

Sulfur Reduction in Naphtha produced from Al-Qayarah Refinery Units by the Simplest Possible and Economically Feasible Methods

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Abstract

Production of low sulfur content of untreated naphtha from Al -Qayarah Refinery units has been studied in this research by using oxidation, oxidation-adsorption, and adsorption methods. The influence of time, temperature, sorbent type on sulfur reduction was investigated. The results showed that oxidation- adsorption was an efficient method for the desulfurization of naphtha where high removal efficiencies of about 93% were obtained. Also, it was concluded that by increasing temperature (up to 60C), and time (up to 5 hr) led to decreasing sulfur content from 1194ppm to about 76ppm. The results indicated that the best sequence of sulfur removal on sorbent materials were as follow: Ni/AC> AC > Ni/ γ Al₂O₃> γ Al₂O₃.

Keywords: Desulfurization, Oxidation, Adsorption, Naphtha

Introduction

Crude oil contains sulfur that exists in two main forms: the first is termed as “active sulfur” which can react with metal directly; the second is “inactive sulfur” which can not directly react with the metal. Active sulfur includes sulfur, hydrogen sulfide and mercaptan. Non-active includes sulfide, carbon disulfide, thiophene (TH). The presence of sulfur in crude oil reduces its price in the world market, and sulfur compounds will appear in the petroleum fractions after distillation, which will cause corrosion in pipelines and equipment and after burning, it will pollute the environment (1, 2).

Sulfur containing compounds are undesirable in gasoline and diesel fuels because of the emission of sulfur dioxide (SO_x) gases. In order to protect the human health and reduce the environmental hazards, environmental regulation that tend to limit the sulfur levels to very low ones have already been introduced in many countries during the last few decades. Also sulfur must be removed from the petroleum fractions as it causes poisoning of catalysts, corrosion of surfaces, and air pollution (3,4)

Deep desulfurization of refinery streams becomes possible when the severity of the HDS process increased. Unfortunately, more severe conditions result not only in a higher level of desulfurization but also in undesired side reactions. When FCC gasoline is desulfurized at higher pressure, many olefins are saturated and the octane number decreases. Higher temperature processing leads to increased coke formation and subsequent catalyst deactivation (5, 6).

Various methods were suggested for the desulfurization and deep desulfurization of the oil and refinery streams. These strategies include:-

1. *Hydrodesulfurization (HDS).*
2. *Adsorptive desulfurization (ADS).*
3. *Biodesulfurization (BDS).*
4. *Oxidative desulfurization (ODS).*

5. *Supercritical water desulfurization (SCW).*

6. *Extractive desulfurization.*

7. *Precipitation desulfurization.*

Among these methods, Oxidative desulfurization (ODS) has been demonstrated to be a promising method for ultra- deep desulfurization technology because of its mild operation conditions, i.e. no hydrogen required and low cost of operation. During the process, the organ sulfur compounds are oxidized to their corresponding sulfoxides or sulfones. The process is carried out in the presence of a catalyst and an oxidant agent, and the oxidized sulfur compounds are subsequently removed by extraction, adsorption, distillation, or decomposition (7, 8).

ADS has become a promising approach in the ultra-deep desulfurization, A crucial issue in a successful adsorption process is to identify and develop a novel adsorbent, which has high adsorptive capacity, high selectivity and good regenerability(9). The objective of this work is to study the desulfurization of untreated naphtha from Al-Qayarah units. Two processes were adopted: Oxidation –adsorption and adsorption using different adsorbents. Activated Carbon (AC), gamma alumina and nickel loaded on both materials.

Experimental Work

Materials

Naphtha

Naphtha was supplied from the North Refineries Company - Baiji Refinery (Qayarah Refinery). Some properties of naphtha are listed in Table (1).

Table (1):- Properties of Naphtha

Property		Value
Sulfur content(ppm)		1194
Density(g/cm ³)		0.6956
Boiling point(°C)		63-142
PONA (wt %)	n-praffin	22.54
	i-paraffin	63.16
	Naphthene	12.08
	Aromatic	2.22
	Total	100

Gamma alumina (γ -Al₂O₃)

Formulated Spherical shape of gamma alumina was used as a carrier for the prepared catalyst; physical properties of γ -Al₂O₃ are shown in Table (2).

Table (2):- Physical Properties of γ -Al₂O₃

Property	Value
Surface area, m ² /g	194.852
Pore volume, cm ³ /g	0.483
Bulk density, g/cm ³	0.5976

Activated carbon (AC)

Granular activated carbon AC of industrial grade used in the present work. The AC dried in an oven at 120°C for 3 hr to remove any moisture and stored in desiccators, physical properties of AC are shown in Table (3).

Table (3):- Physical Properties of Activated carbon

Property	Value
Surface area, m ² /g	933.56
Pore volume, cm ³ /g	0.454
Bulk density, g/cm ³	0.692

Chemicals

The chemical compounds which used in this research are listed in Table (4).

Table (4):- Chemical Compounds

Chemical	Formula	Molecular weight g/mol	Purity/ Concentration
Cobalt nitrate hexahydrate	Co(NO ₃) ₂ ·6H ₂ O	291.03	----
Hydrogen peroxide	H ₂ O ₂	34.01	45%
Acetic acid	CH ₃ COOH	60.05	99.5%
Nickel nitrate hexahydrate	Ni(NO ₃) ₂ ·6H ₂ O	290.81	99.7%

Equipments

The equipments used were:

- Controlled Magnetic stirrer heater,
- Vacuum pump,
- Three neck round – bottom flask (250 ml),
- Beakers, condenser, Buchner funnel system,
- Electric furnace.

Experimental Procedure

Oxidation Experiments

Untreated Naphtha (100 ml) was introduced into a three – necked round bottom flask reactor equipped with condenser, stirred continuously at constant mixing speed (550 rpm) and heated to a temperature of 60 °C using magnetic stirrer heater. When the mixture reached the desired temperature, 4ml of hydrogen peroxide as oxidant and Acetic Acid (1ml) as homogenous catalyst were added to the reaction mixture. These amounts were fixed following the results of previous studies⁽¹⁰⁾. Then, the solution was allowed to settle in a 100 ml separating funnel, where clear distinguishable phases were obtained. After that sample was withdrawn from the organic phase and it sent for analysis or to the next adsorption step. The experimental setup is shown in figure (1).



(A)



(B)

Fig. (1) Apparatus of Oxidation unit.

Adsorbent Preparation

Preparation of Ni/ γ -Al₂O₃ Catalyst

Nickel loaded on gamma alumina was prepared by the impregnation method shown in Figure (2). Trials were made to obtain the desired loading percent of 7.5%⁽¹¹⁾, 50g of γ -Al₂O₃ was soaked in 60 wt% Ni/ (NO₃)₂.6H₂O aqueous solution in a 500 ml round flask The mixture was stirred for 48 hr. Next to the impregnation step was the filtration using Buchner funnel with a vacuum pump, followed by overnight drying in an oven at 110 °C and finally calcinations in a programmable electrical furnace at 550°C for 5 hrs.

Preparation of Ni/AC Catalyst

Nickel loaded on activated carbon (AC) was prepared. 46 g of AC was impregnated in the solution prepared by dissolving 18.8g of Ni/ (NO₃)₂.6H₂O in 100ml distilled water. Other steps were the same as described in the previous section except that 350 ° C was the calcination temperature. Experimental setup is shown in Figure (2).

Preparation of Co/AC Catalyst

Trials were made for loading cobalt on AC but this experiments didn't give good results of impregnation (very low loading was obtained may be because of bad storage of cobalt nitrate material) so, it was not used in the next steps. 44.88 g of cobalt nitrate hexahydrate was dissolved in distilled water (complete volume to 100 ml) with continuous stirring. After that 20 g of AC was placed in a flask and the prepared solution was added gradually to AC with shaking for (24) hours. This process was done at ambient temperature and then filtered by filter paper in Buchner funnel. The apparatus used for impregnation was shown in Figure (2). The impregnated AC was dried at 120°C in an oven for 2 hr to eliminate water and crystallize the salt in the pore surface. The dried catalyst was calcined at (400)°C in a furnace for (4) hr to convert the salt to oxides over catalysts support and to acquire the catalyst physical and chemical properties.



(A)



(B)



(C)

Fig. (2) The apparatus used for preparation of Ni/γ-Al₂O₃, Ni/AC, and Co/AC

Batch adsorption experiments

These experiments were carried out to investigate the effect of time (1, 3, 5, hr), temperature (normal, 20 °C, 40 °C) and sorbent type. Several batches using (50 ml) naphtha with (1 g) of each type of sorbent were taken in a round bottom flask, heated and kept under stirred condition (750 rpm) for different period of time using the same apparatuses of oxidation shown in Fig(1 A) but changing the condition as suitable for adsorption. The total sulfur content in samples before and after adsorption was measured by sulfur analyzer XRF.

Tests

All tests were made at petroleum research and development center (PRDC). Sulfur content in Naphtha was measured by sulfur analyzer (XRF) at refining and gas researches department which is shown in Figure (3), PONA analysis and metals content were measured by laboratory

analysis department. Surface area, pore volume, and bulk density of catalyst were measured by catalyst center section.



Fig. (3) Sulfur analyzer.

Results and Discussion

The experiments were carried out for desulfurization of naphtha in two methods testing, Oxidation and adsorption. Batch method was used for Oxidation and adsorption runs at different conditions.

Oxidation

Effect of time

The effect of increasing the oxidation time was found to enhance the desulfurization of naphtha as the sulfur content decreased from 1194 ppm of feed to 139, 128.5, and 125.2 after 1, 3, and 5 hr. respectively. This is shown in Table (5) and Figure (4). This is explained by

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that, when increasing the reaction time there is more chance for sulfur compounds to react with H_2O_2 and to be oxidized to sulfones. This reaction like any other reactions needs enough time for completion and is promoted as time goes on. Maximum sulfur removal of 89.5% was obtained after 5 hours, however the removal of 89.2% after 3 hours can also be considered as a good result and the small difference may be due to the experimental error.

Table (5): Effect of time on sulfur removal at Oxidation reaction

time(hr)	sulfur content (ppm)	sulfur removal %
0	1194	0
1	139	88.35845896
3	128.5	89.23785595
5	125.2	89.51423786

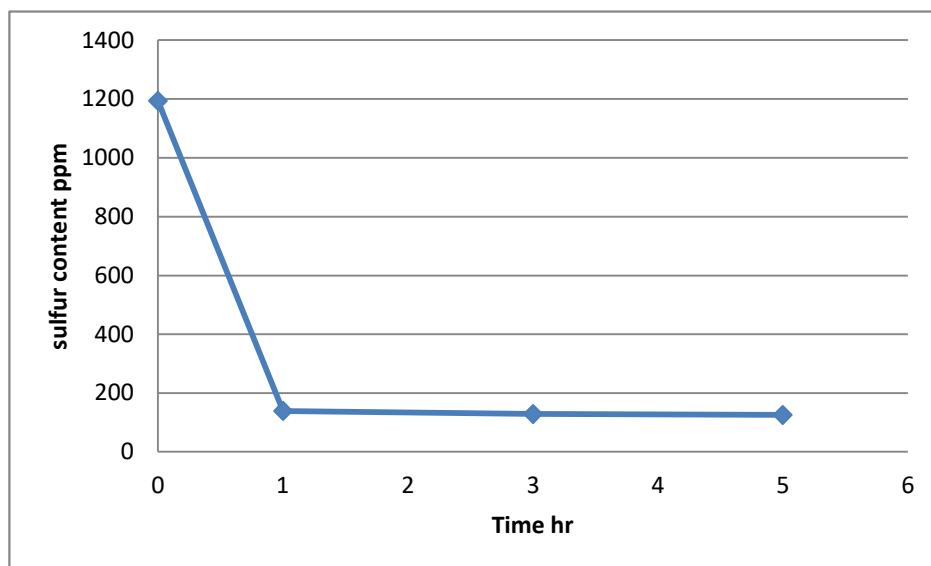


Fig. (4) Effect of time on sulfur removal at Oxidation reaction.

Adsorption desulfurization

- **After oxidation**

This step is a complementary to the oxidation step. Sulfone, as being produced from the oxidation reaction, will be removed by adsorption. In order to investigate the role of sorption, adsorption experiments were carried out using AC, Ni/AC, γ -Al₂O₃, Ni/ γ Al₂O₃ as sorption materials. A comparison of sulfur removal from naphtha with these sorption materials are shown in Figure (5) and Table (6). Figure (5) shows the differences in sulfur content with sorption materials, keeping all other variables constant (feed volume=50ml, sorbent amount=1gm, Temp. =20°C, time=3hr, stirring speed=750 rpm). The results indicate the sequence of sulfur removal as follow: Ni/AC > AC > Ni/ γ Al₂O₃ > γ Al₂O₃. Activated carbon has high surface area and pore volume, therefore, it is found to have the highest removal efficiency among other adsorbents as this result agrees with many studies in literature (11).

A small improvement in sulfur removal was obtained from 92.79% to 93.6% in case of using Ni/AC and from 90.75% to 91.46% in case of using Ni/ γ -Al₂O₃. Many past studies had

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shown the effect of loading nickel (and cobalt) in improving the catalytic activity and selectivity of the adsorbent materials (10, 12).

Table (7) shows the effect of time on PONA content in the oxidation-adsorption process at the condition, feed volume=50ml, activated Carbon=1gm, Temp=20 °C, time=(3hr,and 5hr),stirring speed=750 rpm. This table shows that a decrease in the percentage of n-paraffin and increase in aromatics had occurred, which may be attributed to the adsorption of n-paraffin into activated carbon. This is considered as a benefit for better quality of such fuel.

Table (6): Effect of type of sorbent on sulfur removal at adsorption process on the result of Oxidation reaction.

type of sorbent	sulfur content (ppm)	sulfur removal %
Ni/AC	76.4	93.60134003
AC	86	92.79731993
Ni/ γ Al ₂ O ₃	101.9	91.46566164
γ Al ₂ O ₃	110.4	90.75376884

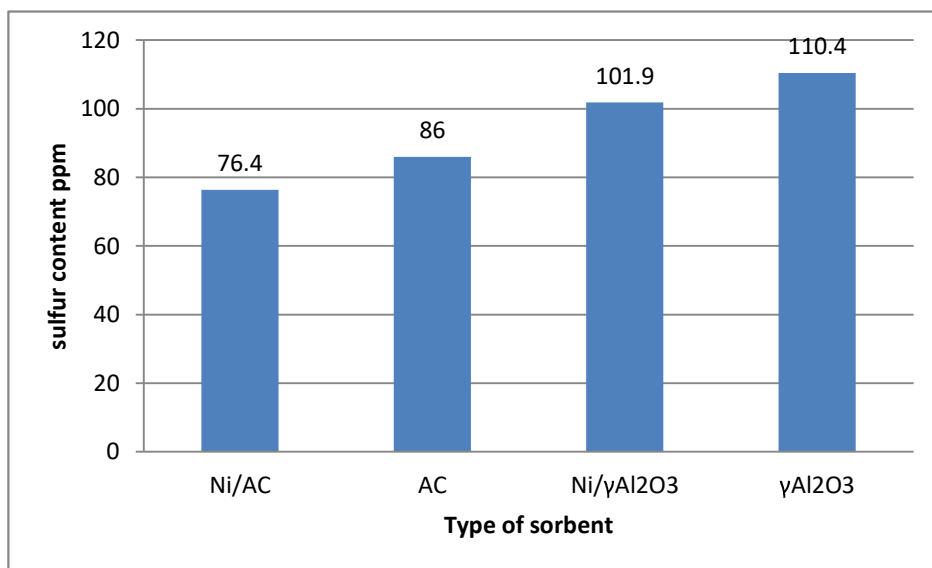


Fig. (5) Effect of type of sorbent on sulfur removal at adsorption process on the result of Oxidation reaction.

Table (7): Effect of time and oxidation-adsorption process on PONA content.

PONA (wt %)	oxidation- adsorption 3 hr	oxidation- adsorption 5hr
n-praffin	18.18	18.20
i-paraffin	66.11	67.00
Naphthene	13.36	12.08
Aromatic	2.35	2.72
Total	100	100

- Adsorption Without Oxidation

Effect of Temperature

Figure (6) and Table (8) show the difference in sulfur performance between AC and Al₂O₃ sorbents at different temperatures. The conditions for these tests were as follow (feed volume=50ml, sorbent amount=1gm, time=3hr, stirring speed=750 rpm), while the temperature was increased progressively (20,40, and 60). This figure displays that AC sorbent is better than γ Al₂O₃, and also that more sulfur can be removed from naphtha by both sorbents with increasing temperature.

Table (8): Effect of temperature on sulfur removal at adsorption process for AC and γ Al₂O₃ sorbents.

Temp. C°	sulfur content (ppm)		sulfur removal %	
	AC	γ Al ₂ O ₃	AC	γ Al ₂ O ₃
0	1194	1194	0	0
20	1079.6	1133.8	9.58124	5.041876
40	911.9	961.3	23.62647	19.48911
60	870.3	950.9	27.11055	20.36013

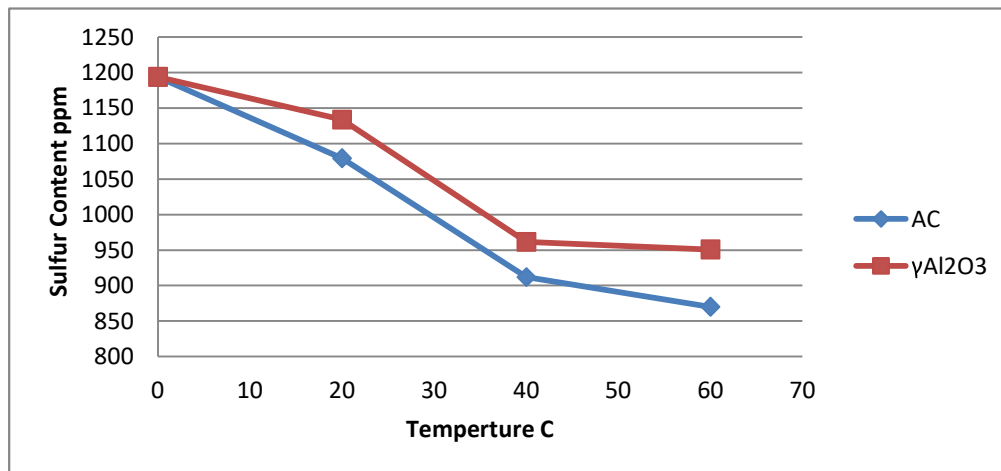


Fig.(6) Effect of temperature on sulfur removal at adsorption process for AC and γ Al₂O₃ sorbents

Effect of time

By comparing Figure (7,8) and Table (9,10) we can see that sulfur removal was increased by increasing temperature as mentioned above, and if we compare both adsorbents we will notice that they have the same behavior in that a decrease in sulfur content occurs as the time increased. However, AC has higher removal efficiency of 26.3% and 30.05% after 5 hrs at 40°C and 60°C respectively.

Table (9):- Effect of time on sulfur removal at adsorption process for AC and γ Al₂O₃ sorbents at (temperature = 40 C)

time(hr)	sulfur content (ppm)		sulfur removal %	
	AC	γ Al ₂ O ₃	AC	γ Al ₂ O ₃
0	1194	1194	0	0
1	1099.3	1153.7	7.931323	3.375209
3	911.9	961.3	23.62647	19.48911
5	879.8	952.5	26.31491	20.22613

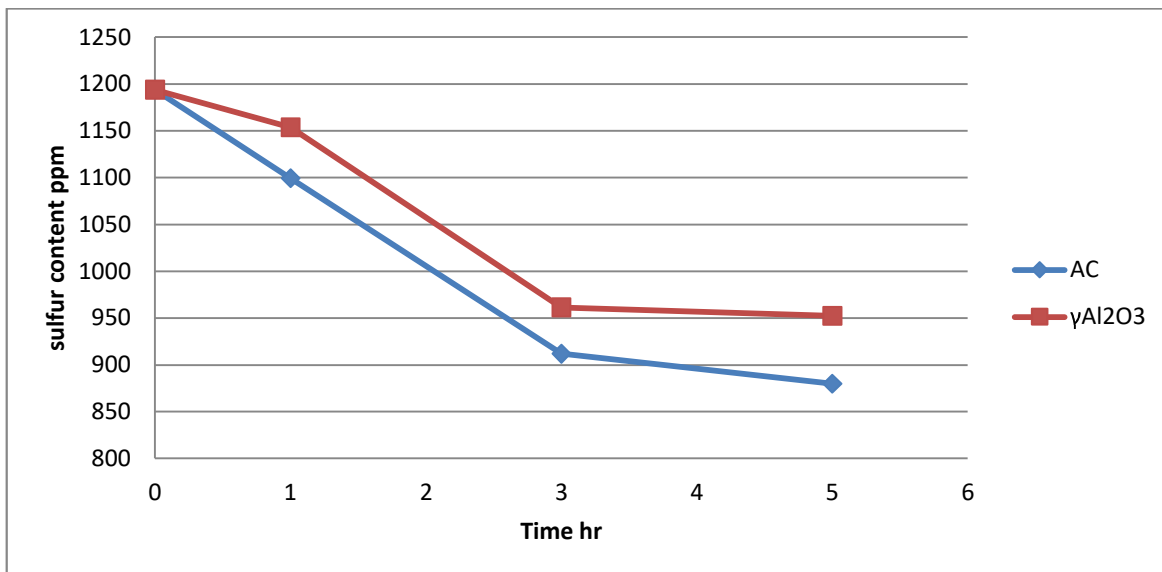


Fig. (7) Effect of time on sulfur removal at adsorption process for AC and γ Al₂O₃ sorbents at (temperature = 40 C°)

Table (10):- Effect of time on sulfur removal at adsorption process for AC and γ Al₂O₃ sorbents at (temperature = 60 C°)

time(hr)	sulfur content (ppm)		sulfur removal %	
	AC	γ Al ₂ O ₃	AC	γ Al ₂ O ₃
0	1194	1194	0	0
1	1040.4	1115.8	12.86432	6.549414
3	870.3	950.6	27.11055	20.38526
5	835.1	921.4	30.05863	22.83082

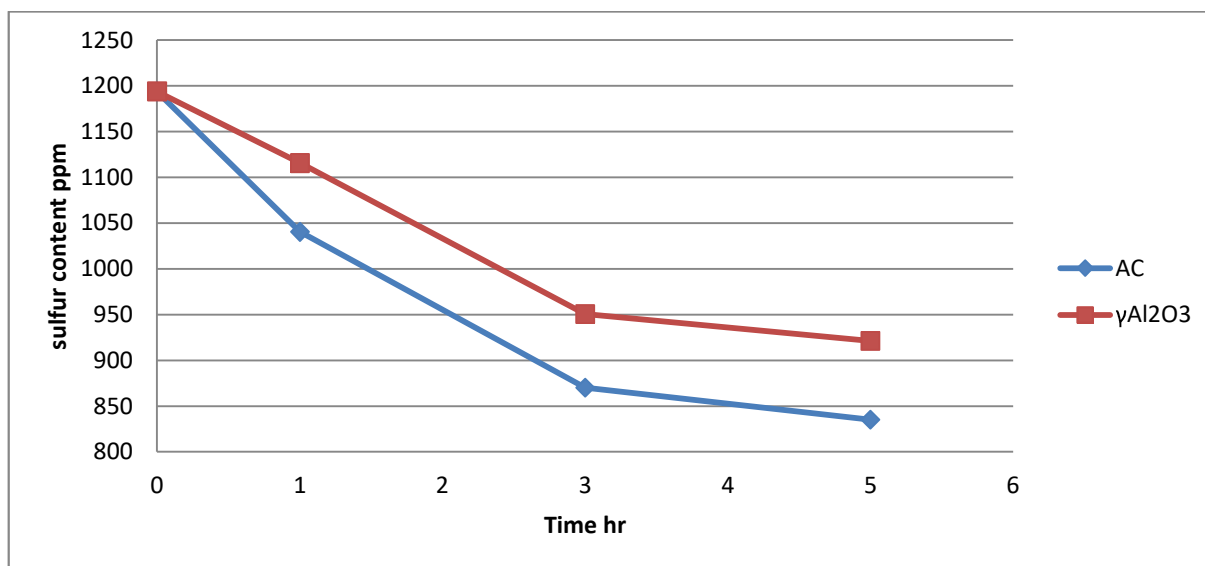


Fig. (8) Effect of time on sulfur removal at adsorption process for AC and γ Al₂O₃ sorbents at (temperature = 60 °C)

Conclusions

1. Oxidation – adsorption is an efficient desulfurization technique for Al-Qayara Naphtha.
2. Oxidation process reduces sulfur content from 1194 ppm to 128.5 ppm corresponding to 89.2% removal using operating conditions, 60° C, 4 ml of H₂O₂ and 3hr,
3. Further removal of sulfur compounds is achieved by adsorption process using Ni/AC which has been found effective among other adsorbents AC, γ -Al₂O₃, Ni/ γ -Al₂O₃ obtaining 93.2%. Sulfur in Al-Qayarah naphtha after this step is reduced to 76.4ppm.
4. Adsorption desulfurization (without oxidation) achieved 30% removal of sulfur compounds for the sulfur content reduced to 835ppm using a temperature of 60 °C in a batch mode operation.
5. Considering the economic point of view, prices of AC and γ -Al₂O₃ must be reviewed to select the most economic adsorbent for some differences were noticed which may be ignored if it affects the economy of the process as the higher removal is obtained using the oxidation process.

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