Hydroisomerization of Sudanese Light Naphtha Over Improved Beta(Pt/H-β Co-Crystalline) Zeolite Catalyst

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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 Khartoum Refinery) was chosen as the case study in this paper. The aims of this study were to produce isomers that high octane number. Type Beta Zeolite Improved (Pt/H-β Co-Crystalline), catalyst 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 OD 3.5cm, ID 1cm, reactor total volume 22.765 cm^3 and 30cm length. All experiments were made at atmospheric pressure and reaction temperature of 160°C. The results show that the conversion of the main light naphtha components to (n-C_4,isopentane, n-C_5, 2,2DMC_4,3MC_5), at 160°C. Also, it was noted that the selectivity to isomers over improved Beta (Pt/H-β Co-Crystalline) Zeolite increases at temperature 160°C. The orginal light naphtha gives Research Octane Number (RON 67.49) and the light naphtha over Beta (Pt/H-β Co-Crystalline) Zeolite catalyst gives (RON 89.52) which is a very good result.

Keywords: hydroisomerization; light naphtha; impregnation; Beta zeolite; zeolites.

INTRODUCTION

The hydroisomerization of normal alkanes proceeds ideally by the bifunctional mechanism in which a noble metal, usually platinum, provides the hydrogenation/dehydrogenation functions of the catalyst, and a zeolites support provides the acidic function responsible for carbonium ion rearrangements [14], [18]. The hydroisomerization reaction of light naphthaprocess 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 [1], [2], [3], [7].The bifunctional Beta zeolite catalyst is crystalline aluminosilicates [6],[5] that have unique pore structures and catalytic properties, promoting their use in many industries, most importantly in hydroisomerization process in oil refinery [4],[10]. The literature mentions many studies which were focused to investigate the hydroisomerization of n-paraffins [12], [17], [19], [15]. Few investigations have used light naphtha as a feedstock for the process. The hydroisomerization process is an efficient and economically acceptable way of increasing the octane number of motor gasoline, and gasoline isomerate represents an ideal product that can satisfy the most stringent environmental requirements [11], [16]. The main objective of this investigation is to study the hydroisomerization of Sudanese light naphtha over bifunctional Beta zeolite catalysts to produce high octane gasoline.

MATERIALS AND METHODS

Materials

In the present work, different materials and compounds are used. Sudanese-Light-Naphtha is used as a feedstock in the present investigation paper. It was supplied by Khartoum Refinery. Tables (1) and (2) show impurity and chemical composition of Sudanese-light naphtha**.** The other material used is bifunctional zeolite catalysts Beta (Pt/H-β Co-Crystalline) zeolite. Table (3) shows the chemical composition of Beta support (Pt/H-β Co-Crystalline) zeolite and Figure (1) shows X-ray Diffraction (XRD) patterns of (Pt/H-β Co-Crystalline) Zeolite. Figure (2) and (3) shows Scanning Electronic Microscopy (SEM) monograph and Energy Dispersive X-ray (EDAX) of (Pt/H-β Co-Crystalline) Zeolite.

Table (1): Impurity 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): The chemical composition of Sudanese-light naphtha [Khartoum Refinery, 2016]

Component	Composition
C_3	1.21
n-C_4	2.30
Isopentane	19.10
n-C_5	73.78
3MC_5	1.43
Benzene	2.18
Total	100
Research Octane Number (RON)	65
Sp Gr at 15˚C	0.671

Table (3): The Chemical composition% of β Co-Crystalline Zeolite raw

Composition	Al_2O_3	SiO_2	TiO_2	Fe_2O_3	P_2O_5	K_2O	La_2O_3	L.O.I
β Co-Crystalline Zeolite	51.179	41.210	0.316	0.595	2.142	0.389	1.31	2.859

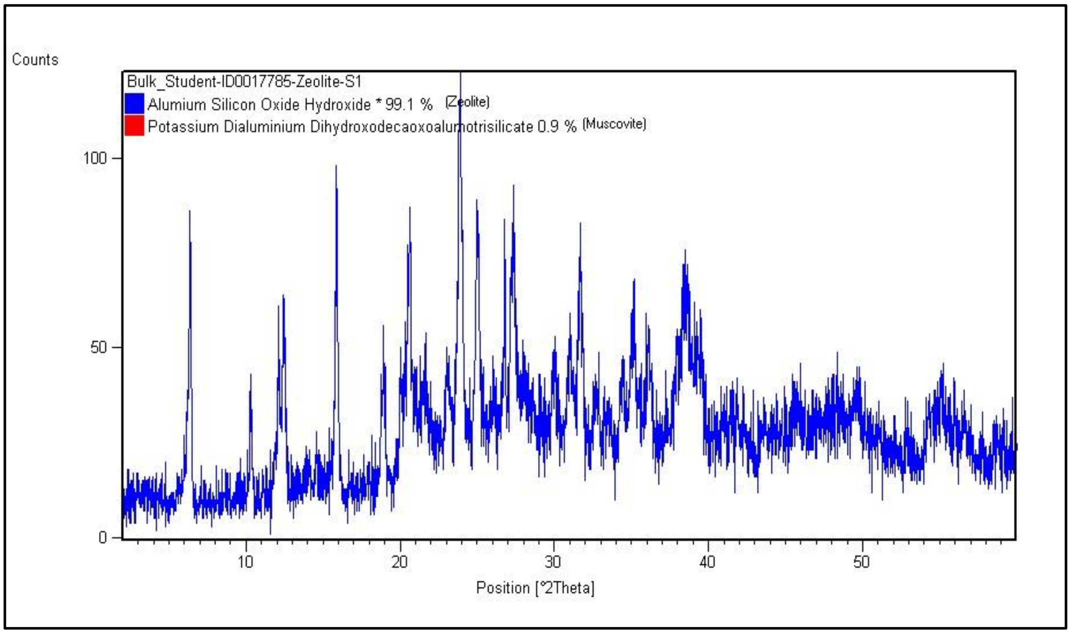

Fig. (1): XRD patterns of β Co-Crystalline Zeolite

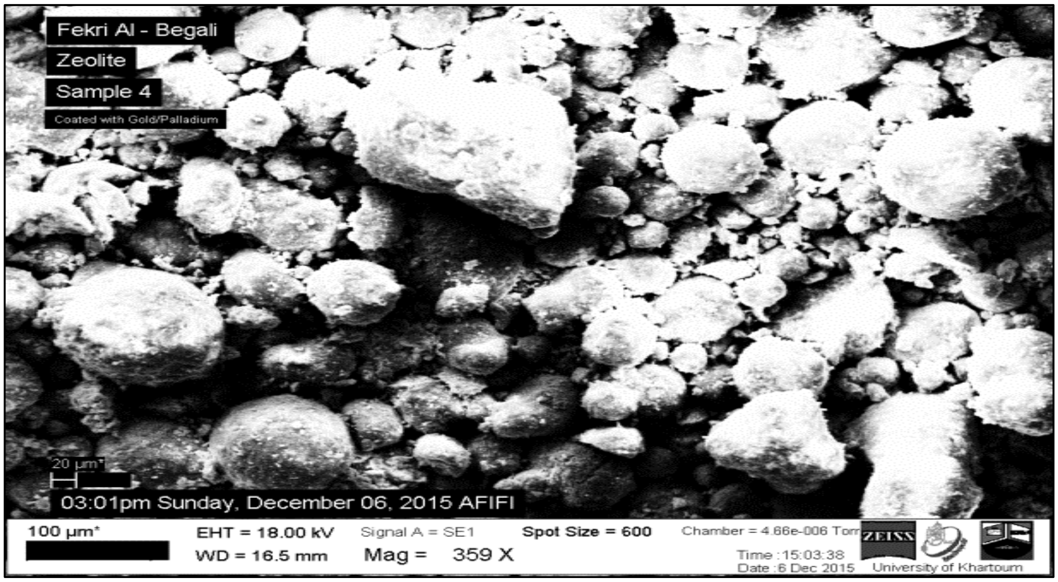

Fig. (2): SEM monograph of Pt/H-β Co-Crystalline Zeolite

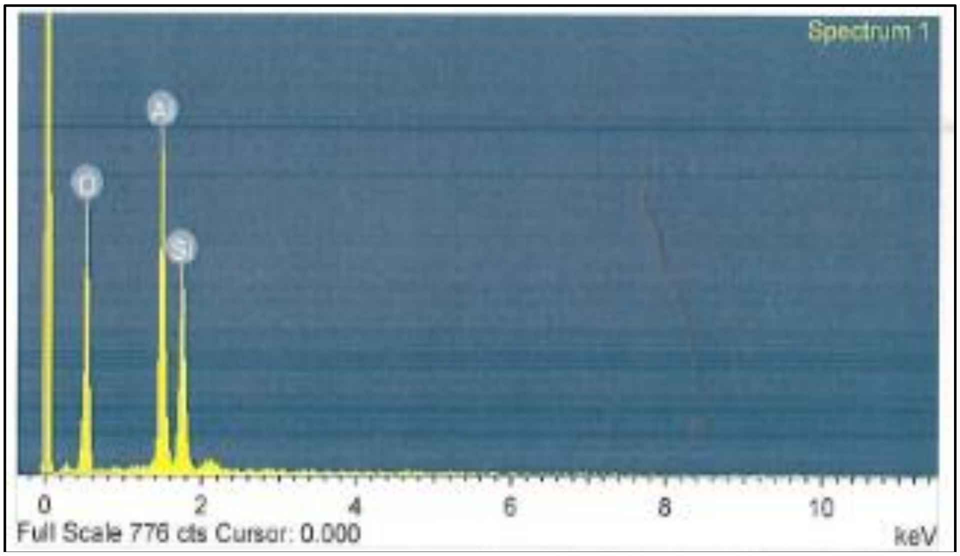

Fig. (3): (EDAX) Pt/H-β Co-Crystalline Zeolite

Experimental Section

Experimental Details 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 catalytic fixed bed tubular reactor Table (5) shows 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 for 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 heat by mantle plate Heater with a maximum temperature of 300°C, it was possible to measure the temperature of oil paraffin which is considered the same temperature of the catalyst bed using calibrated thermometer 360°C in order to measure and control reaction temperature. The reactor was fitted with an accurate means for control of gas pressure and liquid flow rate. The liquid (light naphtha) was injected with an especial inject ampule.

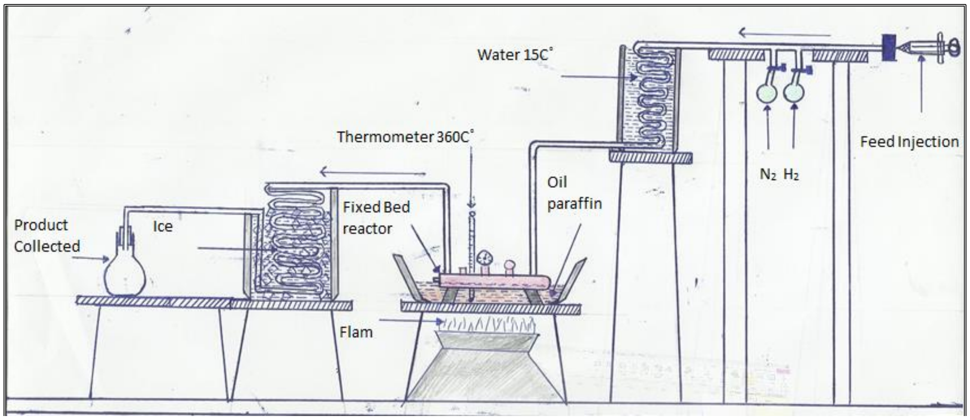

Figure (4): A schematic diagram of the hydroisomerization unit apparatus.

Table (4): Design Specifications for the Atmospheric hydro-isomerization 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	1.0 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

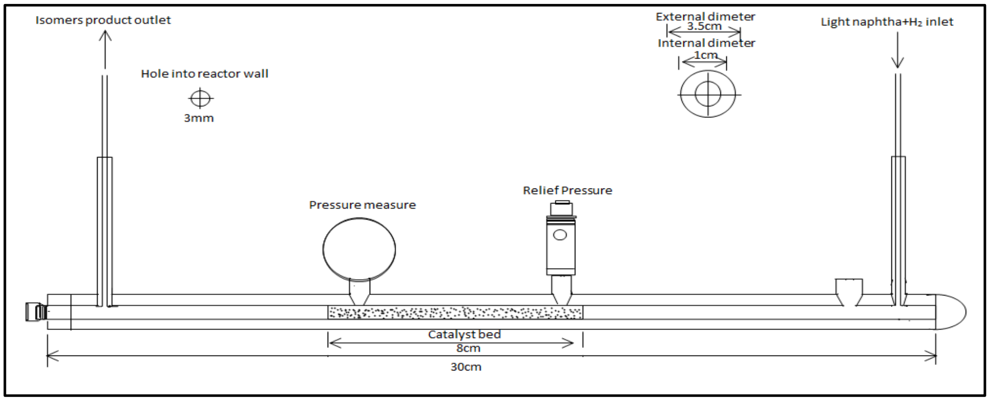

Figure (5): Design of the hydro-isomerization atmospheric reactor.

Catalytic isomerization of light naphtha method

Five grams of freshly prepared catalyst [8] were charged into the middle zone of the reactor. The feed, Sudanese light-naphtha (15ml) was injected into the reactor at atmospheric pressure. The feed sample before it passed to the reactor passed through the molecular sieve filter (HPLC-0.22µm) type to remove any impurities. The hydrogen gas flow to the unit was enough amounts, about 10–1000 ml/min.The Sudanese light-naphtha pass to meet hydrogen gas and were mixed before the reactor inlet. The mixture was flowing at 25°C before entering the reactor, and then passed through the catalyst bed. The performance of catalysts was tested under constant operating temperatures of 160°C and hydrocarbons flow rate of 1ml/min, (15ml of light-naphtha at constant time 15min). 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 of 300°C. Injector front injector type 1177 with temperature 275°C and retention time for thehydrocarbons is shown in Table (6). The Helium gas (He) 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): Retention times of hydrocarbons in the catalytic isomerization of light naphtha

Components	Retention times (min)
Isobutene	5.2150
n-C_4	5.4640
Isopentane	6.6378
n-C_5	6.8750
2,2DMC_4	7.2950
3MC_5	8.8020

RESULTS ANDDISCUSSION

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 bifunctional zeolite catalysts are displayed. The orginal light naphtha gives Research Octane Number (RON 67.49) and the light naphtha over Beta (Pt/H-β Co-Crystalline) Zeolite catalyst gives (RON 89.52) which is a very good result.

Characterization of Catalysts

In order to know the characterization of catalyst Beta (Pt/H-β Co-Crystalline) Zeolite, It has been well-established that the specific surface area of support has important effects on the final properties of the supported catalysts [8].Compositions shown in Table (3) The X-ray diffraction analysis (XRD) shown in Figure (1), were used to determine the crystalline structure of Beta (β Co-Crystalline) Zeolite on 2θ scale. From the results obtained, the zeolite specification and crystalline structure were Beta(β Co-Crystalline) Zeolite: Aluminum Oxide and Silicon Oxide 99.1% crystallite with Potassium Dialuminium Didydroxide 0.9% Muscovite. Figure (2) shows the specific surface area of the supports of Beta (Pt/H-β Co-Crystalline) Zeolite. Scanning Electronic Microscopy (SEM) was examined, and the results show that Platinum particles were seen homogeneously distributed, where the white spots represent platinum particles and black zone represents the support, where the average diameter is 8.5µm.These results are in accordance with that the faujasite crystallite size range (5-10) µm. SEM is used to ensure good impregnation of active components. Also, from Figure (3) it is clear that Al_2O_3 and SiO_2 are the main components.The Brunauer-Emmett-Teller (BET) results of surface area equals 427.98 m^2/mg and pore volume in cm^3/gm of 0.6603. It is clearly seen to be of high surface area and large pore volume.

Effect of Operating Conditions

The performance of catalysts was tested under constant operating temperatures 160°C and hydrocarbons flow rate 1.0 ml/min, 15ml of light-naphtha at constant time 15min. The product samples were analyzed using Gas Chromatograph.Tables (7) and (8) show components and Research Octane Number.

Table (7): Components listed in chromatographic order

Min.	Index	Component	Area	Wt %	Vol. %	Mol. %	Shift
5.465	400.00	n-C_4	3544	0.650	0.708	0.862	0.000
6.380	464.87	Isopentane	75169	13.682	13.955	14.622	-0.029
6.875	500.00	n-C_5	248504	45.234	45.675	48.340	0.000
7.299	530.06	2,2DMC_4	218990	39.678	38.942	35.500	4.630
8.807	636.93	3MC_5	4175	0.757	0.720	0.677	0.040
Total			5508382	100.00	100.00	100.00	

Table (8): The results of orginal light-naphtha and light naphta overpt/H-β.Crystalline zeolite

Items	Value
Research Octane Number (RON), original	67.49
Research Octane Number (RON), over pt/H-β crystalline zeolite	89.52
Motor Octane Number (MON)	N/A
Reid Vapor Pressure (psi)	16.87
Reid Vapor Pressure (RVP), kPa	116.32
Weight% Hydrogen (Wt%H)	16.61
Weight% Oxygen (Wt%O)	0.00
Carbon/Hydrogen Mole Ratio (C/H Ratio)	0.42
Temperature @ V/L=20 (deg C)	25.78

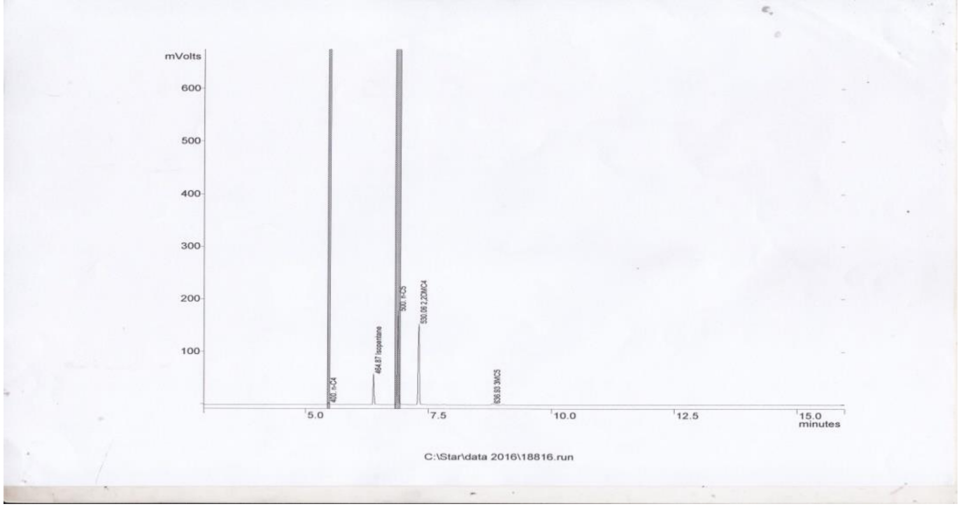

Fig. (6): Identified components listed in chromatographic order over pt/H-β. \ Crystalline zeolite

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. It was noted that, the RON increased to 89.52. This is in agreement with the investigation of [9], and [13]; also the RON in the limit of gasoline fuel specifications (88 to 100).

Conclusions

The Hydroisomerization of Sudanese Light Naphtha over Pt/H-β. Crystalline zeolite catalysts was studied. The characterization of Pt/H-β. Crystalline zeolite show the high selectivity to produce isomer and convert 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 improved zeolites prepared in this study. Many kinds of zeolite species are not available industrially, these are modified zeolite which can be used in a variety of applications such as hydroisomerization unit, petrochemical cracking, and other applications. The hydroisomerization of Sudanese light naphtha over Pt/H-β. Crystalline zeolite was carried out to give high selectivity toward isomers. Therefore, the results of the present work can be applied to the designing of hydroisomerization unit in Sudanese refinery oil.

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هيدروأيزمرية النافتا السودانية الخفيفة لتحسينها بحفاز بيتا (Pt/H−β Co−Crystalline) زيولايت

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الخلاصة

تعتبر عمليه الأزمرة للبرافينات الخفيفة هامه في عمليات تكرير النفط للحصول على الاكانات المتفرعة والتي ترفع الرقم الأوكتاني للجازولين. النافثا الخفيفة المنتجة من الخام السوداني في (مصفاة الخرطوم) اختيرت لعمل الدراسة في هذه الورقة. تهدف هذه الدراسة الى انتاج الأيزومرات ذات الرقم الأوكتاني العالي. تم استخدام حفاز معدل نوع بيتا زيولايت (Pt/H−β Co−Crystalline)والحاوي على نسبة 0.5% وزنا من البلاتين والمحضر بطريقة الترطيب. تم اجراءالتجارب في منظومة مختبرية تحتوي على مفاعل ذو حشوة ثابتة مصنوع من مادة النحاس الزهر المقاوم للصدأ حيث تَم تصميمه لعملية الأزمرة ، القطر الداخلي للمفاعل1.0 سم والقطر الخارجي 3.5سم والطول 30سم. تمت جميع التجارب تحت الضغط الجوي الاعتيادي وعند درجة حرارة 160م°. أوضحت النتائج تحول مكونات النافثا الخفيفة الى (nC_4 ,Isopentane, $n-C_5$, $2,2DMC_4$,$3MC_5$) كما لوحظ زيادة الانتقائية للزيولايت نحو تحويل ($n-C_4$) الى ($2,2DMC_4$) إيزومرات بنسبة (39.678Wt %)، عملية الأزمرة للنافثا السودانية الخفيفة على الزيولايت المعدل نوع (Pt/H−β Co−Crystalline) أعطت الرقم الأوكتاني (RON) يساوي 89.52 وتعتبر نتيجة جيدة جدا.