Upgrading of Basrah-Kirkuk Blend Crude Oil Through Mechanical-Acoustical Effect and (LABS) as Surfactant

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ABSTRACT

Non-Convential method has been used in this study for upgrading mixture of Basrah-Kirkuk crude oil through mechanical - acoustical effect using hydrodynamical coaxial turbo machine type Rotary Pulsation Apparatus (RPA) implementing ultra-high reliability in shearing rotor-stator operation.

The analysis of the crude oil after treatment in RPA showed that on increasing the rotation time from 5 to 10 min with rotor speed of 7610 rpm, leading to an increase in the total yield of light and intermediate petroleum cuts from 30 to 39 vol%, with an increase in API gravity from 29 to 40, reduce flash point from 75 to 54°C and reduce pour point from -10 to -32°C.

The results also showed that, adding LABS surfactant leads to a further increase in API gravity to 45, reduced flash point to 50°C, reduced pour point to -36 °C and increased yield of light and intermediate fraction to 40 vol% within 10 min and 7610 rpm.

Keywords: Non-Convential Upgrading, Rotary Pulsation Apparatus, Surfactant

تحسين خواص خليط نفط خام بصرة – كركوك بأستخدام التأثير الميكانيكي و الصوتي المشترك مع المادة الخافضة للشد السطحي (LABS)

الخلاصة

تمت دراسة تكسير النفط الخام ل(خليط بصرة- كركوك) بواسطة طريقة لاتقليدية تعتمد على التائير الميكانيكي – الصوتي المشترك باستخدام منظومة خلط توربينية خاصة (جهاز نابض دوار نفاث RPA) ذات مواصفات واجهاد قص شديد. فقد تمت الدراسة في زمن (5–10) دقيقة وبسرع متدرجة تصل الى (7610 دورة/دقيقة) بدون او مع اضافة مادة (الكيل بنزين صوديوم سلفونيت) كمادة خافضة للشد السطحي للنفط الخام. لقد تم تقييم انتاجية النفط الخام المعالج باستخدام طريقة التقطير(ASTM) القياسية ,فوجد إن النسبة الحجمية للقطفات الخفيفة ازداد من(

30%)إلى (39%) عند زيادة زمن وسرعة الدوران و التي بالنتيجة ادت إلى زيادة API من (29) إلى (40) وزيادة في نسبة القطفات الخفيفة والمتوسطة وخفض نقطة الوميض من (75°C) إلى (54°C) وكذلك خفض درجة الضباب والانسكاب من (10 °C−) إلى (32°C−) .بالإضافة إلى ذلك فان استخدام (LABS) كمادة خافضة للشد السطحي, ساعدت في تسهيل عملية معالجة النفط الخام بالمنظومة .والنتائج أظهرت ازدياد (API) إلى (45) و انخفضت نقطة الوميض إلى (50 °C) وكذلك نقطة الضباب والانسكاب انخفضت إلى (36 °C−) و نسبة القطفات الخفيفة والمتوسطة ازدادت إلى (40%).

الكلمات المرشدة:.تكسير النفط الخام, جهاز نابض دوار نفاث, مادة خافضة للشد السطحي

INTRODUCTION

The flexibility of upgrading as a process for refining petroleum has resulted in its phenomenal growth during the past years. Feedstock's that can be converted to lower boiling or more desirable products range from residue to naphtha. Products include such widely diverse material such as gasoline, kerosene, middle distillate, lubricating oil, fuel oil, and various chemicals.

One of the non-convential upgrading methods of heavy crude oil is a hydrodynamical coaxial turbo machine type rotary pulsation apparatus (RPA).

The performance of RPA is essentially a milling machine that physically grinds the oil through the modern stationary stator housing with a motor driven rotor, which is concentrically mounted inside the stator. The mating surfaces of the rotor and stator have special channeled grinding surface.

During the RPA operation, the oil passing through channel and exposed to higher hydrodynamic power; shearing and frictional forces; acceleration power and high frequency ultrasonic waves [1].

The fundamentals of dispersion mechanism along RPA occurs into two combined stages, mechanical and acoustical. The action of a mechanical agitation occurs in the clearance between rotor and stator. Both directions of the rotor have a number of teeth were uniformly distributed over the circumference of the rotor disc as well as the stator disc [2].

The RPA rotor is provided for simultaneous adjustment of the gap spaces of the inner and outer grinding zones, where radial oriented shape, and merge into an outer inclined grinding zone. Feeds to be ground is introduced into a central inlet position and is accelerated through the inner and outer zones by centrifugal forces generated by a pair of grinding members which rotate relative to one and other [3].

Between the rotors - stator interactions, the flow in RPA turbo-machines is unsteady and highly turbulent. [4]

The disruption with the RPA field involves hydraulic and mechanical shear as well as acoustical with high-energy ultrasonic pressure gradients generating cavitation. Because of the rotor turns at a very high rotational speed, the material is rapidly reduced in size by

a combination of extreme turbulence, cavitation and mechanical shearing occurring within the narrow gap between the rotor and the stator. [5]

Changing the physicochemical parameters of liquids in RPA including:

1. Mechanical action on particles of a heterogeneous medium (impact, shear, and pulverizing loads and contacts with working parts of RPA;
2. Hydrodynamic effect (large shear stresses in a liquid, developed turbulence, and pressure and velocity pulsations in liquid flow); and
3. Hydroacoustic effect on a liquid (pressure pulsations, heavy cavitation, shock waves, and nonlinear acoustic effects) [6].

The action of dynamic radial pressure pulsations in RPA plays a main role from elements side of the flowing area to the liquid system by cavitations and ultrasonic emission. The circumferential of the rotation of the rotor and the vibration of the stator ensures a deeper and effective treatment of the medium in the apparatus. In this stage, the final dispersion and size reduction of the dispersed particles occurs [7].

Under the cavitation conditions, two events may occur simultaneously, thermal scission of bonds of heavy oil according to rice mechanism of cracking, and the generation of hydrogen atom. These are essential for the upgrading of heavy molecule in heavy oil and other residua. Furthermore, the ultrasound can be applied in situ for generation of oil by reduction of viscosity [8].

Nowadays, additives as surfactants are widely used in extraction, desulfurization, and scale removal [9–10] because of their excellent solubility and catalytic properties in a wide temperature range.

Improvement of petroleum refining processes indexes for primary crude oil distillation and for catalytic and thermal cracking is achieved by pretreating the feed with surfactant additive that are blended into the feed at the optimal concentration.

Surfactant prevents the agglomeration of the asphaltenes through forming free radicals of lower molecular weight by bond cleavage under ultrasound. The free radical reactions could be terminated by recombination or disproportionation. The purpose of hydrogen radicals is to terminate the free-radical reactions after bond cleavage as well as to saturate the product. [11].

Surfactants significantly improve the efficiency of the distillation caused by a stabilization of liquid film so providing an increased interfacial area for mass transfer [12].

Under long-term vigorous cavitation, the C-C bonds are broken in the wax molecules, as a result of which the physicochemical parameters are altered (the molecular mass, pour point, etc.), and the properties of the petroleum derivatives (viscosity, density, flash point) are lowered [13]. After treatment, the paraffin molecules in crude oil are surrounded by a solvated layer in frontier, which makes reduce agglomerating possibility of high molecular weight paraffin, so the crude oil pour point and viscosity were reduced as the result [14].

EXPERIMENTAL WORK

Work was done on an experimental RPA as shown in figure (1), for upgrading blend of Basrah-Kirkuk crudes supplied by Daura refinery. The main properties are listed in Table (1).

The aim of this work is to investigate the effects of RPA treatment time and rotation speed in the presence and absence of linear alkyl benzene sulfonate (LABS) surfactant on percentage yield of light and intermediate fractions; namely gasoline, naphtha, kerosene, and gasoil; using ASTM standard distillation curve method (ASTM D86), NDJ-4 rotational viscometer, API gravity, Cleveland open-cup flash point analyzer (ASTM D92) and pour point (ASTM D97).

RESULTS AND DISCUSSION

API Gravity

The effect of RPA rotation speed, time and/or adding surfactant LABS on API gravity of crude oil is shown in figure (2). The API for untreated crude oil was 29, and after RPA treating increased with speed and time. The results show that API increased to 30 and 38 at 1614 rpm and 7610 rpm ,respectively within 5 min., also when increasing rotation time to 10 min, API increases to 32 for sample tested at 1614 rpm. It is clear from figure (2) that the maximum API obtained was 40 for sample without adding LABS at 7610 rpm and 10 min. The increase in API gravity was upgraded when adding LABS. The maximum API was 45 at 10 min., 7610 rpm.

Viscosity

The dynamic viscosity of the oil sample was measured at 30 ^{o}C. figure (3) showed the reduction in viscosity for crude oil upgraded at 5 and 10 min with various RPA rotation speeds. From figure, it can be shown that the reduction in viscosity increases with increasing rotation speed and time; where the dispersion and homogenizing process increase. The maximum reduction achieved was from 75 to 41 cp within 10 min and 7610 rpm.

The addition of LABS improves crude oil viscosity as shown in figure(4), from which the maximum reduction is found to be 34 cp with rotation speed 7610 rpm, compared with 41 cp for lighter sample tested at the same time and speed without LABS.

(ASTM) Distillation Curve

Data obtained by distillation of crude oil enable the estimation of the yield and quality of products.

Figures (5-6) refer to the ASTM distillation curves for crude oil samples before and after treatment with RPA within rotation time of 5 and 10 min. respectively. From figure (5) it can be seen that before RPA treatment the increasing in total volume distilled of light and intermediate fractions namely; gasoline (IBP-104°C), naphtha (104-157°C), kerosene (157-232°C) and gasoil (232-350°C); was 30 vol% but with speed 7610 rpm after rotation time 5, 10 min, the total volume distilled reach to 36 and 39 vol% respectively as shown in figure (6).

From Table (2), the yield of light and intermediate fraction increases for crude oil after treatment from 3.2 to 4.5 for naphtha, 11.5 to 14.1 for kerosene and from 14.7 to 19.8 for light gasoil for sample treated in RPA at 7610 rpm and 10 min.

Figure (7) shows the comparison in percentage yield for light and intermediate fraction for crude oil before and after treated with RPA at rotation time 5 to 10 min. from which it indicate that the percentage yield for light and intermediate fraction achieved with/without adding 2 gm/lit LABS as a surfactant for sample treated at 10 min and 7610 rpm is 40 vol% and 39 vol% respectively. However, as shown in figure (8), the maximum total volume distilled for sample treated in RPA at same operating conditions but with rotation time 5 min was 37 vol%.

Table (3) shows the relation of percentage yield with RPA rotation time and rotation speed and with or without addition of LABS. The data indicate that the maximum total percentage yield without adding LABS was to 39 vol%, compared to 40 vol% with addition LABS at the same condition ,10 min and 7610 rpm.

The percentage yield after RPA treatment increased from 3.2 to 4.8 for naphtha, 11.5 to 14.4 for kerosene and from 14.7 to 20.2 for light gasoil at 10 min and 7610 rpm with adding surfactant LABS.

Figure (9) shows the percentage yield for light and intermediate fraction within 5 to10 min with adding LABS. From which it's clear that the effect of addition of LABS as a surfactant in increasing yield of light and intermediate fraction, ie from 4.5 to 4.8 for naphtha, 14.1 to 14.4 for kerosene and from 19.8 to 20.2 for light gasoil within 10min and 7610 rpm.

Flash Point

Figure (11) shows the effect of rotation time and speed on flash point, with and without adding LABS. Figure (11) shows that the flash point decreased after treatment with RPA and the education increases with rotation time. The flash point decreased from 75°C to 57°C and 54 °C after treatment for 5 and 10 min respectively at same rotation speed of RPA. The addition of LABS increases the reduction in flash points at same rotation speed of RPA and rotation time. The flash point decreased to 52°C and 50°C within 5 and 10 min respectively.

Pour Point

Figure (12) shows the effect rotation time and RPA speed on pour points for crude oil before and after treatment in RPA with and without addition (LABS). It is clear from figure that the reduction in pour points after treatment with RPA increases with time , where the pour point for crude oil before upgrading was (-10°C) and after within 5 min was (-30°C) and pour point decreased at 10 min to(-32°C) at same rotation speed for (RPA). However, the addition of LABS increases at same rotation speed and time, the pour point was (-33°C) and (-36°C) within (5 to 10 min), respectively.

CONCLUSIONS

The following conclusions could be obtained

1. The density, specific gravity, viscosity, flash point and pour point for crude oil

decrease after treatment in RPA with increasing rotation time and rotation speed.

2. The effect of addition LABS as surfactant leads to enhancement of upgrading crude oil with RPA, where the results show that API gravity and the total percentage yield for light and intermediate fraction increase more than treatment without LABS at the same rotation time and rotation speed.
3. Flash point, pour point, viscosity decrease with the effect of LABS more than that without it in RPA at the same rotation time and rotation speed.
4. The addition of LABS, with increasing rotation time and speed leads to an increase of percentage yield of light and intermediate fraction, reduces flash point, reduces pour point.

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Table (1): Properties of Crude Oil Sample

Properties	Value
API	29
Density (gm/cm^3)	0.8807
Pour point(˚C)	-10
Flash point(˚C)	75
Viscosity (c p)	75

Table (2): Percentage Yield of fraction cuts for samples treated in RPA at Selected Rotation Time and Speeds in the Absence LABS Surfactant.

Rotation speed rpm	0	1614	3925	5267	7610	1614	3925	5267	7610
Temperature for fraction (C˚)	Percentage yield % of crude oil initially	Percentage yield % after rotation time 5 min				Percentage yield % after rotation time 10 min			
Gasoline (IBP-104)	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Naphtha (104-157)	3.2	3.5	3.7	4	4.2	3.7	4	4.3	4.5
Kerosene (157-232)	11.5	12	12.5	13	13.5	12.3	13	13.5	14.1
Light Gasoil (232-343)	14.7	15.9	16.7	17.4	17.7	16.4	17.4	18.1	19.8
Total	30	32	33.5	35	36	33	35	36.5	39

Table (3): Percentage Yield of fraction cuts for samples treated in RPA at Selected Rotation Time and Speeds in the Presence LABS Surfactant

Rotation speed rpm	0	1614	3925	5267	7610	1614	3925	5267	7610
Temperature for fraction	Percentage yield % of crude oil initially	Percentage yield % after rotation time 5 min				Percentage yield % after rotation time 10 min			
Gasoline (IBP-104 C°)	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Naphtha (104-157 C°)	3.2	3.6	3.9	4.2	4.4	3.9	4.2	4.5	4.8
Kerosene (157-232 C°)	11.5	12.4	12.9	13.3	13.6	12.6	13.5	14	14.4
Light Gasoil (232-343 C°)	14.7	16.4	17.1	17.9	18.4	16.9	18.2	18.9	20.2
Total	30	33	34.5	36	37	34	36.5	38	40

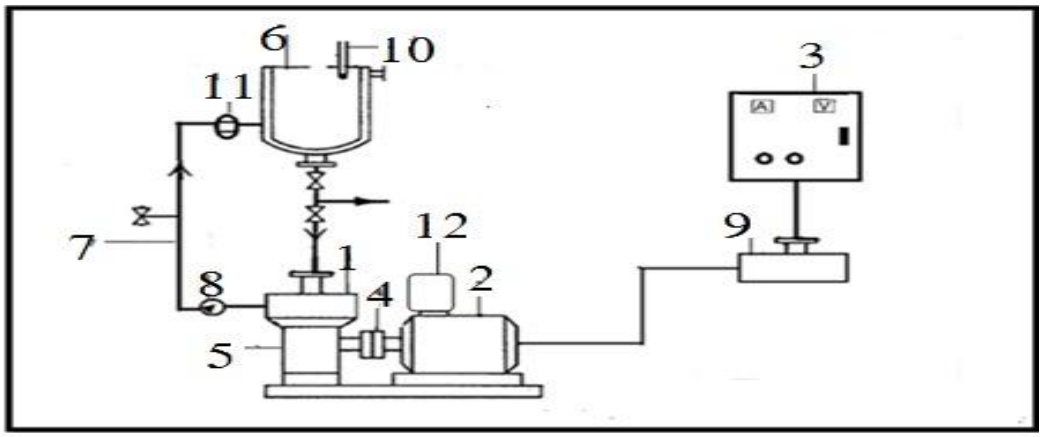

Figure (1): Schematic Diagram for the Equipment 1: RPA Elements (Rotor and Stator), 2: Electric Motor of Direct Current DC, 3: The Instrument Board and Regulators, 4: Shift to Achieve High Rotational Shift Speed, 5: Gearbox, 6: Tank, 7: U-Shape Tube, 8: Pressure Controller, 9: Rotational Speed Controller, 10: Thermometer, 11: Flow Meter, 12: Fan.

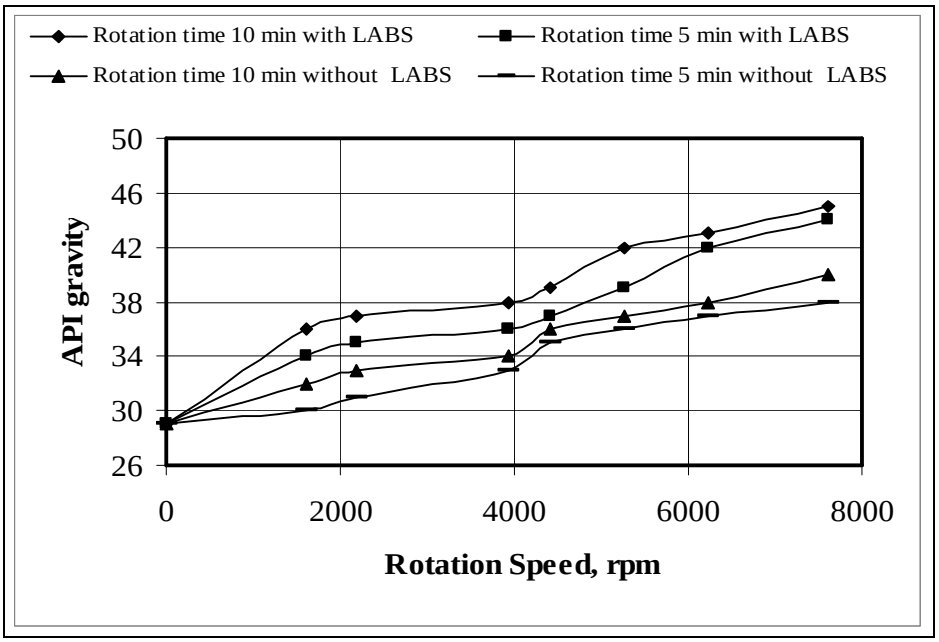

Figure (2): API Gravity of Crude Oil with Different RPA Rotation Speed of Rotation Time 5 min and 10 min in the Presence and Absence of LABS Surfactant

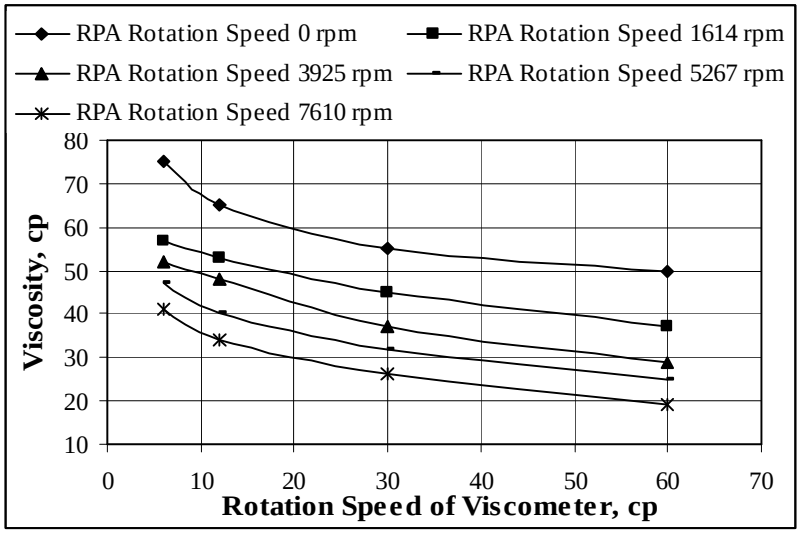

Figure (3): Viscosity of Crude Oil with Different Viscometer Rotation Speed of Different RPA Rotation Speeds in the Absence of LABS Surfactant

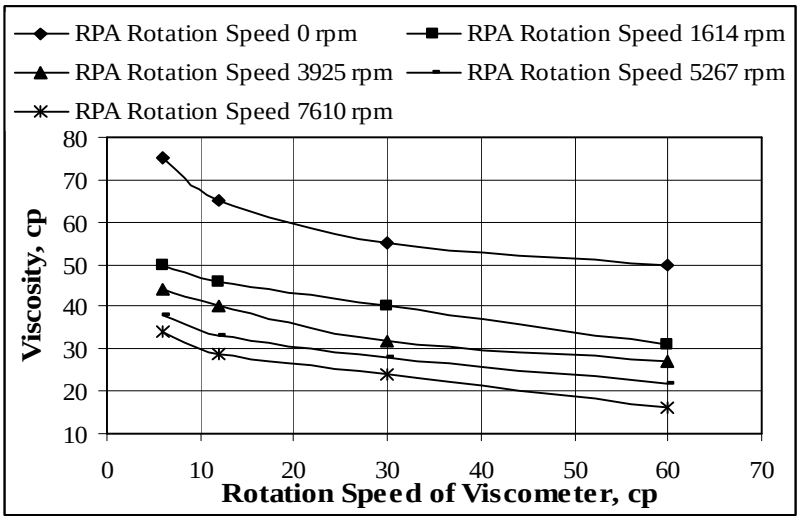

Figure (4): Viscosity of Crude Oil with Different Viscometer Rotation Speed of Different RPA Rotation Speeds In the Presence of LABS Surfactant

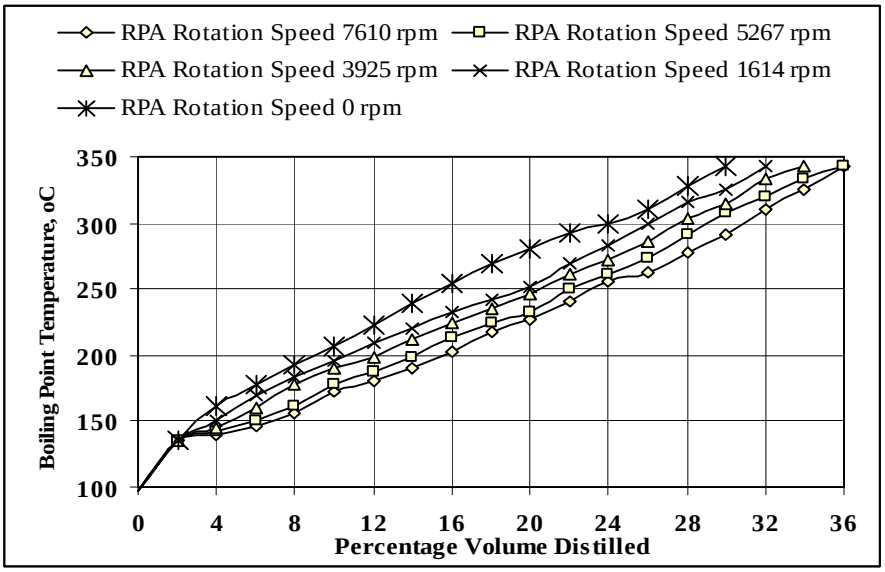

Figure (5): Boiling Point Temperature of Crude Oil with Different Percentage Volume Distilled of Different RPA Rotation Speeds Treated and Rotation Time 5 min in the Absence of LABS Surfactant

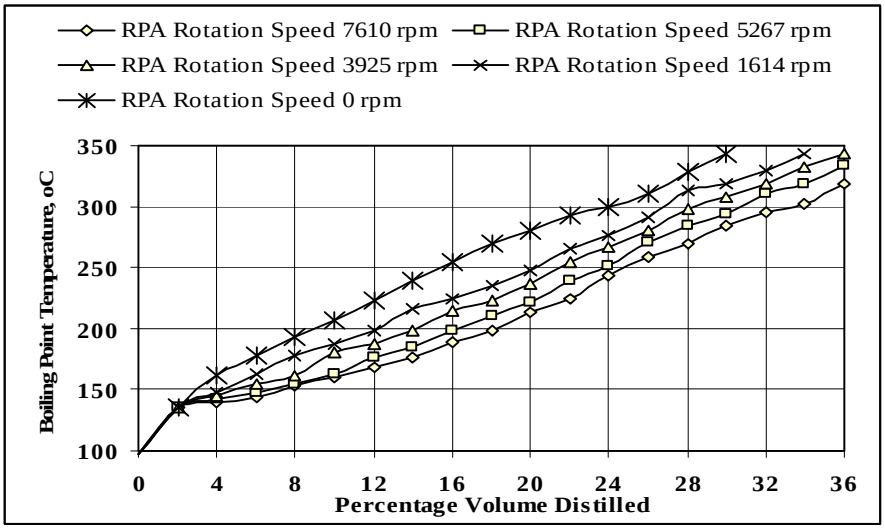

Figure (6): Boiling Point Temperature of Crude Oil with Different Percentage Volume Distilled of Different RPA Rotation Speeds Treated and Rotation Time 10 min in the Absence of LABS Surfactant

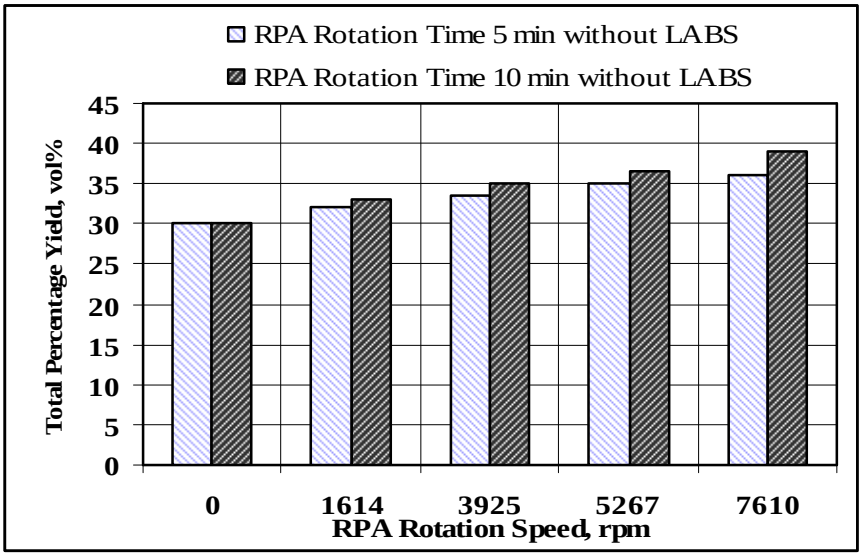

Figure (7): Comparison between Total Percentage Volume Yields for Crude Oil Treated on RPA at Rotation Time 5min, 10 min in the Absence of LABS Surfactant for Various Rotation Speeds

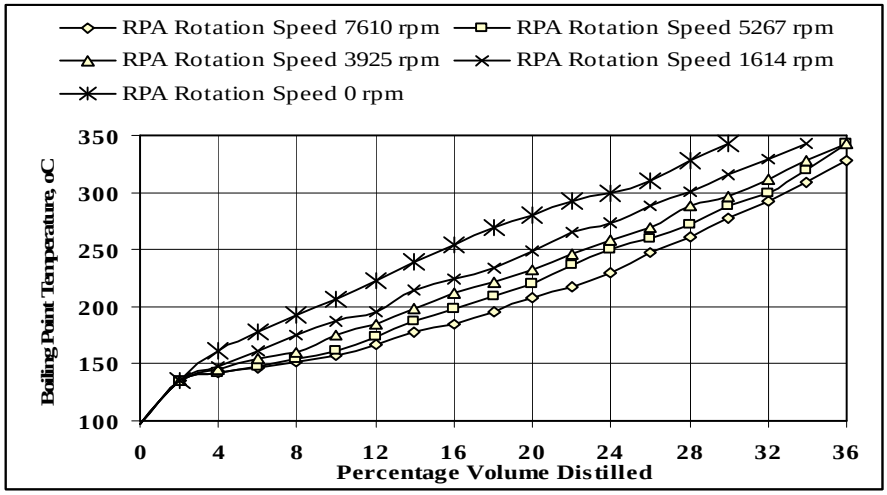

Figure (8): Boiling Point Temperature of Crude Oil with Different Percentage Volume Distilled of Different RPA Rotation Speeds Treated and Rotation Time 5 min in the Presence of LABS Surfactant.

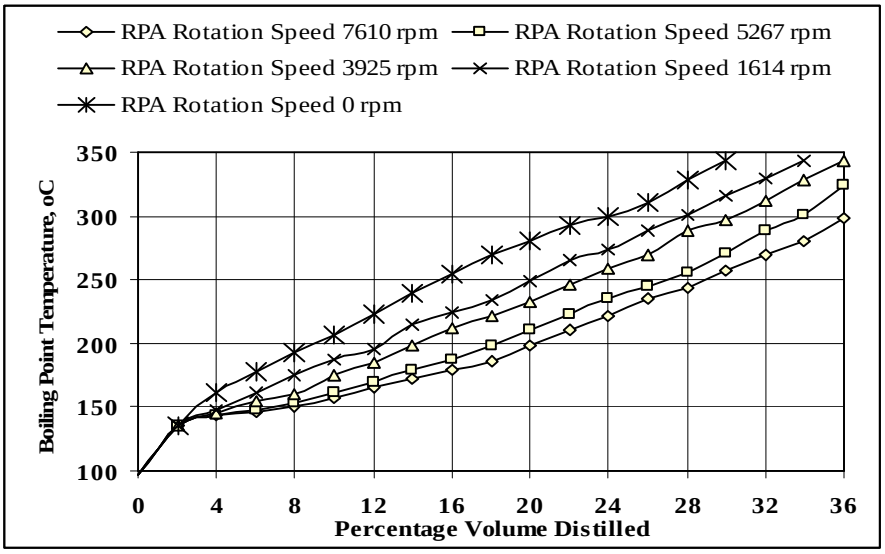

Figure (9): Boiling Point Temperature of Crude Oil with Different Percentage Volume Distilled of Different RPA Rotation Speeds Treated and Rotation Time 10 min in the Presence of LABS Surfactant

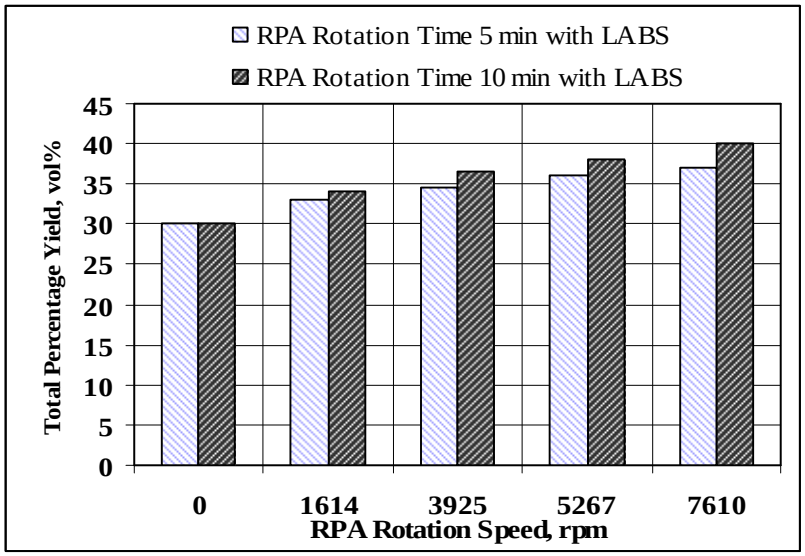

Figure (10): Comparison between Total Percentage Volume Yield for Crude Oil Treated on RPA at Rotation Time 5min, 10 min in the Presence of LABS Surfactant for Various Rotation Speeds

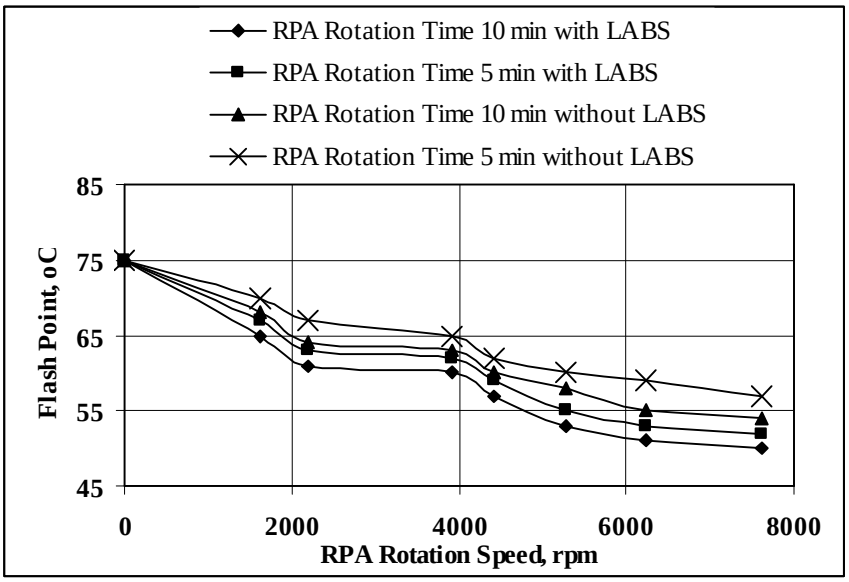

Figure (11): Effect of RPA Rotation Speed and Time on Flash Point for Crude Oil Treated in the Presence and Absence of LABS Surfactant

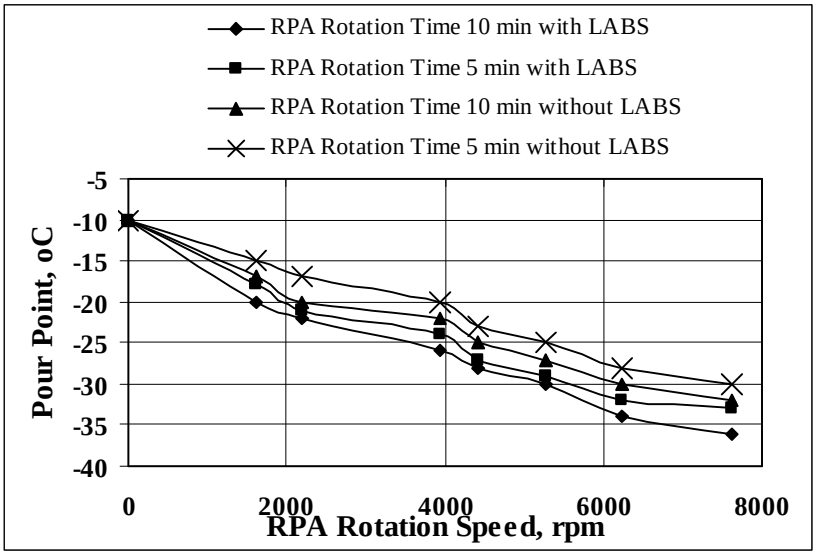

Figure (12): Effect of RPA Rotation Speed and Time on Pour Point for Crude Oil Treated in the Presence and Absenceof LABS Surfactant