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Crude Oil Desalting Using Multi-Surfactant Based on a Best Dosage, Solvent and Mixing Ratio

Ali Hussein Khalaf*
Mohammed Salah Rajab

North refinery company
Baiji
Salahaldeen
Iraq

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ABSTRACT

Crude oil desalting is the first processing step in a refinery. The objectives of crude desalting are the removal of salts, solids, and the formation of water from unrefined crude oil before the crude is introduced in the crude distillation unit of the refinery. The experimental work is divided into three schemes covering the effect of surfactant dosage, test different types of surfactants, and the effect of salt content on desalting efficiency. The results show that the crude oil desalting efficiency, increased with increasing surfactant quantity. The results indicate that desalting efficiency has lowered with increasing the salt content in crude oil. Also, the results show that the best solvent was toluene, and the best mixing ratio of solvent was 10 Vol. %.

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إزالة الاملاح من النفط الخام باستخدام كواسر متعددة للشد السطحي بالاعتماد على كمية الحقن، المذيب ونسبة الخلط

علي صالح خلف   محمد صالح رجب   شركة مصافي الشمال/ بيجي / صلاح الدين / العراق

الخلاصة

تعد ازالة الاملاح من النفط الخام(تحلية النفط)تعتبر اول خطوة للمعالجة في المصافي النفطية. تتمثل اهداف ازالة الاملاح من النفط الخام بإزالة الملح والمواد الصلبة والمياه المتشكلة في النفوط غير المكررة قبل ادخال النفط الخام الى وحدات التصفية والتكرير. ينقسم الجزء العملي الى ثلاث مخططات تغطي تأثير نسبة حقن مادة مخفف الشد السطحي، تجريب أنواع متعددة من مخفف الشد السطحي، وتأثير المحتوى الملحي في كفائة أزالة الأملاح. بينت النتائج أن كفائة أزالة الاملاح من النفط الخام تزداد بزيادة حقن مخفف الشد السطحي، علاوة على ذلك أظهرت النتائج أن كفائة ازالة الاملاح قد انخفضت مع زيادة المحتوى الملحي في النفط الخام، بينت النتائج ان افضل مذيب هو التلوين وافضل نسبة خلط حجمية للمذيب هي 10%.

* Corresponding Author : E-mail: aljobriali@gmail.com

1.Introduction

Desalting is a water-washing operation performed initially in the production field and thereafter at the refinery site for additional crude oil cleanup, where the salt and water content specifications are even more rigid because of their negative effect in the downstream processes due to scale formation, corrosion, and catalyst deactivation. Desalting involves.

Mixing heated crude oil with washing water, using a mixing valve or static mixers to ensure a proper contact between the crude oil and the water, and then passing it to a separating vessel, where a proper separation between the aqueous and organic phases is achieved [1].

Since emulsions can be formed in this process, there is a risk of water carryover in the organic phase. In order to overcome this problem chemical demulsifiers are added to promote the emulsion breaking. When this operation is performed at a refinery, an electric field across the settling vessel is applied to coalesce the polar salty water droplets, and, therefore, a decreasing in water and salt content is achieved [2].

As the crude oil is refined into useful fractions, the salts present therein tend to dissolve in steam under high temperatures, which are characteristic of the refining process. These interactions result in the production of highly corrosive hydrochloric acid. The presence of impurities like naphthenic acids and clays, further catalyze hydrolysis reactions, enhancing the release of the acid [3].

In addition to the salts of carbonate, sulfate, and organic acids can precipitate and deposit on the surface of equipment, such as heat exchangers and furnaces, resulting in cracking of furnace tube, fouling, scaling, and coking which leads to decrease the heat transfer rate [4].

After distillation, the majority of salts is left in residues and heavy stocks, which degrade the end-product such as petroleum coke and bitumen. It is clear that alkali and alkaline earth metals in crudes have stronger alkalinity, which leads to acidic catalyst deactivation, especially to catalytic cracking of heavy oil. On the other hand, silicon and aluminum oxide will react with the catalyst at higher temperature and thus produce a eutectic. Calcium in crude can accumulate on the surface of the catalyst during the catalyst regeneration of catalytic and hydrocracking [5].

2.Experimental Work

2.1.Experimental Apparatus

The main Experimental Apparatus has been set up and used at the laboratory of Baiji oil refinery which contain of high voltage power supply variable output (1-10 KV); electrodes flat plate made of stainless steel AISI 304 of 7 cm length and 5 cm width. The distance between electrodes is 5 cm; Beaker 500 ml; water bath made by Kohler; and wires high tension type. They are constructed as shown in Fig. 1.

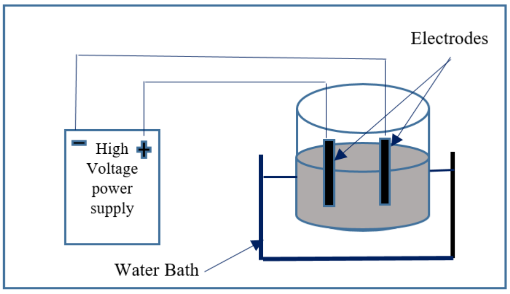

Fig. (1) Experimental apparatus setup

2.2.Other Supplementary Apparatus

Other apparatus used in the present work are salt content analyzer type Kohler (k-23050); electrical mixer with 1000 rpm trade market Huber; centrifugal separator type Kohler (k-61106); clock timer; different glass accessories.

2.3Materials

Crude Oil

The experimental work was carried out on samples of Kirkuk crude oil supplied to Baiji oil refineries. Crude oil samples for different salt concentration are used in the present work. Four samples of crude oil are used and some of the physical properties of these samples are listed in Table 1.

Table 1
Some of the physical properties of Kirkuk crude oil

Sample	Specific Gravity	API	Salt content ppm
A	0.847	35.56	7.9
B	0.85	35.0	16.2
C	0.86	33.0	24.3
D	0.866	32.3	35.0

Surfactants

Commercial demulsifies "surfactants" were used, with the Following of physical properties listed in Table 2.

Table 2
Surfactants Physical Properties

Surfactant	Code	Appearance	Specific Gravity @ 20 ^{0}	Vis 20 C^0 (cst)	Pour Point C^0
CHIMEC 2642	S_1	Brown Liq.	0.95	50	-30
NUR NC 3BK	S_2	Amber Liq.	0.935-0.95	27.5	-25
XBI	S_3	Brown Liq.	1.00	47	-36
Nalco 537 DA	S_4	Brown Liq.	0.855-0.863	42	-33

Other Chemicals

Other chemicals used in the present work are solvents to upgrade the performance of demulsifiers. Some of them are used for the evaluation of salt content and BS&W in crude oil. These chemicals and some of their properties are listed in Table 3.

Table 3
Some properties of solvents

Substance	Molecular weight	Specific Gravity @ 20 °C	Supplier	Purity %
Butanol	74.12	0.81	BIOSOLVE	99.9
Methanol	32.04	0.792	B.D.H	99.9
Ethanol	46.069	0.718	G.C.C	99.9
Toluene	44	0.866	G.C.C	99.0
Xylene	106.16	0.881	BIOSOLVE	99.0

3.Experimental Procedure

The experimental was carried out according to the following procedure:
Crude oil sample 250 ml was washed by fresh water with 4 Vol. % at room temperature. And then, adding the demulsifier "surfactant". Mixing the blend by electric mixer of 1000 rpm which was operated for 3 minutes to homogenize the mixture and providing a good contact between surfactant and crude oil and helping to dissolve free salt crystals in fresh water and to distribute the fresh water. The pH of the mixture was kept at 7 and the electrodes are inserted in the mixture vertically so as all the electrodes are covered by crude oil giving total surface area for each electrode of $70cm^2$.The mixture is heated by controlling constant temperature at 60 C^0 using water bath. It is well known that increasing the temperature is one of-the used methods in breaking emulsions. Many studies use temperature as high as 100 ºC [2,6].

However, 60 C^0 is used in the present work in order to reduce the evaporation of oil and water. High voltage power supply operated at electrical field strength of 1.2 kV/cm for 4 minutes. The electrical field strength is supplied to accelerate the coalescence. The mixture was let for 30 second to rest and allowing drops to coalescence. The electrodes were removed from the mixture and the mixture was separated using glass funnel for 3 minutes to settle water drops by gravity. After that the settled water was removed through a valve located below the glass funnel and getting a clear crude oil. Finally, the salt content in crude oil was tested.

4.Experimental Scheme

The experimental scheme was divided into three schemes:

First scheme: in this scheme, the effect of four type C commercial surfactants dosage (2-10 ppm) on desalting efficiency under the following operating conditions were utilized fresh water added 4 Vol.%, electrical field strength 2 KV/cm is employed and contact time 4 minutes. This scheme is performed on four types of crude oil A, B, C and D .

- **Second scheme:** depending on the results of the first scheme, the best surfactant dosage, and best surfactant performance was used to test the effect of the solvents (xylene, toluene, methanol, and butanol) on surfactants. In this scheme 75 Vol.% of surfactant was blended with 25 Vol.% of solvent.
- **Third scheme:** the best results in second scheme were used to test different mixing ratio of solvent with surfactant. The values of solvent mixing ratio were (0-30) Vol.%

5.Results and Discussions

5.1First scheme

In this scheme, the effect of surfactants dosage in the range 2-10 ppm was investigated at four types of crude oil. Four types of surfactants were used. The salt removal efficiency was tested under the following operating conditions: fresh water 4 Vol.%, electrical field strength 1.2 kV/cm, and contact time 4 minutes. The results were shown in Table 4 and graphically presented in Figs. 2-5. From these Figs. it has been observed that desalting efficiency was increased with increasing the surfactant dosage for each type of surfactants. It has also been noticed that the best dosage was 10 ppm and best surfactant performance was S_4. This is due to the increase of the molecules of surfactants that attack the film between the water drops and crude oil and cause a decrease of the thickness of the film and increase of coalesce of the water drops. The increase of surfactant dosage causes a decrease of the viscosity of emulsions and reduces the interfacial film stability that means increasing the demulsification rate. This results in good agreement with [5,7].

Moreover, From the figures it has been noticed that the desalting efficiency was decreased with increasing the salt content. This may be caused by the decrease of the surfactants solubility in aqueous phase and as result this increase the salinity.

Table 4
First scheme results

—	DESALTING EFFICIENCY AT 2 PPM				DESALTING EFFICIENCY AT 4 PPM				DESALTING EFFICIENCY AT 6 PPM				DESALTING EFFICIENCY AT 8 PPM			
	S_1	S_2	S_3	S_4	S_1	S_2	S_3	S_4	S_1	S_2	S_3	S_4	S_1	S_2	S_3	S_4
A	52.2	50.9	54.1	54.5	54.1	52.7	56.3	56.9	56.2	54.9	58.8	59.9	58.6	57.2	61.3	62
B	51.1	48.2	52.6	53.7	53.2	50.2	54.1	55.2	54.4	52.7	55.8	57.3	56.2	55.8	59.2	59.7
C	45	47.1	48.4	50.0	47.3	48.9	51	52.1	49	50.9	53	53.8	52.3	53.5	56	57.4
D	35.5	36.9	40	42	37.2	40	42.5	44.3	40.6	42.3	45.1	46.9	43.3	44.8	48.3	48.9

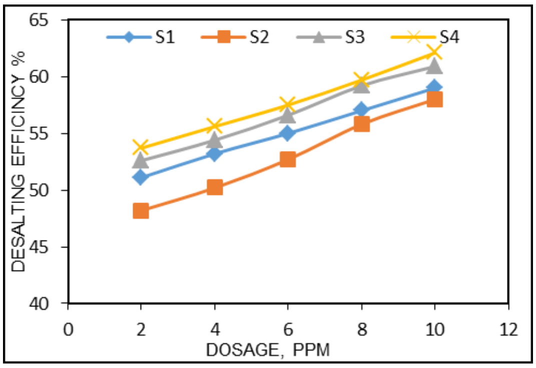

Fig.2. Effect of Surfactant Dosage on Desalting Efficiency at Crude Oil Type A

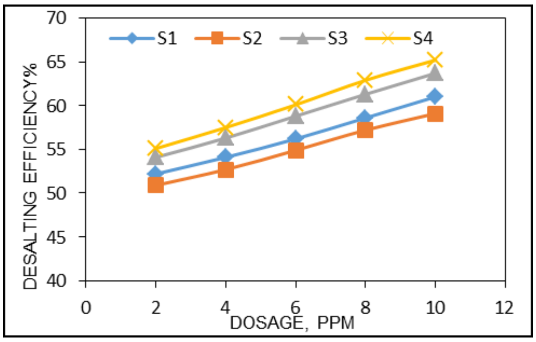

Fig. 3. Effect of Surfactant Dosage on Desalting Efficiency at Crude Oil Type B

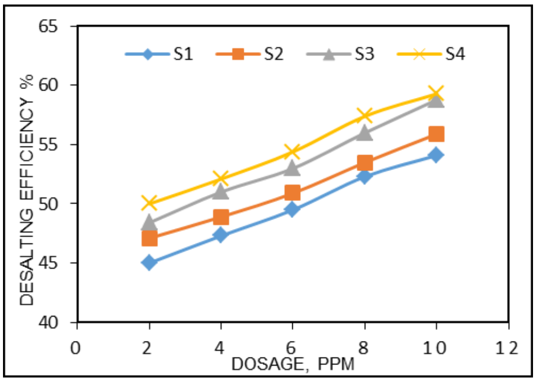

Fig.4. Effect of Surfactant Dosage on Desalting Efficiency at Crude Oil Type C

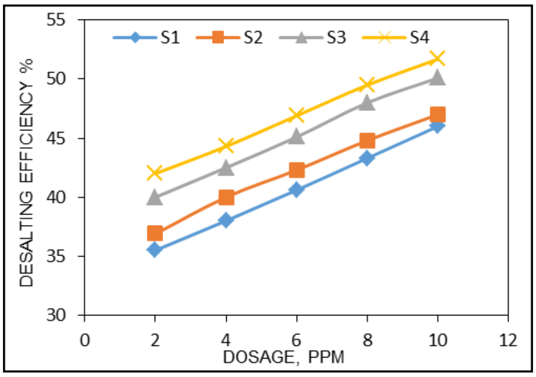

Fig.5. Effect of Surfactant Dosage on Desalting Efficiency at Crude Oil Type D

5.2.Second Scheme

According to the results from the first scheme the best surfactant dosage was 10 ppm, and the best surfactant performance was S_4. In this scheme the effect of solvents (xylene, toluene, methanol, and butanol) on surfactant of each type of crude oil was clarified and investigated. In this scheme 75 Vol.% of surfactant was blended with 25 Vol.% of solvent. The results are graphically presented in Fig. 6. From Fig. 6, it has been noticed that the performance of the surfactant and desalting efficiency have increased by blending the solvents, and the best solvent used in this scheme was toluene. This increase in desalting and dehydration efficiency is due to the enhancing of the solubility of the surfactant which is reflected in better dispersion of surfactant in the crude oil and consequently, in a better demulsification performance. This result is good agreement with result obtained by [1,8].

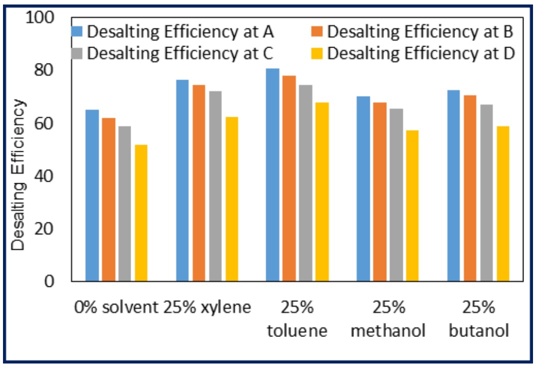

Fig. 6. Effect of Solvents on Surfactant Performance and Desalting Efficiency

5.3Third Scheme

According to the results of the second scheme the best solvent was toluene. In this scheme, the best mixing ratio of toluene has ranged to be (0, 5, 10, 15,25, and 30 Vol.% of toluene). It is performed on the crude oil type A, B, C, and D. The results in this scheme were graphically presented in Fig. 7. It has been noticed that increasing the mixing ratio of solvent has decreased the desalting efficiency. It was found that the best mixing ratio is 10 Vol.% toluene and 90% surfactant. This is due to the increase of the aspheltenes molecules adsorption on water droplets surface. This will lead to more emulsion stability through the formation of viscoelastic interracial films. Aspheltenes are soluble in light aromatic hydrocarbons (Toluene). The stabilization of emulsions by aspheltenes is strongly mediated by their interfacial activity, aggregation state and partitioning at the water-oil interface. Aspheltenes compounds stabilize the emulsion through steric interactions. This results in a good agreement with the results obtained by [9].

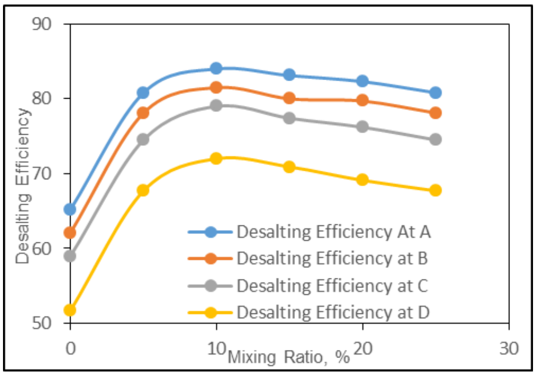

Fig. 7. Effect of mixing ratio of solvent on desalting efficiency

6.Conclusion

This research mainly concludes that desalting efficiency increased with the increasing of the surfactant dosage, and maximum desalting efficiency is obtained when surfactant dosage is 10 ppm. Based on the present facts desalting efficiency is decreased with the increase of the salt concentration in crude oil.

The performance of surfactant is improved when toluene solvent is used. The mixing ratio of toluene has an effect on desalting efficiency. A mixture of 10% toluene and 90% Nalco 537 DA gives best results.

Temperature increasing is a good factor for future study, since desalting efficiency increased by temperature increasing, for the present work temperature increasing is prevented due to laboratory work which leads to start evaporating the crude oil.

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