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Additives of Base and Acid to Oxidative Desulphurization Process of Al-Sumoud Refinery at NRC Baiji

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Abstract

The removal of sulfur compounds from kerosene via extraction is based on the fact that sulfur compounds are more soluble than hydrocarbons in appropriate solvents. The most attractive feature of extractive desulphurization is its applicability at low temperatures and low pressure. The kerosene samples used in this research were obtained from the North Refineries Company, Baiji (NRC), Al-Sumoud refinery. Production of high-quality kerosene fuel decreases its sulphur content of it, and thus burns with the least amount of CO2. One of the main risks to the combustion properties of kerosene and to the atmosphere is the presence of secondary pollutants, such as sulfur and other impurities. Sulfur contamination produces a strong odor that may cause problems if not removed. In this study, additives were incorporated into kerosene to reduce the sulfur content and improve its fuel properties. In this research, the best temperature of removal was 70 °C for base and acid, the removal average of sulfur was from 1880 ppm, while the removal average of sulfur was from 1600 to less than 600 ppm for the Al-Sumoud refinery, without effect on the other specifications, especially specific gravity is considered the main property, ruler test.

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1-Introduction

As fossil fuel prices continue to rise, oil companies will for environmental protection, desulfurization plays a critical role in mitigating the impacts of toxic pollutants. To this end, several experiments have been conducted on single metal oxides and mixed metal oxides as sorbents [1]. Kerosene is a liquid hydrocarbon fuel with multiple uses, including powering jet and rocket engines, heating homes, heating water, and cooking. To protect human health and reduce environmental hazards, environmental regulations that limit sulfur content to very low levels have been introduced in many countries over the past few decades [2]. Additionally, sulfur should be removed from petroleum fractions, as it can poison catalysts, corrode surfaces, and cause air pollution [3]. Abraham Gesner discovered kerosene, a petroleum byproduct, in 1853. Gesner, a British

surgeon, developed a method for removing asphalt from inflammable liquids [4]. Mercaptans, sulfides, disulfides, products is undesirable because of the pollution they cause. However, this can represent significant challenges for petrochemical operations in meeting environmental criteria. The desulfurization procedure determines how these sulfur compounds are removed [5]. Gesner devised a method to separate the inflammable liquid from asphalt. The term kerosene comes from the Greek word kerosene. Kerosene (also known as jet fuel) is a flammable hydrocarbon liquid that is commonly used to power jet engines in aircraft and some rocket engines. It is also widely used as a cooking and lighting fuel for fire toys [6]. Kerosene is a liquid hydrocarbon fuel that is commonly used to power jet aircraft engines (jet fuel) and some rocket engines [7]. It is also widely used in fire toys as a cooking and lighting fuel [8]. Recently, researchers have sought and thiophenes are the most prevalent chemicals found in gasoline. The presence of these groups in petroleum alternative approaches to improve product quality [9]. The process does not change the chemical structure of fuel oil components. To make the separation process efficient, the solvent must be carefully selected to meet several requirements. The solvent must have a boiling point different than that of the sulphur-containing compounds, and it must be inexpensive to ensure the economic feasibility of the process [10]. The Sulphur compounds must be highly soluble in the solvent [11]. The aim of this study was to improve the kerosene product at Al Sumoud Refinery of the North Refineries Company, Baiji, by reducing its sulphur content. Thus, increasing combustion efficiency and reducing CO2 emissions, as well as reducing acidic residues and calcification resulting from sulfur in kerosene fuel.

Materials and Methods

2.1 Kerosene sample preparation

The sample of kerosene was used in this research, collected from North Refineries Company (NRC) Baiji. Obtained from Al-Sumoud refinery Kerosene sample with density of 0.7845 @15.6 °C g/cm3, tank number 3107 FA [12].

2.2 Additive processes

Figure 1 depicts the sweetening process of kerosene with varying percentages of acid and base additives. The percentage addition method was used, as following steps. The raw material was stored in the feed tank, and the heat exchanger exchanged temperatures with the final product. P1 exchanged the raw material's temperature with hot oil to reach a temperature of 60-70 °C. P H2SO4 1 mixes the feed material with H2SO4 at a concentration of 98 %, with an addition of 1%. Decanter No [13]. 1 straddled the product. The feed material is mixed with H2SO4 at a concentration of 98 % by mixer No. 2, with a 0.8 % addition by P H2SO4 2. Decanter No. 2 straddled the product. The feed material is mixed with H2SO4 at a concentration of 98% by mixer No. 3 with a 0.7% addition by P H2SO4 3. To extract the gases, the product was straddled by a decanter (3a - 3b) with a vacuum pump. The feed material is mixed with NaOH at a concentration of 25 % by mixer No. 4, with a 0.8% addition by P NaOH 1. Decanter No. 4 straddled the product. The nutrient is mixed with water at a 0.4% addition ratio by mixer No. 5. A decanter straddled the finished product (5a – 5b). P4 pumped the finished product to the heat exchanger, which reduced the temperature before delivering it to the distribution stations

2.3 Analytical procedure

The specific gravity (Sp.gr) of the kerosene test was calculated according to the standard method (ASTM D 1298) [12]. The physical properties were carried out based on the international code and standard American Society for Testing and Materials (ASTM D-3080) [15]. At the laboratories and quality control department in NRC Baiji. The FTIR test has been conducted before and after the desulphurization process via extraction.

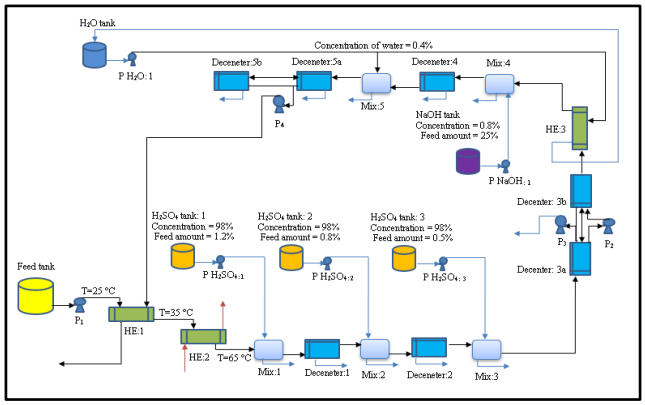

Figure 1:Desulphurization process of the Kerosene product unit

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3. Results and discussions

3.1 Physical properties of kerosene sample

Table 1 shows the physical properties of the kerosene sample produced from Al-Sumoud refinery at NRC Baiji, before the desulphurization process. This specification was done depending on the (ASTM D-978) [16].

No.	Test	Kerosene
1	Density@15.6 °C g/cm^3	0.7845
2	A.P.I	48.8
3	Dr.Test	+ve RSH
4	Total Sulfur ppm	1600
5	Mercaptan ppm	336.4
6	H_2S ppm	Nil
7	Flash Point °C	52
8	Color	+12

3.2 FTIR spectrum

The FTIR spectra of the kerosene samples before and after the process are shown in Figure 2. The results indicate the presence of mercaptans, as evidenced by a prominent band at 3398.57 cm-1 due to desulphurization. A less intense medium band at 1376 cm-1 represents the S=O asymmetric vibration, which gives an indication of the sulphone's chlorides, sulphonates, sulphones, or sulphoxides. A wideband at 3417 cm-1 shows the presence of the NH or OH, which may correspond to the bond associated with sulphonamides31. The FTIR spectra of the kerosene oil treated with HgCl2 (10 %) and Ca (OH)2 (5%) is indicated in Figure 2 before and after. The spectra show that bands in this range, indicating mercaptans S-H (at 2365 cm-1) and S=O (at 1376 cm-1), are weaker in intensity in (after) as compared to the spectra of the original sample. In the spectrum (before), the band at 2356 cm-1 is absent, indicating that substituted thiols have undergone desulfurization. The FTIR results also indicated that the functional groups of the NRC Baiji fuel samples were identical [17].

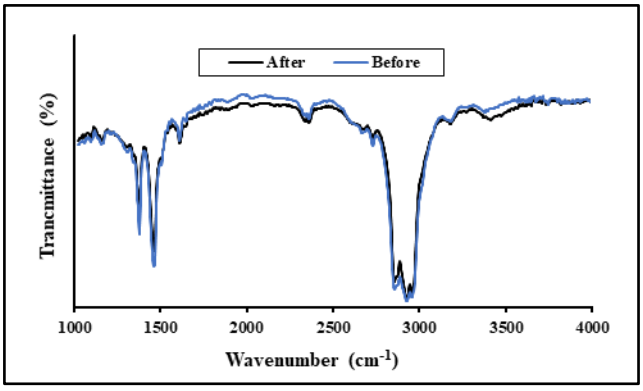

Figure 2: FTIR Spectrum of raw material kerosene and after desulphurization process

3.3 The oxidative desulphurization process

The oxidative desulphurization processes were conducted using an acid-base additive to the kerosene sample in order to reduce the sulfur content [18]. The effects of factors such as temperature, sodium hydroxide concentration, Sulfuric acid concentration, and water content on sulfur content were studied.

3.3.1 Effect of temperatures

The effect of temperature on sulfur removal is determined as shown in Figure 3. The sulfur content was reduced, as shown in Figure 2. 2.5 of H2SO4 at a concentration of 98 % (a fixed amount) was added with 0.8 of NaOH at a concentration of 25 % (a fixed amount) with 0.4 of water (a fixed amount) to varying temperatures. The sulfur content of kerosene decreased, as shown in Table 5. The results showed that at 50 °C, sulfur content was 1000 ppm; at 60 °C, 800 ppm; at 70 °C, 580 ppm; and at 80 °C, 700 ppm, due to temperature and concentration effects. The best temperature was 70 °C with a low sulfur content of 580 ppm [19]. The sulfur concentration decreased from 1000 to below 600 ppm as the temperature increased, reaching 800 ppm at 80 °C, indicating that 70 °C is the optimal temperature for the reaction.

Table 2: Percentage of H2SO4, NaOH, and H2O added to kerosene at different temperature Sulpur

Tempreture (°C)	H_2SO_4 Concentration (99%)	NaOH Concentration (25 %)	H_2O (L)	Sulpur (ppm)
70	1.0	0.8	0.4	1200
70	1.5	0.8	0.4	900
70	2.0	0.8	0.4	700
70	2.5	0.8	0.4	580

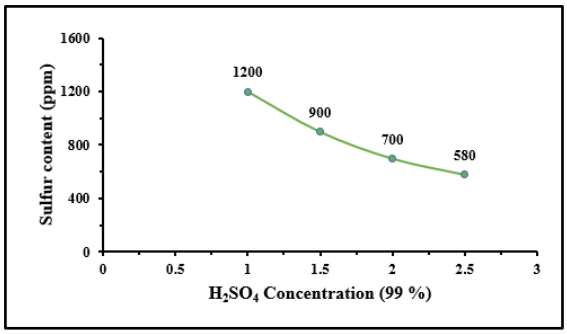

Figure 3: Relation between H2SO4,with NaOH, and H2O at different temperature

3.3.2 Effect of sulfuric acid additive with 99 % H2SO4

The best temperature was 70 °C to the reduced percentage of sulfur content in kerosene as in Figure 4. The temperature was fixed at 70 °C with 0.8 of NaOH at a concentration of 25 % (a fixed amount), with 0.4 of water (a fixed amount), with varying H2SO4 1.0, 1.5, 2.0, and 2.5 with 99 % concentration. The results showed a decrease in the sulfur content in kerosene according to the results shown in Table 3. These results showed sulfur content was 1200 ppm at 1.0 of H2SO4, sulfur content was 900 ppm at 1.5 of H2SO4, sulfur content was 700 ppm at 2.0 of H2SO4, sulfur content was 580 ppm at 2.5 of H2SO4. The best removal process was 580 ppm of sulfur at 2.5 of H2SO4 at 70 °C [20].

Table 3: Percentage 99% of H2SO4, NaOH, and H2O added to kerosene at 70 °C
Sulpur

Table 4: Percantage 0.8 of NaOH, H_2SO_4, and H_2O added to kerosene at 70 °C

Tempreture (°C)	**H_2SO_4 Concentration (99%)**	**NaOH Concentration (25 %)**	**H_2O (L)**	**Sulpur (ppm)**
70	2.5	0.3	0.4	880
70	2.5	0.5	0.4	750
70	2.5	0.7	0.4	620
70	2.5	0.8	0.4	580

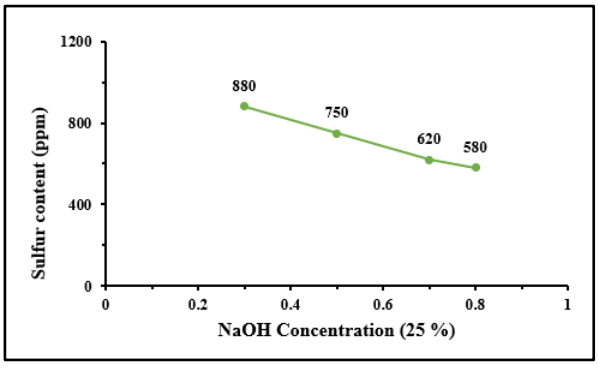

Figure 4: Relation between H2SO4, NaOH, and H2O at 70 °C

3.3.3 Effect of sodium hydroxide additive with 0.8 NaOH

The best temperature was 70 °C to the reduce percentage of sulfur content in kerosene as in Figuer 5. The temperature was fixed at 70 °C with 2.5 of H2SO4 at a concentration of 99 % (a fixed amount), with 0.4 of water (a fixed amount), with varying NaOH 0.3, 0.5, 0.7, and 0.8 with concentration 25 %. The results showed a decrease in the sulfur content in kerosene according to the results shows in Table 4. These results showed that sulfur content was 880 ppm at 0.3 NaOH, 750 ppm at 0.5 NaOH, 620 ppm at 0.7 NaOH, and 580 ppm at 0.8 NaOH. The best removal process was 580 ppm of sulfur at 0.8 of NaOH at 70 °C [21].

Table 4: Percentage 0.8 of NaOH, H2SO4, and H2O added to kerosene at 70 °C Sulpur

Table 5: Specifications of kerosene sample results before and after desulphurization processing

No.	Test	Before processing	After processing
1	Density@15 °C g/cm^3	0.7845	0.7845
2	A.P.I	48.8	48.8
3	Dr.Test	+ve RSH	Neg RSH
4	Total Sulfur ppm	1600	Less Than 600
5	Mercaptan ppm	336.4	Less Than 3
6	H_2S ppm	Nil	Nil
7	Flash Point °C	52	52
8	Color	+12	>+30
9	Distillation		
	I.B.P °C	160	160
	5%	170	170
	10%	174	174
	50%	194	194
	90%	235	235
	E.P °C	255	255
	T.D%	98	98
	Loss%	0.5	0.5
	Res%	1.5	1.5

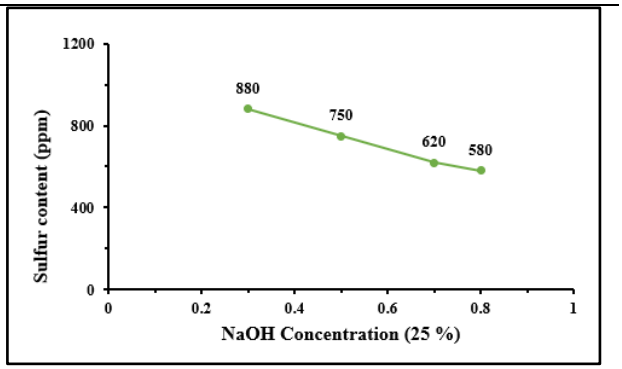

Figure 5: Relation between H2SO4, NaOH, and H2O at 70 °C

4. Conclusion

The desulphurization of kerosene was studied via base and acid by washing. It was found that the washing method is a more effective. The kerosene sample has sulfur content was decreased from 1200 to 750 at 70 °C. The results showed that there was no effect on the density of kerosene, as well as the effect of distillation specifications. This indicates the effectiveness of the desulphurization process without affecting the basic specifications. This contributes to producing high-quality kerosene fuel and ignites by releasing fewer amounts of CO2 gas and does not cause damage to equipment because it contains a low percentage of sulfur.

5. Acknowledgment

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إضافات القواعد والأحماض إلى عملية نزع الكبريت بالأكسدة في مصفى الصمود في شركة مصافي الشمال – بيجي

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[1]شركة توزيع المنتجات النفطية، فرع صلاح الدين تكريت وزارة النفط، [2] قسم هندسة النفط، كلية الهندسة، جامعة النور [3] شركة مصافي الشمال وزارة النفط

الخلاصة

تعتمد إزالة مركبات الكبريت من الكيروسين عن طريق الاستخلاص على حقيقة أن مركبات الكبريت أكثر قابلية للذوبان من الهيدروكربونات في المذيبات المناسبة. وتُعد أكثر المزايا جاذبية لعملية نزع الكبريت بالاستخلاص هي إمكانية تطبيقها عند درجات حرارة وضغوط منخفضة. وقد استُخدمت في هذا البحث عينات من الكيروسين مأخوذة من شركة مصافي الشمال – بيجي(NRC) ، مصفى الصمود. إن إنتاج وقود كيروسين عالي الجودة يؤدي إلى خفض محتواه من الكبريت، وبالتالي احتراقه مع أقل كمية ممكنة من ثاني أوكسيد الكربون .(CO_2) ويُعد من أهم المخاطر التي تؤثر في خصائص احتراق الكيروسين وفي البيئة الملوّثات الثانوية مثل الكبريت والشوائب الأخرى. إذ إن تلوث الوقود بالكبريت يُسبب رائحة نفاذة قد تؤدي إلى مشكلات عدة في حال عدم إزالته. في هذه الدراسة، أُضيفت مواد مضافة إلى الكيروسين بهدف تقليل نسبة محتوى الكبريت وتحسين خصائصه الوقودية. وقد أظهرت نتائج البحث أن أفضل درجة حرارة لعملية الإزالة باستخدام القاعدة والحامض كانت 70°م، حيث بلغ متوسط إزالة الكبريت من 1880 جزءاً بالمليون، في حين تراوح متوسط إزالة الكبريت في مصفى الصمود من 1600 إلى أقل من 600 جزء بالمليون، دون التأثير في المواصفات الأخرى، ولاسيما الكثافة النوعية التي تُعد الخاصية الرئيسة في اختبار الحاكم (Ruler Test).