Enhancing Demulsification of Water-in-oil Emulsion by Eliminating Trace Value of Percentage Residual Water

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Authors’ contributions

This work was carried out in collaboration among all authors. Author JDI designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author JUA managed presentation of the analyses of the study, scrutinized the literature searches, citations and referencing. Author BRE vetted the final draft of the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

The elimination of residual free water and Basic Sediments (BS&W) after field demulsification process and characterization is being investigated with a diluent, to enhance field treatment for quality assurance and crude oil custody transfer. The American Standard for Testing Materials (ASTM) D 4007 is used as separation technique for three field emulsion samples from two Niger Delta basin oil facilities. After an initial bottle test, free water content in crude oil samples on arrival were 0.65%, 0.70% and 0.55% for samples A, B and C respectively. Tests and analysis were carried out at room temperature of 28°C and a water-bath temperature at 60°C. Maximum water separation efficiency of 91% was achieved at diluent and emulsion concentration ratio of 1:9 in first 60 minutes to 720 minutes. BS&W reduced from an average of 0.6% to 0.25%. Emulsion separation index (ESI) provided emulsion stability measurement of respective samples with a contrast between static-laboratory and field-dynamic conditions. From the study, sample B has API of 39 and ESI=40 while recording greater separation than in A and C crude oil samples. Hence, separation efficiency increased with the amount of xylene added and free water percentages reduced in top dry oil with significant changes in BS&W.

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Keywords: Stability; water separation efficiency; emulsion separation index; demulsification; custody transfer.

ABBREVIATIONS

API : American Petroleum Institute
ASTM : American Standard for Testing Materials
BS&W : Basic Sediments and Water
ESI : Emulsion separation Index
IFT : Interfacial tension
PPM : Parts per million
RCF : Relative centrifugal force
TPH : Total Petroleum Hydrocarbon
W/O : Water-in-Oil Emulsions

1. INTRODUCTION

Water-in-oil (w/o) emulsions are formed when crude oil is produced along with water. Under the production conditions, a proportion of this water is usually intimately dispersed throughout the crude oil as small droplets. In order to minimize the production problems related to crude oil emulsions and environmental concerns, petroleum operators need to prevent the formation of emulsion or breaking down of these emulsions. The emulsification of water in oil is normally difficult due to the immiscibility between these two liquid phases. However, shear mixing imposed on the fluids during production and the existence of natural surfactants in the petroleum’s composition contributes to formation of such emulsions [1,2]. Naturally occurring emulsifiers are concentrated in the higher-boiling polar fraction of the crude oil [3,4,5,6]. These include asphaltenes, resins and oil-soluble organic acids (e.g. naphthenic, carboxylic and bases) which are the main constituents of the interfacial films surrounding the water droplets that provide emulsion stability.

Emulsion is one of many problems directly associated with the petroleum industry, in both the oil field production and refinery environments. Whether these emulsions are created inadvertently as in the oil-field production area, or deliberately, as in refinery desalting operations, the economic necessity is to eliminate emulsions or maximize oil-water separation. Viscous crude oils tend to emulsify readily, creating problems that are related to increased emulsion viscosity, expected especially at higher water cuts in case of high inversion point. In addition to that, the temperature of crude oil varies widely along the flow line from the reservoir to production platform. So, crude oil has to flow for several hundred meters through pipelines at the subsea condition where the temperature could be as low as 4°C [7]. Hence, chemical demulsification is the most suitable method from both operational and economic point of view to break the crude oil emulsion. Among chemical agents, interfacial-active demulsifiers (which weaken the stabilizing films to enhance droplets coalescence) are preferred due to lower addition rates needed.

Water-in-oil emulsion is formed during the production of crude oil, which is often accompanied with water. The stability of the emulsion is ranging from a few minutes to years depending on the nature of the crude oil and to some extent the nature of water [8]. An equivalent volume of water accompanies the daily global production of some 60 million barrels of crude oil [9]. Under the production conditions, a proportion of this water can become intimately dispersed throughout the crude oil as small droplets. The natural petroleum emulsion resulting from the secondary production consists of crude oil as dispersion medium and brine as dispersed phase, normally stabilized by natural chemicals such as asphaltenes, resins, solid such as clays and waxes [8]. For asphaltenes in particular, the presence of hetero-atoms in the essentially aromatic structure imparts amphiphilic characteristics [1].

Emulsions are undesirable because the volume of dispersed water occupies space in the processing equipment and pipelines, thereby increasing operating and capital costs. Moreover, the characteristics and physical properties of oil change significantly upon emulsification. The density of emulsion can increase from 800 kg/m³ for the original oil to 1030 kg/m³ for the emulsion. The most significant change is observed in viscosity, which typically increases from a few mPa.s to about 1000 mPa.s [10,11].

This study is influenced by the effectiveness of emulsion breaking which is increasingly important in many practical applications as in the petroleum industry. It is imperative to develop this research to effectively demulsify emulsion by developing the technique from the study’s findings in order to eliminate water-in-oil emulsion at the storage stage even after initial demulsification. This means traceable amount of residual water and sediments under optimal
conditions can be either very significantly reduced possibly below the threshold value since very low BS&W and salt content is a standard requirement to reduce corrosion and salt deposition for flow assurance and custody transfer. In the industrial application of any demulsifier, the user can choose the proper balance between the increased cost of using a higher concentration, such as the application of chemical solvents like diluents in the study to save time and equipment capacity and/or a lower concentration and cost of demulsifier, which will result in longer separation time and probably a higher investment in the capacity of equipment.

2. MATERIALS AND METHODS

The ASTM guidelines of Practice D 4057 and Practice D 4177, Crude oil emulsion w/o samples were fetched from stock tank of three oil field Terminals/ flow stations denoted as fields A, B, and C. At the sampling points in the oil fields, crude oil was collected in such a way as to ensure only pure emulsion interface with turbulence and high fluid velocity in the pipe also ensured that the sample is homogenous and representative. The best sampling method was used by bleeding the sample line very slowly into the sample container. The idea is to minimize shear and reduce emulsification that may be caused by the sampling procedures. Samples were collected in a tightly sealed 1 litre plastic container each at various times of sampling. The experiment was scheduled to be carried out within 7 hours from the time of sampling to avoid staling of the crude oil.

2.1 Bottle Test for Emulsion Stability

100 ml each of emulsion samples was tested for their stability after 50 shaking and left to settle under gravity at room temperature 28°C for 12 hrs (720) minutes and the amount of water obtained in (ml) was the measure of the emulsion stability. Each of the crude oil samples were analysed differently. Chemical property variations such as; temperature, rate of chemical injection, nature of process terminal and processing capacity, as well as the residence time was evaluated. A water bath was set up and maintained at a temperature of 60°C to represent the average process temperature. This temperature was held constant to neglect the effect of temperature on the viscosity of the crude oil emulsion samples. Similarly, representative samples of the emulsion were treated for percentage free water separation of (BS&W), this time with a 100 ml volume of crude oil and identified the test conditions; Test bottles are filled with oil after mixing the samples. The contents of the bottles is required to be kept at room temperature of 28°C while 2 ml of xylene demulsifier was added to each bottle and shaken by hand (50-100 times). Observation and records were made and record for immediate changes in emulsion: colour, droplet size, and appearance of free water. The bottles were heated in an oven at a stable temperature of 60°C and allowed to settle, thus, recording the rate of water separation at periodic intervals of every 5 minutes. BS&W was determined for a second experiment but this time (without xylene) and recorded for oil quality under “Analysis of Treated Phase”. Generally good oil quality is <1% BS&W.

Note. During the samples collection from the bottom layer, the syringe needle is inserted well below the oil layer and residual oil is wiped off the needle before dispensing contents. Failure to do so may result in a false reading; hence, the container should be oil-free.

2.2 Centrifuge Test for Emulsion Stability

Using the ASTM D 4007, six test bottles of capacity 100 ml were labelled with A, B, and C, with suffixes 1 to 6 prepared to denote the times of the experiment rerun and each time with addition of different specific volumes of the diluent demulsifier. The suffix 1 denotes 0 ml of diluent, 2 is 2 ml, 3 is 4 ml, 4 is 6 ml, 5 is 8 ml, and 6 is 10 ml of diluent volume additions to the already measured emulsion samples each. (Emulsion + Xylene) mixtures were placed in a wooden product bottle shaker and agitated vigorously to homogenize the diluent with the continuous phase of the emulsion at room temperature 28°C. After the homogenization of the total volume of 100 ml emulsion and diluent mixed, measurements were done in glass beakers and recorded as percentage free water after centrifuge spins of 1,500 rpm for 15 minutes each for every rerun to investigate emulsion breaking enhancement with xylene. The volume of the water which settled at the bottom was observed and readings taken from the scale in the graduated tube at different times after undergoing spins in a centrifuge machine. The amount of water separation (BS&W) in percentage was calculated as separation efficiency from the water observed in the beaker. The dynamic viscosities reading of various combinations of the blend of demulsifier emulsion, and diluent were determined by a
Rotational Digital Viscometer with spindles and water thermostat to obtain readings. Total petroleum hydrocarbon (TPH) of each sample was determined by using TPH analyser at 60°C using 5 ml of Xylene. A sample each of the emulsion water droplets from the fields were taken and fed into this analyzer and the reading recorded in parts per million, ppm.

Specific gravities of w/o emulsion were determined by calibration and application of digital density meter. To obtain the API of the emulsion sample being analysed, at first the specific gravity of the oil emulsion had to be determined in g/cm$^3$ at 15.5°C.

$$\text{API} = \frac{14.5}{\text{SG}} - 131.5$$  \hspace{1cm} (1)

Where $\text{SG} = \text{Specific gravity}$.

For % free water separation efficiency $= \frac{V_2}{V_1} \times 100$  \hspace{1cm} (2)

Where:

$V_2 =$ water separated (ml)
$V_1 =$ emulsion tested (ml)

For change in viscosity: $\text{cP} \% = \frac{V_i - V_f}{V_i} \times 100$  \hspace{1cm} (3)

Where:

$\text{cP} \% = \text{change in viscosity}$
$V_i =$ viscosity of fresh emulsion
$V_f =$ viscosity of stored emulsion

These standard equations are applied to achieve important results where they cannot be directly obtained from the experiments. Hence, other relevant experiment data are used for derivation.

3. RESULTS AND DISCUSSION

3.1 Bottle Stability Test

For reference purpose, a bottle test was initially done at room temperature to determine percentage residual water and sediment after an efficient homogenization of 100 shakes for the emulsions analysed at 28°C with retention time of 12 hrs without adding diluent demulsifier. As the emulsions eventually stratified during the period, results were recorded as 0.65%, 0.7% and 0.55% respectively for 100 ml each of crude oil emulsion as shown in Appendix A. The crude oil and water were slowly separated into two phases of emulsion and water without heating.

The results from bottle test indicate the suitability of using the demulsifier in terms of quality and quantity of water separation in the oil fields crude oil sample.

The reasons for this behaviour is connected with the presence of special demulsifiers from oil field operations prior to sampling at field which was done using the ASTM practice D4057 method. Thus, water droplets level that was observed from graduated millilitre cylinder were recorded at the approximate duration for the first 60 minutes as shown in Appendix B and shown in Fig. 1. Final reading is done after 720 minutes, for which emulsion stabilized to achieve first results without introducing Xylene. Separation rates were compared when 2ml drops of diluent demulsifier were added to 100 ml each of crude oil emulsion samples and thoroughly mixed to achieve good homogeneity and left to settle for 720 minutes of retention time.

3.2 Separation Rate of Water

Observations and readings were taken after five minutes intervals of the first 60 minutes to represent retention time 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60 minutes as shown in Appendix B. For test without Xylene, there was small but significant amount of water droplet across the three crude oil emulsion samples only after 30 minutes interval; it increased from zero to 0.05, 0.08 and 0.03% respectively after the interval at 30 minutes and furthermore to 0.20%, 0.30% and 0.15% at the end of 60 minutes as compared to the test with addition of 2 ml of Xylene, which was 0.30%, 0.40% and 0.20% respectively. The test involving separation rate as shown in Fig. 1, showed little changes in separation between both runs, indicating that sample B emulsion with diluent was faster in coalescing for the first 60 and significantly separated with average time of 15 minutes. The samples without Xylene lagged slightly but reached free water separation greater than 0.10% for sample A at 50 minutes interval as compared to the test with Xylene and free water separation of up to 0.20%. It can be deduced that addition of more demulsifier reduces the percentage of free water in the oil phase.

To butress the findings from the test, Fig. 2 shows a relationship with emulsion separation and the diluent demulsifier volumes. Generally, it was observed that the coalescence of water to form droplets from the emulsion was a function of...
time and temperature. For an emulsion ratio of 98:2 ml to volume of diluent added, which was the minimum from the experiment's design. The rate required for water to drop out of the emulsion decreased. This is in comparison with the applied ASTM D 4007 method, where relative centrifugal force (rcf) was utilized and subsequent doses of Xylene added in even proportions. Hence, there is a quicker rate of separation when compared to the initial referenced values of the first bottle test, of with and without Xylene. Water droplet level reading was recorded using the eye-to-meniscus separation depicting the water phase from the surface of emulsion formed. The effect of adding Xylene on each crude oil sample was monitored as well as the rate of water separation. There is evidence of an enhancement of the separation process as shown in Appendix C.

![Graphs showing water separation over time with and without diluent](image)

**Fig. 1(a, b, c).** Rate of water separation profile; using xylene diluent demulsifier and without xylene against retention time for period of 60 minutes. $T=28^\circ C$
The maximum BS&W separation from crude oil emulsion for crude sample B was 0.7% of 100 ml crude emulsion determined from a centrifuge test with Xylene as diluent demulsifier. BS&W reduced in the crude oil emulsion as diluent was introduced and as the dose increased from 2 ml to 10 ml, the water separation in the crude oil emulsion improved from 0.2% to 0.65%. There was also a reduction of BS&W in the oil phase of crude oil samples A and C, from 0.2% and 0.1% respectively for 2 ml dose of Xylene to 0.6% and 0.6% respectively for 10 ml of demulsifier. After the addition of up to 4 ml of demulsifiers to each sample, the percentage value was 0.4% and 0.3% respectively. When the volume of diluent reached maximum dose of 10 ml there was a 0.05% difference in reference to the initial bottle test. Hence, crude sample A required the lowest amount of diluent demulsifier to achieve complete creaming due to interfacial relationship.

Fig. 2 shows the behaviour change in diluent concentration at 10 ml (maximum demulsifier dose) with rate of water droplet for emulsion samples collected for sample B to be faster than the others due to lower viscosity and lesser molecular weight of polar components encapsulated in the TPH content. Furthermore, from the experimental design, a diluent demulsifier addition test of between 2 ml and 10 ml of volume of Xylene, this time using a centrifuge machine for each sample which proved to be practically quicker and further increased the separation of BS&W in the emulsion composition as shown in Fig. 2. Since the centrifuge tube was filled with proportions other than a 50:50 ratio of sample and solvent, the results were read directly from the graduated centrifuge tube. Equation 4 was used to adjust for the incorrect mixture:

\[
\text{Sediment and water, } \% = \frac{S}{V} \times 100 \tag{4}
\]

Where:

- \( S \) = Volume of sediment and water found, (ml)
- \( V \) = Volume of oil tested, (ml).

The suffixes after the field samples denotations A, B, and C indicated the variations of diluent concentration added to the emulsion samples which read 1, 2, 3, 4, 5, and 6 for diluent concentrations (0, 2, 4, 6, 8, and 10 ml) respectively. From Fig. 2 (a, b & c), depending on the amount of diluent demulsifier mixed with the emulsion, there was a corresponding increase in the rate of water droplet size with time for all three crude emulsion samples. In addition, it was observed that Xylene as a diluent demulsifier converted solid films to mobile soap films which are weak and can be ruptured easily, hence, promoted coalescence. The emulsion stability for crude oils A, B and C were examined as a function of processing time and the diluent demulsifier applied. Stability was evaluated via the total BS&W separated and it was observed that the introduction of diluent has a creaming effect on BS&W of the crude oil emulsions.
of the aqueous phase or dynamic viscosity reduction as diluent increases, as shown in Appendix C.

### 3.3 Water Quality

The quality of water droplet from observation at the oil and water interface after separation for the three crude oil emulsions samples are shown in Table 1. For the three crude oil emulsion samples when diluent is not mixed with the emulsion, the water quality is dirty and the interface between the water droplet and oil phase is cloudy after 5 to 10 minutes.

As a homogenous mix of the diluent in emulsion increased, there was an improvement in the quality of water change from dirty to clean (i.e. no residual emulsion or oil in the water) and the interface between oil and water droplets changes from fairly clear to clean (i.e., there is a distinct difference between water phase and oil phase as shown in Fig. 3 (d)).

### 3.4 Emulsion Rheology

#### 3.4.1 Effect of diluent demulsifier volume on emulsion viscosity

Effect of diluent on viscosity of each sample is shown in Fig. 4. Xylene volumes added to the three crude oil emulsions, were measured in ‘ml’ of 2, 4, 6, 8, 10 to make a diluent demulsifier-emulsion volume ratio with a total of 100 ml. There is a reduction in viscosity when Xylene is introduced. Viscosity values showed a proportional decrease as the diluent demulsifier increased. The true effect of viscosity on the analysed emulsion is dynamic showing that temperature reduces the oil and interfacial viscosities and increases the droplet collision frequency with Xylene demulsifier. Thus, viscosity reductions are in turn a function of its initial viscosity as shown in Appendix C. The fresh emulsion viscosity values without diluent, decreased during the centrifuge test from an initial 16.8cP, 14.7cP and 17.3cP to 10.2cP, 9.0cP and 11.5cP respectively for 10 ml of diluent dose. The dynamic viscosity profile is shown in Fig. 4 where the viscosity changes in (cP) are plotted against diluent-demulsifier doses acting on each crude sample with shearing effect. From Fig. 4, both crude samples A and C viscosity was a function to the shearing effect compared to crude oil sample B. The type of crude oil can be a good reason for behaviour of crude oil, which in this case is Brent crude. Field crude sample B has lower viscosity and as a light crude oil compared with crude oil A and C which are light but more viscous. This is represented in the API of all three samples as shown in Appendix C. As the dispersed phase function (water) of dispersion is increased, the dispersion rheology changes significantly due to the

| Demulsifier volume (ml) | Water quality A | Water quality B | Water quality C |
|------------------------|-----------------|-----------------|-----------------|
| 0                      | Dirty           | Dirty           | Dirty           |
| 2                      | Dirty           | Dirty           | Dirty           |
| 4                      | Cloudy          | Fair            | Cloudy          |
| 6                      | Fair            | Clean           | Cloudy          |
| 8                      | Fair            | Clean           | Fair            |
| 10                     | Clean           | Clean           | Clean           |

Table 1. Relative residual water quality per volume of diluent for crude samples A, B and C

![Fig. 3. Water qualities improving with increased dose of diluent demulsifier](image)
frequency of droplet interaction. Therefore, as the results coalesces faster in high water cut, the number of the droplets in aggregates change with time. Since any change in the dependence of the viscosity on rate of shear could not be observed, the decrease in viscosity is likely to bring about the broadening of the droplet size distribution.

3.5 Total Petroleum Hydrocarbon

The TPH values were analysed twice for each sample, firstly without xylene and with 10 ml of demulsifier concentration which is shown in Appendix C that there was a reduction. Crude oil emulsion sample A has TPH value of 59.5 ppm for fresh field sample with no diluent, which eventually reduced to 46.5 ppm at diluent concentration of 10 ml, with a difference of 13.0 ppm in TPH. Crude emulsion B and C reduced in values of TPH from 53.4 ppm and 62.3 ppm with no diluent concentration to 38.4 ppm and 49.3 ppm with 10ml of diluent dose respectively. Hence, the difference in TPH between initial and final concentration for both samples are 15.0 ppm and 13.0 ppm respectively. This observation is believed to be a function of a significant volume of Xylene in the mixture at final run, coalescing with the aqueous phase. The TPH values of B and C both reduced as that of A, while sample C exhibited tightness making water droplets of that crude oil emulsion sample resist a quicker retention time for separation. In summary, there is a decrease in the value of TPH in field samples A, B and C between no diluent and 10 ml of diluent demulsifier dose as shown in Fig. 5. This also deduces that apart from tightness in sample C, diluent demulsifier action on the interfacial tension can reduce TPH values. The crude oil emulsions samples A, B and C have API values 38°, 39° and 35° respectively.

3.6 Effect of Asphaltene Content

Since asphaltene was recognized as the main chemical constituent of crude oil, which acted as a natural emulsifier causing the production of W/O emulsion in crude oil, it may be reasonable that, the presence of a significant content of asphaltene will result in much stable w/o emulsions. The sample has demulsifying water in crude oil emulsions containing about 3% asphaltene. However, in some particular cases, crude oil emulsions were formed by much less content of asphaltene. Evidently it may be shown that only smaller amounts of demulsifiers (2 ml to 10 ml dose) were sufficient to break such types of emulsions. The latter must be necessarily less stable than those formed by a great content of asphaltene. The break of emulsions took only an average of 15 minutes with the application of only 10 ml of demulsifiers.

![Fig. 4. Shear effect of diluent-demulsifier volumes on dynamic viscosities of each emulsion field samples. T= 60°C](image-url)
Fig. 5. Effect of diluent demulsifier on emulsion quality; for 0 ml and 10 ml of diluent volumes

Fig. 6. Changes in ESI calculated by volumetric method for 2 ml of diluent at 60 minutes interval. T=28°C

3.7 Emulsion Separation Index

The volumetric method was used to evaluate the emulsion separation index (ESI). The emulsion stability was evaluated by visually monitoring the growth of the clarified serum layer at the bottom of the emulsion with time.

The ESI was calculated using equation (5):

\[
ESI = \left[ 1 - \frac{V_w}{V_e} \right] \times 100
\]  \hspace{1cm} (5)

Where: \( V_w \) and \( V_e \) is volume of water separated and total volume of emulsion respectively. As shown in Fig. 6, the emulsion separation index decreases with increasing water cut. The ESI measures from 0 (indicating full separation, or no stability), to 100% (indicating no separation, or very stable).

A number of factors were observed from the study; free water content, shear rate, stress, and temperature effect were investigated and their influences on the emulsion samples stability and rheology of water-in-oil emulsions were assessed. Where there is high water cuts in the emulsions, results indicated slightly higher viscosities and lower stability with less...
demulsifier dose. Though at lower water cuts, the emulsions behaved as Newtonian fluids; where the power law index for Newtonian fluids is \((n=1)\) for fluid behaviour under shear stress as a function of strain rate.

Direct comparison was made in the first two tests for demulsifier dosage (i.e. dosage obtained in the laboratory with field observations) since laboratory experiments where made under static conditions and field usage observations are under dynamic conditions. However, the laboratory testing method has screened samples for relative emulsion tightness; evaluating the diluent demulsifier, Xylene and evaluating the effect of different variables on the emulsion samples resolution because all the conditions are kept constant except the variable under investigation e.g. Xylene concentration to BS&W. The observations also takes note that though sampling and experiments were carried out within 7hrs of sample collection, there is a definite effect of aging. The longer the emulsion samples stays in the laboratory before and during testing; the higher the demulsifier dosage required for emulsion breaking. Hence, ESI test is a requirement on fresh emulsion samples as expressed in equation (6):

\[
\text{ESI (I)} = \frac{\sum_{w}}{\sum_{n}} \times 100
\]  

Where;

\[
I = \text{Emulsion separation index} \\
\sum_{w} = \text{Summation of water separation at given demulsifier dosage/time as a percentage of BS&W} \\
\sum_{n} = \text{Summation of number of experiments}
\]

The emulsion separation index calculations for each sample provides a measure of the stability of emulsion field samples; viz sample B which showed highest rate of separation (less stability) amongst three field samples analysed in the laboratory.

The ESI calculated using Equation 6 with reference to Appendix B, were ESI was done for 2 ml of diluent addition for all three crude samples A, B and C within 7 hrs of sampling under static condition.

For field crude sample A:

\[
I = \frac{\sum_{w}}{\sum_{n}} = \frac{1.26}{0.3 \times 12} \times 100 = 35
\]

For field crude sample B:

\[
I = \frac{\sum_{w}}{\sum_{n}} = \frac{1.92}{0.4 \times 12} \times 100 = 40
\]

For field crude sample C:

\[
I = \frac{\sum_{w}}{\sum_{n}} = \frac{1.03}{0.2 \times 12} \times 100 = 42.9
\]

The results of calculation depicts that ESI varied with the retention time while each sample was loosening the vicious oil phase for movement of the water droplets. The ESI was calculated for all three samples with addition of 2 ml of diluent dose, resulting in the separation of water from oil hastily in contrast with no diluent addition. While this favours the coalescence process, the results of the calculation show that the ESI increased with the increase of storage/retention time.

4. CONCLUSION

From this study the following conclusions can be made:

(i) Quantity of Xylene required is directly proportional to the emulsion to be treated and separation efficiency increased with the amount of xylene added.

(ii) A maximum water separation efficiency of 91% was achieved at diluent and emulsion concentration ratio of 1: 9 in 60 minutes.

(iii) Free water percentage was reduced in all the crude oil samples. Hence, the already treated emulsion field samples have been enhanced beyond the initial trace value using a commercially available aromatic solvent for custody transfer.

(iv) The rate of demulsification and corresponding value of viscosity of oil was affected by temperature and this caused changes in the emulsion stability to either invert or break the emulsion.

(v) Since the solubility of the surfactant normally changes, the stability of emulsion also changes with dynamic viscosity. As diluent dose increased, the viscosity of crude oil sample A and C was a function to the shear rate compared to crude oil sample B.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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APPENDICES

APPENDIX A

Table A. Initial bottle test for crude emulsion stability at full 720 minutes without diluent addition

| Crude oil emulsion samples | EMULSION vol (ml) | Crude oil | Water level(ml) | BS&W |
|----------------------------|------------------|-----------|----------------|------|
| A                          | 100              | 99        | 0.65           | 0.65 |
| B                          | 100              | 99        | 0.70           | 0.70 |
| C                          | 100              | 99        | 0.55           | 0.55 |

APPENDIX B

Table B. Water separation rate with and without diluent analysis using bottle test readings of the first 60 minutes interval from 720 minutes

| Retention time(min) | A H2O separation (v2/v1)% | B H2O separation (v2/v1)% | C H2O separation (v2/v1)% | A H2O separation (v2/v1)% | B H2O separation (v2/v1)% | C H2O separation (v2/v1)% |
|---------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
|                     | With no diluent demulsifier | With no diluent demulsifier | With no diluent demulsifier | With 2 ml diluent demulsifier | With 2 ml diluent demulsifier | With 2 ml diluent demulsifier |
| 5                   | 0                          | 0                          | 0                          | 0                          | 0                          | 0                          |
| 10                  | 0.01                       | 0.01                       | 0.01                       | 0.01                       | 0.01                       | 0.01                       |
| 15                  | 0.01                       | 0.02                       | 0.01                       | 0.01                       | 0.03                       | 0.01                       |
| 20                  | 0.02                       | 0.03                       | 0.01                       | 0.03                       | 0.05                       | 0.03                       |
| 25                  | 0.03                       | 0.05                       | 0.02                       | 0.05                       | 0.08                       | 0.05                       |
| 30                  | 0.05                       | 0.05                       | 0.03                       | 0.08                       | 0.10                       | 0.05                       |
| 35                  | 0.05                       | 0.08                       | 0.05                       | 0.08                       | 0.15                       | 0.08                       |
| 40                  | 0.08                       | 0.10                       | 0.05                       | 0.10                       | 0.20                       | 0.10                       |
| 45                  | 0.08                       | 0.15                       | 0.08                       | 0.15                       | 0.25                       | 0.15                       |
| 50                  | 0.10                       | 0.20                       | 0.10                       | 0.20                       | 0.30                       | 0.15                       |
| 55                  | 0.15                       | 0.25                       | 0.15                       | 0.25                       | 0.35                       | 0.20                       |
| 60                  | 0.20                       | 0.30                       | 0.15                       | 0.30                       | 0.40                       | 0.20                       |
### APPENDIX C

Table C. Centrifuge analysis result of crude oil samples according to diluent volume

| Diluent vol. of xylene (ml) | Emulsion volume (ml) | Crude oil level (ml) | Water droplet level (ml) | BS&W % | Spec gravity of oil (g/m³) | API° | TPH (ppm) | Viscosity (cp) |
|---------------------------|----------------------|---------------------|-------------------------|--------|--------------------------|------|---------|-------------|
| 0 ml                      | 100                  |                     |                         | 0.836  | 38                       | 59.5 | 16.8    |              |
| 2 ml                      | 98                   | 98                  | 0.15                    | 0.2    |                          |      | 15.8    |              |
| 4 ml                      | 96                   | 96                  | 0.25                    | 0.3    |                          |      | 13.3    |              |
| 6 ml                      | 94                   | 94                  | 0.40                    | 0.4    |                          |      | 12.5    |              |
| 8 ml                      | 92                   | 92                  | 0.40                    | 0.4    |                          |      | 12.1    |              |
| 10 ml                     | 90                   | 89                  | 0.55                    | 0.6    |                          | 46.5 | 10.2    |              |
| 0 ml                      | 100                  |                     |                         | 0.828  | 39                       | 53.4 | 14.7    |              |
| 2 ml                      | 98                   | 98                  | 0.20                    | 0.2    |                          |      | 13.1    |              |
| 4 ml                      | 96                   | 96                  | 0.35                    | 0.4    |                          |      | 12.8    |              |
| 6 ml                      | 94                   | 93                  | 0.55                    | 0.6    |                          |      | 11.3    |              |
| 8 ml                      | 92                   | 91                  | 0.65                    | 0.7    |                          |      | 9.5     |              |
| 10 ml                     | 90                   | 89                  | 0.65                    | 0.7    |                          | 38.4 | 9.0     |              |
| 0 ml                      | 100                  |                     |                         | 0.849  | 35                       | 62.3 | 17.3    |              |
| 2 ml                      | 98                   | 98                  | 0.10                    | 0.1    |                          |      | 13.2    |              |
| 4 ml                      | 96                   | 96                  | 0.25                    | 0.3    |                          |      | 12.8    |              |
| 6 ml                      | 94                   | 94                  | 0.30                    | 0.3    |                          |      | 12.1    |              |
| 8 ml                      | 92                   | 92                  | 0.40                    | 0.4    |                          |      | 11.9    |              |
| 10 ml                     | 90                   | 89                  | 0.55                    | 0.6    |                          | 49.3 | 11.5    |              |

Emulsion separation data after centrifuge separation (ASTM D4007); T=60°C

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