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Upgrading of Sharqy Baghdad Heavy Oil via N-Hexane Solvent

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Abstract

Asphaltenes are a solubility class described as a component of crude oil with undesired characteristics. In this study, Sharqy Baghdad heavy oil upgrading was achieved utilizing the solvent deasphalting approach as asphaltenes are insoluble in paraffinic solvents; they may be removed from heavy crude oil by adding N-Hexane as a solvent to create deasphalted oil (DAO)of higher quality. This method is known as Solvent De-asphalting (SDA). Different effects have been assessed for the SDA process, such as solvent to oil ratio (4-16/1 ml/g), the extraction temperature (23 ºC) room temperature and (68 ºC) reflux temperature at (0.5 h mixing time with 400 rpm mixing speed). The best solvent deasphalting results were obtained at room temperature and 12 ml/g solvents to oil ratio. As a result, the API of DAO was increased by 9.3º compared to the API of Sharqy Baghdad heavy oil. The asphaltene reduction was 61.56%. The Sulfur removal was 32.8%, the Vanadium removal was 36.48%, and the Nickel removal was 46.21%.

Keywords: Upgrading, Deaspdalted oil, Asphaltene, Solvent deasphalting, and N-Hexane.

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1- Introduction

Crude oil refers to a broad range of non-uniform substances that are naturally found. Crude oil is a combination of different hydrocarbons with varied structures and degrees of saturation and a variety of contaminants that may be present.

The structure of the hydrocarbons included in crude oil influences the bulk characteristics of the oil, most significantly its viscosity and density[1]. Oil is classified according to its API scale; API gravity less than 10° is generally considered a bitumen; API gravity between 10° and 22.3° is regarded as heavy oil; API gravity between 22.3° and 31.1° is considered medium oil, and API gravity greater than 31.1° is regarded as light oil[2]. Nearly 70% of the world's oil reserves are heavy oil, extra-heavy oil, and bitumen[3].

Heavy oil and extra heavy oil are defined as any liquid petroleum that is complex, has a high viscosity, a dark colour, is highly dense, has a high molecular weight, has a large proportion of asphaltene (>15% by mass) and resins (>40% by mass). Additionally, this liquid petroleum contains metals such as (Ni, V, Fe) as well as heteroatoms such as (N, O, S)[4][5]. By definition, crude oil contains a mixture of dissolved gases, liquids, and solids. Saturates, aromatics and resins are types of liquids.

Additionally, many types of solids may be included in crude oil; generally, the most common is solid asphaltene[6]. Asphaltene is the most aromatic of crude oil's heaviest components and has the highest molecular weight[7][8].

Asphaltene is a crude oil fraction that is insoluble in n-alkanes but soluble in aromatic solvents (for example, toluene or benzene)[9]. Asphaltene is a black, friable solid that forms when the pressure, temperature, and composition of the oil vary, causing it to deposit. Pipelines, heat exchangers, and the bottoms of distillation columns are susceptible to asphaltene precipitation, resulting in decreased efficiency and increased production costs; aggregates of asphaltene are undesirable because they block pipelines, accumulate in storage tanks, and deactivate catalysts [10].

The need to upgrade heavy oil into cleaner and more valuable light oil is increasing continuously in order to sustain future fuel needs. However, heavy oils and bitumen properties include high viscosity/low fluidity, high density/low API gravity, high asphaltenes, Sulfur, and metal. Therefore, the objectives of upgrading are 1) to reduce the viscosity to aid production and pipeline transportation without diluents addition and 2) to produce synthetic crude oil that meets the qualities of refinery feedstock[11]. Furthermore, the profitability of upgrading heavy crude oil/bitumen is further dependent on market value[12].

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Over the years, various technologies for upgrading heavy oil have been developed. However, these technologies have mostly been based on hydrogen addition and carbon rejection with or without catalysts[13].

The solvent deasphalting Process (SDA), based on liquid-liquid extraction via contact with a paraffinic solvent, is one of the most effective methods for reducing the asphaltene content of heavy oil[14]. Solvent deasphalting occurs when a light hydrocarbon solvent is added to the feed material. DAO is the improved product, whereas asphalt is the carbon rejection product[15].

The use of solvent deasphalting to upgrade heavy, highly viscous crude oil and natural bitumen improves the properties[16]. The SDA process is cost-effective for removing concentrated asphaltene or pitch from heavy oil(HO) and extra heavy oil(EHO). Therefore, it is suitable for extracting large amounts of high-quality oil that can be improved [17]. SDA's operating expenses are also cheap since they are used at relatively low pressure and temperature. In addition, the process is simple to design and scale up, and it is considered a feasible solution since the recovery and recycling of solvents may decrease operating costs[18].

The research group Firdews et al. [19] upgraded sharky Baghdad heavy crude oil with 22 API and asphaltene content of 3.382 wt.% by using a solvent deasphalting process with N-Pentane as a solvent. The API was enhanced to 32 while the asphaltene content decreased to 1.065 wt. % .

Hussain et al.[20] enhanced Sharqy Baghdad heavy crude oil with an API of 22 by solvent extraction process using Iraqi light naphtha solvent, API of DAO increased to 30. Radhi [21] used Sharqy Baghdad heavy crude oil (reduce crude oil, 9.6 API, 23wt. % asphaltene content,90 ppm V,35.2 ppm Ni content) using N-Hexane as a deasphalting solvent in liquid-liquid extraction, the API gravity of deasphalted oil increased by 20 degrees compared to reduced crude oil, while the asphaltenes content reduced by 78% and the Vanadium and Nickel metals concentration decreased by 78% and 76%, respectively.

This study aims to upgrade Sharqy Baghdad heavy crude oil using N-Hexane by solvent deasphalting process and study the effect of different operating conditions on the characteristics of the produced DAO.

2- Experimental Work

2.1. Materials

a. Crude Oil

The heavy crude oil was supplied from the Midland Oil Company. The crude oil characteristics are listed in Table **1**.

Table 1. Characteristics of Sharqy Baghdad Heavy Crude Oil

Property	Value
Specific gravity at 15.6 / 15.6 ºC	0.922
API at 15.6 ºC	22
Viscosity at 40 ºC , Cs	27.927
Asphaltene Content , wt. %	3.382
Sulfur Content , wt. %	4
Caradson Carbon Residue , wt. %	8.98
Ash Content , wt. %	0.0921
Vanadium , ppm	64.554
Nickle , ppm	27.887

b. Hydrocarbon Solvent

For deasphalting, N-Hexane (purity 99%, Chem-Lab/Belgium) the low-boiling petroleum solvents were used.

2.2. Procedure

Solvent Deasphalting Process: The procedure is divided into four stages: mixing, filtration, drying, and solvent recovery, as below

The mixing unit for the solvent deasphalting process, which includes a 500 mL 2-neck for mixing crude (20g) was used in all of the experiments with solvent (N-Hexane) in the proper solvent/oil ratio(SOR) (ml/g) (4/1, 8/1, 10/1, 12/1, and 16/1). The flask was placed on a heated magnetic stirrer set at 400 rpm for a period of time (30 minutes).

To limit the solvent losses to a minimum, a vertical condenser, which runs at total reflux, was installed on the upper neck of the mixing flask. The mixing was investigated at room to (68 ºC)reflux temperatures. The schematic diagram of the laboratory mixing setup is depicted in Fig. (1),

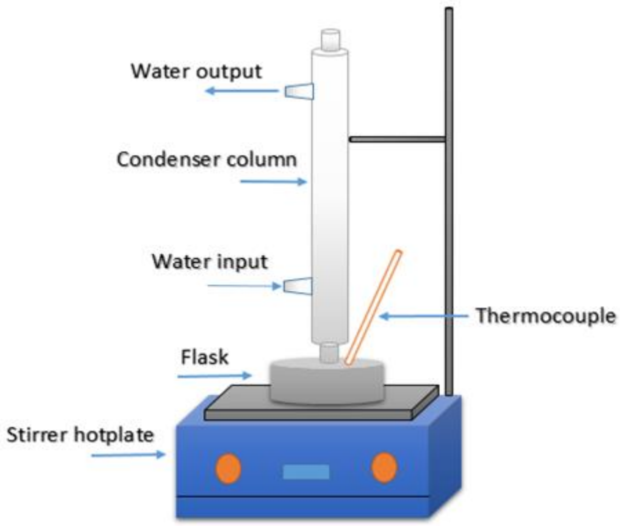


Fig. 1. The schematic diagram of the mixing stage unit

The mixture produced from the mixing unit was sent to the filtration unit, comprised of a filtration flask, Buchner funnel, vacuum pump, and trap. Through the filtration process, filter paper (Chm 2054) was used, and it was wetted in a solvent before use. Next, a (25ml) washing solvent (N-Hexane) was added to the mixing flask to ensure completing filtration. The filter paper was dried using an electric oven at 80°C and for 20 min to remove the remaining solvent associated with the pitch on the filter paper. Then filter paper is weighted to measure the percentage of pitch precipitate in the dried filter paper.

Finally, the mixture of DAO and solvent was introduced to the simple distillation unit to recover solvent from the DAO. It consists of a 500 ml distillation flask heated by the heating mantle. A thermometer is located at the top, an efficient condenser is connected from the side, and the solvent is collected in a receiver at the end. The stripped DAO is weighted to determine DAO yield and the required analyses.

2.3. Analytical Instruments

The deasphalted oil (DAO) was analyzed by different measurement devices such as asphaltene measurement (IP 143 method) (APD-600A), API Gravity Measurement (ASTM 4025) using a Digital Anton Paar, Sulfur Content Measurement (ASTM D7039) (SINDIE OTG), and Metal Content Measurement (Analytik Jena novAA 350-Flame).

3- Results and Discussion

3.1. Effect of Solvent to Oil Ratio (SOR)

Experiments were done using N-Hexane solvent at room temperature (23 ℃) with SOR (4-16 ml/g), mixing time of 0.5 hours, and mixing speed of 400 rpm. The impact of the SOR on the API, asphaltene content, precipitated pitch, Sulfur content, and metal content (Vanadium and Nickel) of DAO is explained below.

a. API Gravity

The effect of solvent to oil ratio on API of DAO at room temperature with SOR (4-16 ml/g) and a mixing duration of 0.5 hours is investigated. Fig. **2** displays the result. According to the findings, increasing the ratio of solvent to oil resulted in an improvement in the API of DAO. With an increase in SOR from 4 to 12 ml/g, the API increase sharply, but it increases slightly with SOR of 16 ml/g. At SOR 16 ml/ g, the higher API obtained was 31.5, which improved by 9.5º.

The enhancement of API comes about as a result of rising the solvent power and selectivity for asphaltene removal with increasing SOR, the dissolution of asphaltene agglomerates and the decrease in the presence of micelle-like clusters were essential steps in the process of improving the API of heavy crude oil and, subsequently, reaching a stable state at a steady state at 16 ml/g SOR. This was consistent with the findings of [19] [20][21].

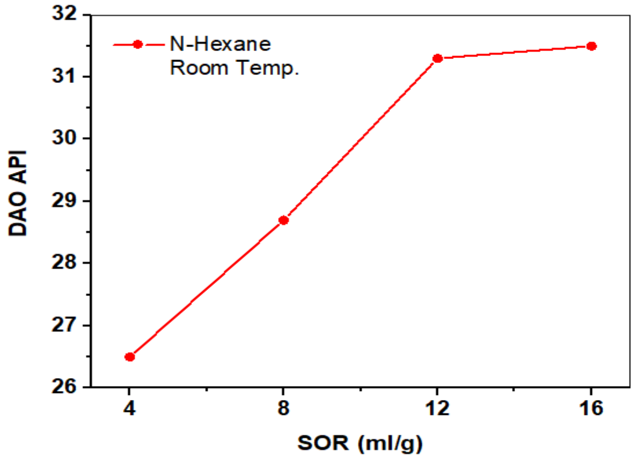


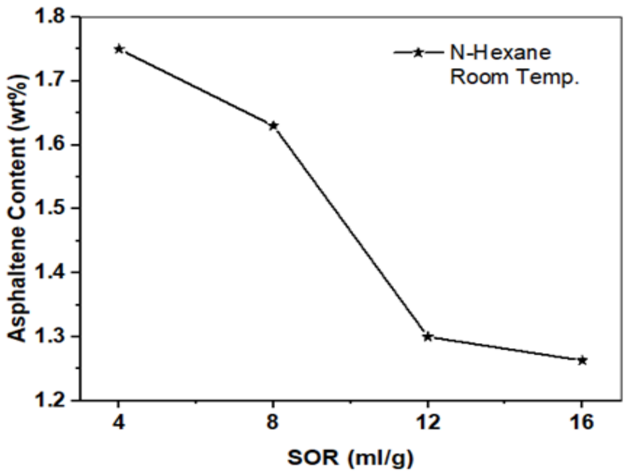
Fig. 2. The effect of solvent to oil ratio on DAO API at room temperature and 0.5 h. mixing time

b. Asphaltene Content and Pitch Precipitate

The solvent to oil ratio affects the asphaltene concentration of DAO, and the pitch precipitated at room temperature, as shown in Fig. **3** (a, b).

According to the results, increasing the solvent to oil ratio (4-12 ml/g) resulted in a significant decrease in asphaltene concentration and an increase in pitch precipitate. Furthermore, an increase in SOR from (4-12 ml/g) resulted in a significant drop in asphaltene content, while a slight decrease at SOR (16 ml: 1 g). At (16ml/g)SOR, the higher asphaltene content in DAO was 1.2631 wt. %, with a removal percentage of 62.65 %, and the higher pitch precipitated to 10.2 wt.%

The increasing solvent to oil ratio results in an increase in the degradation of asphaltene molecules with increasing solvent added, which could lead to the creation of activated centres on both the remaining asphaltenes and the freed sheets, thus leading to increase an overall reduction in the average number of layer and increased pitch precipitate. As a result, the DAO quality improved. These are agreed with the results reported by[19] [22][23][24].



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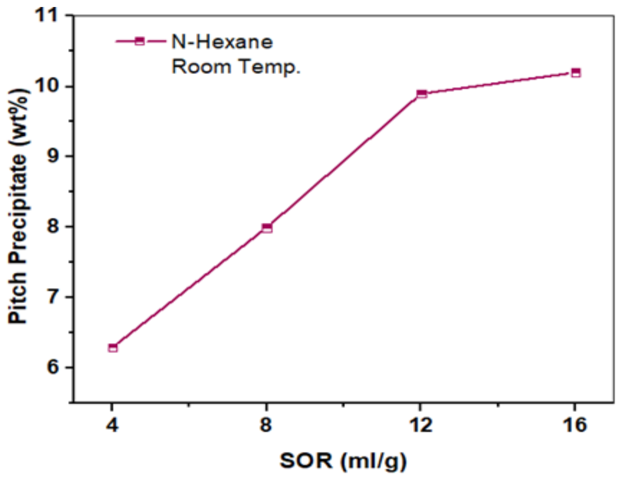
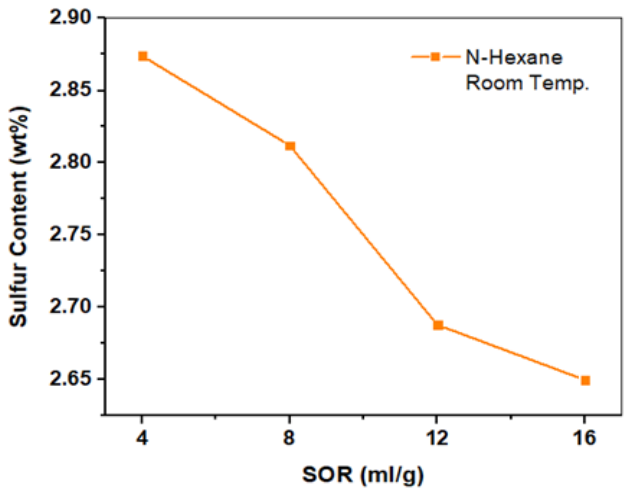


(b)

Fig. 3. The effect of solvent to oil ratio on (a) Asphaltene content and (b) pitch precipitate at room temperature and 0.5 h. mixing time

c. Sulfur and Metals Content

At room temperature, the effect of the solvent-to-oil ratio on the Sulfur and metals (Vanadium and Nickel) content of DAO is being studied. Fig. **4** (a-c) results According to the findings of the tests, raising the SOR significantly decreased the amount of Sulfur and metals in DAO. Increased SOR (4-12 ml/ g) led to a significant drop in Sulfur with metals concentration, while SOR (16 ml/ g) led to a minor decrease. At SOR (16 ml/g), DAO had the highest Sulfur content (wt. %) of 2.65 and the highest removal rate of 33.75 %. There were 40.70 ppm of Vanadium and 14.54 ppm of Nickel in DAO following the removal of 36.95 and 47.87 %, respectively. The drop in Sulfur and metal content in DAO is directly proportional to asphaltene concentration. As the asphaltene content of DAO decreased, so were the concentrations of Sulfur and metals. This agreement is comparable to the results confirmed by [20] [23].



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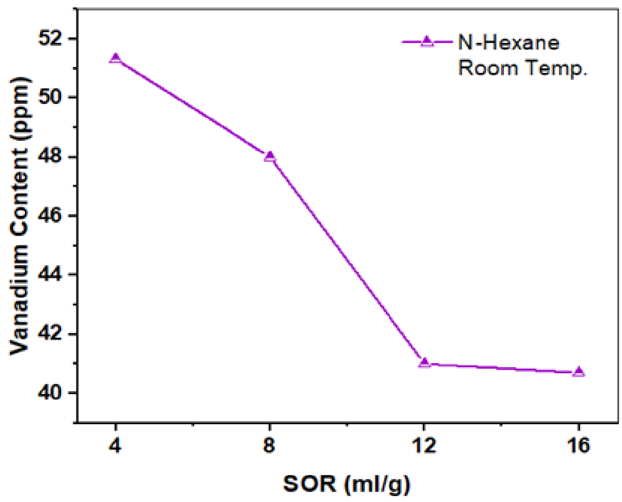

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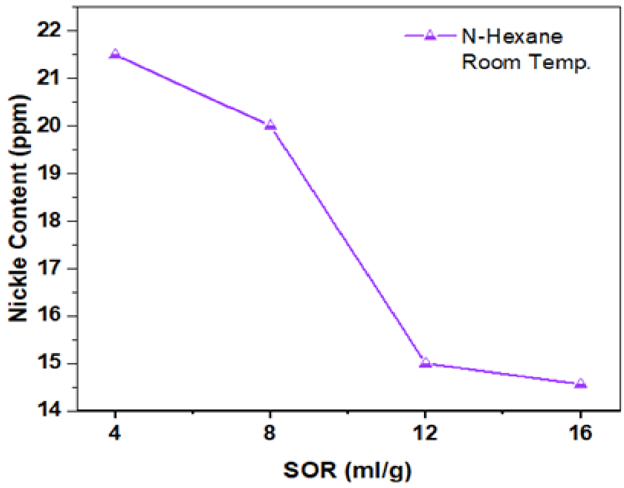


(c)

Fig. 4. The effect of solvent to oil ratio on (a) Sulfur, (b) Vanadium, and (c) Nickel content of DAO at room temperature and 0.5 h. mixing time

3.2 Effect of Temperature

The studies were done at (23 ºC) room temperature and (68 ºC) reflux temperatures with SOR (4-16 ml/g), mixing time of 0.5 h and 400 rpm mixing speed. By using N-Hexane as solvent, the effect of temperature on the DAO characteristics: API, asphaltene content and precipitated pitch, Sulfur content, and metal content (Vanadium and Nickel) is detailed below.

a. API Gravity

The effect of changing temperature from (23 ºC) room temperature to 68 ºC on DAO API is being investigated.

Fig. **5** illustrates the result. The research indicated that when the temperature is raised from room temperature to 68 ° C, the API of DAO decreases by all SOR. The higher API values of DAO at (16 ml/g) SOR fall from 31.5 to 31 and reduce the improvement degree from 9.5º to 9º at room temperature and 68 ºC, respectively. The API of DAO falls when the temperature is raised Due to lower asphaltene removal.

This is because the solubility of asphaltene rises with temperature. Consequently, more resins separated from asphaltene molecules, influencing the API of the oil phase. This is in accordance with[19] [23][25].

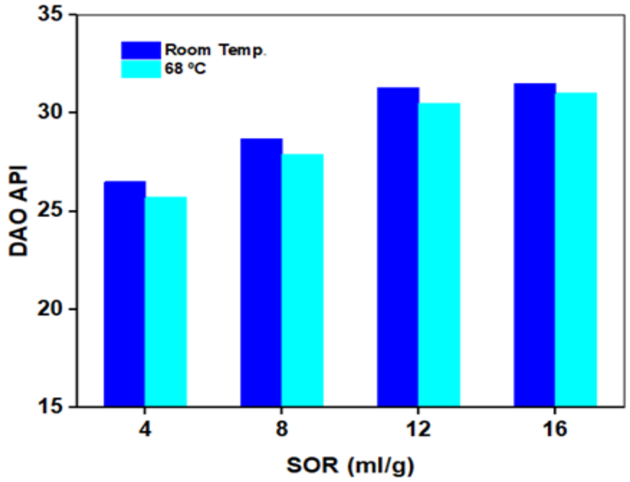
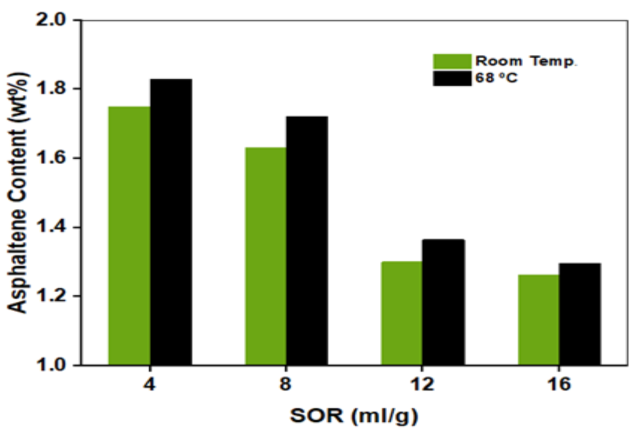


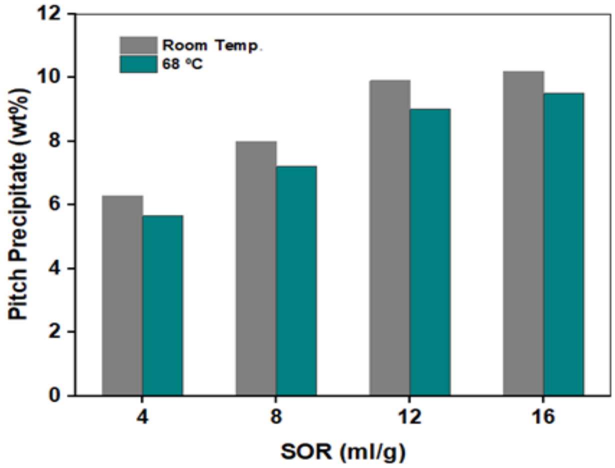
Fig. 5. Effect of temperature on DAO API using N-Hexane at (4-16 ml/g) SOR and 0.5 h, mixing time

b. Asphaltene Content and Pitch Precipitate

Fig. **6** (a, b) represented the influence of changing temperature from room temperature to 68 ºC on the asphaltene content of DAO and precipitated pitch is being evaluated. The results indicate that the asphaltene content of DAO increases when the temperature is increased from room temperature to 68 ºC for all SOR. At (16 mL/g)SOR, the higher asphaltene content in DAO were 1.2631 wt. % and 1.2954 wt. %, with a percentage removal of 62.65% and 61.697% at room temperature and 68 ºC, respectively. While the higher pitch precipitate was 10.2 and 9.5 wt. % at room temperature and 68 ºC, respectively. When the temperature increases, the asphaltene removal is reduced, and its concentration in DAO increases. As the temperature rises, the oil's solubility increases, enabling asphaltenes and resinous compounds to escape into the oil phase. The pitch precipitation reduced as the temperature increased, consistent with previous observations[23][25].



(a)

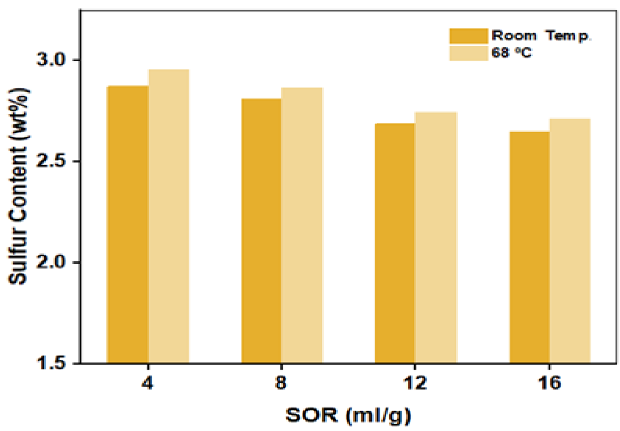


(b)

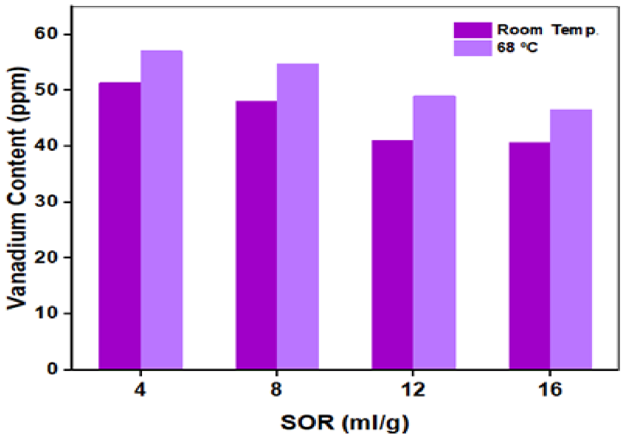
Fig. 6. Effect of temperature on(a) asphaltene content and (b)pitch precipitate by using N-Hexane at (4-16 ml/g) SOR and 0.5 h, mixing time

c. Sulfur and Metals Content

The Sulfur and metals (Vanadium and Nickle) content of DAO are being studied in relation to temperature. The results were in Fig. **7** (a-c). The Sulfur and metals content of DAO increases when the temperature increases from room temperature to 68 ºC. At room temperature and (16ml/g)SOR, the higher Sulfur content of DAO was 2.65 wt. % with percentage removal was 33.75 %, Vanadium content in DAO was 40.7 ppm with removal percentage was 36.95%. The Nickle content in DAO was 14.56 ppm, and their removal percentage was 47.789%. In contrast, at 68 ºC, the higher Sulfur content was increased to 2.711 wt. % and lowered their reduction percentage to 32.225 %. The Vanadium content in DAO was 46.5 ppm; their removed percentage was lowered to 27.967%. The Nickle content in DAO was 17 ppm, with a removal percentage was 39%. As the temperature increased, the Sulfur and metal content of DAO increased. This is consistent with the direct relationship between Sulfur and metals with asphaltene content being dissolved in DAO; rising temperatures increase the amount of asphaltene in the DAO. This agrees with the literature results by [23][25].



(a)



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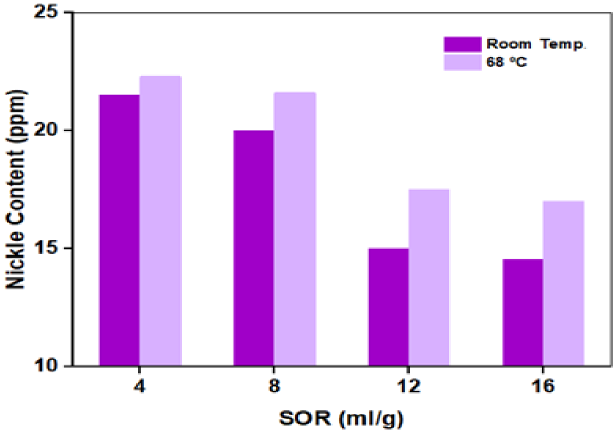

(c)

Fig. 7. Effect of temperature on (a) Sulfur, (b)Vanadium, and (c) Nickel content by using N-Hexane at (4-16 ml/g) SOR and 0.5 h. mixing time

4- Conclusion

The deasphalting process is considered an efficient method to upgrade heavy crude oil depending on asphaltene removal. It favours low temperatures (room temperature), resulting in the highest upgraded characteristics of DAO. Increases in the SOR (4–16 ml/g) increased the API of DAO, precipitated pitch, and decreased the asphaltene content, Sulfur, and metals (Vanadium and Nickel) content, and SOR of 12 ml/g is considered the best. DAO's API was enhanced by 9.3°, 61.56 % was the reduction of asphaltene. There was a 32.8 % reduction in Sulfur, a 36.48% reduction in Vanadium, and a 46.21% reduction in Nickel removal.

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تحسين نفط شرقي بغداد الثقيل بواسطة مذيب الهكسان الاعتيادي

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[3] مركز البحث والتطوير النفطي، وزارة النفط ، بغداد ، العراق.

الخلاصة

الأسفلتينات تصنف على اساس قابلية الذوبان كمكون من مكونات النفط الخام تتصف بخصائص غير مرغوب فيها. في هذه الدراسة ، تم تحسين نفط شرق بغداد الثقيل باستخدام طريقةازالة الأسفلتينات بالمذيبات حيث أن الأسفلتينات غير قابلة للذوبان في المذيبات البرافينية. يمكن إزالتها من النفط الخام الثقيل عن طريق إضافة مذيب الهكسان الاعتيادي للحصول نفط منزوع الاسفلتين (DAO) ذو جودة اعلى. تُعرف هذه الطريقة باسم إزالة الأسفلتينات بالمذيبات ((SDA . تم دراسة تأثيرات مختلفة لعملية SDA ، مثل نسبة المذيب إلى النفط (4-16 / 1 مل / جم) ، درجة حرارة الاستخلاص وهي (23 درجة مئوية) درجة حرارة الغرفة و(68 درجة مئوية) درجة حرارة الارتجاع عند (وقت خلط 0.5 ساعة وسرعة خلط 400 r.p.m). تم الحصول على أفضل نتائج نزع الأسفلت بالمذيب عند درجة حرارة الغرفة و 12 مل / جم نسبة المذيبات إلى النفط. نتيجة لذلك ، تمت تحسين API لـ DAO إلى 31.3. بلغت ازالة الأسفلتينات 61.56٪. كانت نسبة إزالة الكبريت 32.8٪ ، وإزالة الفاناديوم 36.48٪ ، وإزالة النيكل 46.21٪.

الكلمات الدالة: التحسين ، النفط المنزوع الاسفلتين ،الأسفلتينات ، عملية إزالة الاسفلتين بالمذيبات ، والهكسان الاعتيادي.