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Deasphalting of Atmospheric Iraqi Residue using Different Solvents

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ABSTRACT

Different solvents (light naphtha, n-heptane, and n-hexane) are used to treat Iraqi Atmospheric oil residue by the deasphalting process. Oil residue from Al-Dura refinery with specific gravity 0.9705, API 14.9, and 0.5 wt. % sulfur content was used. Deasphalting oil (DAO) was examined on a laboratory scale by using solvents with different operation conditions (temperature, concentration of solvent, solvent to oil ratio, and duration time). This study investigates the effects of these parameters on asphaltene yield. The results show that an increase in temperature for all solvents increases the extraction of asphaltene yield. The higher reduction in asphaltene content is obtained with hexane solvent at operating conditions of (90 °C, 4/1 solvent to oil ratio), where the asphaltene yield was 93%. The highest recorded value of API value at 150 ml for all solvents at the highest temperature and duration time; this value is 32 when using n-heptane solvent at 15/1.

Keywords: Deasphalting, Solvent Deasphalting, Atmospheric Residue.

إزالة الاسفلتينات من متبقي النفط الجوي العراقي باستخدام مذيبات مختلفة

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الخلاصة

استخدمت عدة مذيبات (النافثا الخفيف ، الهبتان والهكسان) لمعالجة بقايا عمليه التقطير بالضغط الجوي للنفط العراقي عن طريق عملية نزع الأسفلت. بقايا النفط تم اخذها من مصفى الدورة ذات الوزن النوعي 0.9705 ، *API* 14.9، ومحتوى الكبريت 50 % نسبة وزنية. تم فحص زيت إزالة الأسفلت (*DAO*) داخل منظومة مختبرية باستخدام المذيبات و بظروف التشغيل (درجة الحرارة ، تركيز المذيب ، نسبة المذيبات إلى الزيت والمدة الزمنية) ، هذه الدراسة تبحث في تأثير هذه المتغيرات على إنتاجية الإسفلت. أظهرت النتائج أن زيادة درجة الحرارة لجميع المذيبات تؤدي إلى زيادة استخلاص انتاجية الإسفلت ويتم الحصول على انخفاض أعلى في محتوى الإسفلت بمذيب الهكسان في ظروف التشغيل (90 درجة مئوية ، نسبة المذيب الى الزيت 1/4) حيث كان إنتاج الأسفلت 93 ٪ ، ثم الهيبتان وأخيرًا النافثا الخفيفة ، أعلى قيمة مسجلة لقيمة *API* عند 150 مل لكل مذيب عند أعلى درجة حرارة ومدة زمنية ، وهذه القيمة هي 32 عند استخدام مذيب الهيبتان بنسبة 1/15.

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الكلمات الرئيسية: ازالة الاسفلت, المذيبات في ازالة الاسفلت, متبقي التقطير الجوي

INTRODUCTION

Solvent deasphalting (SDA) is a cost-effective solution for heavy oils and residues processing. It is one of Bottom-to-Barrel's most relevant technologies **(Mckenna, *et al*., 2013)**. Higher sulfur crudes are used in refineries and more efficient residue processing technology **(Speight, 2007).**
One example is the well-known process of solvent degradation in the lubrication of oil refining. The SDA technology is being used more and more by refineries since the SDA technology has lower investment costs than other waste technology (e.g., hydrocracker, Coker, and Visbreaker) **(Barrera, *et al*., 2013)**.
Since asphaltenes consist of many species and is self-associate, an asphaltene fraction has a wide distribution of properties. The two properties of interest, other than molecular weight, are density and solubility parameter. The density distribution of asphaltenes ranges from 1050 to 1250 kg/m^3**.** The average densities of asphaltenes is typically from 1130 to 1200 kg/m^3 **(Akbarzadeh, *et al*., 2004).** Recently, **(Powers, *et al*., 2016)** reported asphaltenes densities from thermo-cracked, Insitu-converted, and hydrocracked oils ranging from 1120 to 1250 kg/m^3. Asphaltene solubility parameters are determined indirectly by modeling asphaltene precipitation data using regular solution-based theory models **(Akbarzadeh, *et al*., 2004; Artok, *et al*., 1999).**
The solvent deasphalting process (SDA) based on using paraffinic solvents (C4–C7) or polar solvents is considered an efficient method to reduce metal and asphaltene contents of heavy petroleum fractions **(Riazi, 2005)**. The raw oil fraction asphalt is a dark brown to black fried solid, without a certain melting point, and usually spray and swell in heating to leave a residual carbonate **(Hammami, *et al*., 2000)**. Asphaltenes are known to have undesirable properties, a class of solubility in bitumen. Since asphaltene is insoluble in paraffinic solvents, a solvant such as n-pentane, n-heptane, propane , butane and many other substances can be isolated from bitumen or residue for the improvement of the production of asphalted oil (DAO) **(Tharanivasan, *et al*., 2011; Joshi, *et al*., 2001)**. Several parameters that influence the SDA process are solvent type, solvent to oil (S/O) ratio, mixing time, temperature, and pressure. Asphaltene's polar sites are more available **(Peng Luo, *et al*, 2006).**
Increasing the molecular weight of solvents increases the recovery yield of deasphalted oil and allows more resinous feedstock components to stay in the deasphalted oil. But also, since these heavier substances have higher contaminant levels, the deasphalted oil's consistency decreases. The chosen selection of solvents, therefore, requires balancing increased product yield and reduced product quality. The precipitation greatly increases with a solvent/feed ratio up to 10 times higher. Moreover, precipitation develops in very small quantities **(Gonzalez, *et al*., 2004).**
Another example is asphaltene precipitation from oils diluted with a paraffinic solvent or other incompatible fluid such as carbon dioxide. In some cases, such as solvent deasphalting and paraffinic froth treatment processes, the asphaltenes are precipitated deliberately. In other cases, such as refinery blending, dilution of heavy oil for transportation, and batch pipeline operations, the precipitation is undesirable **(Rafael Martínez-Palou, *et al*., 2011).**
Maximum efficiency can be thought of in combination with solvent molecules at all polar sites. In naphtha that is reasonably well solved with asphalt, this is easier to obtain **(Gateau P., and Argillier J.F., 2004).** The present work aims to study the asphaltene precipitation of heavy crude oil in Iraqi atmospheric oil residue supplied from the Al-Dura refinery. Different polar hydrocarbons (light naphtha, n-heptane and n-hexane), different solvent to oil ratio (4/1, 8/1, 10/1, 12/1, and 15/1), different duration time of perception (15, 30, 60, 90, and 120 min) and different temperatures (30, 45, 60, and 90 ˚C) were used in the precipitation of asphaltene.

2. EXPERIMANTAL WORK

The characteristics of oil residue are tabulated in **Table 1,** and the data are provided from **the** Al-Dura Refinery.

Table 1. The properties of atmospheric oil residue

Characteristics	value
Specific gravity at $60^0/60\ ^0F$	0.9705
API gravity	14.9
Kinematic viscosity, c.st.at 100 ^0C	32.73
Sulfur content, wt.%	0.5
Flashpoint ^0C	190

2.1 Petroleum Solvents

Three types of petroleum solvents were used in this study, which is tabulated in **Table 2**.

Table 2. Types of petroleum solvents.

Petroleum Solvent	Purity	Supplier
Light Naphtha	99 %	AL-Dura refinery
n-heptane	99 %	(POCH SA) company
n-hexane	99 %	MERCK

2.2 Experimental Setup

The deasphalting unit process consisted of mixing oil residue with appropriate solvent to oil ratio (4/1, 8/1, 10/1, 12/1, and 15/1) in a 2-neck flask glass. The flask was mounted on a heating magnetic stirrer with a speed of 450 rpm. The duration time of perception was (15, 30, 60, 90, and 120 min). To increase the separation efficiency, two efficient condensers were connected to the upper neck of the flask, the other side neck was fitted with a thermocouple to set an appropriate chosen temperature (30, 45, 60, and 90℃). The deasphalting apparatus and its scheme are shown in **Fig. 1**.

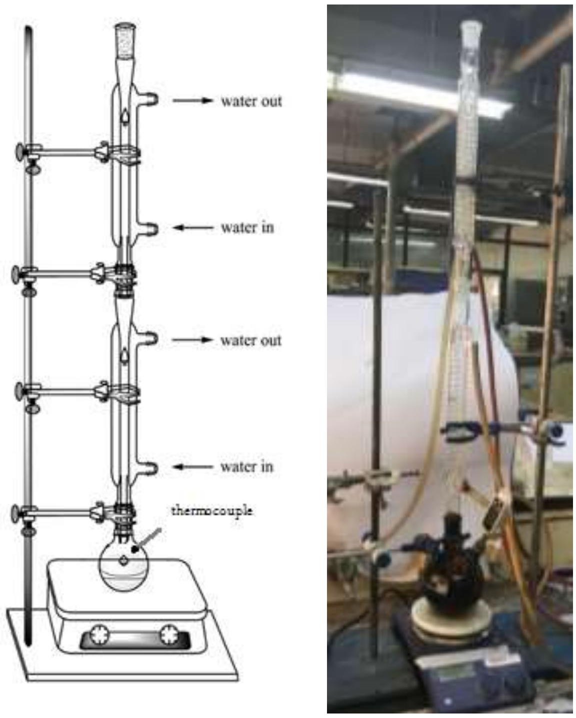

Figure 1. The deasphalting apparatus and its scheme.

After performing each experiment, the sample was taken to a vacuum filter at 5 mm Hg to filtrate the crude oil using filter paper. The vacuum pump reduces the time required for filtration. The solvent and the remaining filtrate through the flask and asphalt remain on the filter paper surface of which was weighted; the filtration unit is shown in **Fig. 2**.

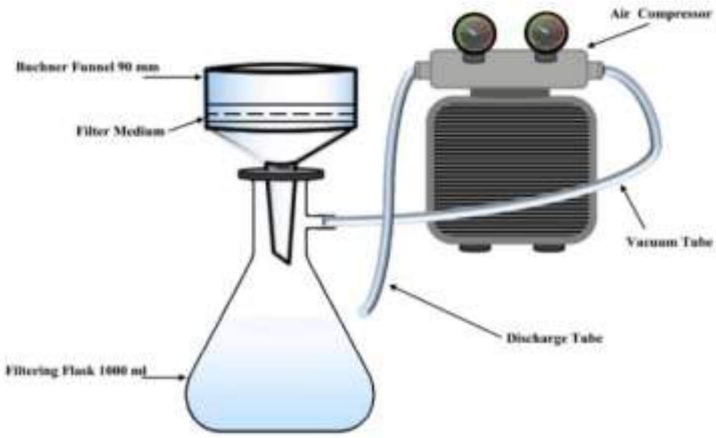

Figure 2. Filtration unit setup.

The asphaltene yield was calculated based on the standard separation of all the asphaltene in the sample, divided by the asphaltene from in gram from each experiment.

3. RESULT AND DISCUSSION
3.1 Effect of Solvent Type

Fig. **3-5** displays the effect on the asphaltene yield percentage of various polar solvent forms at a different concentration. Different solvents at different amounts and temperatures are exposed to the feedstock. These solvents decreased the asphalt content of the polar solvents to dispose of asphalt agglomerates, as well as their temperature.

From **Fig. 3,** the higher reduction in asphaltene content is obtained with n-hexane at 90°C, 4/1 ratio, where the asphaltene yield was 93%. It's noticed from the figure that the increase in temperature at any solvent increases the extraction of asphaltene. The best asphaltene extract was at 90℃ for n-hexane, followed by n-heptane and, at last, light naphtha.

Fig. 4 shows the extraction of asphaltene that was studied using a different solvent to oil ratio (solvent in ml /10 ml sample). At any solvent volume, the n-hexane has the best performance at 80 ml (90% yield), followed by heptane (76% yield) and finally light naphtha (55% yield).

Unique types of compounds are well known to break down asphaltene agglomerates. In the polyaromatic systems of asphaltene agglomerates, the electrons' presence may play a role in the interaction between the compounds added to and n electrons. Compounds held in one ring to preserve the dimensions of molecules allow a wider distribution by the crude oil matrix and the incorporation into the asphalt agglomerates **(Hussein, *et al*., 2014)**.

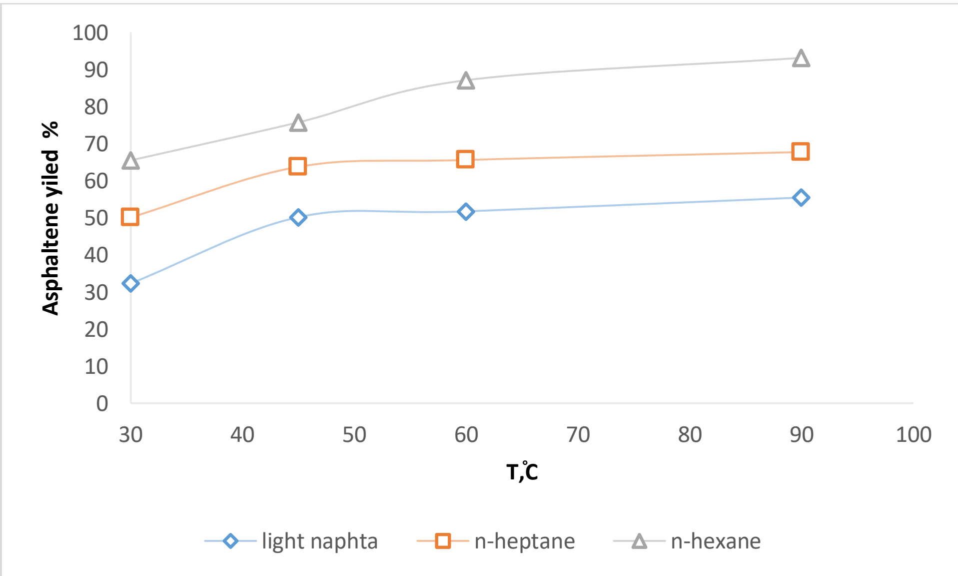

Figure 3. Effect of solvent type on asphaltene at different temperature.

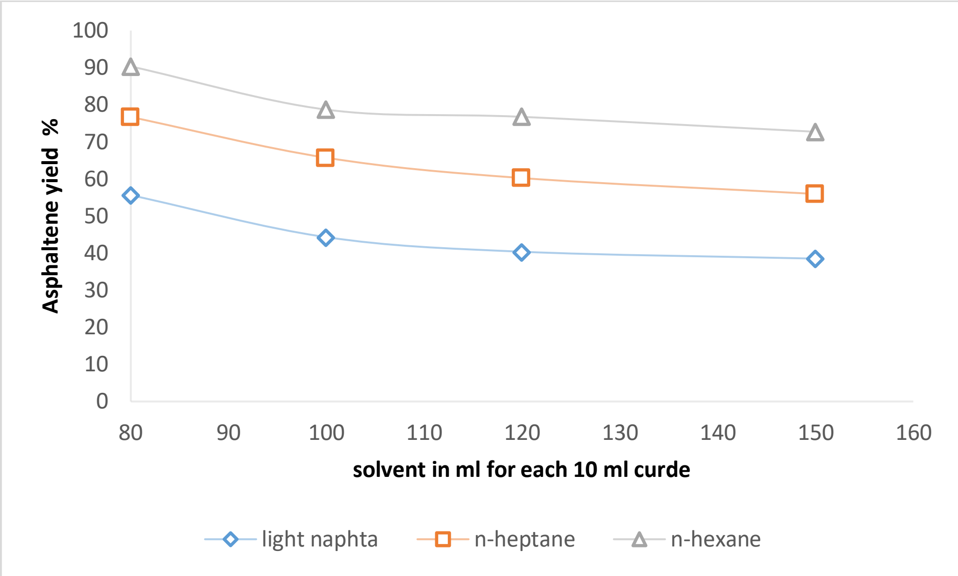

Figure 4. Effect of solvent to crude sample ratio on the asphaltene.

The effect of treatment time was studied, as shown in **Fig. 5** for each solvent. The treatment time in general increases the amount of asphalt precipitation at any solvent **(Naief, *et al*., 2019)**.
These values show that the average solubility decreases as more content are precipitated. The asphaltenes' solubility parameter decreases on average with solvent power decreases and more molecules (with high solubility in hexane) transfer to drop. Contrary to the solvent / crude oil ratio impact, there were no major variations in the profile as demonstrated by the example presented in comparison of asphalt solution profiles in a given solvent / crude oil ratio at different times. These results were agreed with the results obtained by **(Rogel, *et al*., 2017).**

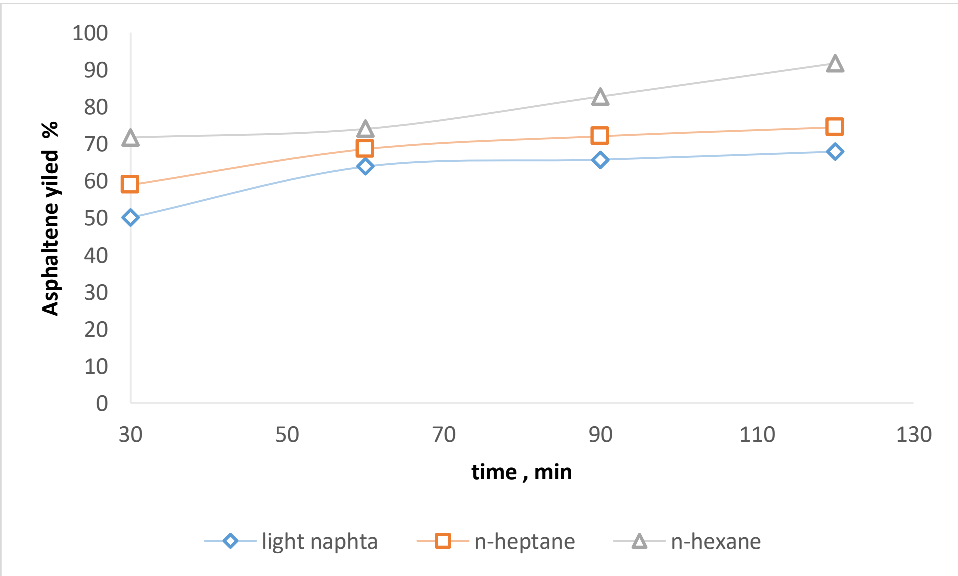

Figure 5. Effect of asphaltene with duration time in min using different solvent.

These values show that the average solubility decreases as more content is precipitated. The asphaltenes' solubility parameter decreases on average with solvent power decreases and more molecules (with high solubility in hexane) transfer to drop. Contrary to the solvent / crude oil ratio impact, there were no major variations in the profile as demonstrated by the example presented in comparison of asphalt solution profiles in a given solvent / crude oil ratio at different times. Increased content of asphaltene was found related to the relative increase in species or aggregates of high molecular weight. Experimental evidence suggests that asphaltene precipitation is a dynamic process involving the aggregation and the reorganization of aggregates **(Puron *et al*., 2014)**.

3.2 Effect of Solvent Concentration

Fig. 6-8 shows the effect on API values' improvement at various temperatures, solvent ratios, and mix times of solvent concentration. With raising solvent concentration at different temperatures, the API for heavy crude oil was increased.

The highest API value was recorded at 150 ml for all solvents at the highest temperature and duration. The value was 32 when using n-heptane solvent at 15/1 ratio followed by light naphtha after 120 min treatment time.

The breakdown of asphalt agglomerates and the reduction in the existence of micelle-like clusters were crucial in improving the API of heavy crude oil, where polar solvents dispersed asphaltene molecules, reduced their molecular size, and decreased the amount of asphaltene, causing an increase in the API of heavy crude oil **(Singh *et al*., 2012).**

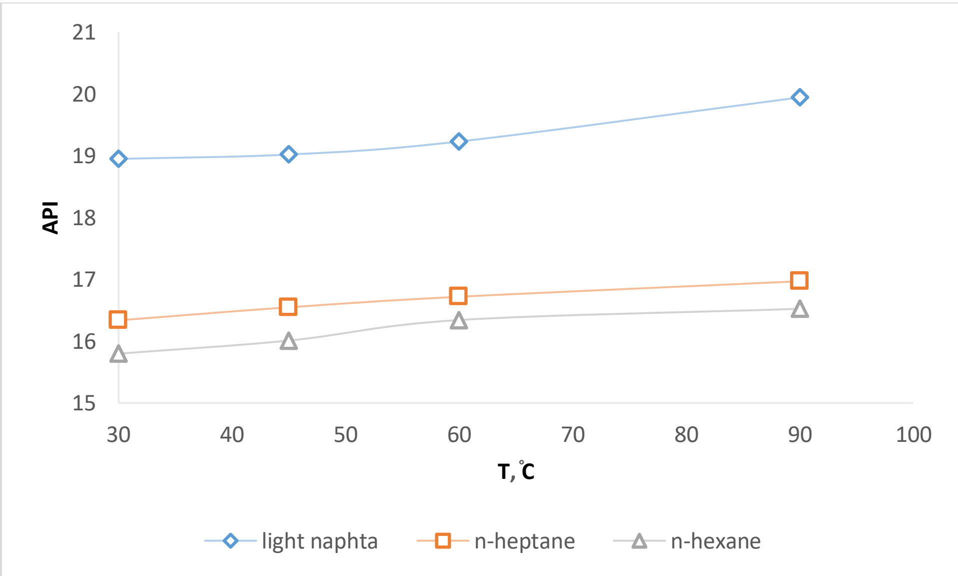

Figure 6. Effect of solvent type with temperature on the API.

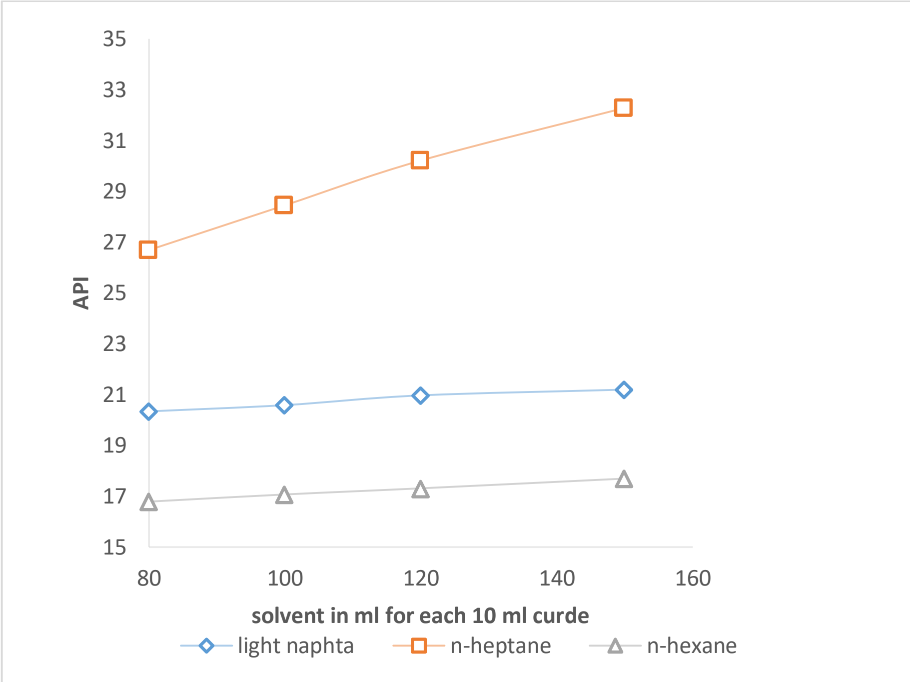

Figure 7. Effect of solvent ratio on API.

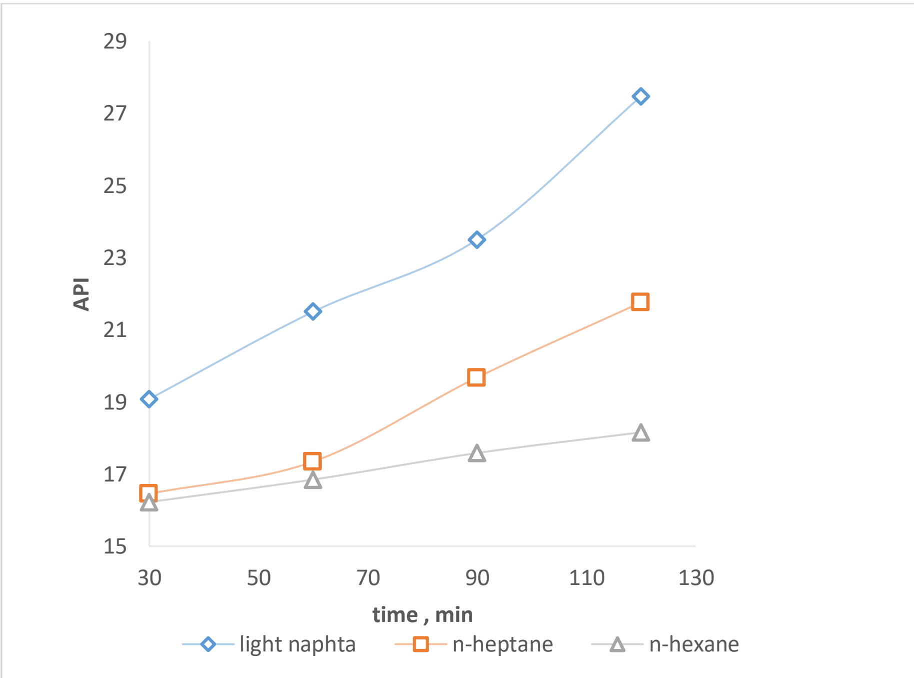

Figure 8. Effect of duration treatment on API at different solvent.

4. CONCLUSIONS:

From the study results, the agglomeration of asphalt particles, which is due to the entanglement of solvency asphalt particles in atmospheric oil residue. Asphaltene was the best precipitate for n-hexane, n-heptane, and light naphtha. The highest API value was recorded at 150 ml for all solvents at the highest temperature and duration. The value was 32 when using n-heptane solvent at 15/1, followed by light naphtha after 120 min. of treatment time. The higher reduction in asphaltene content is obtained with hexane at 30°C, 10/1, where the asphaltene yield was 93%.

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NOMENCLATURE

API	The American Petroleum Institute
DAO	Deasphalting oil
SDA	Solvent deasphalting
S/O	solvent to oil ratio