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Plant extraction as a new demulsifier formulation for water-in-oil 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 plant extracts. Single plant screening of two groups of plant samples; A, B, C (Calotropis procera: dry and fresh extract and Citrus limonum: fresh extract) and D, E, F (Jathropha curcas: dry and fresh extract and Thevetia ferifolia: fresh extract) using bottle test and centrifuge methods was conducted at 70^0C for 300 seconds. The effect of modifier (ether, ethylacetate, ethylene glycol, ethanol and buthanol) was determined using the same methods. The optimum concentrations in g/ml for combination of oil and water-soluble demulsifier was determined using prediction profiler plot. Model formulation was based on 2^3 full factorial (custom) experimental design for the two groups and the final product was compared with commercial demulsifier; product code W054 in emulsion treatments. Results show that single plant screening shows that A, B and C are oil-soluble and D, E and F are water-soluble. From the modifier screening, ether (60% vol) has the highest volume of water separation while butanol (64% vol) has the highest oil separation. The optimum concentrations for oil and water-soluble demulsifier obtained from the prediction profiler plot was (A=3.1, B=1.95 and C=2.1) and (D=1.5, E=01.0 and F=3.65) respectively. The combination of oil and water-soluble demulsifiers for optimum emulsion resolution was based on the combination of B, C, D, E and F using the predicted concentrations.

Keywords: plant, new, extraction, demulsifer, development

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.

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.

Background of study

Testing procedures are available to select appropriate chemicals. These tests include bottle tests, dynamic simulators, and actual plant tests. For the demulsifier to work effectively, it must make intimate contact with the emulsion and reach the oil/water interface. The amount of chemical added is also important. Too little demulsifier will leave the emulsion unresolved. Conversely, a large dose of demulsifier (an overtreat condition) may be detrimental. Because demulsifiers are surface-active agents like the emulsifiers, excess demulsifier may produce very stable emulsions. The amount or dosage of demulsifier required is very site-specific and depends on several factors, some of which are discussed in this section of the study. On the basis of an evaluation of the literature, the demulsifier rates quoted vary from less than 10 to more than 100 ppm (based on total production rates). To ensure good overall performance, a demulsifier should meet the following criteria.

i. Dissolve in the continuous oil phase.

ii. Have a concentration large enough to diffuse to the oil/water interface. However, it should not be higher than the critical aggregate concentration.

iii. Partition into the water phase (partition coefficient close to unity).

iv. Possess a high rate of adsorption at the interface.

v. Have an interfacial activity high enough to suppress the IFT gradient, thus accelerating the rate of film drainage and promoting coalescence

Demulsifiers are typically formulated with polymeric chains of ethylene oxides and propylene oxides of alcohols and amines, ethoxylated resins, ethoxylated phenols, polyhydric alcohols and sulphonic acids salts.

Aim and objectives

This study is designed to primarily formulate and apply local demulsifier from specific plant extracts to break water-in-oil emulsion.

Specific objectives include:

i. Identification and screening of plants.

ii. Determination of water and oil separation from emulsions using plants extracts at different concentrations.

iii. Study of some base chemicals (modifiers) used in formulation of existing chemical demulsifiers.

iv. Optimization of demulsifier formulation.

v. Application of formulated demulsifier on different crude oil emulsion systems.

vi. Comparison of the formulated demulsifier with a standard commercially available demulsifier.

Literature rewiew

The most common method of emulsion treatment is adding demulsifiers. The effect of chemical demulsifier in demulsification of water in oil emulsions experimentally has been studied by a few investigators [3, 4]. Four groups of demulsifier with different functional groups were used namely; amines, polyhydric alcohols suphonates and polymer. The results obtained have shown the capability of chemical demulsifier in destabilization of water-in-oil emulsions. These chemicals are designed to neutralize the stabilizing effect of emulsifying agents. Demulsifiers are surface-active compounds that, when added to the emulsion, migrate to the oil/ water interface, rupture or weaken the rigid film, and enhance water droplet coalescence. Optimum emulsion breaking with a demulsifier requires a properly selected chemical for the given emulsion; adequate quantity of this chemical; adequate mixing of the chemical in the emulsion; and sufficient retention time in separators to settle water droplets. It may also require the addition of heat, electric grids, and coalescers to facilitate or completely resolve the emulsion.

The authors in [5] investigated three different macromolecular structures of poly (ethylene oxide-b-propylene oxide) copolymers, used in formulations of commercial demulsifiers for breaking water-in-crude oil emulsions. The interfacial activity (a), the lower interfacial tension (gm), the critical micelle concentration (CMC), the interfacial concentration (I) and the molecular area (A) adsorbed at the interface of the surfactant solutions were evaluated. These results were correlated to surfactant performance in coalescing three different asphaltene model emulsions. The Poly (ethylene oxide-b-propylene oxide) PEO-b-PPO commercial demulsifiers that were capable to dewater asphaltene model emulsions, exhibited interfacial activity to the oil-water interface, reduced the interfacial tension to low values, reached the CMC at low concentration and presented low molecular area adsorbed at the interface.

Selection of the right demulsifier is crucial to emulsion breaking. Table 1 shows the development and evaluation of chemical demulsifier [6].

The selection process for chemicals is still viewed as an art rather than a science. However, with the increasing understanding of emulsion mechanisms, the availability of new and improved chemicals, new technology, and research, and development efforts, selection of the right chemical is becoming more scientific. Many of the failures of the past have been eliminated.

Demulsifier chemicals contain the following components: solvents, surface-active ingredients, and flocculants. Solvents, such as benzene, toluene, xylene, short-chain alcohols, and heavy aromatic naptha, are generally carriers for the active ingredients of the demulsifier. Some solvents change the solubility conditions of the natural emulsifiers (e.g., asphaltenes) that are accumulated at the oil/brine interface. These solvents dissolve the indigenous surface-active agents back into the bulk phase, affecting the properties of the interfacial film that can facilitate coalescence and water separation. Surface-active ingredients are chemicals that have surface-active properties characterized by hydrophilic-lipophilic balance (HLB) values. Flocculants are chemicals that flocculate the water droplets and facilitate coalescence.

3.0 Materials and methods

In order to achieve the objectives of this study, several materials, experimental and analytical procedures used in this study are presented in this section.

3.1 General chemicals

The chemicals used were obtained of analar grade; acetone (99.5%) as sterilizing solvent; n-hexane (99%), required in asphaltenes and saturates recovery; dichloromethane (99%) as solvent in resin recovery; methanol (99.5%) for aromatics recovery. Silica gel, ethanol (98%), butanol (99.5%), ether (98%), ethylacetate (98%) and ethylene glycol (99%), were used in demulsification.

3.2 Chemical demulsifier

The demulsifier chosen and used in this study to benchmark the formulated local demulsifier was obtained from Schlumberger with product code W054.

3.3 Crude oil samples

Crude oil samples for emulsion preparation were obtained from Ibigwe field, and Forcados terminal in the Niger-Delta area of Nigeria. The properties of these crudes as well as the SARA analysis, were determined at the Central Laboratory University of Ibadan.

3.4 Plants extracts

The plants used for this study as listed in Table 1.1 were collected within and outside the University of Ibadan. Most of these plants were extracted fresh while others were air dried for seven days before extraction.

3.5 Oil field brine

Synthetic oilfield brine used in preparing the emulsion system was prepared by dissolving NaCl in deionized water in order to obtain the required salinity similar to the average Niger-delta field which is about 2.4% (Oruwori and Ikiensikiama, 2010) by using equation 1[9].

Salinity equation; $Y = 8.3566X - 0.3582$ (1)

Where:

Y = Salinity (%w/w); % in per thousand

X = NaCl concentration (g/100 ml)

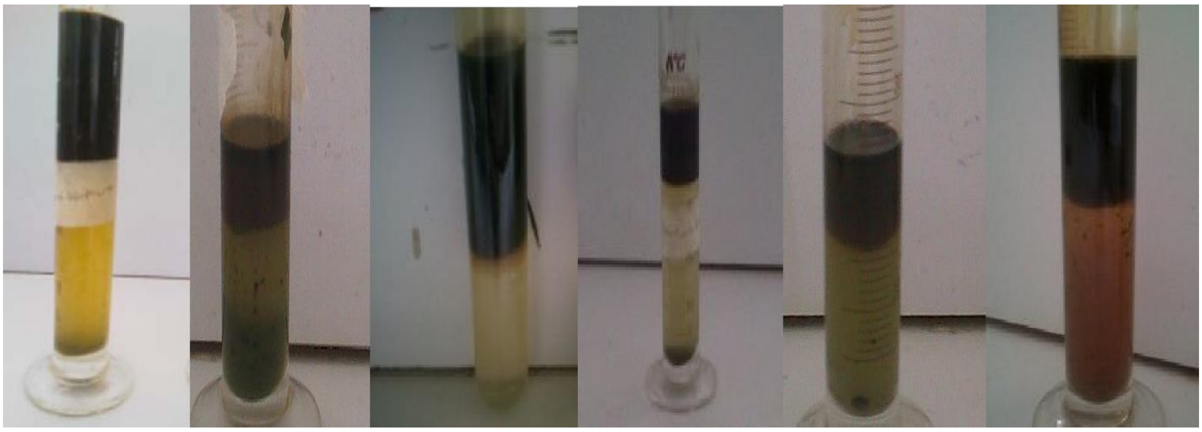
Table 1.1: Botanical names and common names of plant used

Botanical names	Common names
Calotropis procera	Apple of Sodom
Jathropha curcas	Barbados nut, physic nut
Thevetia ferifolia	Yellow oleander, lucky nut
Termanalia catappa	Almond
Carica papaya	papaya
Citrus limonium	Lemon

3.6 Experimental methods

3.6.1 Effect of Concentration of Plant Extracts on Demulsification Performance

Four different concentrations were used to examine the effects of the plant extracts on the emulsion system. The concentration varied from 1 to 4g/ml. The temperature was fixed at 70^{o}C. The volume of water and oil separation from the emulsion system was observed, recorded and the % water and oil separated were plotted against time.



A B C D E F

Figure 2: Single Plant Extracts Screening for A, B, C, D, E and F respectively

4 Results and discussions

4.1 Crude Oil Properties

Table 7 shows the properties of these crudes as well as the SARA analysis, which were determined at the Central Laboratory University of Ibadan.

4.2 Oil-soluble demulsifier and water-soluble demulsifier: Effect of various concentrations

The results of percent water and oil separation using oil-soluble demulsifiers and water-soluble demulsifiers at concentrations of 1-4g/ml are shown in Figures 3a –3d.

From figures 3a and 3b, it was observed that the percent volume of oil separated by A, B and C is about 80 % and it's more than the percentage of water separated of which A has the highest percentage by volume and its about 60%. The concentration of 4g/ml is the highest concentration considered in the study, therefore, this concentration alongside with other concentrations (3g/ml, 2g/ml, and 1g/ml) are been used in classifying the different plants extract as either water soluble or oil soluble

demulsifier. From these figures, A, B and C is classified as oil soluble demulsifier. This is because the percentage of water separated from A, B and C is more compared D, E and F.

Table 7: Crude Oil Properties

Properties	Crude A	Crude B	Crude C
Location	Ibigwe field	Forcados terminal	Forcados terminal
Saturates hydrocarbon (%w/w)	26.45	93.52	7.30
Aromatic hydrocarbon (%w/w)	14.85	13.07	88.86
Resin (%w/w)	41.12	21.38	17.74
Asphaltene (%w/w)	0.00	28.47	0.00
Viscosity (cp)	5.10	20.44	14.14
Density (g/ml)	0.864	0.889	0.927
Specific gravity	0.838	0.893	0.894
API gravity	37.35	26.95	26.77

From figures 3c and 3d, it was observed that the percentage volume of water separated by D, E and F; 40%, 37.5%, 0%, is less than the percentage of oil separated; 60%, 75% and 50% respectively . From these figures, D, E and F are classified as water soluble demulsifier based on the same reason stated above.

4.3 Effects of modifier

The effect of ethanol, butanol and ethylene glycol, ether and ethyl acetate were investigated. Figure 4 shows the percent of water separation. From the plot, ether, ethyl acetate, ethylene glycol and ethanol addition resulted into 60, 55, 50 and 10% water separation while butanol has no effect. This shows that ether, ethyl acetate and ethylene glycol have a good ability in promoting water separation. From literature, this is because short chain alcohols are very soluble in water and long chain alcohols are very soluble in oil. Figure 5 shows oil separation as follows: butanol (64%), ethylene glycol (55%), ether (52%), ethanol (44%) and ethyl acetate (20%).

4.4 Effect of new formulation and commercial demulsifier on different crude oil system

The results obtained from optimization for water soluble demulsifier putting into consideration P-value and regression coefficient values show that X3 (< 0.0001, 8.198) contribute largely to water separation, followed by the X2X3 interaction (0.0001, 7.046) and then X2 (0.0001, 5.759) respectively. Since the interaction effect involves X2X3, the best demulsifier in this group is X2 and X3.

Also from the optimization of oil soluble demulsifier, considering the same parameters; P-value and regression coefficient; X3 (<0.0001, 7.483) has the highest significant contribution. This is followed by X1(< 0.0001, 6.166) and the interaction effect of X1X2X3 (0.0001, 4.171). From this, consideration was made for the three (X1, X2, X3).

Putting into consideration the prediction profiler, it predicted for oil soluble demulsifier that the combination of A, B and C (2.1, 1.95 and 3.1) respectively will produce an average 54.58696 % volume, with a minimum and maximum percentage volume separation at 51.8716 and 57.3023 % volume respectively. Prediction for water soluble demulsifier; D, E and F (1.475, 0.975 and 3.65) respectively will produce an average of 62.83028 perceentage volume of water, with a minimum and maximum percentage volume separation at 59.6774 and 65.9612 % volume respectively.

For formulation effect determination, B, C, D, E and F have the highest significance in water separation from

the synthetic crude oil emulsion. These extracts are combined together as predicted by the profiler. Table 10 shows the concentration of each extract used; this shows that F (Thevetia ferifolia) contributes largely to water separation than all others, followed by C (lemon). Figures 10 to 15 show the result of percentage volume of water and oil separated for three different crude oil samples and their comparison with a commercially available demulsifier. From figures 10, 12 and 14, after 300 seconds, the new formulation caused 51.7%, 49.2%, and 54.4% volume of water to separate from the synthetic crude A, B and C water-in-oil emulsion while 63%, 60% and 66.2% volume was separated by the commercial demulsifier used (W054). Also, figures 11, 13 and 15, after 300 seconds, the new formulation caused 36.3%, 60%, and 70.2% volume of oil to separate from the synthetic crude A, B and C water-in-oil emulsion while 85%, 95% and 80% volume was separated by the commercial demulsifier (W054) respectively.

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Table 10: Plants extract used for the new formulation and their concentration

Plants extract	Botanical Name	Concentration (g/ml)
B	Calotropis Procera (fresh extract)	1.95
C	Lemon	2.10
D	Jathropha curcas (dry extract)	1.48
E	Jathropha curcas (fresh extract)	0.98
F	Thevetia ferifolia	3.65

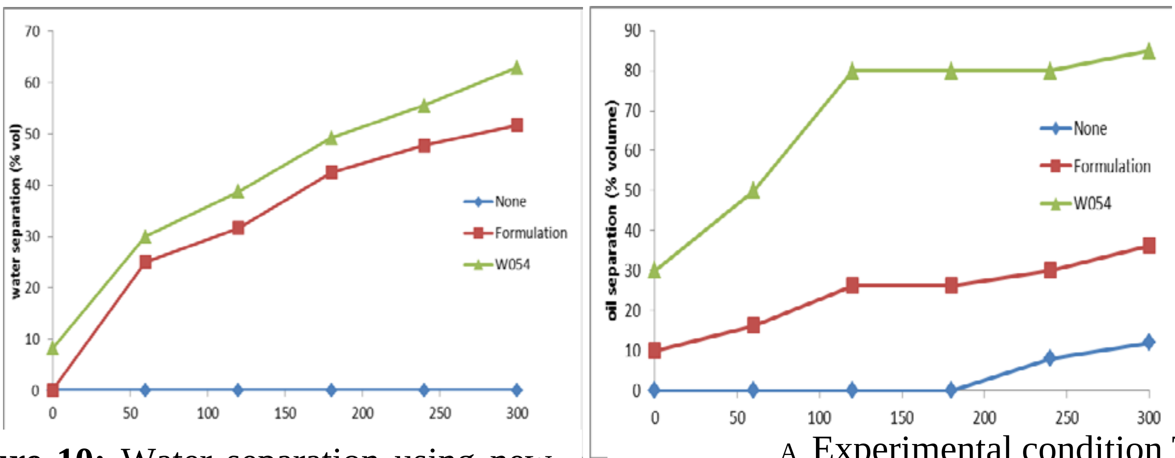

Figure 10: Water separation using new formulation commercial demulsifier on crude oil

A. Experimental condition T=70°C

Figure 11: Oil separation using new formulation commercial demulsifier on crude oil A. Experimental condition T=70°C

5 Conclusions and recommendations

5.1 Conclusions

This study investigate the use of plant extract in separation of water-in-oil emulsion on three crude oil systems and then comparison with chemically available demulsifier was made. From the two classifications; oil soluble

demulsifier and water soluble demulsifier, Calotropis Procera (fresh extract), lemon and Jathropha curcas (dry extract), Jathropha curcas (fresh extract), Thevetia ferifolia are the best in each group respectively and they were chosen in formulating the local demulsifier. The concentrations used are shown in table 10 which when combined together gives percentage water separation of 51.7% volume, 49.2% volume and 66.2 % volume of water for crudes A, B and C respectively. Also the percentage oil separated obtained are; 36.3% volume, 66% volume and 70.2% volume. This indicates that the new formulation separate water more than oil for crude A, oil more than water for crude B and C. This new formulation when extracted with a better solvent would perform better.

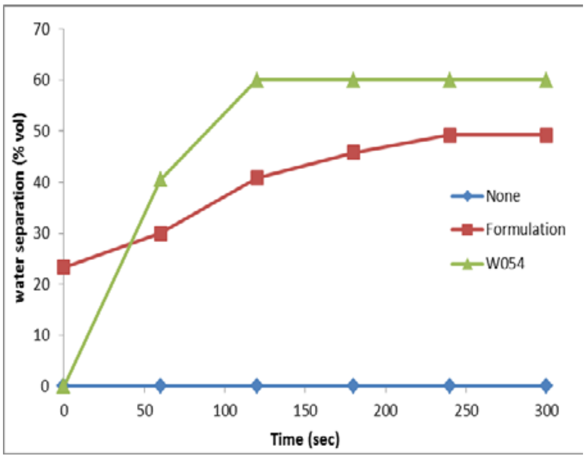

Figure 12: Water separation using new formulation commercial demulsifier on crude oil B. Experimental condition T=70°C

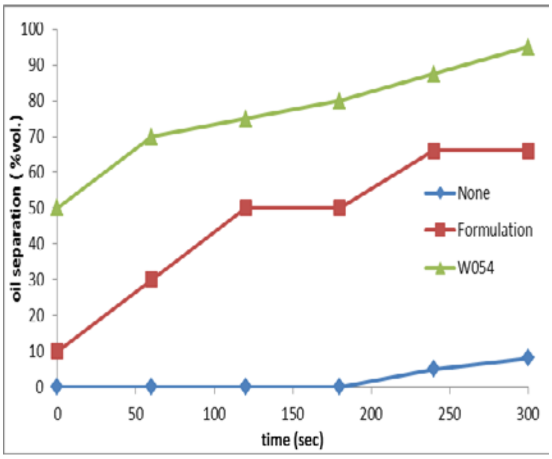

Figure 13: Oil separation using new formulation commercial demulsifier on crude oil B. Experimental condition T=70°C

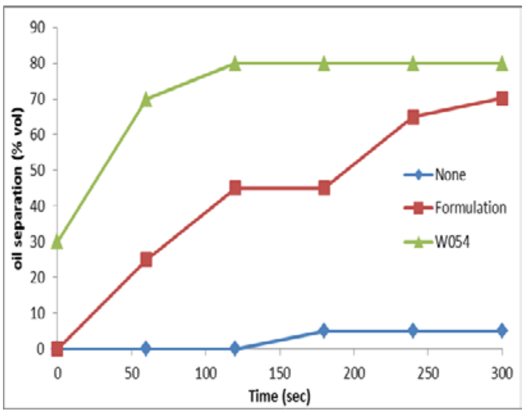

Figure 14: Water separation using new formulation commercial demulsifier on crude oil C. Experimental condition T=70°C

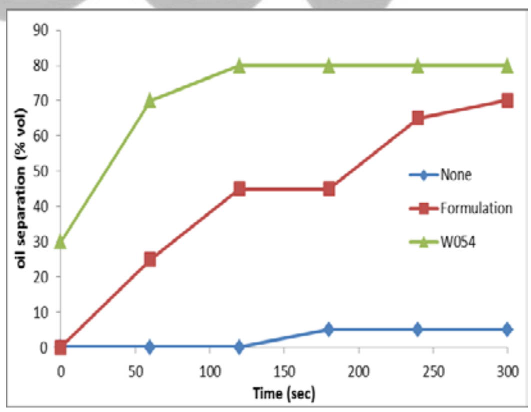

Figure 15: Oil separation using new formulation commercial demulsifier on crude oil B. Experimental condition T=70°C

The results obtained indicate that the plant extracts are good material for treating crude oil emulsion problems. These plants when extracted using a good solvent would function better.

Based on literature study, most of the commercially available chemical demulsifiers use different types of chemical modifiers to increase the efficiency of the chemical demulsifier. In this research work, the singular

effect of some of these modifiers was considered. It shows that ether separated water more than any other andbutanol has the highest volume of oil separated.

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