



IMPACT OF LOCALLY FORMULATED DEMULSIFIERS FROM LOCALLY SOURCED RAW MATERIALS ON EMULSION DEMULSIFICATION

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ABSTRACT

Separation of water from oil before transportation or refining is very essential for economic and operational reasons. 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. 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. 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, showing

the effectiveness of locally formulated demulsifier and better water separation capability than the commercially available imported demulsifier known.

Keywords: Local materials, Coalescence, Demulsifier, Emulsion, Flocculation, Niger Delta.

1. Introduction

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, (R. Grace and Schramm, L.L. 1992).

Whether these emulsions are created inadvertently or are unavoidable, as in the oil-field production area, or are deliberately induced, as in refinery desalting operations, the economic necessity to eliminate emulsions or maximize oil-water separation is present. Emulsion problems in crude oil production and transportation requires expensive emulsion separation equipment such as water treaters, separators and coalescers. Hence, chemical demulsification is the most suitable method from both operational and economic point of view to break the crude oil emulsion (I.H. Auflem. 2002). Among chemical agents, interfacial-active demulsifiers, which weaken the stabilizing films to enhance droplets coalescence, are preferred due to lower addition rates needed. However, these demulsifiers are costly and pose significant threat to the environment. It becomes imperative to develop cheap and environmentally friendly demulsifiers from locally source raw material.

1.1 Background of Study

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'enant, 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.

1.1.2 Characteristics of Emulsion

Crude oil emulsions are complex and should be characterized as completely as possible. Droplet-size distribution, interfacial phenomena, and the nature of organic and inorganic components are important. The viscosity of the emulsion is affected by both the water content and droplet size distribution [S. D. Taylor, 1988, D. G. Thompson, A. S. Taylor, and D. E. Graham, 1987]. The increase in aqueous phase of the emulsion leads to an increase in viscosity of emulsion which in turn aggravates flow of emulsion in conduct either at the sand face or through the surface facilities [R. Espinoza and W. Kleinitz, 2003, K. Sunil, A. Abdullah, and N. S. Meeranpillal,

2007]. Stable water-in-oil emulsions have been generally found to exhibit high interfacial viscosity and/or elasticity modulus. Viscosity of crude oil emulsion was found to increase with increase in water and decreased with increase in speed of rotation of spindle when demulsifier is added [N. H. Abdurahman and W. K. Mahmood, 2012].

An emulsion's characteristics change continually from the time of formation to the instant of complete resolution. Accordingly, aged emulsions can exhibit very different characteristics from those that fresh samples do. This is because any given oil contains many types of adsorbable materials and because the adsorption rate of the emulsifier and its persistence at the interface can vary. The emulsion characteristics also change when the liquid is subjected to changes in the following:

- Temperature
- Pressure
- Degree of agitation

1.1.3 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.

1.1.4 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 μm to more than 1000 μm . 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

1.1.5 Emulsion Classification

Emulsion viscosity can be substantially greater than the viscosity of either the oil or the water because emulsions show non-Newtonian behavior. This behavior is a result of droplet crowding or structural viscosity. A fluid is considered non-Newtonian when its viscosity is a function of shear rate. A closely related and very important property, especially for demulsification, is the interfacial viscosity, or the viscosity of the fluid at the oil/water interface. As mentioned water-in-oil emulsions form rigid interfacial films encapsulating the water droplets. These interfacial films stabilize an emulsion by lowering IFT and increasing interfacial viscosity. These films retard the rate of oil-film drainage during the coalescence of water droplets, thereby greatly

reducing the rate of emulsion breakdown. The oil-drainage rate depends on the interfacial shear viscosity. High interfacial viscosities significantly slow the liquid drainage rate and thus have a stabilizing effect on the emulsion. Emulsion interfacial viscosity plays a very important role in demulsification.

Produced oilfield emulsions can be classified into three broad groups:

- Water-in-oil
- Oil-in-water
- Multiple or complex emulsions

Water-in-oil emulsions consist of water droplets in a continuous oil phase, and oil-in-water emulsions consist of oil droplets in a water-continuous phase. **Figs. 1 and 2** show the two basic (water-in-oil and oil-in-water) types of emulsions. In the oil industry, water-in-oil emulsions are more common (most produced oilfield emulsions are of this kind); therefore, the oil-in-water emulsions are sometimes referred to as "reverse" emulsions.

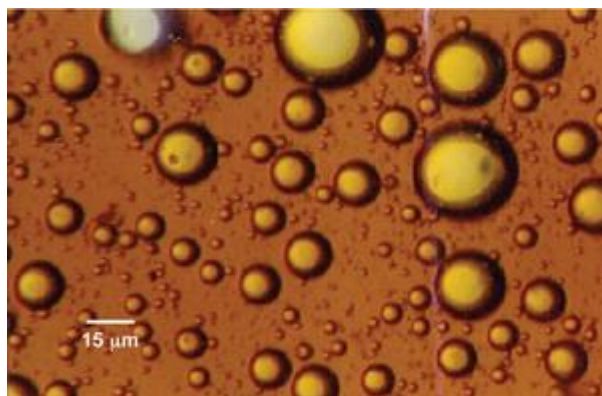


Fig. 1.1 – Photomicrograph of water-in-oil emulsion.

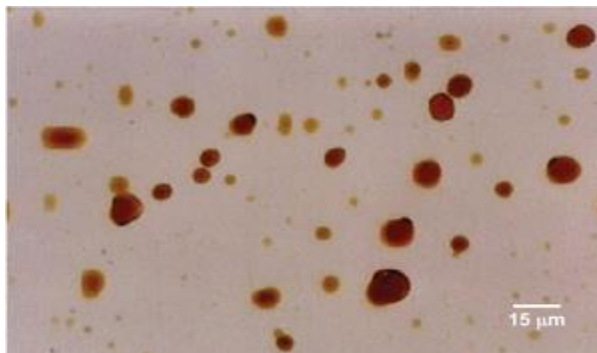


Fig. 1.2 – Photomicrograph of oil-in-water emulsion.

Multiple emulsions are more complex and consist of tiny droplets suspended in bigger droplets that are suspended in a continuous phase. For example, a water-in-oil-in-water emulsion consists of water droplets suspended in larger oil droplets that, in turn, are suspended in a continuous water phase. **Fig. 3** shows an example of a multiple emulsion.

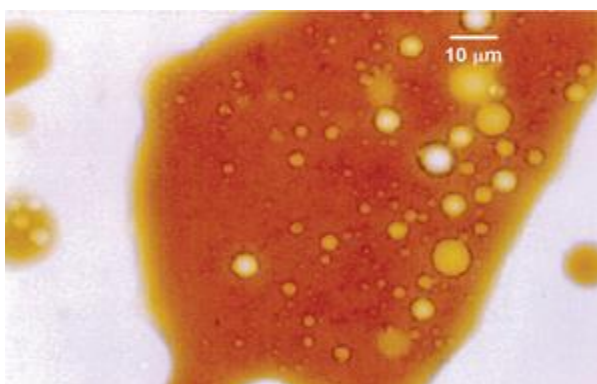


Fig. 1.3 – Photomicrograph of water-in-oil-in-water emulsion.

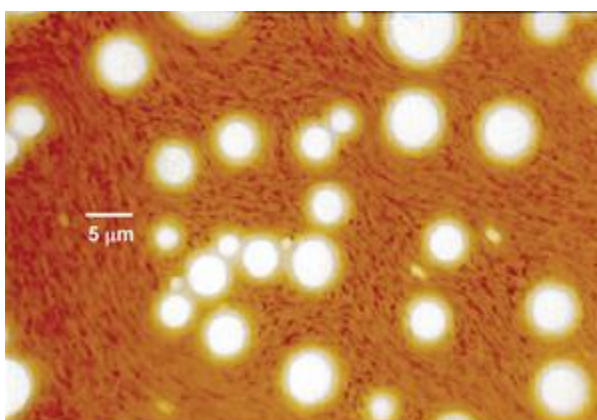


Fig. 1.4 – Photomicrograph of emulsion showing the presence of solids.

Water-in-oil crude oil emulsions may be encountered at all stages in the petroleum production and in processing industry. With presence of water, they are typically undesirable and can result in high pumping costs and pipeline corrossions and increase the cost of transportation. Reduced throughput is needed to introduce special handling equipment, contribute to plugging of gravel pack at the sand phase, and affect oil spill cleanup.

1.2 Objectives of Study

This research is focused primarily to formulate local demulsifier from locally sourced raw materials and apply the formulated local demulsifier on water-in-oil emulsion for demulsification.

2.1 Demulsification process

A number of general rules help to form the basic philosophy of how emulsion behave within commercial emulsion breaking (Grace, 1992). Firstly, petroleum emulsions are composed primarily of immiscible liquids. Separation should be the natural tendency of these liquids, by providing the density different between the liquid that are exists. Secondly, the gravitational settling rate is dependent on the surface tension of the droplets that form the internal phase of the emulsion. Large droplets have less surface tension as a function of mass than small droplets.

Therefore, anything that can be done to increase the droplets size or coalescence will increase the rate of separation. Thirdly, an emulsion is stable within a given environment. Varying the environment may affect the stability of an emulsion and allow the phases separation. Finally, a stable emulsion exists only when emulsifying agents are present. Neutralization, alteration or elimination of the emulsifying agents will allow immiscible liquids to separate.

From the above four generalizations it becomes noticeable that a number of options exist in emulsion breaking. Any single change in these areas may result in the resolution of an emulsion.

2.2 Demulsifier formulation

Demulsifiers can be used singularly or in combinations of two or more.

Finding a demulsifier system that works well is often done by trial and error. Grace (1992) stated that the selection process has historically been viewed as a “black art”, which produces as many failures as successes. But the failures can be eliminated with the increasing understanding of emulsions and emulsion-breaking chemicals, the development of new test procedures and devices, and well-organized method of chemical selection. The best demulsifiers are one that can reduce the interfacial shear viscosity, increases the interfacial mobility and destabilizing the water-in-oil emulsion.

2.3 Demulsifiers performance

Different types of demulsifiers will give the different way in demulsification process. Knowledge of formation and stability of crude oil emulsions, types of demulsifiers, demulsification mechanisms and so on are very important since it can be useful in the demulsification process of crude oil emulsions. Thus, it is frequently observed in studies of parameters that can affect the formation of stability of the crude oil emulsion.

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

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 mark and heated to 60°C for 2 hours.

4.0 RESULTS AND DISCUSSION

The Bottle Test results using the two locally formulated demulsifiers (CONK1 and CONK2) 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, and 4.2 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.

	Separated water Volume				
Volume of Demulsifier (ml)	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

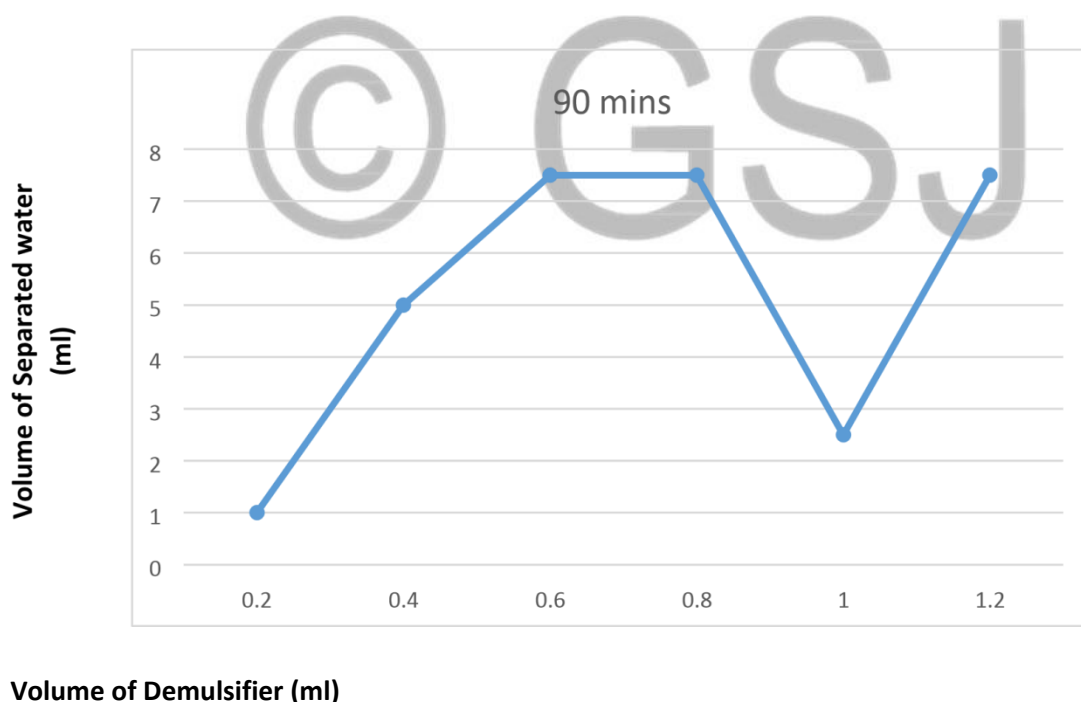
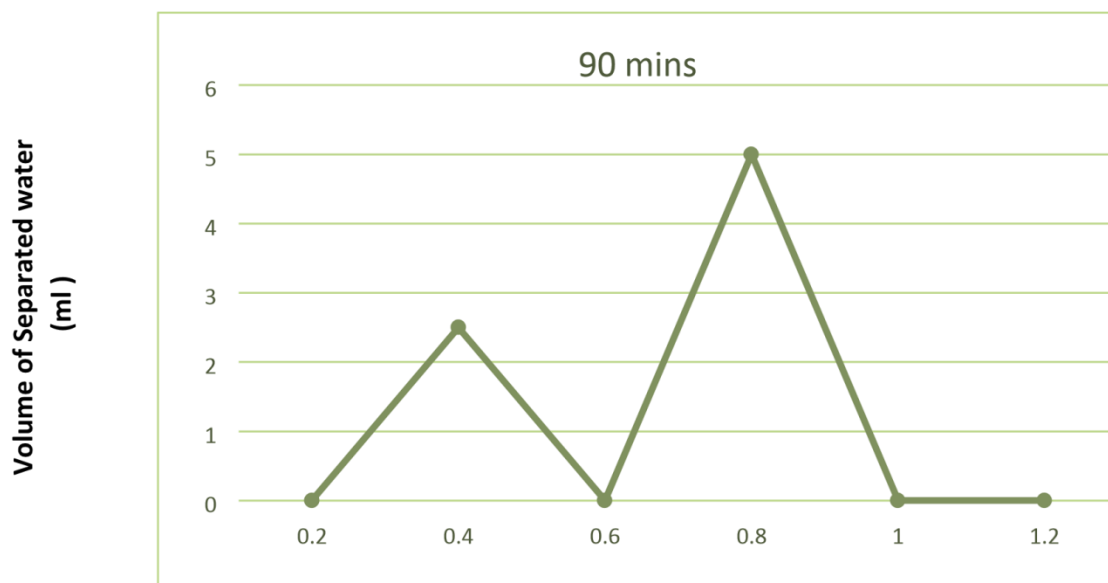


Figure 4.1 showing the volume of separated water using locally formulated CONK1 demulsifier

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

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.

CONCLUSION

In this work, two demulsifiers were formulated from locally sourced material. They were tested on a crude oil emulsion sample from a Niger Delta Field (Oben Field) and subjected to a temperature of 60° F. This result 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.

The results clearly demonstrated that cheap locally chemicals with demulsification properties can be used to successfully to break emulsions and enhance the quality of the produced crude.

The demulsifiers (CONK1 and CONK2) contained no organic chloride, bromides, iodides, or lead, hence will not cause any refining problems.

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