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COMPARATIVE ANALYSIS OF THE EFFECT OF DEMULSIFIERS IN THE TREATMENT OF CRUDE OIL EMULSION

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ABSTRACT

This paper is aimed at highlighting the problems of crude oil emulsion and identification of the most effective combination of treatment method through the comparative analysis of various brands of demulsifiers that give the best quality oil. The best quality oil is oil with the lowest Basis sediment and water (BS and W) and low API gravity values. In the process of analysis (bottle test), a combination of factors were used to determine the best treatment condition. They are: Residence time, chemical requirement, heat effect etc. The result of the comparative analysis showed that V44O4 at a temperature of 60°C at a close rate of 50PPM was found most suitable.

Keywords: demulsifiers, emulsion, crude oil.

INTRODUCTION

Emulsions are among man-made commodities such as food, goods [8, 13], paints [16], agricultural sprays [7], asphalt preparations [15] and pharmaceuticals [3, 16]. Emulsions are also found as undesired byproducts of industrial processes, including crude oil production [23, 24] and liquid-liquid extraction operations [10]. Information on the microstructure and composition of an emulsion is relevant whether its making is sought or unwanted, because such information can be related to important properties of the dispersion such as its viscosity [17, 18 and 21], and its stability and phase separation [19, 26], and also to control standards. For example, the colour [14] and texture [11] of food emulsions are known to depend on the distribution of droplet sizes; crude oil streams with emulsified water content in excess of a given threshold are not suited for processing in refining equipment and transportation in pipelines [12]. The latter of these areas is the focus of this work. The intent of most characterization is to relate some property or group of properties back to the fluids behaviors in production or refining. Establishing a valid cause-and-effect relationship can lead to greater confidence when assessing the economic and technical risks associated with new projects or modifications to existing systems.

One of the main requirements in upstream production involves the dehydration of oil to meet pipeline water specifications. Numerous parameters have been cited as playing a role in emulsion stability [20]. Sorting through the influence of some of the parameters can be accomplished with the field bottle test. However, the bottle test does not prescribe to a set procedure that is maintained for all emulsion studies. There is no standard method for conducting a bottle test in the literature [20]; the bottle test is as much a method as a procedure. Some of the variables that are initially examined in the field include the influence of demulsifier chemistry, demulsifier dosage, test length, temperature, and degree of agitation. Experimental design can help in establishing a bottle test procedure that is representative of field conditions (i.e. one that ultimately procedures dry oil and accurately stimulates field conditions) [20].

This study will be carried out based on oil field emulsion samples from OPL 118 field situated in Niger Delta region, Nigeria. The average API of the crude from the field is 22º. Four producing wells from the four off-shore platforms in the OPL 118 fields will be selected and treated with different brands of demulsifiers in order to determine the optimum emulsion breakers. The time and temperature required for the complete breakage of the emulsion will also be determined.

Emulsion stabilizers (emulsifying agents) are so many in nature. They include: oil-wet solids such as sand, silt, shale particles, iron, and zinc etc. and similar materials. All of these stabilizers and many other have their peculiar reaction (strength) different types of treatments. This therefore necessitates the need for a study of the best chemical needed for a particular field or well.

MATERIALS AND METHODS

The content of water or basis sediments and water (BS and W) in oil ready for shipment is very important to oil producing companies. Many an oil producing company, conduct measurements of the water content in crude oil automatically by a lease automatic custody transfer (LACT) unit, which passes oil to the pipelines only if the water content present is below a preset maximum, i.e., minimum BS and W [5, 6]. Although, the automatic unit is a good measuring method, there is still a need for the use of a precautionary method (Bottle test) to ensure measurements are in compliance with the preset minimum BS and W. This is necessary in order to determine the effectiveness of the treating process. It also determines the records of water content in advance at various points in the treatment plant. Correct sample records for analysis are very important because a non representative sample can be very misleading.

Bottle test

The bottle test is used normally to help determine the type of demulsifier that will most effectively break emulsion from a given well, lease or field. The objective is basically to compare the rate of settling of water from oil in the presence of various demulsifiers. The bottle test analysis determines the ratio of treating compound to emulsion; that is, the smallest amount of proper chemical needed to satisfactorily break the volume of emulsion being produced. In another perspective, the field or base engineer could use results of bottle test to study the behavior of various emulsions and the chemicals used to treat them.

The following were put into consideration during the process of carrying out the bottle test:

i) It was ensured that the sample is a true representation of the emulsion to be treated.
ii) It was ensured that the sample is as fresh as possible.
iii) It was ensured that the same condition of agitation and heating as found on the lease was stimulated as much as possible.
iv) It was ensured that all tests performed were identical; since variation in size, samples, intensity of shaking, cleanliness and temperature of the test can influence results.

Sample collection for bottle tests

The samples were taken from the sample withdrawal point located upstream of chemical injection point. This was to ensure that the sample was a true representation of the crude from the well and that there was no contamination whatsoever that could affect the results. If the positioning of the sample point is after the chemical injection point, the chemical injection operation would be stopped for a reasonable length of time to make sure the chemicals already in the system were thoroughly washed away in the line before sample collection.

Big sample containers were used to collect enough crude for the test. To take samples from each point, the valve was opened and the crude allowed gushing out for some time in order for the flowing crude to become homogenized in the flow line. It was ensured that the container to be used in collecting the crude was free of dirt and that what so ever was collected in the bottle are purely the crude and its constituents.

The samples were gotten following strictly the procedure mentioned above. The crude collected was then properly cocked to prevent any form of foreign body from entering inside. The valve at the sample collection point was then firmly locked. The samples were then taken to the laboratory for experimentation and analysis. Samples were collected from 4 different fields. (Platforms) vis-a-viz:

i) Akam ii) Adanga iii) Ebughu iv) Mimbo

All the four platforms were used to carry out the bottle test using a particular well at each platform. The bottle test was carried out on:

i Well number- AK15HT (Akam field)
ii Well number- AD10SS (Adanga field)
iii Well number EB05HT (Ebughu field)
iv Well number MI02RS (Mimbo field).

Brands of chemicals used for the experiments were:

V4404-NALCO and EXXON OF USA
92LTM174-
PROCHINO EN/82/2- CECA Company of France.
DS964- Petrolite.

The analysis

Aim

To carryout bottle test using different brands of chemical demulsifiers on some crude samples at varying temperatures, different intervals of time and also considering the de-hydration rate and clarity of separated water.

Apparatus

i Sample containers.
ii Sample bottle graduated in 100ml scale with caps.
iii Water bath with a thermostatic control.
iv Different brand of demulsifiers. (V4404, 92LTM174, EN/82/2 and DS 964)
v Micro-pipette for taking the required chemicals.
vi A 50 ml graduated cylinder and thermo hydrometer.
vii Stop watch.

Analytical procedures

i An amount of crude was collected using the sample container (care was taken to ensure that crude was collected during flow).
ii The excess water present in the crude was free of water or at least reduced to a minimum in order to carry out the test effectively.
iii The sample bottles were labeled with names of the different chemical demulsifiers according to the number of chemicals used.
iv From the samples, the 4 test bottles were filled up to the 100ml mark and the 4 different demulsifiers were added to the bottles accordingly.
v The samples were shaken vigorously to homogenize.
vi The water bath temperature was set as indicated in the result Tables. The test bottles were kept in the bath followed by using a stop watch to record the corresponding time it took to reach the pre-set temperature.

RESULTS AND DISCUSSIONS

The results of the bottle tests carried out using four brand of demulsifier at temperature of 40ºC and 60 ºC and at different intervals of time (10-60 minutes) are summarized in Tables 1A, 1B, 2A, 2B, 3A, 3B, 4A and 4B. Other results like the colour or quality of separated water, appearance of the oil at the end of the experiment

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could not be quantified. Hence they do not appear on result Tables.

Tables 1A and 1B show the results for AKAM field, Tables 2A and 2B for ADANGA field, Tables 3A and 3B for Ebughu field and Tables 4A and 4B for MIMBO field.

The experiment was carried out at temperatures of 40ºC and 60ºC. The results of 40ºC were then tabulated as "A"s and those of 60ºC as "B"s for each platform.

The brands of demulsifiers used for the test were entered in separate column. Four brands were used. They are: V4404, 92LTM174, DS964, EN/82/2 and for each case the dose rate was maintained at 50 PPM of demulsifiers.

Table-1A. Results of bottle test analysis using demulsifiers at 40ºC and at different time interval using 50PPM demulsifiers.

AKAM FIELD

Time (min)	**Temperature** (ºC)	**Separated water in percentage**			
		V4404	**92LTM174**	**DS964**	**EN/82/2**
10	40	0.40	0.20	-	0.09
20	40	1.30	1.00	0.10	0.10
30	40	3.05	2.00	0.19	0.12
40	40	8.10	7.55	0.61	0.12
60	40	15.0	13.80	1.80	0.12

Table-1B. Results of bottle test analysis using different demulsifiers at 60ºC and at different time interval using 50PPM demulsifiers.

AKAM FIELD

Time (min)	**Temperature** (ºC)	**Separated water in percentage**			
		V4404	**92LTM174**	**DS964**	**EN/82/2**
10	60	0.8	0.6	0.01	0.10
20	60	1.50	1.46	0.14	0.13
30	60	3.06	2.75	0.21	0.30
40	60	6.10	5.50	0.8	0.32
60	60	16.20	14.98	2.0	0.40

Table-2A. Results of bottle test analysis using different demulsifiers at 40 ºC and at different time interval using 50PPM of demulsifiers.

ADANGA FIELD

Time (min)	**Temperature** (ºC)	**Separated water in percentage**			
		V4404	**92LTM174**	**DS964**	**EN/82/2**
10	40	0.50	0.40	0.01	0.06
20	40	1.78	1.56	0.30	0.13
30	40	3.81	2.71	0.40	0.10
40	40	9.68	6.20	0.40	0.10
60	40	15.48	13.62	1.90	0.10

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Table-2B. Results of bottle test analysis using different demulsifiers at 60 ºC and at different time interval using 50PPM demulsifiers.

ADANGA FIELD

Time (min)	**Temperature** (ºC)	**Separated water in percentage**			
		V4404	**92LTM174**	**DS964**	**EN/82/2**
10	60	0.90	0.80	0.01	0.10
20	60	1.78	1.65	0.16	0.15
30	60	3.50	3.14	0.34	0.80
40	60	11.54	7.62	1.90	0.80
60	60	18.00	16.77	3.89	0.90

Table-3A. Results of bottle test analysis using different demulsifiers at 40 ºC and at different time interval using 50PPM demulsifiers.

EBUGHU FIELD

Time (min)	**Temperature** (ºC)	**Separated water in percentage**			
		V4404	**92LTM174**	**DS964**	**EN/82/2**
10	40	0.30	0.20	Negligible.	0.06
20	40	1.00	0.10	0.01	0.09
30	40	2.62	1.79	0.14	0.10
40	40	10.30	4.21	0.71	0.10
60	40	14.00	10.76	1.52	0.10

Table-3B. Results of bottle test analysis using different demulsifiers at 60 ºC and at different time interval using 50PPM demulsifiers.

EBUGHU FIELD

Time (min)	**Temperature** (ºC)	**Separated water in percentage**			
		V4404	**92LTM174**	**DS964**	**EN/82/2**
10	60	1.02	1.00	0.01	0.10
20	60	2.16	2.06	0.16	0.15
30	60	3.89	3.46	0.30	0.11
40	60	12.60	15.28	2.10	0.91
60	60	21.00	18.72	4.00	1.78

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Table-4A. Results of bottle test analysis using different demulsifiers at 40 ºC and at different time interval using 50PPM demulsifiers.

MIMBO FIELD

Time (min)	**Temperature** (ºC)	**Separated water in percentage**			
		V4404	**92LTM174**	**DS964**	**EN/82/2**
10	40	0.02	0.05	-	0.10
20	40	0.10	1.00	-	0.15
30	40	1.01	1.30	0.05	0.11
40	40	1.80	2.05	0.01	0.85
60	40	2.68	3.10	0.01	1.78

Table-4B. Results of bottle test using different demulsifiers at 60 ºC and at different time interval using 50PPM demulsifiers.

MIMBO FIELD

Time (min)	**Temperature** (ºC)	**Separated water in percentage**			
		V4404	**92LTM174**	**DS964**	**EN/82/2**
10	60	0.18	0.20	-	-
20	60	0.78	0.95	0.04	0.06
30	60	2.00	2.60	0.08	0.10
40	60	4.30	5.55	0.10	0.72
60	60	7.58	9.50	0.12	1.30

From the above tables of results, a lot about emulsion treatment can be learnt. The importance of heat in emulsion treatment in combination with the right chemicals and gravity settling are directly observed. A closer look at Tables "A" and "B" reveal that the separated water in Tables "B" is higher than those from Tables "A" (experiments). This observation could be explained using density phenomena: when the crude is heated, its viscosity becomes reduced, there by making the crude less dense. As a consequence of this, the water contained in the emulsion can drop more freely from it. This fact explains the large quantity of water collected in the "B" Tables as compared to "A" Tables. This therefore show that application of heat to an emulsion after a demulsifier has been mixed with it increases the effectiveness of the chemicals, by reducing the viscosity of emulsion and also promoting intimate mixing of chemicals with emulsion. The reaction at the oil-water interface takes place at a more rapid rate at higher temperatures. The result in Table "A" and "B" clearly agrees to the fact mentioned above.

The importance of retention time was also noticed during the experiment and it can be seen from the results of Tables 1 to 4. (Comparing the volume of water separated after 10 minutes to those after 60 minutes for each of the cases). Even in cases where zero water was noticed, some water is separated with increase in retention time. Although increase in time allows for gravity settling, it is important to note the optimum time so that the time will not be wasted. The idea of increases in retention time having an effect or (in some cases) negative effect on the volume of water is observed. Taking as an example well number AK15HT (Akam field) in bottle test results, EN/82/2 show an increase in the separated water as the retention time increased from 10 to 20 minutes and from 20 to 30 minutes. The value of separated water remained constant at 0.12 % for 30 to 60 minutes at 40^{O}C. and finally 40-60 minutes. The Figure then remained constant i.e. 0.10 at 40ºC. Even in the 60 ºC case, the 20 minutes difference between 40-60 minutes for EN/82/2 could only achieve a 0.1% increase in volume of water separated. This result might be due to re-emulsification. Other cases of negative benefit of increases in retention time include: EBUGHU at 40ºC, 92LTM174 showed a deviation from the expected and showed a decrease in separated water between 10-20 minutes, a reduction from 0.2 to 0.1%. DS964 at 40 ºC MIMBO results, 30-40minutes retention interval showed a reduction from 0.05 to 0.01%.

From the above, emphasis must be placed on the optimum retention time and care should be taken to allow re-emulsification. Observation of the colour and clarity of separated water in each bottle during the test which are not reported here, but only observations are stated, show that the colour and clarity of the separated water in the EN/82/2 and DS964 treated samples was very cloudy and poor as compared to the other two. The poor performance of this two chemicals could be as a result of the crude

(Emulsion) density as explained and the poor compatibility of the chemical with other production chemicals such as corrosion inhibitors, water clarifiers (reverse emulsion breakers), antifoam etc. This is similar to the observations made by [3], [12] and [26]. A Table of production chemicals and their consumption is included in this result.

The average API of the crude from OPL 118 is 22º. This is considered to be in the range of medium to heavy crude. The performance of treating chemicals can also be influenced by the API gravity of the oil, for example, a 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. This explanation further emphasizes the fact that there can be no universal demulsifier since the type and composition of oil 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.

The observations made on the following factor during the bottle test are:

- Colour and appearance of the oil,
- clarity of the water,
- interfacial quality,
- preset temperature of 40 and 60 ºC set,
- settling time, and
- The BS and W contents.

Considering the observations above, the performance of the chemicals, DS964 and EN/82/2 exhibit light colouration of the crude without a clearly defined oil-water interface. The water clarity was also poor although in some cases, at increased temperature, a remarkable improvement was observed when compared to the other two chemicals. DS964 and En/82/2 were clearly not good for this case study.

V4404 and 92LTM174 showed the best result in MIMBO platform followed by V4404. The chemical V4404 exhibited the best performance on AKAM, ADANGA, EBUGHU and second best in MIMBO. Thus, on the average, V4404 is adjudged the best demulsifier considering the prevailing field conditions.

From the results obtained, an economic implication can be applied in selecting the best treatment conditions. It has already been mentioned that the main objective of oil producing companies is to consistently deliver the maximum volume of the highest API gravity oil to the pipelines and at the lowest possible cost. The bottle tests were conducted at uniform temperature for the four (4) chemical demulsifiers at uniform intervals of time using a uniform dose rate of 50PPM. Taking an average from the results, the chemicals V4404 and 92LTM174 were the best treatment chemicals. Their usage thus makes better economic sense.

CONCLUSIONS

It is an established fact that the nature of emulsions are subject to change and no treatment method can be generalized as best for this study, the following conclusions can be made; From the discussion of result, it was pointed out that all the chemical brands were subject to the same chemicals. When the performance of chemicals and the economic considerations are combined for the various brands and compared, V4404 was adjudged the best.

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