Al-Khwarizmi Engineering Journal, Vol. 7, No. 3, PP 19 - 29 (2011)

Al-Khwarizmi Engineering Journal

Upgrading Sharky Baghdad Heavy Crude Oil

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(Received 28 February 2011; accepted 19 Jun 2011)

Abstract

Shaky Baghdad heavy crude oil 22 API is processed by distillation and solvent extraction. The purpose of distillation is to separate the light distillates (light fractions) which represent 35% of heavy crude oil, and to obtain the reduced crude oil. The heavy residue (9 API) is extracted with Iraqi light naphtha to get the deasphaltened oil (DAO), the extraction carried out with temperature range of 20-75 ^{o}C, solvent to oil ratio 5-15:1(ml:g) and a mixing time of 15 minutes. In general, results show that API of DAO increased twice the API of reduced crude oil while sulfur and metals content decreased 20% and 50% respectively. Deasphaltened oil produced from various operating conditions blended with the light distillates obtained from distillation in a constant blending percentage of 35% light for all mixtures. These blends produced synthetic crude oil with API up to 30 suitable for using in the subsequent hydrocarbon processes.

Keyword: *synthetic crude oil, deasphaltening, distillation, extraction.*

1. Introduction

Asphaltenes are high molecular weight polycyclic compounds containing nitrogen, sulfur, oxygen, and metals. The relative concentrations of these compounds vary in terms of the crude oil, and make up a unity which makes it a useful parameter for general comparisons of oils. All of these compounds are present in different oils which vary from light to heavy crudes with a broad spectrum of varying densities in which the conventional unit of gravity API gravity decreases or the oil becomes heavier, making this unit an important correlational factor. Additional general correlational factors describing different types of oils are the H/C ratios, which also decrease as the oil becomes heavier. Further, the polar N, S, O compounds become concentrated in the heavy ends of crudes. The heteroatom contents of these oils are measurable quantities and are also useful for correlational purposes. Thus, as the sulfur and nitrogen concentrations increase, the API value decreases, consistent with an increase in the concentrations of compounds containing heteroatoms and increasing molecular weights. The high molecular weight fractions also concentrate organometallic compounds [1].

Reduction of asphaltenes and metal content can be achieved by disturbing the solvation equilibrium via addition of suitable solvents, e.g., propane, pentane, heptane or carbon dioxide, resulting in the flocculation of asphaltenes [2].The solvent deasphaltation treats the residue through a pressurized liquid-liquid extraction, using specific properties of the solvent. The deasphaltation produces the deasphalted oil and the asphalted residue [3].The Residuum Oil Supercritical Extraction process is the premier deasphalting technology available in industry today. This state-of-art process extracts high-quality deasphalted oil (DAO) from atmospheric or vacuum residues and other feedstocks. The asphaltene products from the ROSE process are often blended to fuel oil, but can also be used in the production of asphaltic blending components, solid fuels, or fuel emulsions. The development of the deasphaltation technology using supercritical fluid appears as a solution to improve the separation of the deasphalted oil (ODES) from the asphaltenes. The use of supercritical fluid has some advantages like: the difference of the densities between the extraction phase and the refining phase is greater than that obtained by the conventional liquid extraction, becoming the separation between the phases easier; the mass transport is faster using the supercritical fluid; the quantity and the quality of the ODES can be easily controlled adjusting the temperature and the pressure of the extraction system and the efficiency to recover the oil is a function of the density of the supercritical fluid [3].

The solvent deasphalting process (SDA) which is based on liquid–liquid extraction by using paraffinic solvents (C4–C7) is one of the most efficient approaches to reduce metal and asphaltene contents of heavy oil cuts before sending them to hydro-desulphurization and Hydrocracking units.

A number of deasphalting process parameters are to be considered, amongst which the DAO process yield and the levels of demetalization and deasphalting could be noted. The important factors influencing the mentioned parameters are solvent composition and ratio of the solvent to the feed, temperature, pressure and the type of extractor equipment.

The precipitation increases substantially as the solvent/feed ratio increases up to 10 folds. Beyond this value, precipitation increases by very small amounts [4].

Extraction temperature must be maintained below the critical temperature of the solvent, however, because at higher temperatures no portion of the residue is soluble in the solvent and no separation occurs[5].

In industrial plants, increasing the solvent to feed ratio compensates for the DAO yield reduction with temperature rise. In consequence, the extraction process selectivity for paraffinic oils escalates and eventually the extracted oil will have an improved quality due to the reduction of undesirable components [6].

Direct hydro-desulphurization followed by Hydrocracking of crude oil heavy cuts and vacuum residues is one of the best methods of heavy residue upgrading in refining industry. But, problem emerges when metal and asphaltene contents of residue are high. In fact, the presence of these compounds adversely influences the activities of the hydro-desulphurization and Hydrocracking catalysts.

The aim of this work is to separate the light distillates from Sharky Baghdad heavy crude oil and to obtain deasphaltened oil by solvent extraction with light naphtha. The light and the blended DAO distillate to produce high API synthetic crude oil with low sulfur and metals content.

2. Experimental Work

2.1. Distillation Process

The distillation process for separation of light distillates (light fractions) from sharky Baghdad heavy crude oil was achieved by a computerized laboratory distillation apparatus (according ASTM 5236) (PIGNAT COMPANY, FRANCE) that consists of distillation flask, heating mantle, distillation column, condenser, thermometers, fraction collector. The physical properties of Sharky Baghdad heavy crude oil and distillation results are shown in Table (1). Figure (1) shows the schematic diagram of the laboratory distillation apparatus.

Table 1,
Physical Properties of Sharky Baghdad Crude Oil.

Property	Value	Preliminary distillation (IP 24/55)	
		Temperature, ºC	Vol. %
Specific gravity 15.6/15.6 ºC	0.922	-	-
API gravity	22	IBP(85 ºC)	-
Viscosity at 37.5 ºC, Cs	47	100	3.5
Sulfur content, wt. %	5.044	125	5
Vanadium, ppm	88	150	8.6
Iron, ppm	25	175	11.6
Nickel, ppm	38	200	15.1
Saturate compounds, wt. %	42.66	225	18.4
Naphthene compounds, wt. %	23.87	250	23
Polar aromatic compounds,wt.%	17.8	275	27.5
Asphultene content,wt. %	15.67	300	33.7

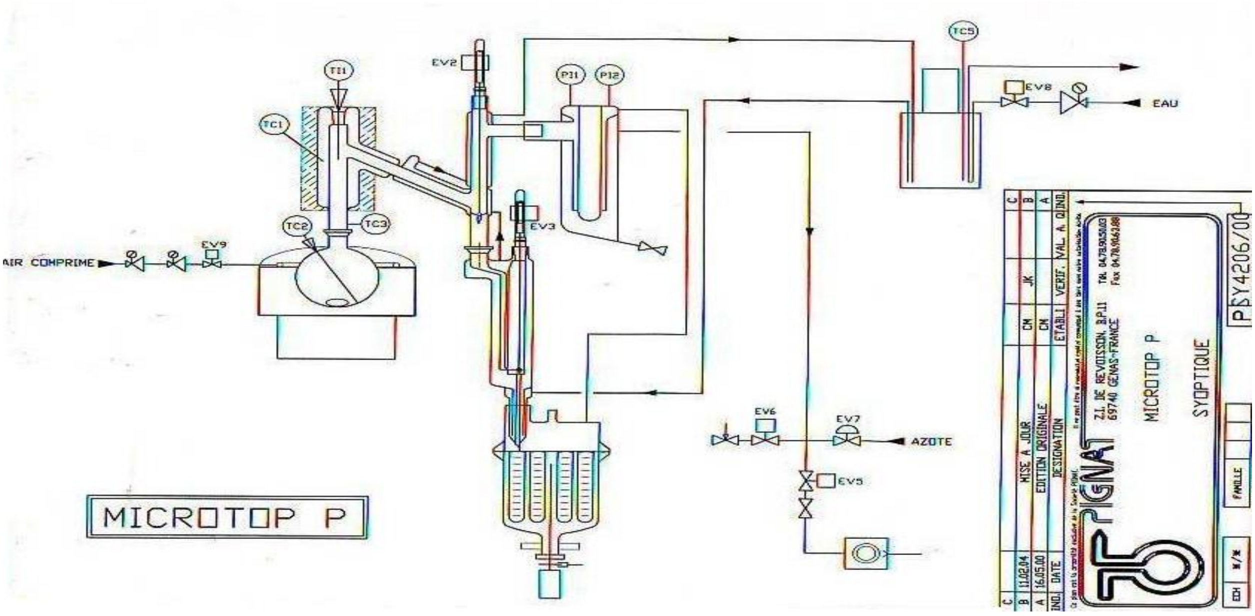

Fig.1. Schematic Diagram of the Laboratory Distillation Unit.

2.2. Extraction Process

Asphaltenes are separated from atmospheric residue (350+oC) obtained from distillation stage by extraction with light naphtha. The composition of light naphtha and the physical properties of atmospheric residue are given in Tables 2 and 3, respectively.

The extraction process consists of three stages mixing, filtration and solvent recovery.

Table 2,
Composition of Iraqi Light Naphtha.

n-Paraffins	wt %	i-Paraffins	wt %	Naphthenes	wt %	Aromatics	wt %
C_3	0.067	i-C4	0.045	CC5	0.302	Benzene	0.683
n-C_4	0.329	i-C5	3.956	NC6	4.37	Toluene	1.904
n-C_5	7.006	$2MC_5$	10.787	CC6	2.844		
n-C_6	14.809	$3MC_5$	7.421	NC7	4.11		
n-C_7	10.192	$2MC_6$	6.976	NC8	7.091		
		$3MC_6$	6.106				

Table 3,
Physical Properties of Atmospheric Residue.

Property	Value
Specific gravity 15.6/15.6 ºC	1.002
API gravity	9.66
Asphaltenes ,wt %	23
Asphaltenes ,g	11.5
Sulfur ,wt %	5.7
Sulfur ,g	2.85
Vanadium ,ppm	90
Nickle ,ppm	35.2
Chrome ,ppm	2.35

A- Mixing Stage

Mixing was carried out with 1-liter 2-neck glass flask, magnetic stirrer, heating mantle, high efficiency condenser and thermometers. 50 g of atmospheric residue was mixed with light naphtha at temperatures of 20, 50, 75oC, Solvent to oil ratio 5, 10, 15:1 (ml:g) and mixing time of 15 minutes with 200 rpm. A high efficient vertical condenser operating at total reflux was mounted on mixing flask in order to decrease the solvent losses to the minimum. Figure (2) shows a scheme of mixing process. When the mixing step was complete, the flask left for 1 hour at ambient temperature to let asphaltenes settle to the bottom of the flask.

Fig.2. Scheme of the Mixing Unit.

B- Filtration

In order to filter the solvent-oil mixture in a reasonable time, a vacuum filtration unit was assembled, which consisted of a filtration flask, Buchner funnel, vacuum pump and trap for condensing the high volatility solvent in order to avoid vacuum pump damage. The filter paper (Whatman no. 1) was wetted with solvent before the filtration step. At the end of the filtration, the filter paper was put in a hot electrical furnace to evaporate the solvent associated with the precipitated asphaltenes. The dried filter paper was then weighed to estimate the percentage of asphaltenes yield.

C- Evaporation

Solvent and deasphaltened oil is introduced to distillation unite in order to separate the solvent from DAO.

2.3. Blending

DAO produced from various operating conditions blended with the light distillates is produced from distillation stage which formed 35% from these mixtures to produce synthetic crude oil.

3. Results and Discussions

The tests results of DAO produced from various operating conditions are shown in Table (4). The effective parameters of process included in these tables are specific gravity, API, asphaltene content, sulfur and metals content.

Table 4,
Tests results of Deasphaltened Oil.

Temperature	**20 °C**		
Oil:Solvent	**01:05**	**01:10**	**01:15**
Specific gravity 15.6/15.6 °C	0.946425	0.933993	0.931105
API	18.01	20	20.47
Asphaltenes removed,g	8.32	10.5	11
Sulfur content, wt%	4.4	4.3	4.4
Vanadium,ppm	35	24.6	24
Nickle,ppm	16	15.2	14.9
Chrome,ppm	0.1	0.1	0.1
After blending API of synthesis crude oil	29.2065	30.5	30.8055
Temperature	**50 °C**		
Oil:Solvent	**01:05**	**01:10**	**01:15**
Specific gravity 15.6/15.6 °C	0.946488	0.937086	0.93461
API	18	19.5	19.9
Asphaltenes removed,g	7.81	8.2	8.4
Sulfur content, wt%	4.5	4.6	4.6
Vanadium,ppm	41.4	31	24.3
Nickle,ppm	18	17.5	17.1
Chrome,ppm	0.6	0.3	0.2
After blending API of synthesis crude oil	29.2	30.175	30.435
Temperature	**75 °C**		
Oil:Solvent	**01:05**	**01:10**	**01:15**
Specific gravity 15.6/15.6 °C	0.95634	0.955436	0.9555
API	16.46	16.6	16.59
Asphaltenes removed,g	5.1	7.3	7.1
Sulfur content, wt%	4.8	4.7	4.6
Vanadium,ppm	58.4	57	50.9
Nickle,ppm	18.2	18	17.5
Chrome,ppm	0.64	0.56	0.3
After blending API of synthesis crude oil	28.199	28.29	28.2835

3.1. Effect of Temperature

Figure (3) shows that asphaltenes yield decreased with increasing temperature. This behavior is due to increasing the solubility of oil with increasing temperature which permits asphaltenes and resinous materials to escape to the oil phase.

Figures 4 and 5 show that API of DAO and synthetic crude oil decreased with increasing temperature respectively due to decreasing of asphaltenes removal with increasing temperature. Figure (6) shows that sulfur content of DAO increased with increasing temperature due to the decreasing removal of asphaltenes. A figure 7, 8 and 9 shows that metals impurity reduction of vanadium, nickel and chrome respectively decreased with increasing temperature. These behaviors due to increasing asphaltenes content with increasing temperature.

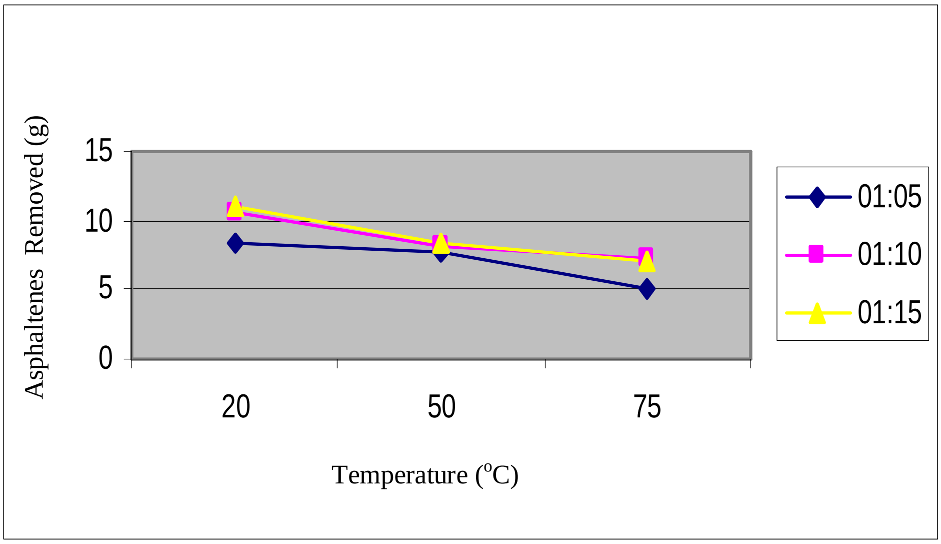

Fig.3. Effect of Temperature on Asphaltenes Removal from RCR at Various Oil to Solvent Ratio.

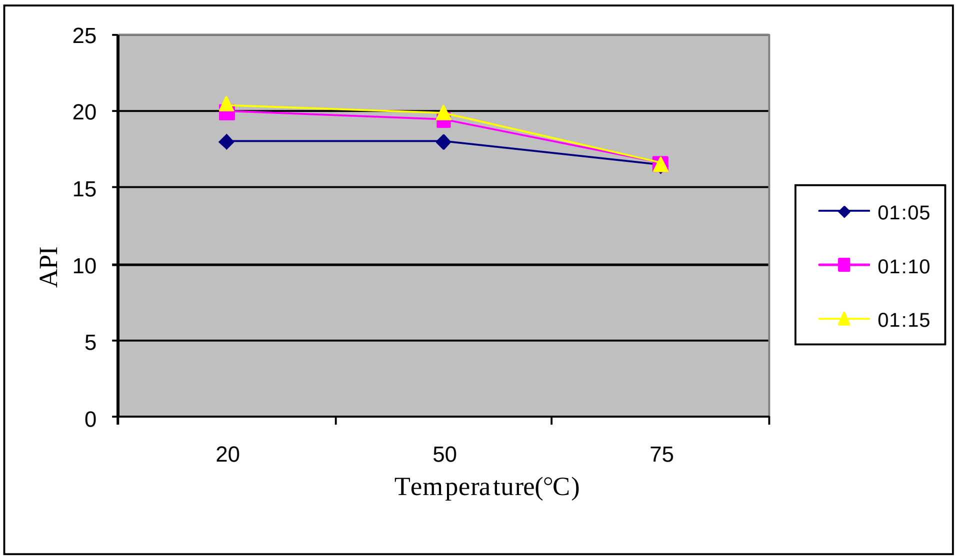

Fig.4. Effect of Temperature on API of Deasphaltened Oil at various Oil to Solvent Ratio.

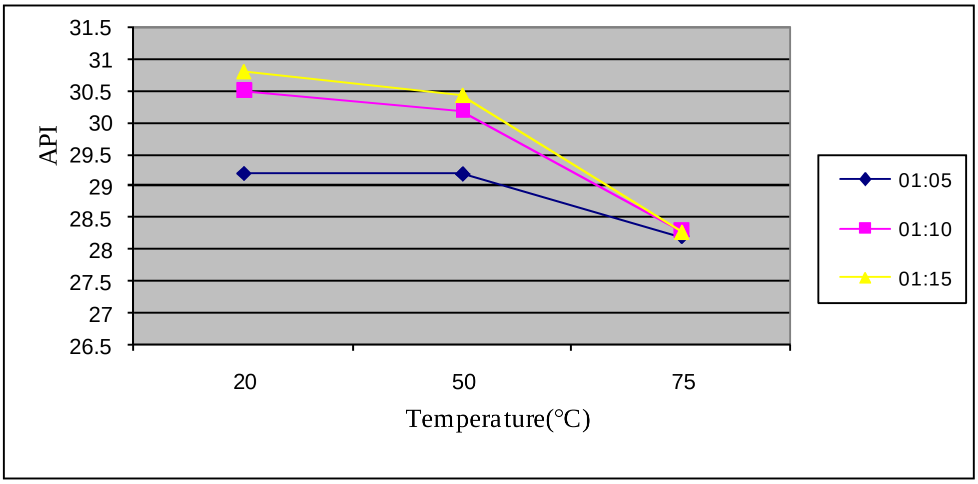

Fig.5. Effect of Temperature on API of Synthesis Crude Oil at various Oil to Solvent Ratio

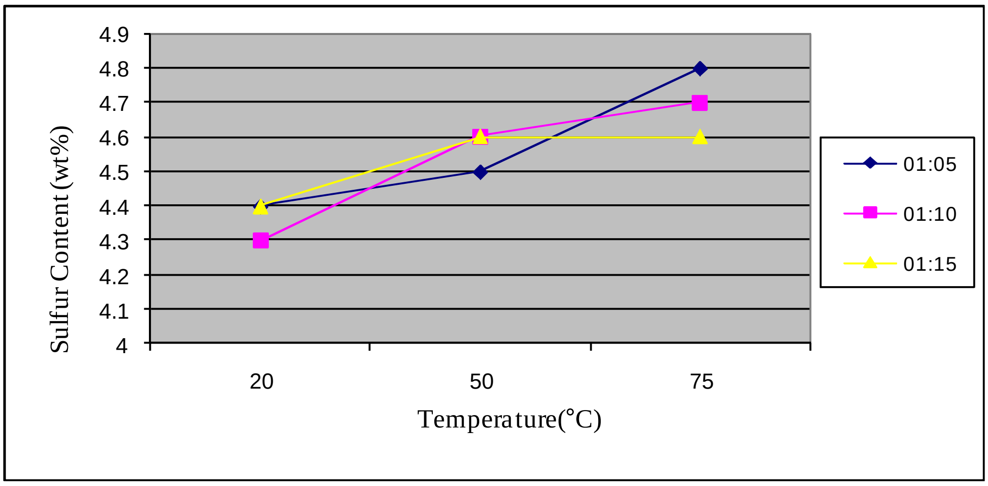

Fig.6. Effect of Temperature on Sulfur Content of Deasphaltened Oil at various Oil to Solvent Ratio.

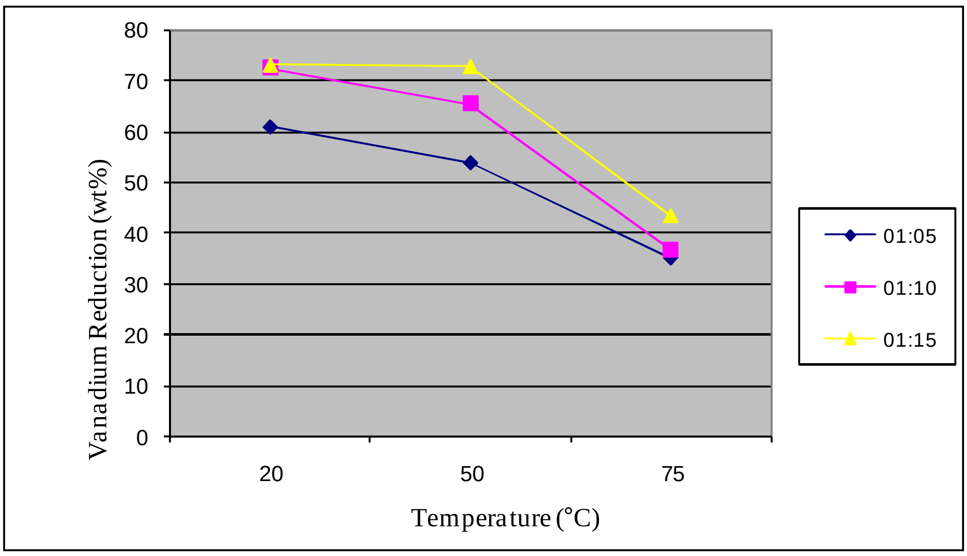

Fig.7. Effect of Temperature on Vanadium Reduction of Deasphaltened Oil at various Oil to Solvent Ratio.

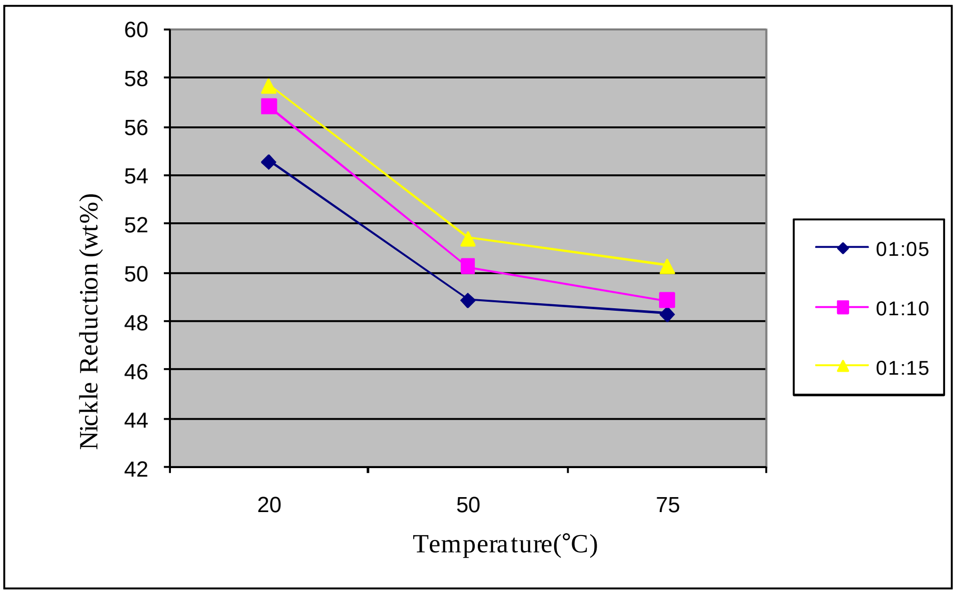

Fig.8. Effect of Temperature on Nickel Reduction of Deasphaltened Oil at various Oil to Solvent Ratio.

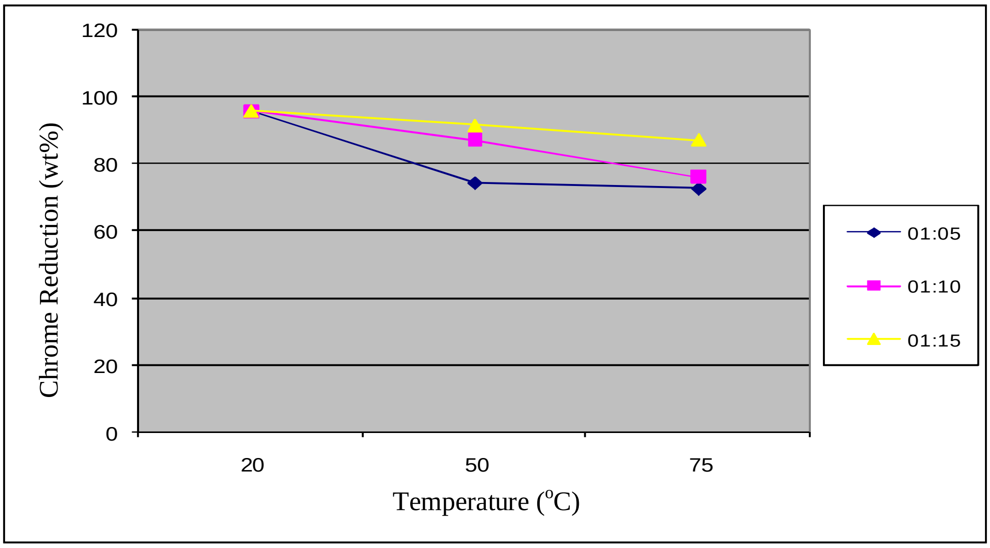

Fig.9. Effect of Temperature on Chrome Reduction of Deasphaltened Oil at various Oil to Solvent Ratio.

3.2. Effect of Solvent to Oil Ratio

Figure (10) shows the effect of increasing solvent to oil ratio on the removing of asphaltene. In this case, increasing solvent to oil ratio led to increasing asphaltenes removal and then to steady state at 10:1. This behavior is due to increasing solvent power and selectivity toward asphaltenes removal.

Figures 11 and 12 shows the effect of increasing the solvent to oil ratio on API of DAO and synthetic crude oil respectively. In this case, the increasing of solvent to oil ratio led to increase of API due to increasing solvent power and selectivity for the removing of asphaltenes and then to steady state.

Figure (13) shows approximately steady state effect of increasing the solvent to oil ratio on sulfur content. Figures 14, 15 and 16 show the effect of increasing solvent to oil ratio on Vanadium, Nickel and Chrome impurity reduction, respectively. In this case, increasing solvent to oil ratio led to the increasing of metals impurity reduction due to increasing the removing of asphaltenes.

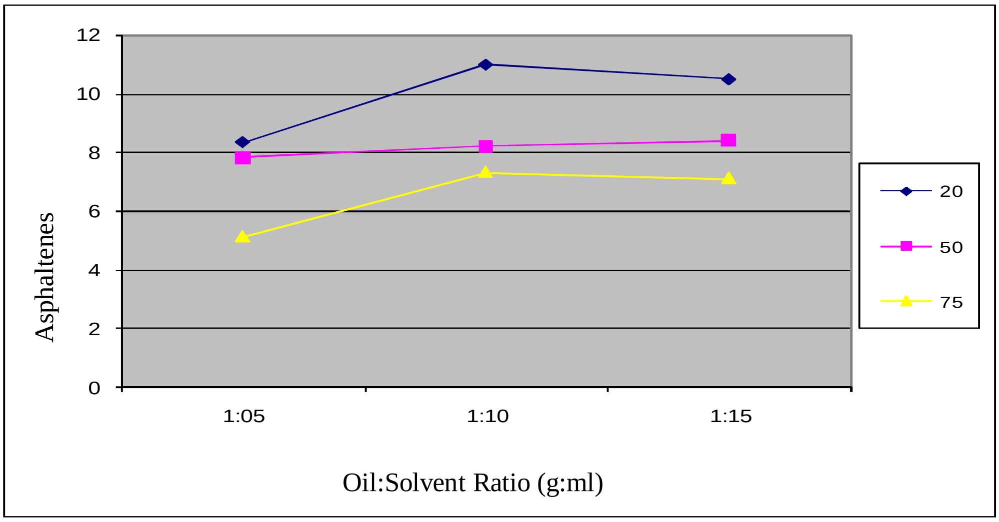

Fig.10. Effect of Oil to Solvent Ratio on Asphaltenes Removal from RCR at Different Temperatures.

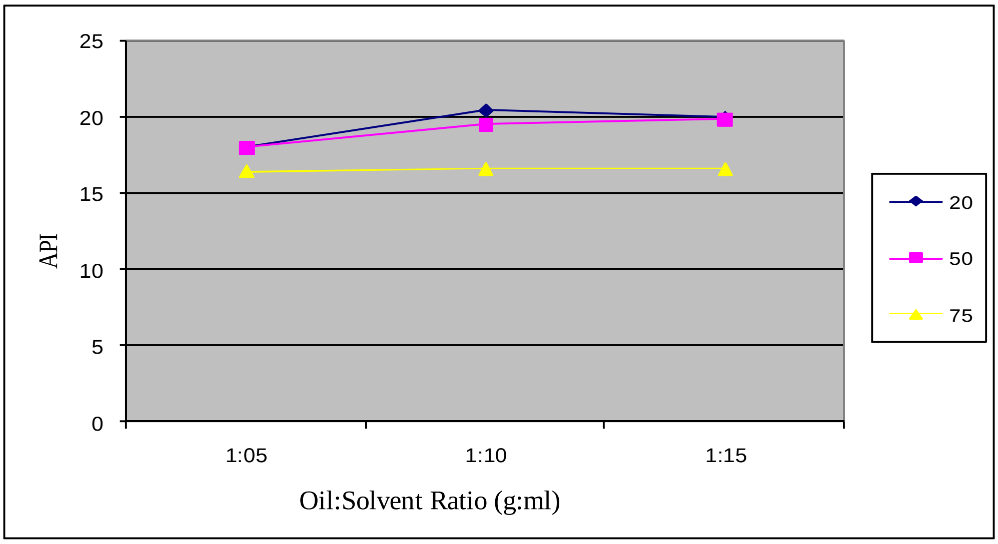

Fig.11. Effect of Oil to Solvent Ratio on API of Deasphaltened Oil at Different Temperatures.

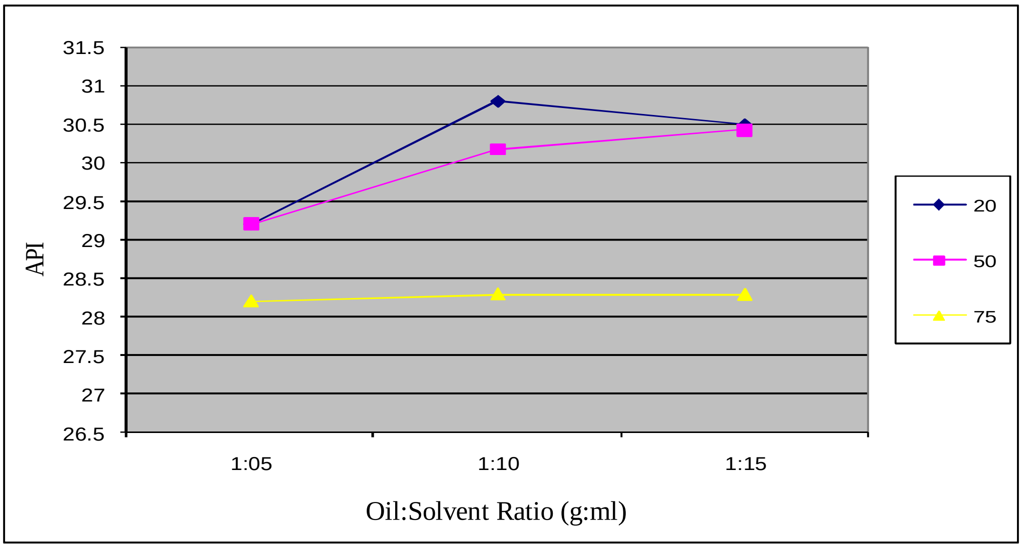

Fig.12. Effect of Oil to Solvent Ratio on API of Synthesis Crude Oil at Different Temperatures.

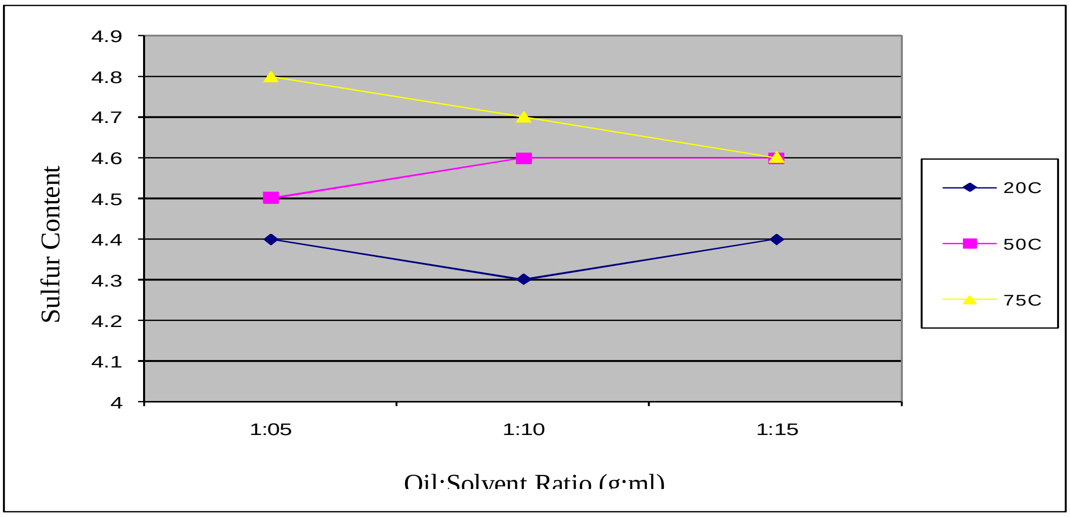

Fig.13. Effect of Oil to Solvent Ratio on Sulfur Content of Deasphaltened Oil at Different Temperatures.

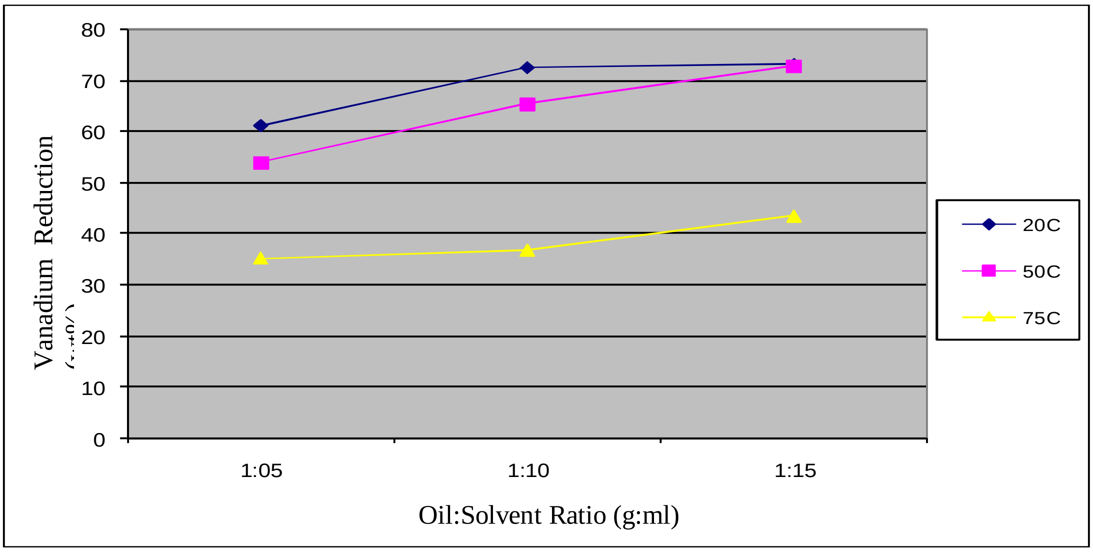

Fig.14. Effect of Oil to Solvent Ratio on Vanadium Reduction of Deasphaltened Oil at Different Temperatures.

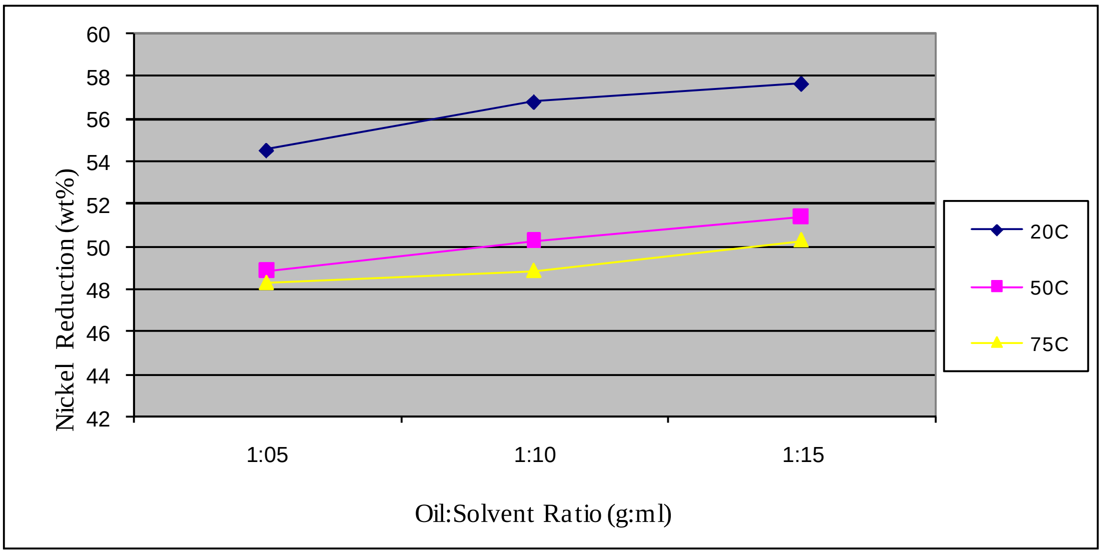

Fig.15. Effect of Oil to Solvent Ratio on Nickel Reduction of Deasphaltened Oil at Different Temperatures.

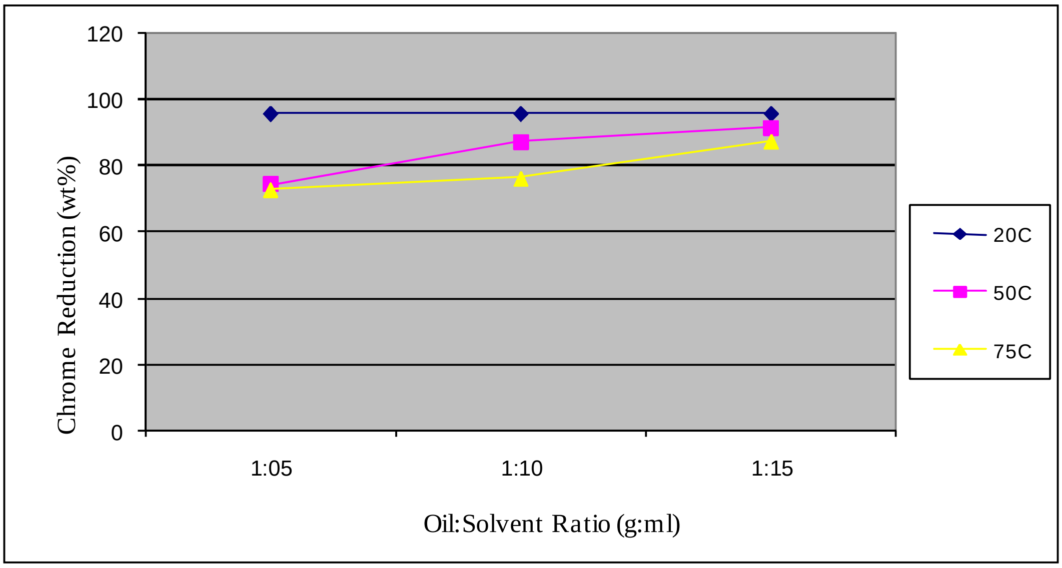

Fig.16. Effect of Oil to Solvent Ratio on Chrome Reduction of Deasphaltened Oil at Different Temperatures.

4. Conclusions

1- Removing asphaltenes from the reduced crude oil produces DAO with 19 API with low sulfur and metals content.
2- Increasing extraction temperature led to decreasing API of DAO and other properties.
3- Increasing solvent to oil ratio led to increasing API of DAO and other properties with no significant changes beyond solvent to oil ratio 10:1 (ml:g).
4- Optimum extraction process is carried out at temperature 20oC and 10:1 solvent to oil ratio.
5- Blending of light distillates in a percentage 35% with DAO led to producing synthetic crude oil with 30 API and low sulfur and metals content.

5. References

[1] E. T. Premuzic and M. S. Lin, “212TH National Acs Meeting Induced Biochemical Interactions In Crude Oils”, August 18-22, 1996, Orlando, FL.

[2] Eckermann B. and Vogelpohl A., “Deasphaltization and Demetalling of Heavy Crude Olis and Distillation Residues with CO2”, Chemical Engineerring and Technology. V13,P.258-264, 1990.

[3] Mendes M. F., Ferreira C. Z. and Pessoa F. L. P., “Deasphaltion of Petroleum Using Supercritical Propane”. 2nd Mercosur Congress on Chemical Engineering, 4 nd Mercosur Congress on Process Systems Engineering, Enpromer, Costa Verde – Brasil, 2005.

[4] Gonzalez, E. B., C. L. Galeana, A. G. Villegas, J. Wu, AICHE Journal, Vol. 50, No. 10 Oct. 2004, p. 2552

[5] Meyers, R. A., “Handbook of petroleum Refining processes”, 10^{th} ed., McGraw-Hill, 2003.

[6] Ditman, J. G., van Hook, J. P. :ACS Meeting Atlanta, April 1981.

رفع خواص نفط خام شرقي بغداد الثقيل

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الخلاصة

معاملة نفط خام شرقي بغداد الثقيل بعمليات التقطير والاستخلاص. ان الغرض من التقطير هو لفصل المقطرات الخفيفة (المقاطع الخفيفة) والتي تمثل ٣٥% من النفط الخام الثقيل, وللحصول على المتبقي الجوي الثقيل. ان المتبقي الثقيل بثقل نوعي ٩ قد استخلص بالنافثا العراقية الخفيفة للحصول على متبقي منزوع الاسفلتينيات, حيث تم الاستخلاص بمدى درجة حرارة ٢٠-٧٥ مئوية, نسبة مذيب الى اللقيم ١:٥-١٥ (مل:غم) وزمن خلط ١٥ دقيقة.بشكل عام فان النتائج اظهرت بان الثقل النوعي للثقيل المنزوع الاسفلتينيات قد ازداد مرتين بالنسبة الى المتبقي الجوي الثقيل بينما انخفض المحتوى الكبريتي والمعادن ٢٠%و٥٠% على التوالي.تم خلط المتبقي منزوع الاسفلتينيات مع المقطرات الخفيفة المستحصلة من عملية التقطير بنسبة خلط مئوية ثابتة ٣٥% خفيف و لجميع الامزجة المحضرة. هذه الامزجة انتجت نفط خام مصنع بثقل نوعي بحدود ٣٠ ملائم للاستخدام في العمليات الهيدروكاربونية اللاحقة.