

**Technical Investigation of crude oil emulsion demulsifier produced in Nigeria on crude oil to water recovery ratio efficiency**

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**ABSTRACT**

The most important objective of any oil production facility is the separation of water and other foreign materials from produced crude. Emulsions of oil and water are one of many problems directly associated with the petroleum industry, in both oil-field production and refinery environments. Several methods in use have suffered from drawbacks such as high costs of production and environmental concerns. The need to develop a cost effective and efficient demulsifier in treating crude oil emulsions without compromising quality and environmental safety is a major concern to the oil industry worldwide. Hence, this study aims at developing and formulating cheap and environmentally safe demulsifier from locally sourced raw materials thereby compare its effectiveness with that of commercially imported foreign demulsifier. Experimental investigation was carried out to ascertain its effectiveness in breaking crude oil emulsion. Materials used included locally made liquid soap, starch, camphor, alum, castor oil, and distilled water. Two different demulsifier formulations were made and tested on a crude oil emulsion sample from a Niger Delta field and subjected to a temperature of 60°F. A foreign demulsifier, Separol, of the same quantity and under the same experimental condition, served as a basis for comparison (control).

The result of the treatment was a successful separation of oil and water using formulated demulsifier. The separated water volume by the local demulsifier (CONK1) was 31ml, while that separated by Separol was 6ml. This showed the locally formulated demulsifier had high effect and better water separation capability than the commercially available imported demulsifier (Separol).

**Keywords:** Coalescence, Local Materials, Demulsifier, Emulsion, Flocculation, Niger Delta, Saparol.

## 1. Introduction

Emulsion is defined as a system in which one liquid is relatively distributed or dispersed, in the form of droplets, in another substantially immiscible liquid. Emulsions have long been of great practical interest due to their widespread occurrence in everyday life which occurs due to reliance of the behaviour of the emulsion on the magnitude and range of the surface interaction. They may be found in important areas such as food, cosmetics, pulp and paper, biological fluids, pharmaceutical, agricultural industry, and petroleum engineering. In production and flow assurance, the two commonly encountered emulsion types are water droplet dispersed in the oil phase and termed as water-in-oil emulsion (W/O) and if the oil is the dispersed phase, it is termed oil-in-water (O/W) emulsion (D. Langevin, S. Poteau, I. H´enaut, and J. F. Argillier, 2004). When there is dispersion (droplets) of one liquid in another immiscible liquid is called emulsion. The phase that is present in the form of droplets is the dispersed or internal phase, and the phase in which the droplets are suspended is called the continuous or external phase. For produced oilfield emulsions, one of the liquids is aqueous and the other is crude oil. The amount of water that emulsifies with crude oil varies widely from facility to facility. It can be less than 1% and sometimes greater than 80%.

In a true emulsion, either the drop size must be small enough that forces from thermal collisions with molecules of the continuous phase produce Brownian motion that prevents settling, or the characteristics of the interfacial surfaces must be modified by surfactants, suspended solids, or another semisoluble material that renders the surface free energy low enough to preclude its acting as a driving force for coalescence.

### 1.1 Appearance and Color

Color and appearance is an easy way to characterize an emulsion. The characterization becomes somewhat easy if the emulsion is transferred into a conical glass centrifuge tube. The color of the emulsion can vary widely depending on:

- Oil/water content

- Characteristics of the oil and water

The common colors of emulsions are dark reddish brown, gray, or blackish brown; however, any color can occur depending on the type of oil and water at a particular facility. Emulsion brightness is sometimes used to characterize an emulsion. An emulsion generally looks murky and opaque because of light scattering at the oil/water interface. When an emulsion has small diameter droplets (large surface area), it has a light color. When an emulsion has large diameter droplets (low total interfacial surface area), it generally looks dark and less bright. Understanding the characteristics of an emulsion by visual observation is an art that improves with experience.

## 1.2 Formation of Emulsions

Crude oil emulsions form when oil and water (brine) come into contact with each other, when there is sufficient mixing, and when an emulsifying agent or emulsifier is present. The amount of mixing and the presence of emulsifier are critical for the formation of an emulsion. During crude oil production, there are several sources of mixing, often referred to as the amount of shear, including: Flow through reservoir rock, Bottomhole perforations/pump, Flow through tubing, flow lines, and production headers, Valves, fittings, and chokes, Surface equipment, Gas bubbles released because of phase change. The amount of mixing depends on several factors and is difficult to avoid. In general, the greater the mixing, the smaller the droplets of water dispersed in the oil and the tighter the emulsion. Emulsion studies have shown that the water droplets can vary in size from less than 1  $\mu\text{m}$  to more than 1000  $\mu\text{m}$ . The second factor important in emulsion formation is the presence of an emulsifier. The presence, amount, and nature of the emulsifier determines, to a large extent, the type and "tightness" of an emulsion. The natural emulsifiers in crude are resident in the heavy fraction. Because there are different types of crudes and because these crudes have different amounts of heavy components, the emulsifying tendencies vary widely. Crude with a small amount of emulsifier forms a less stable emulsion and separates relatively easily. Other crudes contain the right type and amount of emulsifier, which lead to very stable or tight emulsions. Emulsions may be encountered at all stages in the petroleum recovery and processing industry (drilling fluid, production, process plant, and transportation emulsions)

### **1.3 Objectives of Study**

This research is focused primarily to drive comparison of commercially imported foreign available demulsifier effectiveness and water separation capability to locally formulated demulsifier from locally sourced raw materials on water-in-oil emulsion demulsification.

## **2.0 Demulsifiers Development, Formulation and Performance**

### **2.1 Historical development**

Rigorous attempts have been in trying to correlate between demulsifier performance and physical properties such as molecular structure, interfacial tension, Hydrophilic-Lipophilic balance (HLB), interfacial viscosity, partition viscosity, dynamic interfacial tension and relative solubility number.

A quick look on the chemical demulsifiers history reveals that prior to the knowledge of polyether condensates synthesis, chemicals such as Turkey red oil, sulphuric acid, sulphated castor oil, mahogany soaps, polyamines and polyhydric alcohols were used directly as demulsifiers (Monson, 1969).

In early 1940's, the technology of alkylene oxide condensation started to evolve worldwide, and since then almost all demulsifier components were made up of condensation products of ethylene, propylene and butylenes oxide. Most of these are alkoxyated polymers that are mainly etoxyated and propoxyated and sometimes both. They are macromolecules held in chains, industrially synthesized from petroleum chemicals.

After World War II, the whole branch of chemistry was opened to companies involved in surfactant (surface-active agents) technology. With the beginning of condensed polyether made possible by large-scale production of ethylene and propylene oxides (Becker, 1997), a new class of nonionic detergents began to appear. The condensation products of the ethylene oxide were found to be water soluble and the high reactivity of the oxirane ring made it useful in a host of chemical reactions. It was found that the propylene oxide gave poly condensation products that tended to be oil soluble. The polymer most employed in the demulsification industry is surfactant that exhibits

both hydrophilic and hydrophobic groups. The polymeric surfactant when added to the petroleum emulsion located itself in the interface between the water and oil molecules. The hydrophilic groups orient themselves towards water whilst the hydrophobic ones orient themselves towards the oil.

The best polymeric surfactants used nowadays throughout the world are alkoxyated material derivatives. Because they are alkoxyated, they are considered as nonionic polymers. Sometimes mixtures of nonionic, cationic or anionic materials are used together, depending on the oil characteristics. Etoxyated nonionic surfactants are effective multi-purpose and versatile substances. Commercial products are obtained by reaction of ethylene oxide with a hydroprobe having an active hydrogen group (e.g. fatty acids, alkylphenols or fatty alcohols) in the presence of suitable catalysts.

Sjoblöm et al. (1990) stated that a similar destabilization sequence for model and authentic crude oil emulsions can be obtained when medium-chain alcohols and fatty amines are used as destabilizers. The commercial demulsifiers that used to break up water-in-oil emulsion are oil soluble and water soluble demulsifiers. Table 2.2 shows the comparison between those demulsifiers.

**Table 2.1: The development and evaluation of chemical demulsifiers (Selvarajan et al., 2001)**

Year	Demulsifiers
1920-1930	Soap, naphthenic acid salts and alkylaryl sulphonate, sulphated caster oil
1930-1940	Petroleum sulphonates, derivatives of sulpho-acid oxidized caster oil and sulphosucinic acid ester
1940-1950	Fatty acids, fatty alcohols, alkylphenols

1950-1960	Ethylene oxide/propylene oxide copolymer, Alkoxylated cyclic p-alkylphenol formaldehyde resins
1960-1970	Amine alkoxyate
1970-1980	Alkoxylated cyclic p-alkylphenol formaldehyde resins
1980-1990	Polyesteramine and blends

**Table 2.2: Comparison between oil soluble demulsifier and water soluble demulsifiers (Bhattacharyya, 1992)**

No/Type	Oil soluble demulsifiers	Water soluble demulsifiers
1	Moderately 2000-50,000 molecular weight (mw). High mw are the preference.	10,000-15,000 molecular weight. Lower mw are the preference.
2	Polydispersed interfacially active polymers.	Tetrapolymer or pentapolymer
3	Mostly non-ionic block polymer with hydrophilic and hydrophobic segments.	The polymer present hydrophilic (-COOH) and hydrophobic (alkyl) groups.
4	Dangerous and expensive chemicals like ethylene and propylene oxide.	Easy handling chemicals like methyl methacrylate, butyl acrylate, acrylic acid and methacrylic acid.

In water-in-oil emulsion cases, the most effective demulsifiers are oil-soluble or hydrophobic. This is because oil is the continuous phase while water is the dispersed phase. Thus, the surfactants will absorb straightly into the continuous phase without any resistance in optimum temperature.

Typically, these oil soluble demulsifiers are formulated in organic solvent alone such as toluene, xylene, tetrahydrofuran, dioxane, lower alcohols and light gasoline fractions having boiling limits of from 50 to 200°C, or in co-solvents comprising organic solvents and water where in the organic solvent are usually C3 to

C10 alkanols, ethylene diamine, diethylene triamine or ethanolamines including diethanolamine (Mercant et al., 1988).

Among the disadvantages of having organic solvents in a demulsifier formulation are increased cost, flammability, and toxicity. Therefore a demulsifier formulation, which does not include organic solvents, would represent an advance in the art of demulsification.

## **2.2 Formation and Stability of Emulsion**

An emulsifying agent must be present to form stable water-in-crude oil emulsions (Sjöblom et al., 2002). Such agents include clay particles, added chemicals or the crude oil components like asphaltenes, waxes, resins and naphthenic acids (Sjöblom et al., 2002). In the late 1960's, Berridge and his co-workers were the first to measure several physical properties of emulsions (Fingas and Fieldhouse, 2003). They described the formation of emulsions due to the asphaltene and resin content of the oil (Fingas and Fieldhouse, 2003). Mackay and McAuliffe (1988) also stated that the main factors affecting the stability of the emulsion is the presence of substances like crude oil resins, asphaltenes, and natural wax. It was found that asphaltenes were a major factor in emulsion stability (Fingas and Fieldhouse, 2003). Asphaltene fraction contains the highest percentage of hetero-atoms (O, S, and N) and organometallic constituents (Ni, V, Fe) in the crude oil (Sjöblom

et al., 2002). These components combine with organic and/or inorganic solids producing emulsion-stabilizing films at oil-water interface, and contribute to the formation of stable emulsions (Cormack, 1999).

### 3.0 MATERIALS AND METHOD

#### 3.1 Materials

The crude oil emulsion sample used in this research was obtained from an oil field located in Nigeria’s Niger Delta region (code 001) Three demulsifier, two laboratory made (CONK 1 and CONK 2) and a commercially available imported Separol were used in treating this emulsion. The Bottle Test method was used to determine the emulsifier most effective in breaking the emulsion. The result from the test also indicates the smallest amount of demulsifier needed to satisfactorily break the given volume of emulsion.

The materials used in formulating CONK1 and CONK2 are shown in Table 3.1.

Content	Function	Weight/Vol	
		CONK1	CONK2
Alum	To facilitate settling of sediments	5g	5g
Castor Oil	It acts as the lipophilic agent in the demulsifier	30ml	45ml
Starch	Coalescing of the tiny water droplets	5g	5g
Liquid Soap	Destabilization of emulsion film	50ml	25ml
Camphor	It improves the demulsifier performance	10ml	10ml
Xylene	It lightens the oil in the emulsion	-	10

**Table 3.1: CONK1 and CONK2 Materials**



### 3.2 Apparatus

- I. Digital Weigh balance
- II. Measuring Cylinder (50ml graduated)
- III. Beaker
- IV. Magnetic Heat-Stirring machine
- V. Filter paper
- VI. Prescription bottles (200ml graduated)
- VII. Thermostatic Water Bath
- VIII. Stop watch
- IX. Syringe
- X. Micro-pipette
- XI.



### 3.3 Local demulsifier Formulation Procedure

#### 3.3.1 CONK1 Formulation Process

- I. A solution of 10g of camphor dissolved in 30ml of castor oil was stirred and heated (150oF) in a Magnetic heating and stirring machine until homogeneity of solution is obtained.
- II. A mixture of 5g of starch (from cassava flour), 50ml of detergent, and 5ml of Alum solution was prepared in another beaker and added to the camphor- castor oil solution.

- III. The new mixture above was further stirred and heated for 2 hours, after which all precipitates or sediments were filtered off.

### **3.3.2 CONK2 Formulation process**

- I. A solution of 10g of camphor, 10ml of Xylene and 45 ml of cator oil was prepared in a beaker.
- II. A second solution of 5g of starch, 5ml of alum solution, and 25ml of liquid soap was prepared also and stirred.
- III. Both solutions were combined and heat-stirred in the Hotplate Stirred machine for 2 hours, afterwards all remaining precipitates were filtered off.

### **3.4 Analytical Procedure**

- I. Samples were heated in water bath to achieve fluid mobility before placing in the bottles.
- II. A 100ml of emulsion were poured into each of the 18 prescription bottles.
- III. All prescription bottles were labeled according to the concentration of demulsifier to be used for the analysis. Six bottles for each demulsifier were used with concentrations of 0.2ml, 0.4ml, 0.6ml, 0.8ml, 1.0ml, and 1.2ml of demulsifier.
- IV. All bottles containing samples with varying dose of demulsifier were agitated to achieve proper mixture.
- V. The bottles were placed in the water bath, with level at the 100ml ark and heated to 60°C for 2 hours.

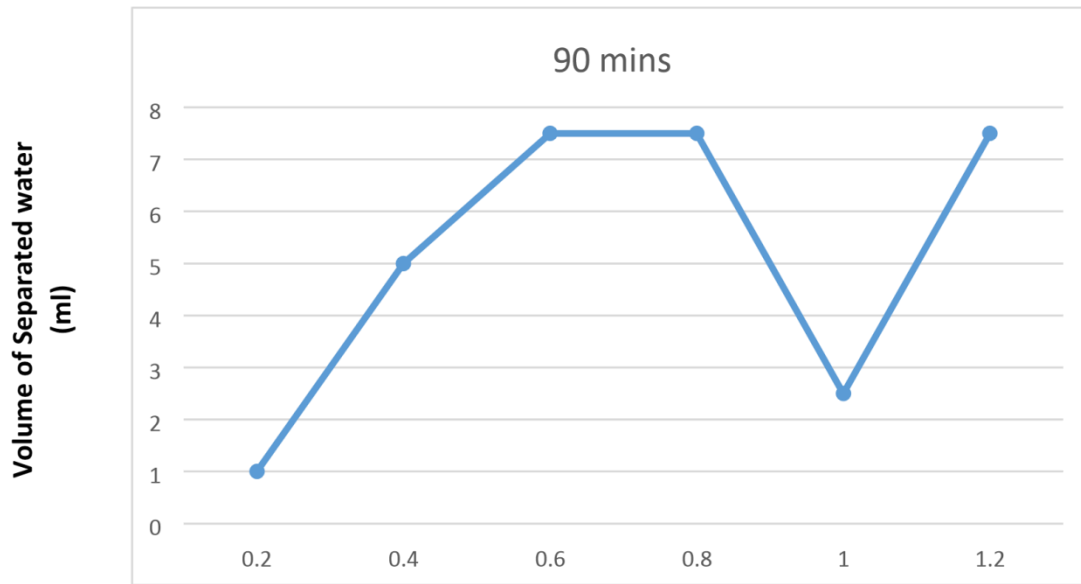
## **4.0 RESULTS AND DISCUSSION**

The Bottle Test results using the three demulsifiers (CONK1, CONK2 and Separol) at a constant treatment temperature of 60°C and at time intervals of 20 minutes after heating for 2 hours are summarized in Table 4.1, 4.2 and 4.3 respectively. Before carrying out any analysis, all samples

were drained of free water after aging for a week. This allowed the water to settle out by gravity. The Basic Sediment and Water (BS&W) and the API of a sample before and after treatment, are summarized in Tables 4.4.

Volume of Demulsifier (ml)	Seperated water Volume				
	1 min	30 mins	60 mins	90 mins	120 mins
0.2	-	-	1.0	1.0	1.0
0.4	2.5	5.0	5.0	5.0	5.0
0.6	2.5	5.0	7.5	7.5	7.5
0.8	7.5	7.5	7.5	7.5	7.5
1.0	2.5	2.5	2.5	2.5	2.5
1.2	7.5	7.5	7.5	7.5	7.5

**Table 4.1: Results of Heat and Chemical Treatment using locally formulated demulsifiers CONK1**

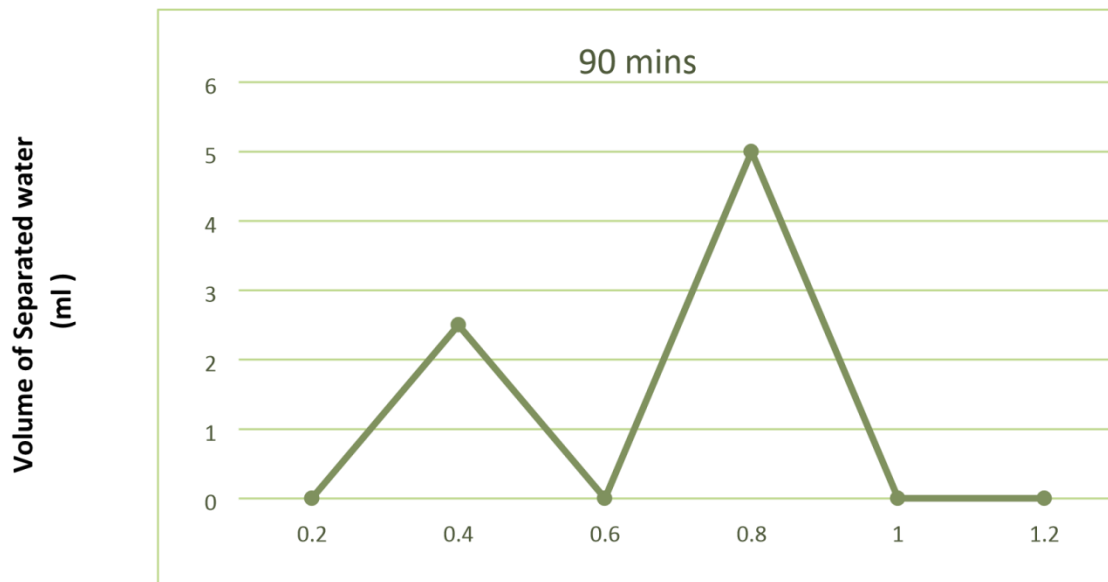


**Volume of Demulsifier (ml)**

Figure 4.1 showing the volume of separated water using locally formulated CONK1 demulsifier

Volume of Demulsifier (ml)	Seperated water Volume				
	1 min	30 mins	60 mins	90 mins	120 mins
0.2	-	-	-	-	-
0.4	2.5	2.5	2.5	2.5	2.5
0.6	-	-	-	-	-
0.8	5.0	5.0	5.0	5.0	5.0
1.0	-	-	-	-	-
1.2	-	-	-	-	-

**Table 4.2: Results of Heat and Chemical Treatment using CONK2**

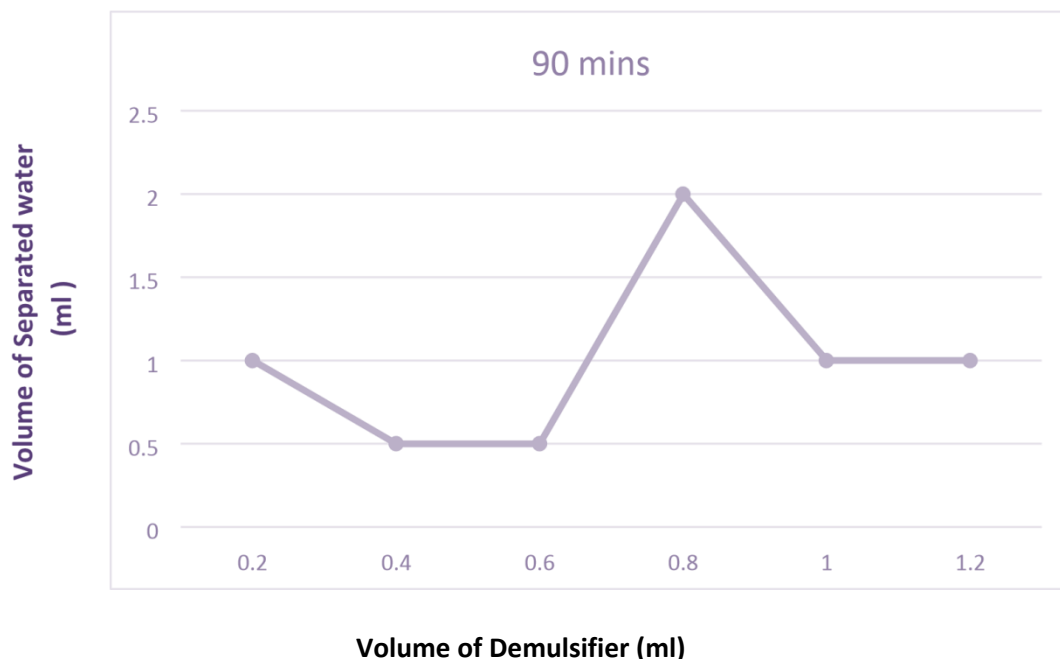


**Volume of Demulsifier (ml)**

Figure 4.2 showing the volume of separated water using locally formulated CONK2 demulsifier

Volume of Demulsifier (ml)	Seperated water Volume				
	1 min	30 mins	60 mins	90 mins	120 mins
0.2	-	1.0	1.0	1.0	1.0
0.4	-	-	-	0.5	0.5
0.6	-	-	-	0.5	0.5
0.8	2.0	2.0	2.0	2.0	2.0
1.0	-	1.0	1.0	1.0	1.0
1.2	-	1.0	1.0	1.0	1.0

**Table 4.3: Results of Heat and Chemical Treatment using Separol**



**Figure 4.3 showing water separation using conventional demulsifier Separol**

As shown in Table 4.1 and figure 4.1, CONK1 was the most effective demulsifier for treating this particular crude oil emulsion sample, despite the heavy nature of the crude and its pour point of 95°F. All samples were heated in the water bath for two hours before readings were taken.

At 1 minute, after heating for two hours, separated water in bottles containing the emulsion with concentrations 0.4ml, 0.6ml, 0.8ml, 1.0ml, and 1.2ml of formula 1 (CONK1), were 2.5M, 2.5m, 7.5m, 2.5m, and 7.5m respectively, at 60 minutes, 1.0m of separated water was observed for emulsion sample injected with 0.2m

Concentration of CONK1 but no further change was observed for the next 60 minutes.

A little deviation from normal was observed in the sample dosed with 1.0m of CONK1 at 1 minute of treatment. As volume of injected demulsifier increased, ideally the volume of separated water ought to increase or be maintained not decrease from 7.5m to 2.5m then back to 7.5m.

This may be due to sludge/sediment content in the emulsion sample. Samples treated with 0.4m and 0.8m of CONK2 (Table 4.2 figure 4.2) separated 2.5m and 5.0m water respectively after 120 minutes. Sediment containing traces of water were observed in other bottles containing CONK2 perhaps an adjustment of the proportion of materials used may have produced a better result after 120. On the other hand, the total separated water volume by Separol after 120 minutes was 6m. This proves that there is no demulsifier which can break all emulsions effectively, ideally for medium to light crude oil emulsions, the API gravity ought to increase due to the separation and extraction of water. However, for heavy crudes (in this case below 20° API) which normally are treated above 180°F, heat may have had a negative effect on difference in density. In special cases, increased heat may cause the density of water to be less than that of oil. Heating well fluids is expensive and can cause a significant loss of the lower boiling-point hydrocarbons. This results in loss of oil volume because the light ends are boiled off, and the remaining liquid has a lower API gravity and thus may have a lower value.

A manual centrifuge was used before and after treatment to determine the BS& W content of crude oil emulsion samples. Also due to the API gravity of the crude and pour point there was very little separated water from the emulsion hence requiring the addition of Xylene after treatment to the samples in order to reduce its pour point temperature to room temperature. Nevertheless, no free water was observed after treatment.

## **CONCLUSION**

In this work, two demulsifiers were formulated from locally sourced raw material. They were tested on a crude oil emulsion sample from a Niger Delta Field and subjected to a temperature of 60° F. this rests of the treatment was the successful separation of the oil emulsion sample into oil and water. The separated water volume by the local emulsifier (CONK1) was 31m, while that separated by a foreign demulsifier (Separol) was 6m. this showed the locally formulated demulsifier had high effect and better water separation capability than the commercially available imported demulsifier (Separol).

The results clearly demonstrated that cheap locally chemicals with demulsification properties can be used to successfully break emulsions and enhance the quality and quantity of crude productivity. The demulsifiers (CONK1 and CONK2) contained no organic chloride, bromides, iodides, or lead, hence will not cause any refining problems.

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