Al_2O_3 catalysts was studied. The characterization of pt/H-γ-Al_2O_3 show the high selectivity to produce isomers and conversion of benzene to cyclohexane. The results show that the best operating temperature for the hydroisomerization process (with high selectivity toward isomerization) is 160 °C with the same improved zeolites prepared in this study. Many kinds of zeolite species are not available industrially; these modified zeolite can be used adequately in a variety of applications such as hydroisomerization units, petrochemical cracking, and other applications. The hydroisomerization of Sudanese light naphtha over Pt/H-γ-Al_2O_3 was carried out to give high selectivity towards isomers. Therefore, the results of the present work can be applicable to the designing of hydroisomerization units in Sudanese oil refineries.

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