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Development of Local Demulsifier For Water - In- Oil Emulsion Treatment

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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.

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In comparison with commercial demulsifier the new formulation gave 51.7%, 49.2%, and 54.4% volume of water and 36.3%, 60%, and 70.2% volume of oil while chemical demulsifier gave 63%, 60% and 66.2% volume of water and 85%, 95% and 80% volume of oil for emulsions of the three crude oils respectively. Some plants when extracted with the appropriate solvents can be used in treating water-in-oil emulsion thus reducing cost and environmental pollution.

***Keywords*:** Plant extracts; Demulsifier; Response Surface Methodology; Water separation

1. Introduction

1.1 Background

Emulsions of oil and water are one of many problems directly associated with the petroleum industry, in both oil-field production and refinery environments [1]. 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 [2]. 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.

1.2 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.

1.3 Scope

The study focus on the use of locally formulated demulsifier from eight plant extracts and base chemicals (modifier) on emulsions from three different crude oil samples (one from Ibigwe field and the two others from Forcados terminal) in the Niger Delta area of Nigeria to determine optimum concentration for emulsion

resolution using full factorial design optimization. Comparison was then made with commercially available demulsifier to validate the effectiveness and efficiency of the local demulsifier.

2. 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.

Table 1: The development and evaluation of chemical demulsifier [6]

YEAR	DEMULSIFIER
1920 -1930	Soap, naphtenic acid salts and alkylary sulphate, sulphated caster oil
1930 - 1940	Petroleum sulphonates, derivatives of sulpho-acid oxidized castor oil and sulphosucinic acid ester
1940 -1950	Petroleum sulphonates, derivatives of sulpho-acid oxidized castor oil and sulphosucinic acid ester.
1950 -1960	Ethylene oxide/propylene oxide copolymer, Alkoxylated cyclic palkylphenol formaldehyde resins
1960 -1970	Amine alkoxylate
1970 – 1980	Alkoxylated cyclic p-alkylphenol formaldehyde resins
1980 - 1990	Polyesteramine and blends

The authors in [7] found that medium-chain alcohol (1-butanol and benzyl alcohol) and amines are speeding up the separation of water. The destabilization mechanisms in these two cases seem to be fundamentally different. The alcohols seem to modify the rigidity of the interfacial film by a diffusion/partitioning process while the amines show a strong and specific interaction with interfacial groups, hence hydrophilizing the whole film. Observed trends in the time dependence of the interfacial tension upon addition of alcohols and amines support these suggestions to destabilization mechanisms.

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 [8].

3. 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

Figure 1 is a flow chart of experimental protocol designed to formulate crude oil emulsion demulsifier used in the treatment of water-in-oil emulsion.

3.6.1 Emulsion preparation

Water in oil emulsion was prepared by mixing crude oil with the synthetic oilfield brine (1:1 v/v, 50ml). The emulsification was carried out by using a Hamilton Beach Scovill mixer set at medium speed for 2.5 minutes to get a stable emulsion [10].

3.6.2 Single plant extracts screening.

The plant extracts were screened using bottle test method. The screening process was performed at fixed temperature and varied plant extract concentrations. The most effective was obtained based on the percent water separation from emulsion system. The bottles containing the emulsion were immersed in water bath at a controlled temperature, 70^{o}C. Then it was placed in a centrifuge machine for 5 minutes, measuring water and oil separation at every 60 seconds interval. Extraction of plant was done using polar solvent (water), and the concentration was prepared based on the gram of plant and volume of water used in extracting the plants; g/ml.

3.6.3 Modifier screening

Some chemicals which form the base for all existing chemical demulsifiers were screened. The screening process is similar to plant screening process.

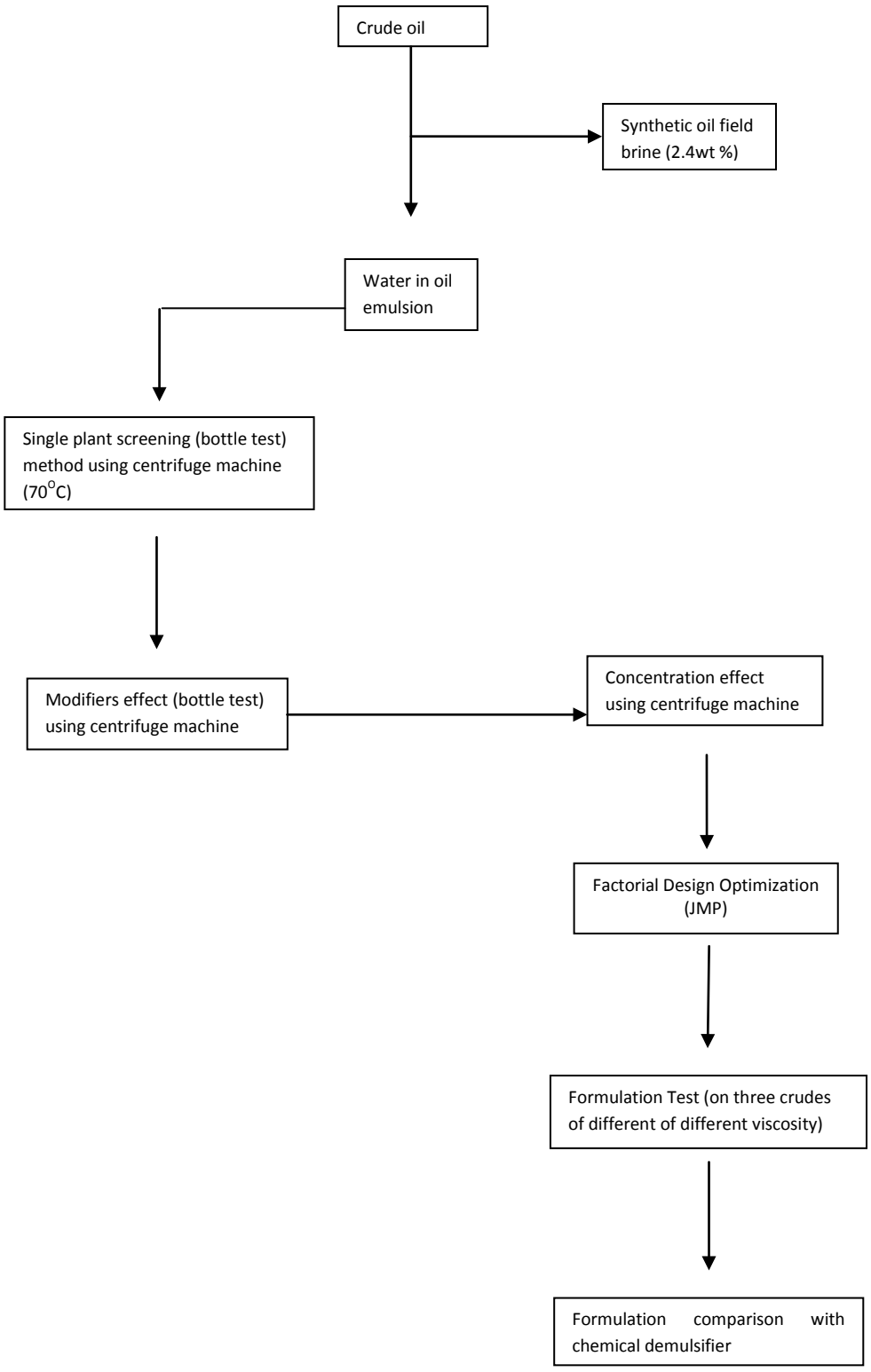
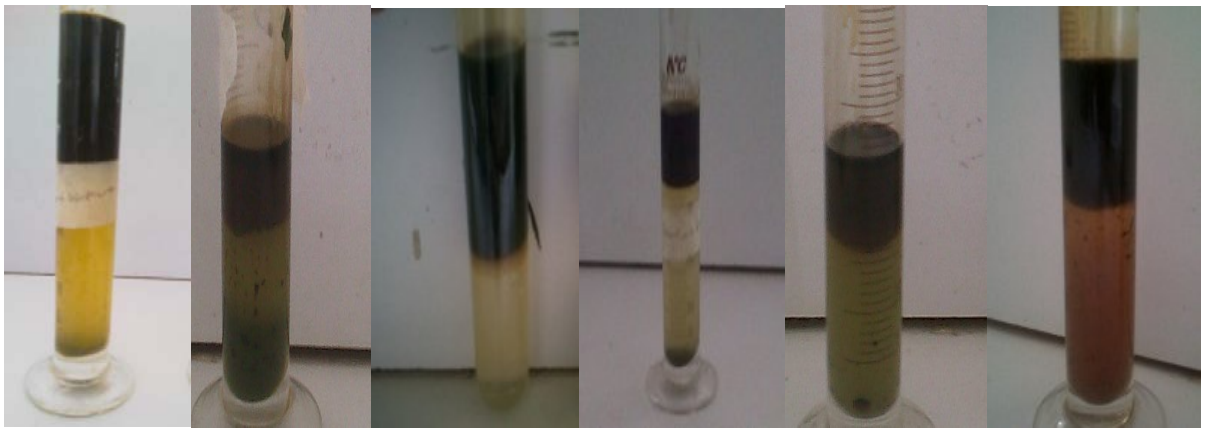


Figure 1: Experimental work flowchart.

3.6.4 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°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

3.7 Optimization of plant extracts formulations

The results from the previous section were used as the factors in optimizing the formulation of local demulsifier for breaking emulsion using experimental design. The Experimental design has been used to minimize the number of experimental conditions, which were investigated. The factors that affect the crude oil plant extract demulsifiers formulation were concentration of the plants used. Two run of Experimental design were used to optimize the concentration by dividing the plants into two groups: group 1 and group 2 (oil soluble demulsifier and water soluble demulsifier respectively). The optimum concentrations for both factors were combined as a new formulation in treating crude oil emulsion systems. The effect of this combination was checked in comparison with the chemical demulsifier (W054).

The design matrix in 2^3 factorial design is shown in Table 2. The range and the levels of variables of oil-soluble and water-soluble demulsifiers investigated in this study was given in Tables 3 and 4 which show the experimental range and levels of independent variables for water-soluble demulsifiers and oil-soluble demulsifier respectively. 2^3 full factorial (custom) design for oil-soluble demulsifiers and water-soluble demulsifiers are shown in Tables 5 and 6, respectively. The concentration values for both oil-soluble demulsifiers and water-soluble demulsifiers are gained from trial and error method by using bottle test.

Table 2: Algebraic signs for calculating effects in the 2^3 design (Myres and Montgomery, (2002)

Factor Run	A	B	C
1	-	-	-
2	+	-	-
3	-	+	-
4	+	+	-
5	-	-	+
6	+	-	+
7	-	+	+
8	+	+	+

Table 3: Experimental range and levels of Independence variables for water soluble demulsifier system

Variables Levels **X, variables(g/ml)**	**-1**	**+1**
X_4, A	1.8	3
X_5, B	2	2.4
X_6, C	1	2

Table 4: Experimental range and levels of Independence variables for oil soluble demulsifier system

Variables Levels **X, variables(g/ml)**	**-1**	**+1**
X_4, D	1.5	1.8
X_5, E	1	1.3
X_6, F	3	3.6

Table 5: 2^3 full factorial design for water- soluble demulsifier

Number of Experiments	Coded Variables A	B	C
1	1.8	2	1
2	3	2	1
3	1.8	2.4	1
4	3	2.4	1
5	1.8	2	2
6	3	2	2
7	1.8	2.4	2
8	3	2.4	2

Table 6: 2^3 full factorial design for oil-soluble demulsifier

Number of Experiments	Coded Variables X_4	X_5	X_6
1	1.5	1	3
2	1.8	1	3
3	1.5	1.3	3
4	1.8	1.3	3
5	1.5	1	3.6
6	1.8	1	3.6
7	1.5	1.3	3.6
8	1.8	1.3	3.6

3.8 Optimization by using response surface methodology (RSM)

The approximate model considered for this work is the first order model with interactions; equation (3). For the case of two independent variables, the first-order model in terms of the coded variables is

$$Y = \beta_o + \beta_1 X_1 + \beta_2 X_2 + € \quad (2)$$

Where;

Y = dependent variable, also refer to as regressand (by Greene).

X = independent variables, also known as explanatory variables or regressors.

β_o = intercept (regression coefficients)

€ = error term.

The form of the first-order model is sometimes called a main effects model, because it includes only the main effects of the two variables. If there is an interaction between these variables, it can be added to the model easily as follows:

$$\mathbf{Y} = \beta_o + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_{2;} \quad (3)$$

This is the first-order model with interaction. Adding the interaction term introduces curvature into the response function. Often the curvature in the true response surface is strong enough that the first-order model (even with the interaction term included) is inadequate. A second-order model will likely be required in these situations. For the case of two variables, the second-order model is

$$Y = \beta_o + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^{\,2} + \beta_{22} X_2^{\,2} + \beta_{12} X_1 X_{2;} \quad (4)$$

In general, the first order model is

$$\mathbf{Y} = \beta_o + \beta_1 X_1 + \beta_2 X_2 + \ldots + \beta_k X_k \quad (5)$$

The parameters of the mathematical model were estimated based on the data obtained by using full factorial (Custom) design (JMP; version 10) software in first order regression analysis.

By using the results obtained from optimization of demulsifier formulation, the formulation was tested on three different synthetic crude oil emulsion system. The emulsion preparation was the same as discussed previously. The volume of water and oil separation from the emulsion system was observed and the graph of % water separation versus time and % oil separation versus time are plotted.

The effectiveness of a commercial demulsifier formulation was examined in order to get the comparison between the new formulation created and the commercially available demulsifier used; product code (W054).

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 Optimization of demulsifier formulation

4.4.1 Optimization for oil-soluble demulsifier formulation.

Table 8 shows water separation results obtained from experimental design. The application of the response surface methodology yielded the following regression equation (equation 6), which is an empirical relationship between water separation yield and the test variables in coded unit.

$$Y= 32.263 + 1.306X_1 – 5.759X_2 – 8.198X_3 – 4.966X_1X_2 – 0.341X_1X_3 – 7.046X_2X_3 – 3.488X_1X_2X_3 \quad (6)$$

The intercept value (32.263), represent the average of all actual responses. The coefficients can be directly compared to assess the relative impact of factors. For instance, X_3 has the highest coefficient (8.198), thus it implies that X_3 has the largest effect on the response.

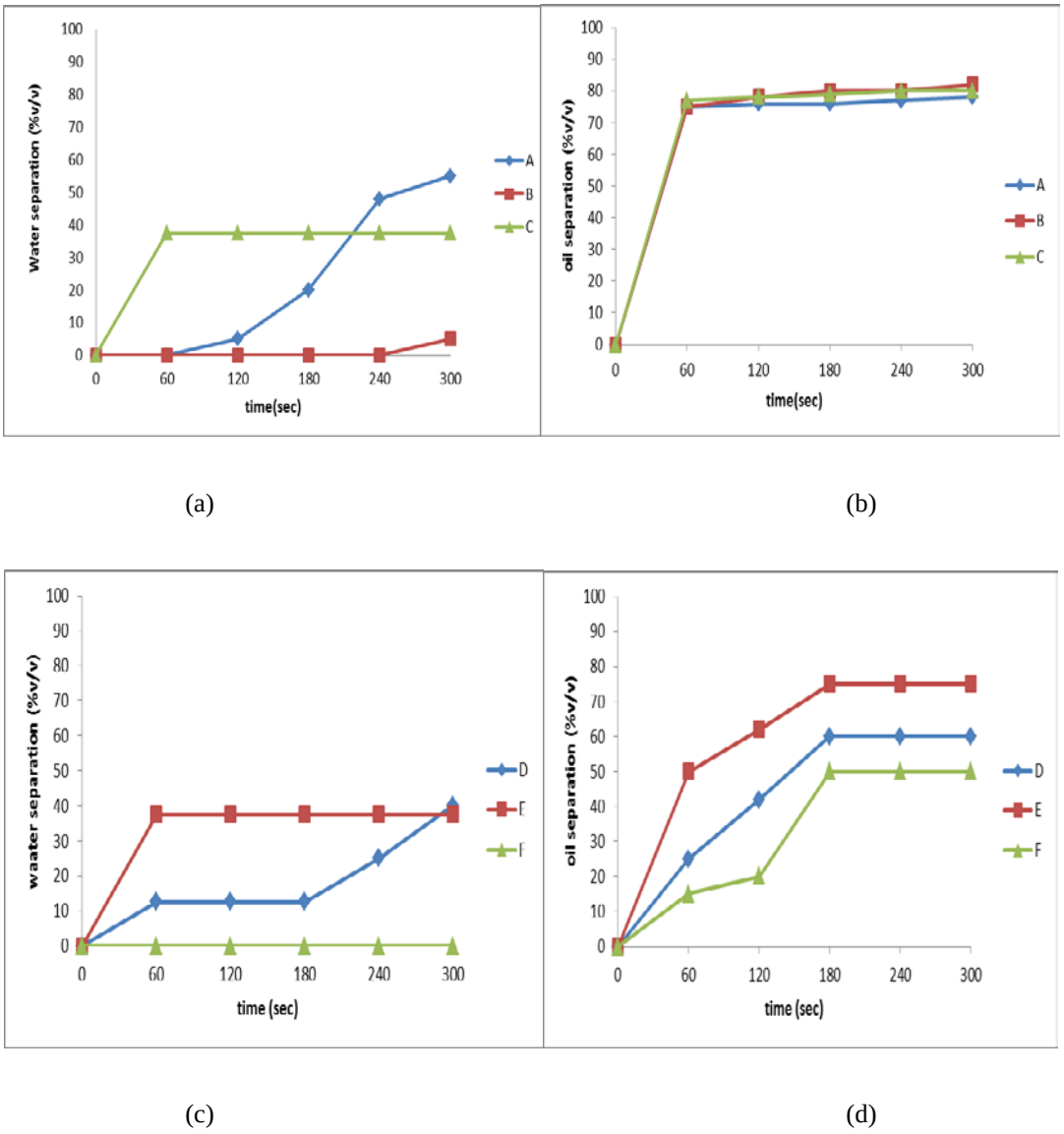


Figure 3: (a) Water separation (%) for A, B and C (b) Oil separation (%) for A, B and C (c) Water separation (%) for D, E and F (d) Oil separation (%) for D, E and F. Experimental conditions: T=70^{o}C, Conc=4g/ml

The actual versus predicted plot in Figure 6 shows the actual percentage volume of water separated versus the predicted percentage volume. As the predicted values come closer to the actual values, the points on the scatterplot fall closer around the red line. Because the points are all very close to the line, the model predicts well the percentage volume of water separated based on the chosen factors.

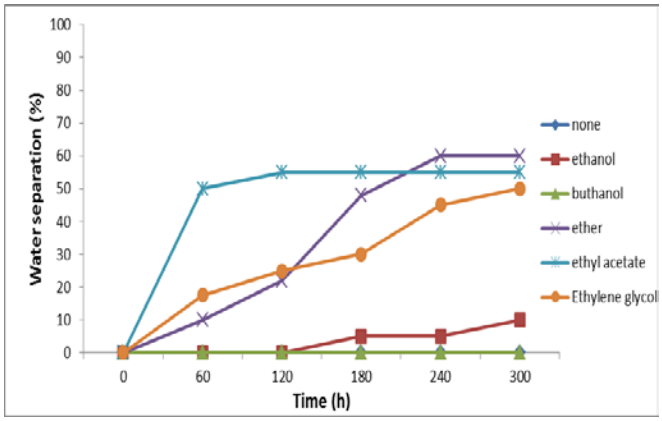


Figure 4: Water separation using modifier. Experimental conditions: T=70^{o}C

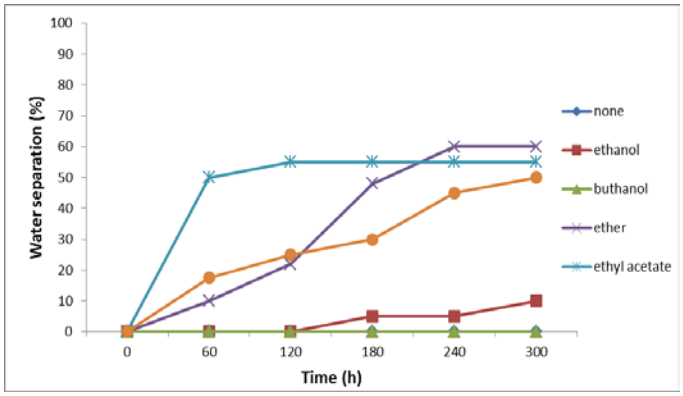


Figure 5: Oil separation using modifier. Experimental conditions: T=70^{o}C

Table 8: 2^3 full factorial design with the response for oil soluble demulsifier

runs	A	B	C	Water separation
1	1.8	2	2	27.5
2	3	2.4	1	42.12
3	3	2.4	2	4.24
4	3	2	1	42.30
5	1.8	2.4	1	41.58
6	3	2	2	46.29
7	1.8	2	1	36.50
8	1.8	2.4	2	17.99
9	1.8	2	1	35.60
10	3	2.4	1	41.71
11	1.8	2.4	2	19.51
12	3	2.4	2	3.3

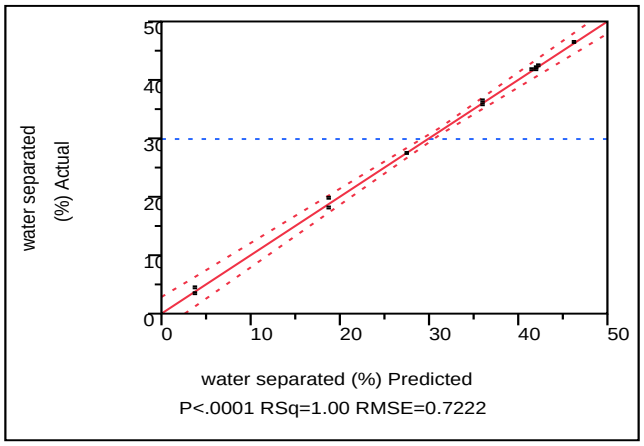


Figure 6: Actual by predicted plot of response water separated (%) for oil soluble demulsifier

Figure 7 is the prediction profiler for oil soluble demulsifier. The highest concentrations of A, B and C at the highest level of desirability is 3.1, 1.95 and 2.1 respectively. These combinations will yield an average value of 54.59% of water separation, in the range of 51.8716 to 57.3023 % volume of water separation.

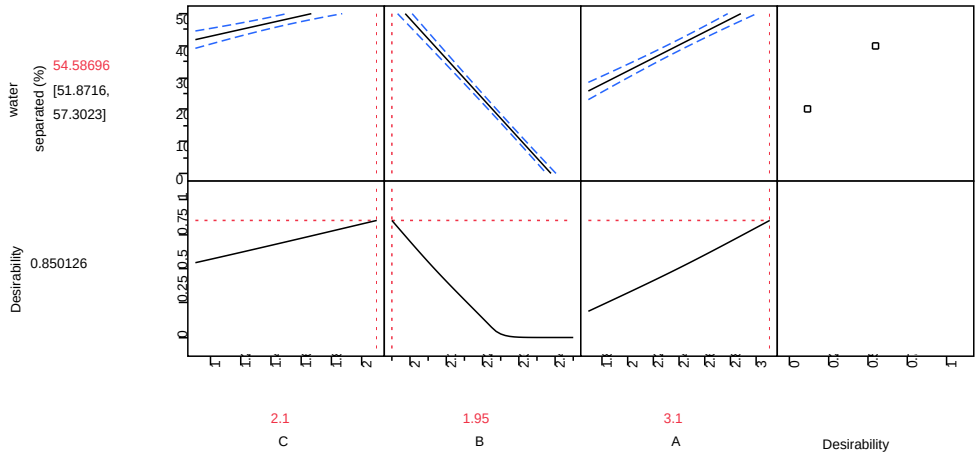


Figure 7: Prediction profiler for oil soluble demulsifier

4.4.2 Optimization for water-soluble demulsifier formulation.

Table 9 shows oil separation results obtained from experimental design. The application of the response surface methodology yielded the following regression equation (equation 7), which is an empirical relationship between water separation yield and the test variables in coded unit.

$$Y = 30.043 - 6.1655X_1 - 3.735X_2 - 7.483X_3 - 2.946X_1X_2 + 2.870X_1X_3 + 1.495X_2X_3 + 4.171X_1X_2X_3 \quad (7)$$

The intercept value (30.043), represent the average of all actual responses. The coefficients can be directly

compared to assess the relative impact of factors. For instance, X_3 has the highest coefficient (7.483), thus it implies that X_3 has the largest effect on the response.

The actual versus predicted plot in Figure 8 shows the actual percentage volume of water separated versus the predicted percentage volume.

Table 9: 2^3 full factorial design with the response for water soluble demulsifier

runs	D	E	F	Water separation
1	1.8	1	3.6	23.37
2	1.5	1.3	3.6	36.64
3	1.8	1	3	25.72
4	1.5	1.3	3	21..85
5	1.5	1.3	3.6	37.77
6	1.5	1	3.6	55.92
7	1.8	1.3	3	12.81
8	1.5	1	3	29.46
9	1.5	1	3	30.26
10	1.8	1.3	3.6	32.36
11	1.8	1	3.6	23.86
12	1.8	1.3	3.6	34.38

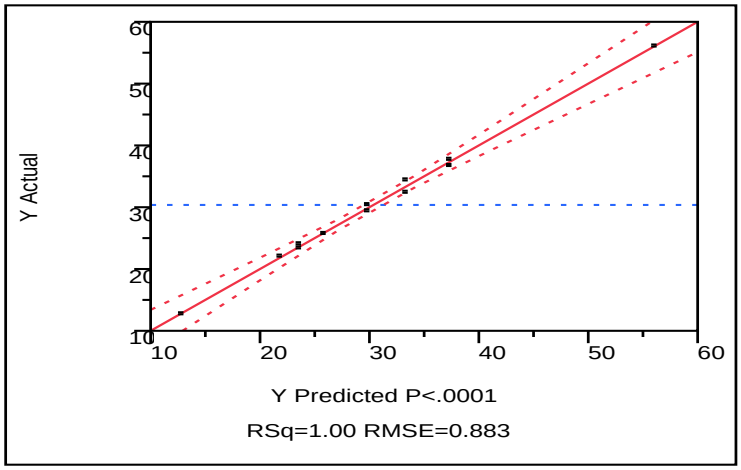


Figure 8: Actual by Predicted Plot of Response water separated (%) for water soluble demulsifier.

Figure 9 is the prediction profiler for water soluble demulsifier. From this figure, the highest desirability is 0.9984. The lowest and highest values on the graph are 0 and 1 respectively. The highest concentrations of D, E and F at the highest level of desirability are 1.475, 0.975 and 3.65 respectively. These combinations will yield an average value of 62.83028% of water separation, given the range of 59.6994 to 65.9612 % volume of water separation.

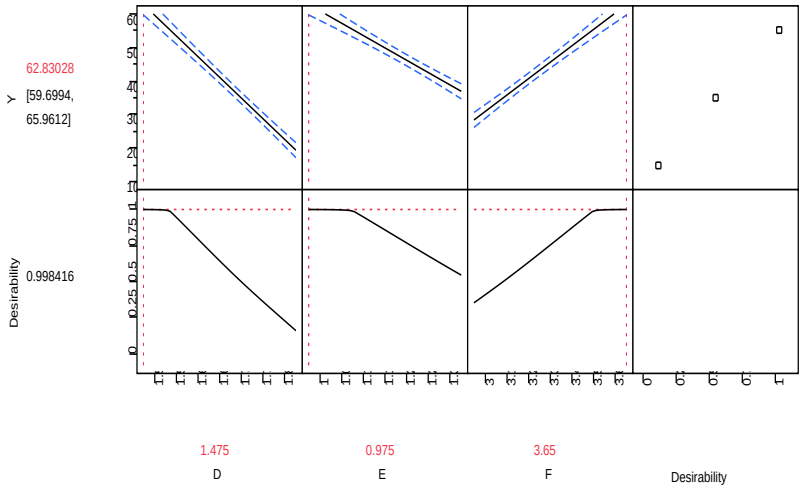


Figure 9: Prediction Profiler for water soluble demulsifier

4.5 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.

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

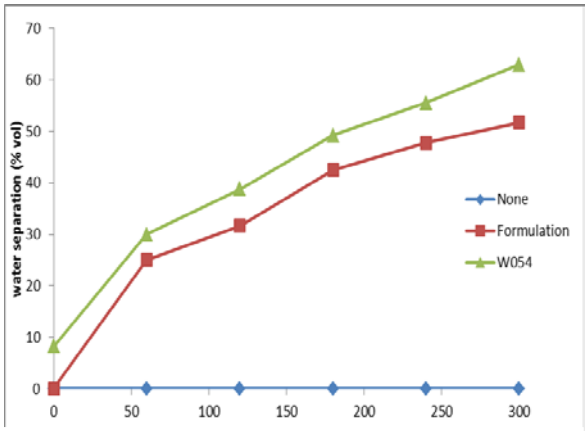


Figure 10: Water separation using new formulation commercial demulsifier on crude oil A. Experimental condition T=70°C

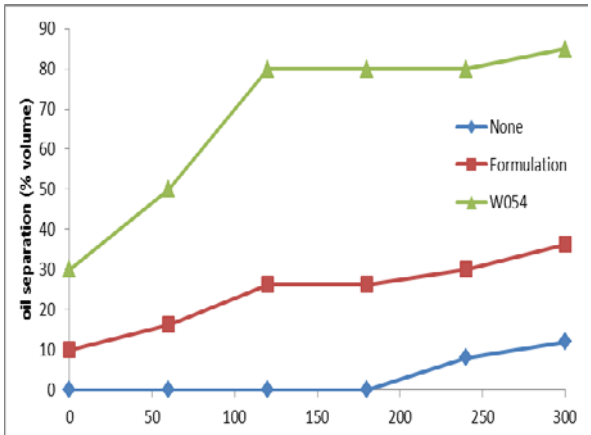


Figure 11: Oil separation using new formulation commercial demulsifier on crude oil A. Experimental condition T=70°C

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.

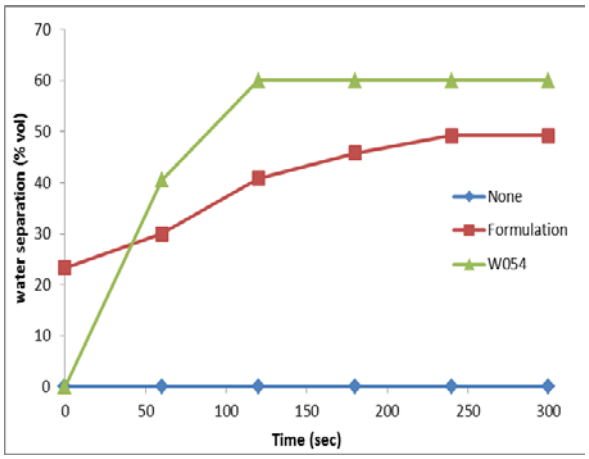


Figure 12: Water separation using new formulation commercial demulsifier on crude oil B. Experimental condition T=70°C

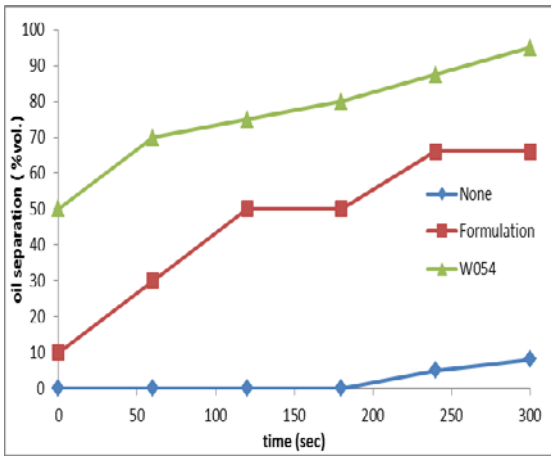


Figure 13: Oil separation using new formulation commercial demulsifier on crude oil B. Experimental condition T=70°C

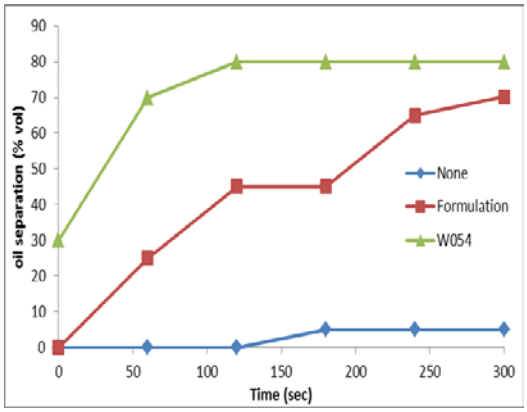


Figure 14: Water separation using new formulation commercial demulsifier on crude oil C. Experimental condition T=70°C

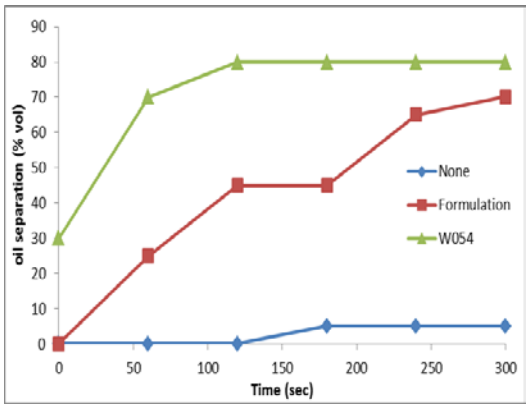


Figure 15: Oil separation using new formulation commercial demulsifier on crude oil B. Experimental condition T=70°C

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 and butanol has the highest volume of oil separated.

5.2 Recommendations for future studies

i. Since most of the plants used are easily accessible, further study should be done on plants and some other local materials that could be used as demulsifier.
ii. Also determination of a better solvent for these extract could help increase the efficiency and effectiveness of these extracts in water separation from crude oil emulsion.
iii. The rheological properties of these extracts should be examined and comparison should be made with that of commercially available demulsifiers.
iv. Further work considering temperature variation on extracts, continuous stirring (which would aid absorption of the extracts into the interface quickly) on water separation should be done.
v. Testing extracts on real emulsion system is a very good way of validating the effectiveness and efficiency of any local demusifier.

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