COMPARISON OF IMPORTED AND LOCALLY MADE DEMULSIFIERS ON ESCRAVOS CRUDE OIL EMULSION

OLAYEBI, O.O.
Department of Chemical Engineering, Federal University of Petroleum Resources, Effurun, Nigeria

ABSTRACT

Emulsion of oil and water is one of many problems encountered in the petroleum industry, in both oil-field production and refinery operations. It is important to develop the demulsifier formulation to solve the emulsion problems. This work focused on a comparison of the effectiveness of both the imported and locally made demulsifiers. This test was carried out using the bottle test and the Basic Sediment and Water (BS&W) test which is based on the use of centrifuge at various concentrations and temperatures. The effectiveness of the demulsifiers were evaluated by measuring the water and oil levels. Other tests carried out include, the determination of salt content, and total hydrocarbon content of the effluent after water separation. Test analysis showed that the water separation efficiency increased with time for both the imported (D2005 and PT) and the locally made (Daf360) demulsifiers with a maximum separation obtained after 30 minutes. Maximum separation efficiency of 18% was obtained at a dosage of 20ppm for Daf360. It was observed that the water separation efficiency increased with temperature with a maximum obtained at 65 ^{0}C and with time. The maximum amount of water removed was 18%, 10% and 2% respectively for Daf360, D2005 and PT. It was also observed that water separation efficiency increased with decreasing salt content for Daf360 sample. The salt content was 9.6 Lbs/1000bbl compared to a content of 26.8 Lbs/1000bbl for D2005. The total hydrocarbon content for the sample treated with Daf360 was 127.89mg/l while that treated with D2005 was 80.82mg/l and that treated with PT was 84.35mg/l. The locally made demulsifier, Daf360 gave very promising results hence, there are prospects for the use of the locally made demulsifier which economically may be worthwhile on the long run due to foreign exchange savings.

Keywords: Asphaltenes, Emulsion, Oil Phase, Water Content
Correspondence: olayebi.oluwafemi@fupre.edu.ng

INTRODUCTION

During the production of crude oil, water which is known as emulsion is produced together with the oil in the form of oil and water emulsion [1]. The dispersed droplets are known as the internal phase. The liquid surrounding the dispersed droplets is the external or continuous phase. The emulsifying agent separates the dispersed droplets from the continuous phase [2]. The interfacial active agents in the crude oil are asphaltenes, resins and naphthenic acid which accumulate at the water-oil interface preventing separation of the droplets.

Among these components, asphaltenes are believed to be the major causes of stabilizing the emulsion. This is because they tend to adsorb at water-in-oil interfaces to form a rigid film surrounding the water droplets and protect the interfacial film from rupturing during droplet-droplet collisions. Consequently, the formation of particularly stable water-in-oil emulsion is facilitated [3]. Demulsifiers are usually formulated such that they can be effective at shorter separation times and smaller dosages [4].

Depending on the nature of the crude oil the stability of the emulsion ranges from a few minutes to years [5]. Emulsions are stabilized by the presence of a film between dispersed droplets and the continuous phase and the density of emulsions can increase to $1030\ kg/m^3$ with the most significant change being the viscosity, which can increase from a few mPa·sec or less to about 1000 mPa·sec [6]. Thus, an effective and efficient demulsifier is needed to separate the oil and water. The treatment of water-in-crude oil emulsions involves the application of mechanical, thermal, electrical, and chemical processes [7], and the best quality oil is oil with the lowest Basis sediment and water (BS and W) and API gravity values.

Classification of petroleum is based on different criteria which include, viscosity, density (specific gravity or API gravity), pH, surface tension and interfacial tension [8]. Crude oil can be divided into four major fractions which are: saturates (including waxes), aromatics, resins and asphaltenes. The four divisions are referred to as SARA fractionation due to their polarity and solubility in the solvent.

Asphaltenes have no definite melting point but decompose when the temperature exceeds (300-400) °C. Many researchers have shown that changes in pressure, temperature and oil composition can cause asphaltene precipitation [8]. Chemically, asphaltenes represent the pentane or hexane insoluble portion of the oil [9]. Resins are black or dark brown semi solid, have a specific gravity near unity, molar mass ranging from 500 to 2000 g/gmol and are very adhesive materials. The content of resin in crude oils ranges from (2- 40) wt% and usually higher than asphaltenes in terms of composition [10].

In the petroleum industry the usual emulsions encountered are water droplets dispersed in the oil phase and termed as water-in-oil emulsion (W/O), conversely, if the oil is the dispersed phase, it is termed oil-in-water (O/W) emulsion. In addition to the usual emulsion types, multiple emulsions for instance, water droplets dispersed in oil droplets that are in turn dispersed in a continuous water phase (W/O/W) can occur. Figure 1 shows a pictorial of three out of the various simple kinds of this emulsion [11].

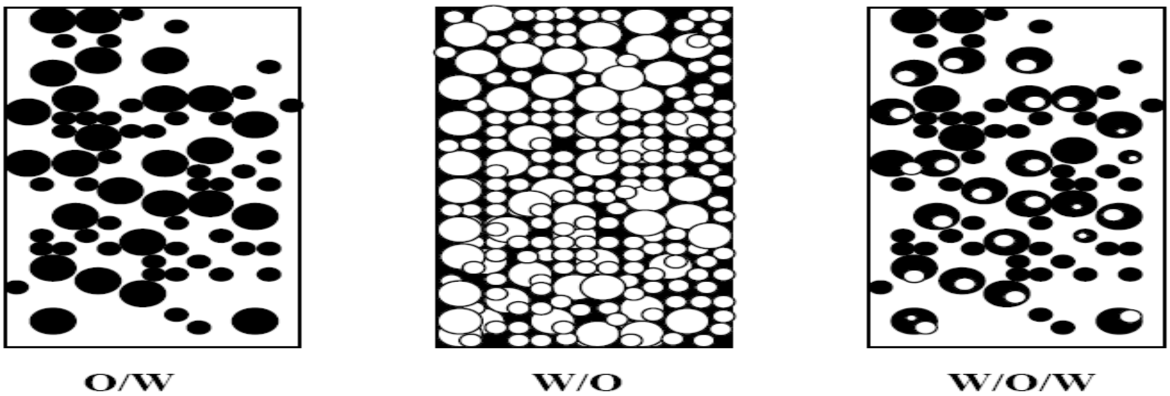

Figure 1: Common Types of Crude Oil Emulsions: Oil-in-Water (O/W), Water-in-Oil (W/O), and less common: Water-in-Oil-in-Water (W/O/W): Source, [11].

The type of emulsion that is formed depends upon a number of factors. If the ratio of phase volume is very large or very small, then the phase having the smaller volume is frequently the dispersed phase and the emulsion type depends more on the nature of the emulsifying agent, so that the phase which an emulsifier is more soluble constitutes the continuous phase [12]. The viscous water in oil emulsions formed are undesirable as they not only cause serious processing problems but also lead to significant cost increases for pumping, transportation [13].

Six factors which may affect the rheological properties of emulsion described in [14], are:

- Viscosity of the external (continuous) phase.
- Volume concentration of the dispersed phase.
- Viscosity of the internal (dispersed) phase.
- Nature of the emulsifying agent and the interfacial film formed at the interface.
- Droplet size distribution in the continuous phase.
- Shear rate.

To ensure the high-quality performance, a demulsifier should possess the following characteristics [15]:

- The demulsifier should be able to partition into the water phase and oil phase.
- Dissolved in the oil phase.
- The concentration of the demulsifier in the droplet must be sufficient to ensure a high enough diffusion flux to the interface.
- The demulsifier must be high enough to suppress the interfacial tension gradient, thus accelerating the rate of film drainage hence promoting coalescence.

The parameters that are being identified to affect demulsifier performance are:

1. Temperature: The suitable temperatures considered for demulsification process for lab-scale are between 50 to 70°C, which are similar to the dehydration processes in the actual refinery process. The interfacial viscosity of the internal phase will decrease with increasing of the temperature. This is because the rate of film drainage is increased proportional to the temperature. The momentum between two water droplets will increase before coalescence is occurred. The two phases of immiscible liquids will be separated due to the different density among them [7].
2. pH: The oil-in-water emulsions are preferential at low pH value ranging between 4 to 6, while water-in-oil emulsions are favored at high pH values that are between pH 8 to 10. It was shown by [16] that the stability of oil-in-water emulsion formed increased as pH was increased from 4 to 6, but further increasing in pH, from 6 to 8 and finally 10 resulted in formation of relatively less stable oil-in-water emulsions and more stable water-in-oil emulsions. Chemical method of resolving crude oil emulsion are based on the addition of reagents (demulsifiers) which destroy the protective action of hydrophobic emulsifying agents and allow the water droplets to coalesce.

Stability is widely used to refer to the persistence of an emulsion in the environment, and has been identified as an important characteristic of water-in-oil emulsions. Recent work has shown that viscosity has a correlation with the stability of an emulsion [17]. Stable emulsion will increase with viscosity over time. Increasing alignment of asphaltenes at the oil-water interface may cause increasing of viscosity. The application of heat and the addition of demulsifiers can reduce the viscosity. Demulsification is carried out through four methods and these are, mechanical, thermal, chemical and electrical methods [10].

i. Mechanical method: There are many kinds of mechanical separation tools that are typical equipment used in destabilization of crude oil emulsion. These include cyclones, gravity settling tanks, centrifugal separators [1].
ii. Thermal method: This is carried out by the addition of heat to enhance emulsion breaking in oil field. An increase in temperature above the paraffin melting point ranging from 50-65°C may completely destabilize an emulsion. So, the optimum operating temperature at refinery is (65°C). However, the application of heat alone is usually not sufficient to break emulsions. There is need for the addition of chemicals demulsifiers [7].
iii. Electrical method: This is done through the principle of electrostatic dehydration. This process does not typically resolve emulsions completely by itself. It also requires the addition of chemicals or heat [7].
iv. Chemical method: This is the most widely applied method of treating water-in-oil and oil-in-water emulsions and involves the use of chemical additives to accelerate the emulsion breaking process. The most common method of demulsification in both oil-field and refinery application is the combination of heat and application of chemical design to neutralize and eliminate the effects of emulsifying agents [7].

The success of the chemical demulsifying method depends on the following:

- An adequate quantity of a properly selected chemical entering into the emulsion.
- Thorough mixing of the chemical in the emulsion must occur.
- Sufficient heat may be required to facilitate or fully resolve an emulsion.
- Sufficient residence time is required.

The demulsification activity promotes coalescence of the water droplets in the emulsion, which in turn causes separation of water and lowering of viscosity. The action of the demulsifier in emulsion breaking is to “unlock” the effect of the emulsifying agents present. This unlocking is accomplished in two fundamental steps, which are flocculation and coalescence [18]. It was shown [19] that the kinetics of chemical demulsification process is caused by three main effects:

- The displacement of the asphaltenic film from the (water/oil) interface by the demulsifier.
- Flocculation.
- Coalescence of water droplets.

Good demulsifier should have sufficient surface pressure and create good partition between the water phase and oil phase. The imported demulsifiers are usually formulated from organic solvents such as toluene, xylene, dioxane etc. The materials used in the production of local demulsifiers are listed in Table 1 while Table 2 presents the chemicals that have been used as demulsifiers since the beginning of the century [20].

Table 1: Materials used in the production of locally made demulsifiers [21].

Materials	**Functions**
Camphor	It acts as a solvent for the camphor and also increases the lipophilic properties of the crude oil.
Olive oil	Forms the lipophillic end of the demulsifiers from local sources
Candle wax	This served as the bulking agent in the locally sourced demulsifier.
Starch	Forms the hydrophilic end of the locally sourced demulsifier due of its strong affinity for water.
Liquid soap	Serves as the binder for locally sourced material to bind the lipophilic and the hydrophilic end.
Distilled water	Used as solvent for the starch solution.

Table 2: The development of chemical demulsifiers [4, 12, 22].

Year	**Demulsifiers**
1920-1930	Soap, naphtenic acid salts and alkylaryl sulphonate, sulphated castor oil
1930-1940	Petroleum sulphonates, derivatives of sulpho-acid oxidized castor oil and sulphosucinic acid ester
1940-1950	Fatty acids, fatty alcohols, alkyl phenols
1950-1960	Ethylene oxide/propylene oxide copolymer, Alkoxylated cyclic alkyl phenol formaldehyde resins
1960-1970	Amine alkoxylate
1970-1980	Alkoxylated cyclic p-alkyl phenol formaldehyde resins
1980-1990	Polyester amine and blends
199	Sodium silicat, sodium hydroxide, phenol
2006	Acrylic acid anhydrous, Methacrylic acid, Butyl acrylate

There are three types of demulsifiers that are used to break the crude oil emulsion. They are anionic, nonionic and cationic demulsifiers [23]:

1. Anionic demulsifiers: These are used in practically every type of detergents, which are the main constituents of demulsifiers and are more in use than other types. The surface-active part of the anionic molecule carries a negative. The anionics have the advantage of being stable foaming agents.
2. Nonionic demulsifiers: These are surfactants that do not have a charged group. Nonionic surface-active agents have a hydrophobic/hydrophilic balance where there is neither a negative nor a positive charge in either part of the molecule, thus giving it the nonionic terminology. These surface-active agents have the advantage that they are not affected by water hardness or changes In pH changes and are considered as medium to low foaming agents.
3. Cationic demulsifiers: These carry positive charge on the active portion of the molecule.Cationic surfactants play an important role as antiseptic agents in cosmetics Basically cationic demulsifiers are classified as Amine salts (primary, secondary and tertiary) and Quaternary ammonium compounds.

MATERIALS AND METHODS

The target was to experimentally investigate and compare the effectiveness of imported and locally made demulsifiers, by looking at the dosage and the time it takes to break crude oil emulsion. Three demulsifiers types were used; two imported types (D2005 and PT) and the other locally made type (Daf360) formulated through methods outlined in [21]. Water separation efficiency, total hydrocarbon content of water effluent, salt content in treated crude oil and pour point of treated crude oil were examined. Many oil producing companies, 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. However, there is still a need for the use of the Bottle test method to ensure measurements are in compliance with the preset minimum Basic Sediment and Water (BS and W).

Materials used in experiments

- Sample bottle graduated in 100ml scale,
- Centrifuge, Demulsifier brands: Daf360
- (Locally made), PT
- (Imported) and D2005 (Imported), Micro-
- pipette, 50 ml graduated cylinder and thermo
- hydrometer, Syringe, Stop watch, Crude oil sample

Table 3: Physical Properties of the Escravos crude oil (From Warri refinery).

Property	**Escravos Crude Oil**
API Gravity	24.5
Specific gravity at 15^{0}C (Kg/lt)	0.907
BSW(%vol)	0.05
Salt content (Lbs/1000bbl)	293.47
Total Sulphur (%wt)	0.19
Kinematic viscosity at 38^{0}C	10.47
Pour point (^{0}C)	-3

Experimental procedure

Chemical demulsification method (Bottle test)

The demulsification tests were performed on the Escravos crude oil. The demulsifiers were tested by using the standard procedure known as Bottle Test method [24, 25]. Figure 2 shows the laboratory equipment used in the experimental work. The purpose of this testing process was to test the effectiveness of demulsifiers in breaking crude oil emulsion. The following procedure was followed:

- Crude oil sample was taken.
- The sample bottles were labeled with names of the different chemical demulsifiers.
- From the samples, the test bottles were filled up to the 50ml mark and with the aid of a micro pipette the 3 demulsifiers were added to 3 bottles accordingly.
- The samples were shaken vigorously for homogeneity and allowed to stand for 5mins while the amount of water separated, emulsion and top oil were read off and recorded. The process was monitored for 30mins at 5minutes interval.
- The experiment was carried out at ambient temperature and repeated for all the samples.
- The experiment was also carried out at a temperature of 65^0C and repeated for all the samples.

Figure 2: Demulsifier Samples used for the Experiments

Determination of BS&W:

Laboratory test was carried out to determine the Basic Sediment and Water (BS&W) of the top oil from the bottle test samples according to standard methods which consist of mixing equal volumes of solvent and crude oil then centrifuging in order to separate any solids, free water, or suspended particles [26]. Figure 3 shows the laboratory equipment used in the determination of BS&W of the treated crude oil. Graduated centrifuge tubes, measuring cylinders (I00ml), centrifuge and stop watch were used to carry out the tests. Four different graduated centrifuge tubes were filled with samples to the 10ml mark. The samples were centrifuged for 10 minutes. The basic sediment content, water content and the sum of the basic sediment and water were read and recorded.

Figure 3: Equipment used in the determination of BS&W

Evaluation of salt content

The salt content in the (W/O) emulsion after breaking emulsion was measured using salt in crude analyzer by Electrometric method as shown in Figure 4. The following procedure was followed

- To a dry, 100ml graduated, glass-stoppered cylinder, 15ml of xylene was added and then 10ml of the crude oil samples.
- The level was made up to 50ml with xylene and shaken vigorously for approximately 60s.
- The sample was diluted to 100ml with alcohol solvent, and again shaken vigorously for approximately 30s. The solution was allowed to stand for approximately 5mins and poured into the dry test beaker.
- The electrodes were placed into the solution in the beaker and the indicated electrode voltage adjusted accordingly. The current at each voltage was recorded to the nearest 0.01mA.
-


Figure 4: Electronic equipment for salt analysis.


Figure 5: Pour point measurement apparatus.

Evaluating the residual water for total hydrocarbon content (THC).

The hydrocarbon content of the produced water was extracted using xylene. The hydrocarbon concentration was determined with the use of a spectrophotometer. The following procedure was followed:

- Single wavelength option on spectrophotometer was selected and wavelength set to 400nm.
- 2ml dose of 50% of sulphuric acid solution was added to the sample and shaken to reduce the PH to about 2.
- The sample was transferred to a 1000ml graduated sample bottle.
- 50ml of xylene was measured into a cylinder.
- Approximately half the xylene from the measuring cylinder was transferred into the sample bottle and shake for 2mins, venting regularly to allow any built-up gas to be released.
- The xylene was transferred from the sample bottle to the separating funnel.
- The above procedure was repeated with the other half of the xylene.
- The separating funnel containing the sample was shaken for about 2mins and allowed to stand until the emulsion was separated.
- The water layer was drained off and the solvent layer collected in a clean, dry beaker.
- The material was filtered through silica gel for THC and through filter paper for O & G.

RESULTS AND DISCUSSION

The results of the bottle tests carried out using three brands of demulsifier at ambient temperature and 65^{0}C and at different time intervals (5-30mins) and centrifuge test are summarized in Tables 4-6

Table 4: Results of Bottle Test and Centrifuge Test Analysis Using Locally Made Demulsifier (Daf360) At 27^{0}C and 65^{0}C for the Crude Oil Emulsion

Product Name	Daf360	Daf360	Daf360	Daf360
Temp	27^{0}C	27^{0}C	65^{0}C	65^{0}C
Dosage (ppm)	10ppm	20ppm	10ppm	20ppm
Colour change	Dark	Dark	Dark	Dark
5 mins				
W	9	6	10	8
O	91	94	90	92
10 mins				
W	10	16	12	18
O	90	84	88	82
15 mins				
W	10	18	12	22
O	90	82	88	78
25 mins				
W	8	18	10	18
O	92	82	90	82
30 mins				
W	9	18	12	20
O	91	91	88	80
H_2O Quality	Good	Good	V. good	V. good
BS &W	0.2%	0.2%	0.06%	0.04%

Note: W (Water), O (Oil)

Table 5: Results of Bottle Test and Centrifuge Test Analysis Using Imported Demulsifier D2005) At 27^{0}C and 65^{0}C for the Crude Oil Emulsion

Product Name	**D2005**	**D2005**	**D2005**	**D2005**
Temp	27^{0}C	27^{0}C	65^{0}C	65^{0}C
Dosage (ppm)	10ppm	20ppm	10ppm	20ppm
Colour change	Dark	Dark	Dark	Dark
5 mins				
W	4	4	6	6
O	96	96	94	94
10 mins				
W	5	10	8	10
O	95	90	92	90
15 mins				
W	6	10	10	14
O	94	90	90	86
25 mins				
W	2	8	4	6
O	98	92	96	94
30 mins				
W	4	10	6	14
O	96	90	94	86

H_2O Quality	Good	Good	Good	Good
BS & W	0.6%	0.7%	0.5%	0.4%

Table 6: Results of Bottle Test and Centrifuge Test Analysis Using Imported Demulsifier (PT) At 27^0C and 65^0C for the Crude Oil Emulsion

Product Name	**PT**	**PT**	**PT**	**PT**
Temp	27^0C	27^0C	65^0C	65^0C
Dosage (ppm)	10ppm	20ppm	10ppm	20ppm
Colour Change	Dark	Dark	Dark	Dark
5 mins				
W	0	0	0	1
O	100	100	100	99
10 mins				
W	0	0	1	2
O	100	100	99	98
15 mins				
W	0	2	2	4
O	100	98	98	96
25 mins				
W	0	1	2	2
O	100	99	98	98
30 mins				
W	0	2	3	5
O	100	98	97	95
	No H_2O	Milky	Good	Good
H_2O Quality				
BS & W	0.9%	0.8%	0.7%	0.6%

The last rows of Tables 4, 5 and 6 show BS & W results of centrifuge test analysis. Table 7 and 8 show the values of salt in crude, pour point of crude oil after water separation and value of total hydrocarbon content in residual water from crude oil.

Effect of heat on water separation efficiency

From Tables 4, 5 and 6 the importance of heat in emulsion treatment in combination with the right chemicals and gravity settling can be observed. The separated water in Daf360 is higher than in D2005 and in PT probably because when crude is heated, its viscosity becomes reduced, thereby making the crude less dense. As a result, the water contained in the emulsion can drop more freely from it. This is likely responsible for the large quantity of water collected in Daf360 sample as compared to D2005 and PT sample. Hence the application of heat to an emulsion after a demulsifier has been applied increases the effectiveness of the chemicals, by reducing the viscosity of emulsion and also promoting intimate mixing of the chemicals with the emulsion. Also, the reaction at the water-oil interface takes place at a more rapid rate at higher temperatures. The importance of retention time was also noticed during the experiments and it can be seen from the Tables when comparing the volume of water separated after 5 minutes to that after 15 minutes for each of the cases. Even in cases where zero water was noticed, some water is separated as retention time increases.

Effect of demulsifiers on water separation efficiency

Figures 6-9 show the effect of Daf360, D2005 and PT on water separation efficiency with time. It can be observed that the water separation efficiency for Daf360, D2005 and PT increases sharply with time until it reaches 15 min. The maximum separation efficiency of 18% was obtained at 30 min and at a dosage of 20ppm for Daf360. Figure 6 shows the separation efficiency of water for 20ppm dosage of D2005 at 10% obtained after 30 min. Similarly, the separation efficiency of water for 20ppm PT increased with time till after 15 min.

A look at the Figures show the effect of temperature. It can be observed that the water separation efficiency increases with temperature and increasing time. There was sharp increase until about 15 min. The maximum separation efficiency obtained was 20% for Daf360, 5% for PT and 14% for D2005 at 30 min. It can be adjudged from the results that Daf360 (local made demulsifier) under the prevailing conditions based on which the experiments were conducted for the samples gave very promising results

Table 7: Results of Total Hydrocarbon Content of Water Effluent after Water Separation with Imported and Locally Made Demulsifiers

Parameter	Unit	Method	D2005	PT	Daf360
Total Hydrocarbon Content (THC)	Mg/l	API RP45	80.82	84.35	127.89

Table 8: Results of Salt in Crude and Pour Point of Crude Oil after Treatment with Imported and Locally Made Demulsifiers

Parameter	Unit	Method	D2005	PT	Daf360
Salt in crude	Lbs/1000bbl	ASTM D3230	26.8	27.5	9.6
Pour point	^{0}C	ASTM D97	<-20	<-20	<-20

Effect of adding demulsifiers doses on water separation

Figures 6 and 7 show the effect of demulsifier dose on water separation efficiency after 30 min for D2005, PT and Daf360. It can be observed that water separation increases with increasing time. The maximum removal of water (18%) was obtained at a dosage of 20ppm Daf360, and that of D2005 10% and PT 2%. The chemical and physical properties of Daf360 may have contributed to this as shown in Table 9 and Table 10 in line with observations by [27].

Table 9: Materials used in production of demulsifier

Materials	Functions
Camphor	Forms the lipophillic end of the demulsifiers from local sources
Olive oil	Acts as a solvent for the camphor and also increases the lipophillic properties of the crude oil.
Candle wax	Serves as the bulking agent in the locally sourced demulsifier.
Starch	Forms the hydrophilic end of the locally sourced demulsifier because of its strong affinity for water
Liquid soap	Serves as the binder of the lipophillic and the hydrophilic end in the demulsifier formulation
Distilled water	Solvent for the starch solution
Polyoxyalkylene Copolymers	Chemical demulsifier
Benzalkonium chloride	Chemical demulsifier
Acetone	Solvent in the chemical demulsifiers preparation.
Polyol	Performance enhancer to demulsifiers

Table 10: Quantities of materials used in producing demulsifer

Material	Quantities (g)
Olive oil	30.00
Camphor	10.00
Candle wax	10.00
Starch	4.86
Water	25.14
Liquid soap	20.00
Total	100

Total hydrocarbon content of effluent water after separation

Table 7 shows the total hydrocarbon content of effluent water after water separation. It can be observed that total hydrocarbon content for Daf360 sample, was found to be 127.89 mg/l compared to the sample treated with D2005 which has 80.82 mg/l while that of PT was 84.35mg/l. Thus, it is observed that D2005 sample (imported demulsifier) has a good water effluent

Salt content after water separation

Table 8 shows salt content of crude oil after water separation. It can be observed that water separation efficiency increases with decreasing salt content for Daf360 sample. The salt content was 9.6 Lbs/1000bbl compared to a content of 26.8 Lbs/1000bbl for D2005. This may be attributed to the chemical activity of the hydrophilic and hydrophobic groups present in the demulsifier.

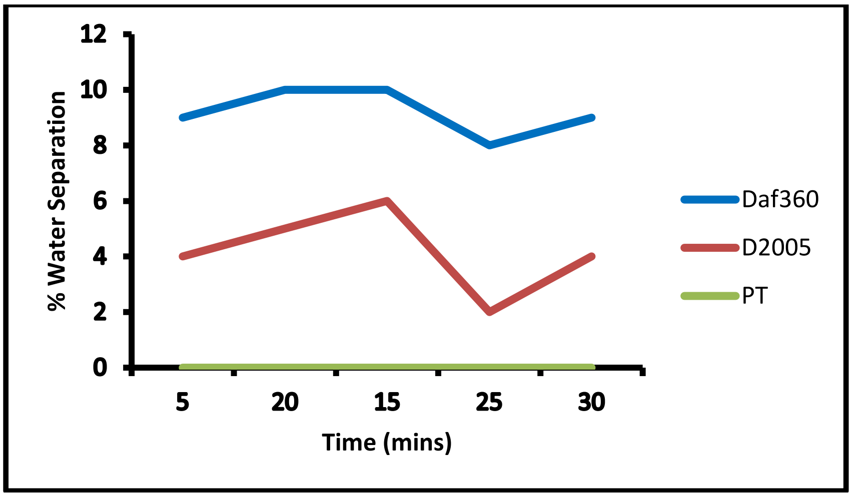

Figure 6: Effect of Adding Daf360, D2005 and PT at 27^{0}C and 10PPM with Time.

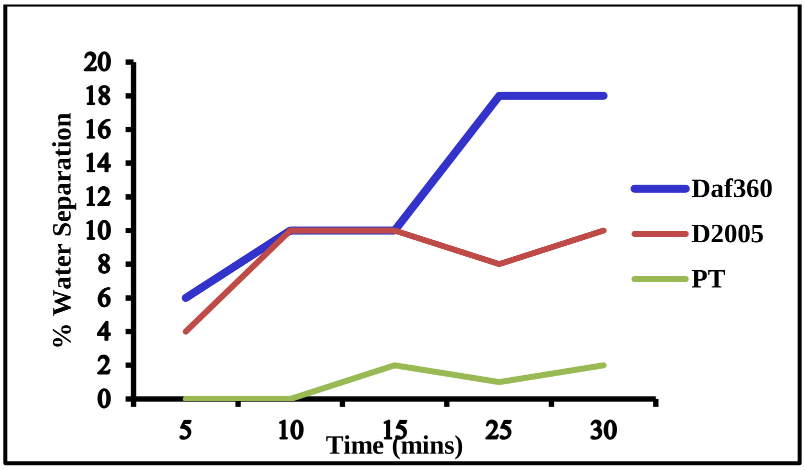

Figure 7: Effect of Adding Daf360, D2005, PT at 27^{0}c and 20PPM with Time.

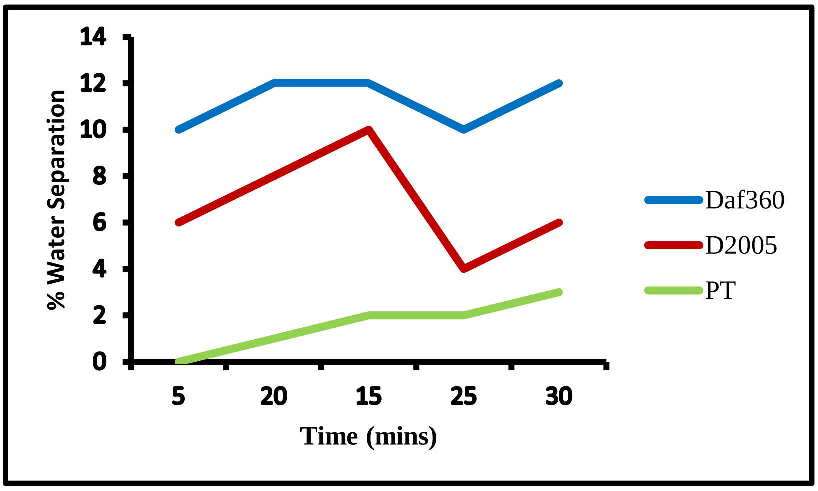

Figure 8: Effect of Adding Daf360, D2005, PT at 65°C and 10PPM with Time.

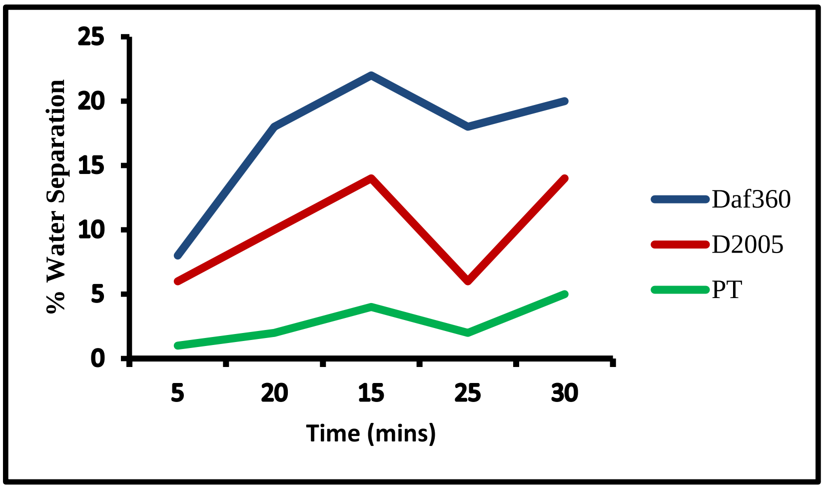

Figure 9: Effect of Adding Daf360, D2005, PT at 65°C and 20PPM with Time.

CONCLUSION

The following are conclusions from the experiments:

1. Water separation efficiency increased with increasing separation time for imported and locally made demulsifiers. The maximum separation was obtained at 30 min.

2. Water separation efficiency increased with increased dosage of demulsifiers. The maximum separation for water was obtained is at 20 ppm for both the imported and locally made demulsifiers.

3. Water separation efficiency increased with increasing heat for both the imported and locally made demulsifiers. The maximum separation was obtained at 65 ^{0}C.

The locally made demulsifier Daf360 gave very promising results. Hence, there are prospects for the use of the locally made demulsifier which economically may be worthwhile on the long run.

ACKNOWLEDGEMENT

The author acknowledges the assistance of Warri Refinery and Petrochemical Company in providing crude sample for this work

REFERENCES

1. AUFLEM, I.H. (2002). Influence of Asphalting Aggregation and Pressure on Crude Oil Emulsion Stability, Norwegian University of Science and Technology: Ph.D. Thesis.
2. KENNETH J. LISSANT (1988). Emulsification and De-emulsification, A Historical Overview. *Colloids and surfaces*, **29:** 15.
3. SJOBLOM, J., MING YUAN, L., HOILAND, H & JOHANSEN, J.E. (1990). Water-in-Crude Oil Emulsions from the Norwegian Continental Shelf, Part III. A Comparative Destabilization of Model Systems. *Surfaces*, **46**: 127-139.
4. SELVARAJAN R., ANANTHA S. & ROBERT A. M. (2001). Aqueous Dispersion of an Oil Soluble Demulsifier for Breaking Crude Oil Emulsions, (US Patent No. 6,294,093).
5. HARDWAJ, A. & HARTLAND, S. (1998). Studies on Build up of Interfacial Film at the Crude Oil/Water Interface. *Journal of Dispersion Sciences and Technology*, **19**(4): 465-473.
6. FINGAS, M., FIELD HOUSE, B., BOBRA, M. & TENNYSON, E. (2003). The Physics and Chemistry of Emulsions. Proceed Workshop on Emulsion, Marine Spill Response Corporation, Washington, DC.
7. GRACE, R. (1992). Commercial Emulsion Breaking. In.: Schramm, L.L., Emulsions Fundamentals and Applications in the Petroleum Industry. American Chemical Society, Washington DC. 313-338.
8. SPEIGHT J.G. (1994). The Chemistry and Technology of Petroleum, Marcel Dekker Inc. New York.
9. EINAR, J.J., MAGNAR, I.S., TORGEIRL, J. SJŐBLOM, H. SŐDERNUD & G. BOSTRŐM, (1988). Water-in-Crude Oil Emulsions from Norwegian Continental Shelf; Part Formation, Characterization and Stability Correlation. *Colloids and Surfaces*, **34**: 353-370.
10. GAFONOVA, O.V. (2000). Role of Asphaltenes and Resins in the Stabilization of Water- in-Hydrocarbon Emulsions, the University of Calgary: MSc Thesis.

11. PAUL, M.S. (2001). The Impact of Asphaltene Chemistry and Solvation on Emulsion and Interfacial Film Formation, of North Carolina State University: Ph.D. Thesis.
12. HANAPI, B.M, (2006). Study on Demulsifier formulation for treating Malaysian Crude Oil Emulsion," University Technology Malaysia: MSc. Thesis
13. PEKDEMIR, T., AKAY, G., DORGRU, M., MERRLLS, R.E. & SCHLEICHER, B., (2003). Demulsification of highly stable water in oil emulsions. *Separation Science and Technology,* **38**(5): 1161-1183.
14. BECKER, J.R. (2005). Crude Oil Waxes, Emulsions, and Asphaltenes. Penn Well Publishing Company. Oklahoma. 126-129.
15. KRAWCZYK, M.A. (1990). Mechanisms of Demulsification, Institute of Technology, 20: Ph.D. Thesis.
16. TAMBE, D.E. & SHARMA, M.K. (1995). Factor Controlling the Stability of Colloid-Stabilized Emulsions, *Journal of Colloids and Interface Science*, **171**: 456-462
17. NRT Science & Technology Committee (1997). Emulsion Breakers and Inhibitors for Treating Oil Spills. Fact Sheet.
18. LEOPOLD, G. (1992). Breaking Produced-Fluid and Process-Stream Emulsions. In. Schramm, L.L. Emulsions Fundamentals and Applications in the Petroleum Industry. American Chemical Society, Washington DC.341-383.
19. ESE, M.H., GALET, L., CLAUSSE, D. & SJOBLOM, J. (2006). Properties of Langmuir Surface and Interfacial Films Built up by Asphaltenes and Resins: Influence of Chemical Demulsifiers, *Journal of Colloids and Interface Science*, **220**: 293-301.
20. SCHRAMM, L.L. (1992). Petroleum Emulsion. In.: Schramm, L.L. Emulsions Fundamentals and Applications in the Petroleum Industry**.** American Chemical Society, Washington DC. 1-45.
21. ODISU, T. & SALAMI, D.O. (2010). Formulation and Production of Crude Oil Demulsifiers from Locally Sourced Materials. *Journal of Physical Science and Innovation*, **2**: 26-37.
22. HANAPI, B.M. (2006). Study on Demulsifier formulation for treating Malaysian Crude Oil Emulsion, University Technology Malaysia: MSc. Thesis
23. PORTER, M.R. (1994). Use of Surfactant Theory. Hand book of Surfactants. Blackie Academic & Professional. United Kingdom. 26-93.
24. LISSANT, K.J. (1983). Demulsfication Industrial Application, Marcel Dekker Ins., New York, USA.
25. RAYNEL, G.D., S. MARQUES, S. AL-KHABAZ, M. AL-THABET & L. OSHINOWO. (2021), A new method to select demulsifiers and optimize dosage at wet crude oil separation facilities, Oil & Gas Science and Technology – Rev. *IFP Energies Nouvelles*, **76**: 19
26. MANUAL OF PETROLEUM MEASUREMENT STANDARDS **(**MPMS) (2013), Determination of Water and/or Sediment in Crude Oil by the Centrifuge Method (Field Procedure) Chapter 10. 4, (4th ed.). Washington, DC: American Petroleum Institute.
27. ABDULKADIR, M. (2010). Comparative Analysis of the Effect of Demulsifiers in the Treatment of Crude Oil Emulsion. ARPN *Journal of Engineering and Applied Science*, **5:** 67-73