Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/petroleum-coal
Petroleum & Coal 57(5) 470-477, 2015

A CASE STUDY EVALUATING WATER AND SALTS REMOVAL CAPABILITIES OF DIFFERENT BRANDS OF COMMERCIALLY AVAILABLE DEMULSIFIERS FROM SLOPE OIL EMULSIONS

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Received July 31, 2015; Accepted October 12, 2015

Abstract

The best quality oil is characterized by the lowest Basis Sediment, Water contents (BS and W) and low API gravity values. The present article highlights the problems of crude oil emulsions and identification of the most effective combination of treatment methods to give the best quality oil through the comparative analysis of various brands of demulsifiers. About 70 different brands of commercially available demulsifiers were used for the cleaning of slope oil emulsions. Bottle test was used in the current study for the screening of demulsifiers. A combination of factors such as residence time, chemical requirement, heat effect *etc.* were used to determine the best treatment condition. Based on the result obtained in a single demulsifiers screening process, the demulsifiers from both groups (water soluble and oil soluble) were combined together as composite which resulted in formulation which was very efficient in treating aspaltenes emulsions. The experimental data of the comparative analysis indicated that demulsifiers of brand names 44479 and 669 were the best chemicals for separate treatment of both light and heavy crude emulsions as compared to the other demulsifiers. These demulsifier also caused the separation of 4.02 Ptb and 3.99Ptb of salts from emulsions respectively. A composite mixture of different demulsifiers also proved to be effective but best results were found in case of mixing of 44479, 669 and 5217 demulsifiers. In combination test when both types of oil (from C-Sump and D-Separator) were mixed at 60:40 ratios the demulsifier D 6193 caused 22% water drop from at 500 ppm injection rate and was suggested to be the most perfect treating chemical for such emulsions.

Key words: De-emulsifiers; Crude oil; Bottle test; Attock Oil Refinery; Emulsions.

1. Introduction

Emulsions can be encountered at numerous stages including drilling, production, transporttation and processing of crude oil. Three factors play an important role during emulsification process e.g. first in order to form an emulsion, it requires the availability of two immiscible liquids, secondly emulsion is formed by applying mechanical energy to generate droplets and third the presence of an agent possessing partial solubility in both phases which know as emulsifier [1-2]. The formation of emulsions creates a lot of problems in oil field industry. On one hand they might increase cost of production, transportation and on the other hand they accumulate in the refinery tank, causes pipeline corrosion and plugging, equipment failure, and also decrease throughputs [3-4]. Refineries around the world produce nearly ten million barrels of unusable oil each year. Slop oil is actually the product obtained during the refining of crude oil, containing water, salts and many impurities. The composition of slop oil is variable depending upon the type and location of crude oil.

All the slop oil can be upgraded and mixed with crude oil to be reprocessed in the refinery for other uses. Slop oil is either stored in oil lagoons or tanks, or it is incinerated. Incineration is very energy-intensive, because the mixture has a high proportion of water. The slop oil emulsions are also found which may be oil in water or water in oil emulsions [5-7]. For economic and operational purposes, it is necessary to remove water completely from the slope oil emulsion through demulsification process. By the way there is no single chemical de-emulsifier that is applicable to break all kind of crude oil emulsions [8]. The mechanism of destabilization by using demulsifier is quite complicated process. Fan *et al*., [6] have reported that chemical demulsification consist of the addition of small amount of breaking agent (usually1-1000 ppm) to enhance phase separation using surfactant, polymers, pure solvent or their mixture.

Generally the incumbent product takes quite longer time to drop salts and require more retention time to clear oil and water interface, hence resulting in emulsion build up due to poor demulsification quality. This causes de-salter vessel to fill up with emulsion, which is eventually carried over with effluent water, creating problems at the downstream processing [9-11]. In order to resolve this problem we intended to identify most suitable demulsifier/de-salter for the treatment of heavy crude oil. In the present work about 70 different types of commercially available of de-emulsifiers were used to break slope oil emulsions. Best demulsifiers were screened through bottle test procedures. Some of the variables that are initially examined in the test include the influence of de-emulsifier chemistry, de-emulsifier dosage, test length, temperature, and degree of agitation.

2. Materials and methods

2.1 Process description

The experimental work was conducted at Attock Oil Refinery laboratories Rawalpindi which is actively engaged in refining of crude oil and marketing of a wide range of petroleum pro-ducts. It has four distillation units namely, HBU-20,000, HBU-5,000 (both processing Light Sweet crude), Lummus-5,000 (Light Sour) and HCU-10,000 process heavy crude only. The flow sheet diagram of ARL is given in Fig. 1.

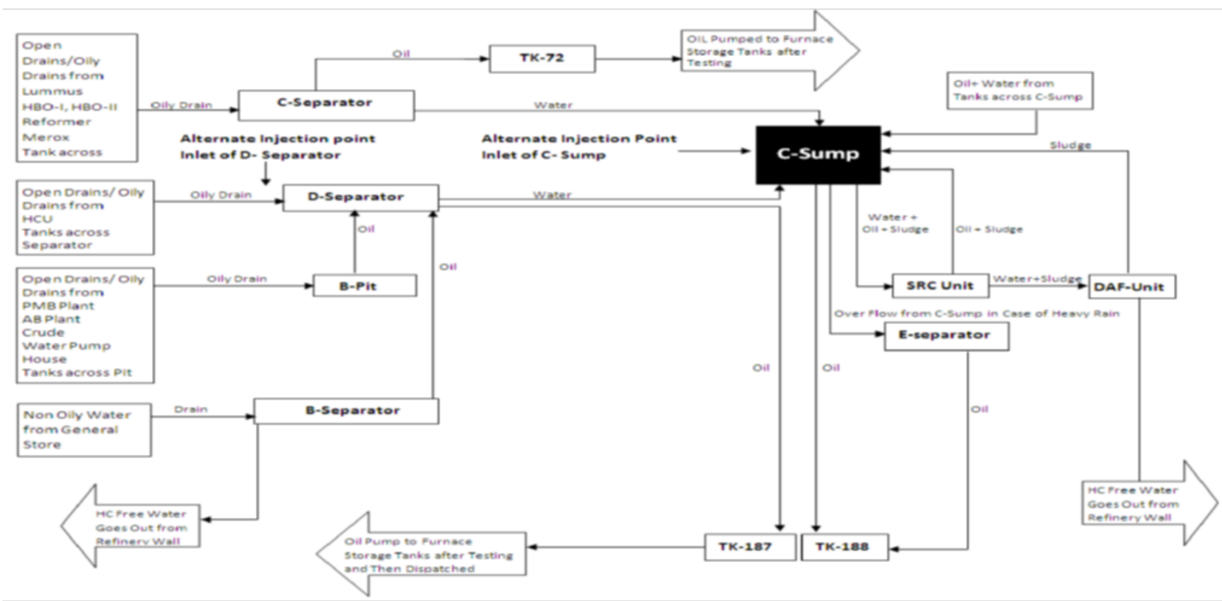

Figure 1 Flow sheet diagram of the Attock Oil Refinery

2.2 Collection of slope oil samples

Slop oil were collected from two main streams of the refinery i.e. C-Sump & D-Separator.

For combination tests the two samples were mixed in the ratio of 40 and 60. We also separately tested the BS & W of C-Sump and D-Separator. C-Sump had tight emulsion, containing traces of water while D-Separator had 15-30 % water drops. The crudes from D-Separator were paraffinic in nature and that of the C-Sump were asphaltic in nature.

Extreme care was taken to ensure that the collected samples were true representation of the slope oil and there was no contamination. Samples were collected in dirt free containers by opening the valves allowing crude gushing out for some time in order become homogenized in the flow line. The containers were then properly cocked to prevent any form of foreign body entering inside. The samples were then taken to the laboratory for experimentation and analysis. About 70 different types of commercially available demulsifiers were used for study but the following 17 brands of demulsifiers namely 5042, 978, 2277, 5217, 6042, 542, D4799, D8020, D5127, D6904, D9021, 3102, 7A297, 44479, 4184, 550, 669 gave satisfactory results.

2.3 Procedure for bottle test

Bottle test (ASTM D-3230-97) was applied for the screening of different brands of comercially available demulsifiers. The effect of temperatures, time and concentration was also investigated.

Centrifuge bottles were used for the screening test. About 10-30ml depending on the type of samples of the emulsion was taken into centrifuge bottles and a carefully determined quantity (in ppm) of the de-emulsifier was added to the sample. Each sample was then stirred vigorously for 1 minute for proper mixing and kept for 15 minutes in a water bath whose temperature was set at the test temperature. The bottles were then centrifuged at 1200 rpm for different residence times for phase separation. The volume of water expelled from the emulsion system as a function of separation time and temperature were measured. The same test was applied to a mixture of slope oil emulsions from both the sources (C-Sump and D-Separator). The observations made on the following factors during the bottle test were recorded:

a) Colour and appearance of the oil,
b) Clarity of the water,
c) Interfacial quality,
d) Preset temperature of 60 ºC,
e) Settling time,

The parameters used during the test are given below:

- Solution of intermediates: 10%
- Injection rate: 20ppm

We performed a reconfirmation tests with product having good desalting ability, such as with:

- Solution: 10%
- Injection rate: 30 ppm.
- Salts of raw crude: 18.89 Ptb.

During combination testing:

- Solution: 10%
- Injection rate:20%
- Salts of Raw crude: 18.89Ptb.
- Tested at 60:40 respectively.

2.4 Determination of salts contents of slope oil

The salts contents in the slope oil emulsions were measured using a calibrated conductivity meter.

3. Results and discussion

The determination of water content and basis sediments (W and BS) in oil is very important step to oil producing companies for the oil ready for shipment. Lease Automatic Custody Transfer (LACT) unit is employed by a number of companies for measurements of the water content in crude oil [12-13]. Though the automatic unit is good measuring method, still a precautionary method (Bottle test) is required to ensure measurements are in compliance with the preset minimum W and BS. This not only determine the effectiveness of the treating process but also determines the records of water content in advance at various points in the treatment plant [14].

The results given in table 1 are of the bottle tests carried out using different brands of commercially available demulsifiers at optimized temperature of 60ºC and at different intervals of time (30-60 minutes).

Table 1 Results of the bottle tests carried out using different brands of commercially available demulsifiers at temperature of 60ºC and at different intervals of time (1-60 minutes).

S. No	Brands of demulsifiers	Top Oil Layer		Interface		Quantity of Water Dropped
Intervals of Time		30 minutes	1 hour	30 minutes	1 hour	1 hour
1	5042	GP	GP	Loose	Loose	3mL hazy water drop
2	978	GP	GP	Loose	Loose	3mL hazy water drop
3	2277	GP	GP	Clear	V.Clear	5mL with clear water drop
4	5217	GP	ETO	Clear	V.Clear	5 mL excellent clear water drop
5	6042	GP	ETO	Clear	Clear	3mL hazy water drop
6	542	GP	GP	Loose	Clear	3mL hazy water drop
7	D4799	GP	GP	Loose	Loose	4mL hazy water drop
8	D8020	GP	GP	Loose	Clear	3mL hazy water drop
9	D5127	GP	GP	Loose	Clear	3mL hazy water drop
10	D6904	GP	GP	Loose	Clear	4mLclear water drop
11	D9021	GP	GP	Loose	Loose	3mL hazy water drop
12	3102	GP	GP	Clear	Clear	5mL hazy water drop
13	7A297	GP	ETO	Loose	Loose	2mL hazy water drop
14	44479	GP	ETO	Clear	Clear	5mL very clear water drop
15	4184	GP	GP	Loose	Loose	2mL water drop
16	550	GP	GP	Loose	V.Clear	3mL water drop
17	669	GP	ETO	Clear	V.Clear	5mL clear water drop
18	DIU	GP	ETO	Clear	Clear	5mL clear water drop

**DIU: Demulsifier In Use, ETO: Excellent Top Oil, GP: Good Polished*

Tables 2 and 3 shows the results of bottle tests carried out using most effective demulsifiers and their composites along with the concentration of salts removed in a single screening of c-sump or d-separator slope oil emulsions. The results in table 4 are of the bottle tests carried out using a mixture of emulsions from both the sources. Table 5 show the effect of concentration (dose rate) of the most effect demulsifier on its performance.

Heating of the emulsion is very important for reducing the viscosity and thus enhancing the gravity settling so that the water contained drop more freely from it. The experiments were performed at different temperatures but good results were obtained at 60ºC. Choice of the right demulsifier also plays an important role. Subsequent heating of the emulsion after demulsifier has been mixed increase its effectiveness as it reduces the viscosity and promote intimate contact of the chemical with the emulsion. Increase in retention time also enhances the gravity settling thereby promoting the separation of large quantity of water as can be seen from the table 1.Optimization of the retention time is an important step in every chemical process. In our study during single screening process one hour was the optimal time to remove maximum quantity of water. While in case of combination tests increasing the retention time up to two hours caused the separation of maximum quantity of water and thus two hours retention time was found to be the optimized time. From table 1 it is clear that holding the sample in centrifuge for 30 minutes and 1 hour time duration respectively resulted in the separation of the oil samples into three distinct layers; the top oil layer, the middle interface and the bottom water layer.

Table 2 Results of the bottle tests carried out using most effective demulsifiers at temperature of 60ºC and at 1 hour interval of time along with the concentration of salts removed

S.No	Brands of Demulsifiers	Top Oil Layer	Interface	Quantity of Water Dropped	Concentration of Salts Removed (Ptb)
1	3102	GP	Clear	5mL hazy water drop	4.14
2	7A297	GP	Loose	2mL water drop	4.79
3	44479	ETO	Clear	5mL clear water drop	4.02
4	4184	GP	Loose	2mL water drop	3.91
5	550	GP,	Clear	3 mL water drop	4.12
6	669	ETO	Clear	5 mL clear water drop	3.99
7	DIU	GP,	Clear	5 mL Clear water drop	4.11

(Ptb): Pounds per thousand barrel

Table 3 Results of the bottle tests carried out using composites of the most effective demul-sifiers at temperature 60ºC and at 1 hour interval of time along with the concentration of salts removed

S.No	Brands of Demulsifiers	Top Oil Layer	Interface	Quantity of Water Dropped	Concentration of Salts Removed (Ptb)
1	44479+5217	ETO	Clear	5mL clear water drop	2.8
2	44479+2277	GP,	Clear	5mL clear water drop	3.41
3	669+5217	GP,	Clear	5mL clear water drop	3.47
4	669+227	GP	Clear	4mL slight hazy water drop	3.59
5	44479+669+5217	ETO	Clear	excellent clear 5 mL water drop	3.10
6	DIU	GP,	Clear	clear 5 mL water drop	4.08

Table4 Results of the bottle tests carried out using a mixtures of slope oil emulsions from C-sump and D-separator with different brands of commercially available demulsifiers at temperature of 60ºC and at different intervals of time (30-120 minutes).

S.No	*Brands of Demulsifiers*	*Top Oil Layer*			*Interface*			*Quantity of Water Dropped*		
Intervals	of Time	30 minutes	1 hour	2 hour	30 minutes	1 hour	2 hour	30 minutes	1 hour	2 hour
1	D 6193	GP	GP	ETO	Tight	Loose	Excellent	8 mL	20 mL	22 mL
2	D 3013	GP	GP	ETO	Tight	Loose	Loose	3 mL	12 mL	18 mL
3	D 6004	GP	GP	ETO	Tight	Loose	Loose	4 mL	8 mL	15 mL
4	D 006	GP	GP	ETO	Tight	Loose	V.Loose	3 mL	6 mL	10 mL
5	D 2162	GP	GP	ETO	Tight	Loose	V.Loose	2 mL	5 mL	8 mL
6	D 2277	GP	GP	ETO	Loose	Loose	Excellent	8 mL	15 mL	20 mL
7	D 6411	GP	GP	ETO	Tight	Loose	V.Loose	5 mL	8 mL	10 mL
8	DQC 420	GP	GP	ETO	Tight	Loose	V.Loose	8 mL	10 mL	15 mL
9	D 70PG	GP	GP	ETO	Tight	Loose	V.Loose	7 mL	10 mL	13 mL
10	D 5042	GP	GP	ETO	Tight	Loose	V.Loose	10 mL	15 mL	17 mL
11	D 8020	GP	GP	ETO	Tight	Loose	V.Loose	7 mL	9 mL	10 mL
12	D 5127	GP	GP	ETO	Tight	Loose	V.Loose	4 mL	5 mL	8 mL
13	D 5217	Re-emulsified			Re-emulsified			Re-emulsified		
14	D 9021	GP	GP	ETO	Tight	Loose	V.Loose	4 mL	5 mL	8 mL

Treatment with a variety of demulsifiers has caused the separation of water from the slope oil. The data shows that increasing the time duration from 30 minutes to 1 hour the quantity of water dropped also increased. In most of the cases there is still partial contamination of the interfacial layer that is not very clear as indicated by the word 'Loose'. Also the quantity of water dropped was not reasonable and looked hazy. As compared to other demulsifiers which have caused the separation of relatively low quantity of water four brands of demulsifiers namely 2277, 5217, 44479 and 669 caused maximum separation of water (5ml) from the slope oil emulsions. Increasing the time of centrifugation up to 1 hour caused the interface to be very clear and with no oil contamination.

Table5 Effect of dosage rate on the performance of Demulsifier D 6193 using a mixtures of slope oil emulsions from C-sump and D-separator at temperature of 60ºC.

S.No	Dosage of the demulsifier added	Top oil	Interface	Water dropped in one hour
1	500 ppm	Excellent top oil	very clear water	18 mL very clear
2	400 ppm	Excellent top oil	very clear water	18 mL very clear
3	300 ppm	Good polished	clear water	16 mL slightly hazy water
4	200 ppm	Polished	slightly hazy water	15 mL hazy water
5	100 ppm	polished	ml hazy water	12 mL hazy water

Thus with these remarks the use of these demulsifiers makes better economic sense. The poor performance of some brands of demulsifiers could be as a result of the crude (emulsion) density and the poor compatibility of the chemical with other production chemicals such as corrosion inhibitors, water clarifiers (reverse emulsion breakers), antifoam *etc.*[15-16]. The performance of demulsifying chemicals is also affected by API gravity of the oil as low molecular weight resin used for treating 35º API oil may exhibit rapid water drop but the same chemical when used in treating an emulsion of 15º API oil may not cause rapid water drop. There is no universal demulsifier as the oil's type and composition understudy which contains the emulsion has more influence on how a certain chemical demulsifier will perform than those of the specific category of components included in the treating chemical. So in light of these observations, aforementioned brands of demulsifiers proved to be effective for breaking slope oil emulsions collected separately from the two sources. We did not confine our study to the separation of water from slope oil emulsions we also measured conductometrically the quantity of salts removed by using demulsifiers.

Binks [17] have studied that o/w droplets increase in size solubilizing more oil with increasing salt concentration while w/o droplets decrease in size. At low and high salt concentrations, the monolayer constrained to lie at the flat interface has a preferred tendency to curve and increase the tension. At intermediate concentrations, the tension is least because the flat monolayer has no tendency to curve. Tambe and Sharma [18] have studied the effect of inorganic salts such as sodium chloride and calcium chloride on emulsion stability for some pH values. They have found that the presence of salt has an adverse effect on emulsion stability and decrease as pH increases. From table-2 it is clear that demulsifiers namely 3102, 7A297, 44479, 4184, 550 and 669 removed maximum quantity of salts from slope oil emulsions. Maximum concentrations of salts (4.79 Ptb) followed by (4.14 Ptb), (4.12 Ptb), (4.02 Ptb) and (3.99Ptb) were removed by demulsifiers namely 7A297, 3102, 550, 44479 and 669 respectively. Thus demulsifiers namely 44479 and 669 were found to be the best in terms of separation of maximum quantity of water and salts as compared to other demulsifiers. The results in table-3 shows that using a composite after mixing different brands of demulsifiers have caused the separation of maximum quantity of water and slats thereby breaking slope oil emulsions. Maximum quantity of salts (3.59 Ptb) followed by 3.47Pt and 3.41 Ptb were removed by a composites of 669+227, 669+5217 and 44479+2277 respectively. A composite of three different demulsifiers i.e. 44479+669+5217 have caused effective separation of water from emulsions. When both types of slope oil emulsions from c-sump and d-separator were mixed in 60:40 ratio and the effect of demulsifiers were studied. The commercial brand namely D 6193 and D 2277 removed maximum quantity of water that is 22ml and 20 ml respectively so we can conclude that these two brand of demulsifiers were the best in terms of economy and times for dewatering and de salting of crude oil. Treatment of the mixture two types of oil with commercial brand D 6193 is more effective as compared to separate treatment. From table-5 it is clear that increasing the concentration of demulsifier up to 500ppm resulted in a more clear interface as indicated by Figure 2.So 500ppm was the optimal concentration for demulsificiation.

4. Conclusions

Bottle test is a quick and accurate technique for comparing the emulsion breaking capabilities of different demulsifiers. This method takes about five minutes per determination. From the present study it is clear that as compared to other brands of demulsifiers which caused the separation of relatively low quantity of water four brands of demulsifiers namely 2277, 5217, 44479 and 669 caused maximum separation of water (5ml) from the slope oil emulsions. Increasing the time of centrifugation up to 1 hour caused the interface to be very clear and with no oil contamination. The demulsifiers 44479 and 669 removed maximum quantity of both water and salts from slope oil emulsions. Thus these two were found to be the best demulsifiers for treating separately the slope oil emulsions from C-sump or D-separator. Composite mixtures of the demulsifiers also proved to be effective such as the composite of 44479+669+5217 caused maximum separation of water from slope oil emulsions. Mixing of heavy oil (D-separator) and light oil (C-sump) creates a strong emulsion which is very difficult to break. Treatment of the mixture with commercial brand D 6193 at 2 hour time duration gives excellent results. Thus treatment of the mixture of slope oil emulsions with demulsifier is suggested to be more effective as compared to the separate treatment of the slope oil emulsions.

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