



Formulation of Green Oilfield Demulsifiers using *Annona Muricata* Seed Oil Extracts

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Abstract

Oilfield emulsions are formed when crude oil makes agitating contact with water in the presence of emulsion stabilizing substances. Emulsions are generally not desirable in the petroleum industry for a number of reasons. The presence of water-in-oil increases the incidence of corrosion and scaling in separation and refining equipments, while reducing the quality index of crude oil samples. In this study, green oilfield demulsifiers were formulated using seed oil extracts from the tropical soursop fruit. Seeds from locally-sourced soursop fruits were dehusked, crushed to obtain seed oil extracts. Using the extracts as base components, two green demulsifiers were formulated for treating oilfield emulsions. A number physicochemical characterization were also carried out on both extracts and demulsifiers. The developed demulsifiers were later compared with two commercial demulsifiers for benchmarking assessment using key indicators like hydrophilic-lipophilic balance (HLB) and dielectric constant. Obtained results showed satisfactory properties of the formulated demulsifiers in terms of hydrophilic-lipophilic balance (HLB) and dielectric constant.

Keywords: soursop seed oil, oilfield chemicals, demulsifier, green chemistry, hydrophilic-lipophilic balance, dielectric constant

Introduction

Emulsions exist between liquids that have low solubility between them (Roostaie et al., 2017). Most of the crude oil is produced initially in the form of water-in-oil (W/O) emulsions in oilfields (Akpoturi, & Ejelonu, 2021). Oilfield emulsion is produced as a result of the contact between two immiscible liquids, in the presence of emulsifying compounds in crude oil (e.g asphaltenes), as well as turbulence during production activities. Due to solubility differences between crude oil components in water, produced water can equally be produced in the form of emulsions (Liu et al., 2019).

Emulsions can be difficult to treat and may cause several operational problems in wet-crude handling facilities and gas/oil separating plants (Duru et al., 2016). Emulsions can create high-pressure drops in flow lines which may lead to an increase in demulsifier usage, and sometimes cause trips or upsets in wet-crude handling facilities. In an untreated emulsion, the density difference between the oil and the water will cause a certain amount of water to separate from the oil by natural coalescence and settling. However, unless some form of treatment is used to accomplish complete separation, a small percentage of water probably will remain in the oil, even after extended settling time (Abdulredha et al., 2020).

Demulsification is the process for the separation of emulsions into their constituent phases (Abdulredha *et al.*, 2022). There are three basic methods for demulsification, including physical, chemical and biological methods. If demulsification is not properly done, this can lead to excessive pumping pressure due to increased viscosity of

emulsions, and heightened risk of corrosion and catalyst poisoning in the refinery. The chemicals usually used for the treatment of emulsions are generally known as demulsifiers or surfactants. According to Oguntade *et al.* (2022), surfactants are organic particles comprising of two parts: a polar part that is attracted to the water phase (hydrophilic) and a non-polar part attracted to the oil (hydrophobic).

Addition of demulsifiers disrupts the stability of the interfacial barrier by separating the emulsion into their separate phases (Admawi & Mohammed, 2023). The basic element of the chemical demulsification mechanism of any type of emulsion is the gradual breaking of water-oil film, thereby causing tremendous changes to the interface viscosity and elasticity (Raya et al., 2020). Emulsion breakers are currently used in large numbers as chemical additives to break the emulsion of water in oils. The resistance to and response to demulsification techniques such as chemical demulsification of emulsions of a W/O emulsion mainly depends on the physico-chemical properties of the oil they are formed from, emulsification, and aging conditions (Rajamanickam, 2021).

The effort and strategies for optimizing the emulsion of crude oil by demulsifiers therefore vary from one oil field to another and requires careful selection of the chemicals (Zhai et al., 2020). For a given emulsion, an appropriate amount of the chemicals and an appropriate mix of chemicals in an emulsion is also needed. Conventional demulsifiers usually consist of hydrophilic and hydrophobic groups, which enable them to adsorb at the oil/water

interface to break the stability of emulsions (Kang et al., 2018). However, despite their high efficiency, they will remain in the oil phase or the water phase after the demulsification, causing additional environmental issues (Saad et al., 2020). Therefore, it is important to develop a highly efficient and environmentally friendly and cost effective demulsifiers.

Materials and Methods

Sample Preparation and Drying

Matured Soursop fruits were purchased from vendors at Itam market, Uyo, Akwa Ibom State, South South Region of Nigeria. The fruit's maturity was determined visually by its dark green skin and fleshy spines. The seeds were removed manually from the ripe soft fruits, washed, dehulled, and oven dried. The matured soursop seeds were oven dried using an electric conventional oven drier set at a constant temperature of 50°C for time of 24hrs, after which an equilibrium dried weight was reached. The seeds were later prepared for oil extraction. The seeds were later crushed and the oil extracted and stored in a measuring cylinder.

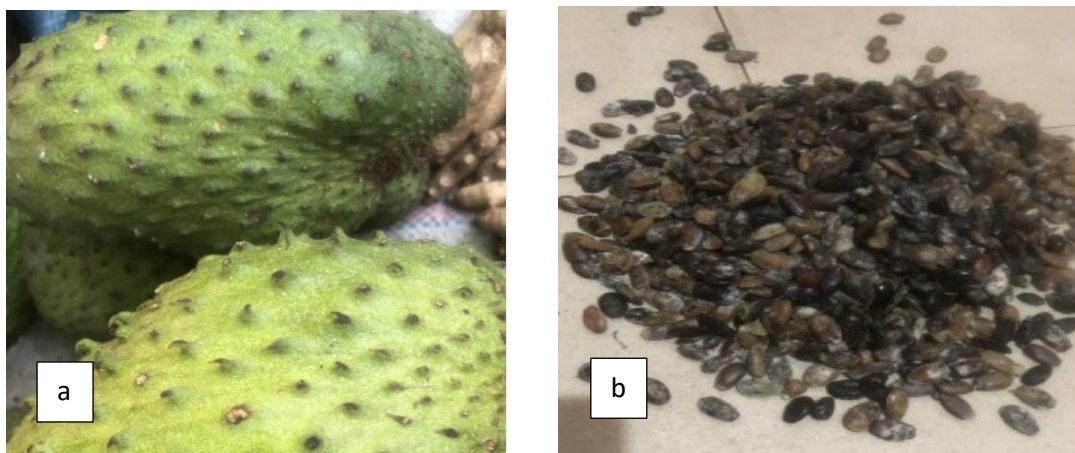


Plate 1: (a) Matured soursop fruits (b) Soursop fruit seeds.

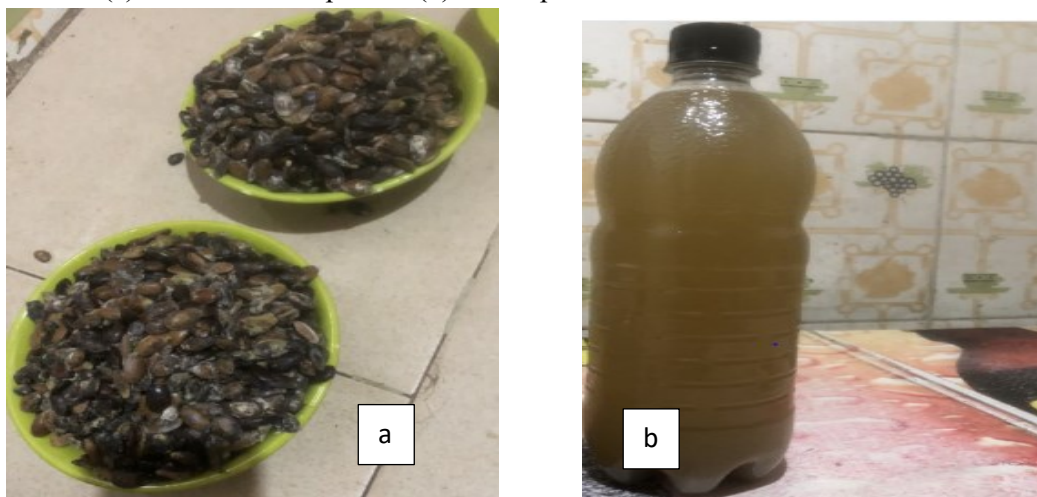


Plate 2: (a) Dehulled soursop fruit seeds (b) Extracted Oil.

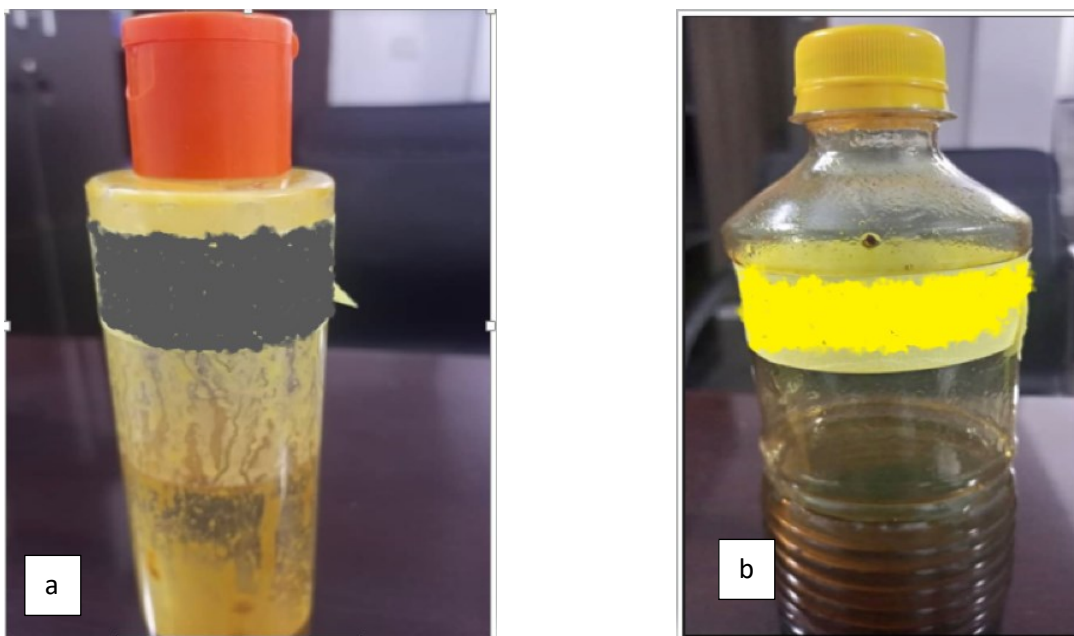


Plate 3 (a) Sample of Formulated Type A (b) Sample of Formulated Type B

Formulation of Type A Demusifier

The materials were selected and bought with reference to literature (Saad *et al.*, 2020). 300ml of non-edible but biodegradable soursop seed oil was measured into a measuring cylinder of 500ml with the addition of 100ml of diethanolamine and 2.5g of p-toluene sulfonic acid. Measured mixture were poured into a flat bottom flask, place on a magnetic stirrer equipped with a thermostat and a stirrer dropped into the mixture. The mixture was heated gradually to 140°C with continuous mixing to achieve homogenous liquid and subsequently cooled. The homogenized mixture was poured into a round bottom flask equipped with a reflux condenser, heated in a heating mantle to 180 °C and continuously heating for two (2) hours till 12ml of water collected. Sample was later removed from the heating mantle, cooled and purified with petroleum ether and evaporated in vacuum evaporator.

Formulation of Type B Demusifier

The materials were selected and bought with reference to literature (Saad *et al.*, 2020). 300ml of non-edible but biodegradable soursop seed oil was measured into a measuring cylinder of 500ml with the addition of 100ml of diethanolamine and 2.5g of sodium hydroxide. The measured mixture were poured into a flat bottom flask, placed on a magnetic stirrer equipped with a thermostat and a stirrer dropped into the mixture. The mixture was heated gradually to 140°C with continuous mixing to achieve homogenous liquid and subsequently cooled. Homogenized mixture poured into a round bottom flask equipped with a reflux condenser, heated in a heating mantle to 180 °C and continuously heating for two (2) hours till 12ml of water collected. Sample removed from heating mantle, cooled and purified with petroleum ether and evaporated in vacuum evaporator.

Sample Characterization

Fourier Transform Infrared Spectrophotometer (FTIR)

For functional unit determination, Fourier transform infrared (FTIR) spectrophotometer (Shimadzu FTIR 8400S) was used to identify the characteristic functional groups in the samples. 10mg of oil sample was homogenized with 10mg of anhydrous potassium bromide (KBr) using mortar, after which the mixtures were pressed by vacuum hydraulic (Graseby Specac) at 1.2psi to obtain transparent pellet. The transparent pellet was scanned through infrared, with its continuing wave by detector connected to computer and giving results of tested sample spectrum. Samples were usually scanned in the absorption area of 600 to 4000 cm^{-1} . The results of analysis consisted of chemical structure, molecular binding form and certain functional groups of the tested sample.

Gas Chromatography-mass Spectrometry (GC-MS)

The sample was analyzed by gas chromatography/mass spectrometry (GC/MS), using Agilent-Technologies of Network GC system, equipped with mass detector and auto injector. Oil sample volume of 10ml was injected into the column with helium at a flow rate of 1.2 mlmin^{-1} . The column temperature was programmed from 150°C to 250°C at a linear ramp rate of 4°C min^{-1} , while the initial and final hold up time was 1min and 5mins, respectively. An electron ionization energy of 70 eV was used for GC/MS detection. Samples were further identified and authenticated using their MS compared to those from mass spectral library of the GC-MS system. Results components were matched with NIST17 database library furnished with GCMS method to analyze the sample's chemical compounds.

Physicochemical and Thermal Properties Determination

Both formulated type A and formulated type B were formulated from oil extracted from non-edible biodegradable soursop seeds. Diethanolamine (liquid), reagent grade > 98.0% purity, and p-toluene sulfonic acid (solid), reagent plus 98%, sodium hydroxide and petroleum ether (40–60) were purchased and two (2) types of commercial demulsifiers (A/B) were collected from the oilfield. Crude oil samples of QUA IBOE Brent were collected from flow lines of four (4) different flowing wells and their manifold in an oil field located in the Niger Delta area of Nigeria. The samples were coded as 16AU, 219A, 343A, 445A and a MIXBLEND, and were properly sampled, packed and preserved for analysis.

Determination of Density

The density of the sample was determined using ASTM method D-129-12b (2017). The sample test portion was transferred to a hydrometer cylinder and both heated to the same temperature. Then hydrometer, with similar temperature, was lowered into the test portion and allowed to settle. At the equilibrium temperature, equilibrium was reached, and the hydrometer scale reading and the temperature of the test portion was taken. The observed

hydrometer reading was referenced with temperature, and the corrected hydrometer scale reading recorded to the nearest 0.1kg/m³ as density.

Determination of Specific Gravity

The specific gravity is calculated as follows:

$$\text{Specific Gravity} = \frac{\text{Weight of 50ml of oil}}{\text{Weight of 50ml of water}} \quad (1)$$

Determination of Acid Value

Sample acid value was determined by ASTM method (ASTM – D 974). About 0.5g of sample was weighed into a 250ml conical flask. 50ml of neutralized ethyl alcohol was added. The mixture was then heated on a water bath to dissolve the sample. The solution was later titrated against 10ml of 0.1M KOH using phenolphthalein as indicator. The acid value was first determined, after which the free fatty acid was calculated respectively as follows:

$$\text{Acid Value} = \frac{A \times M \times 56.1}{\text{Weight of sample (g)}} \quad (2)$$

Where,

A = ml of 0.1M KOH consumed by sample

M = Molarity of KOH

W = weight in grams of the sample

And,

$$\text{Free Fatty Acid} = \frac{\text{Acid Value}}{2} \quad (3)$$

Determination of Saponification Value

Saponification Value of the sample was determine using (ASTM) method- D94 -07 (2017). 5g of the sample was weighed into a conical flask. 25ml of 0.5M KOH was added and the resulting mixture was refluxed for 60 minutes. The resulting solution was subsequently titrated against 0.5M HCl, tested with phenolphthalein as indicator and the resulting end point was obtained when its pink colour changed to colourless. The same procedure was used for the blank. The Saponification value (SV) was then calculated using the expression;

$$\text{Saponification Value (S.V)} = \frac{56.1(B-S)*M \text{ of HCl}}{\text{Weight of sample}} \quad (4)$$

Where;

B = ml of HCl required by blank

S = ml of HCl required by sample

M = Molarity of HCl

56.1= Molar mass of KOH

Determination of Viscosity

Viscosity is the opposite of flow of liquid. Dynamic viscosity is expressed in mm²/sec or Pa/s or kg/ms. The oil viscosity was determined using Brookfield Digital rotational viscometer

(ASTM D- 445). The sample was heated in the hot oil bath and viscometer spindle fitted into the melted wax. The speed was selected and the start button was pressed for the spindle to rotate and give the angle of rotation including the viscosity measurement and operating temperature on the display. However, kinematic viscosity is the ratio of dynamic viscosity to density.

$$\text{Kinematic Viscosity} = \frac{\text{Dynamic Viscosity}}{\text{Density}} \quad (5)$$

Determination of Dielectric Constant

10ml volume of sample was turned into a sample cuvette and a probe inserted into the sample and the capacitor meter was powered. The capacitance of the sample was read from the meter. After taking the reading, the cuvette was emptied and then the probes were dipped into the empty cuvette. The capacitance was then taken for empty cuvette, which is the capacitance of air. The ratio of the capacitance of sample to that of air was then calculated and recorded as the dielectric constant. Mathematically,

$$\text{Dielectric constant} = \frac{\text{Capacitance of the sample}}{\text{Capacitance of air}} \quad (6)$$

Results and Discussion

Table 1: Physicochemical properties of crude oil samples.

S/N	Parameters	Units	Crude oil samples				
			16AU	219	343	445	Mixblend
1	pH	-	6.7	6.6	6.6	6.4	6.2
2	Moisture Content	%	7.12	58	32.2	17.38	21.21
3	Relative Density	g/ml	0.9034	0.9957	0.9029	0.9261	0.9938
4	Specific Gravity	-	0.92	1.018	0.92	0.96	1.016
5	Refractive Index	-	1.533	1.646	1.528	1.595	1.535
6	Viscosity @28 °C	Mpa.s	22.3	21.9	21.6	34.4	33.2
7	Kinematic Viscosity	Cp	24.69	21.99	23.92	37.15	33.41
8	Free fatty Acid	%	4.67	6.15	4.605	4.565	4.71
9	Iodine Value	Mg/gOil	26.28	63.31	23.73	25.36	24.291
10	Peroxide Value	Meq/kg	16	42	16	26	22
11	Flash Point	°C	126.2	152.6	129.4	138.3	122.9
12	Pour Point	°C	-1.9	1.8	2.8	-1.2	3.2
13	Cloud Point	°C	0.62	2.6	3.4	1.1	3.6

The physicochemical properties of the crude oil samples utilized for the study is shown in Table 1. From the table, it can be seen that the crude oil samples exhibit a typical characteristics of a sweet crude and that of Qua Iboe crude in Niger Delta, with pH ranging from 5-8 as discussed explicitly by (Olanisebe & Isehunwa, 2013). The crude oil samples' relative density, specific gravity, viscosity and kinematic viscosity show typical physical

parameters of a light crude (Odebunmi *et al*; 2002). Flash point, pour point and cloud point results shown in the table also agree with expected results for a Nigerian crude (Akpoturi & Ejelonu, 2021). Pour point of a petroleum sample is usually an index of the lowest temperature of its utility for certain applications. Hence, the pour point values of these samples in Table 1 above are low and indicate that the oils can easily be utilized under low temperature conditions.

Table 2: Physicochemical and thermal properties soursop seed oil sample.

Serial Numbers	Parameters	Units	Values
1	Ph	-	6.6
2	Viscosity	mPa.s	5.11
3	Kinematic Viscosity	cSt	2.05
4	Density	g/ml	0.844
5	Specific Gravity	-	0.863
6	Refractive Index	-	1.562
7	Saponification Value	mg KOH/g	194.725
8	Acid Value	mg KOH/g	2.51
9	Iodine Value	gl2/100g	93.38
10	Peroxide Value	meqO2/kg	12.4
11	Heating Value	MK/KJ	34.221
12	Water Content	%	4.27
13	Cloud Point	°C	2.3
14	Pour Point	°C	-2.1
15	Flash Point	°C	117.4
16	Cetane Number		32.1
17	Solubility	Water	Partially
		methanol	soluble
		acetone	soluble

Table 2 shows the physicochemical and thermal properties of the soursop seed oil. It includes variables like pH, kinematic viscosity, density, viscosity, acid value, iodine value, heating value, saponification value, peroxide value, specific gravity refractive index, water content, cloud point, pour point, flash point, cetane number and solubility. They were determined in accordance to ASTM standard procedures. At room temperature, the oil was pale yellow in colour with a refractive index 1.562, the colour observation and refractive index of the oil

agreed with previously published report by Okoro & Osunde (2013). Specific gravity of the oil obtained was 0.863. Viscosity, which measures the oil resistance to shear obtained was 5.11 mPa.s, this makes it a low-viscosity oil.

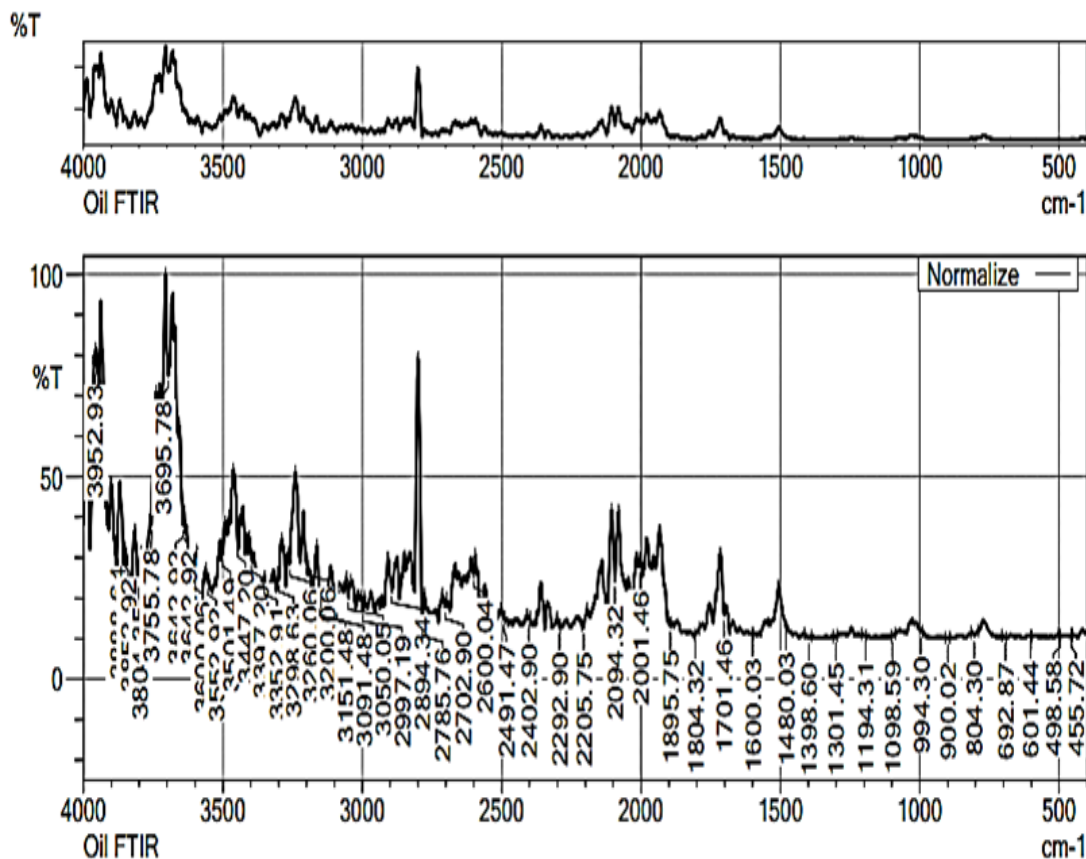


Plate 4.1: Fourier transform infrared (FTIR) of soursop seed oil.

Plate 4.1 shows Fourier transform infrared (FTIR) of soursop seed oil. The peak between 1072-1150 cm^{-1} in Plate 4.1 is assigned to C-O stretching vibration with strong band in aliphatic ether. Peak at 1273-1320 cm^{-1} is attributed to carboxylic acids stretching vibration with medium band. The band at 1334-1430 cm^{-1} is assigned to O-H bending vibration (in plane) with medium bond. The peak at 1635.69 is assigned to C=C symmetry which ranges between 1680-1600 cm^{-1} .

The spectrum at 2144.9 is assigned to $\text{C}\equiv\text{C}$ (symmetry reduces intensity) with ranges from 2100-2250 cm^{-1} . The peak at ranges between 2695 – 2830 cm^{-1} is due to H-C=O stretch and C=O stretch. Absorption peak at 2885.6 cm^{-1} is due to sp^3 C-H stretching vibration with strong band of CH_3 , CH_2 , CH_2 or CH_3 bands. A peak from ranges between 2500 – 3325 cm^{-1} is assigned to O-H stretches. Band with O-H stretch, hydrogen bonded is found within 3356.25 – 3500 cm^{-1} wave number. The peak with stretching vibration of O-H stretches, N-H stretches, and C-H stretches is found between 3200-3800 cm^{-1} wave number.

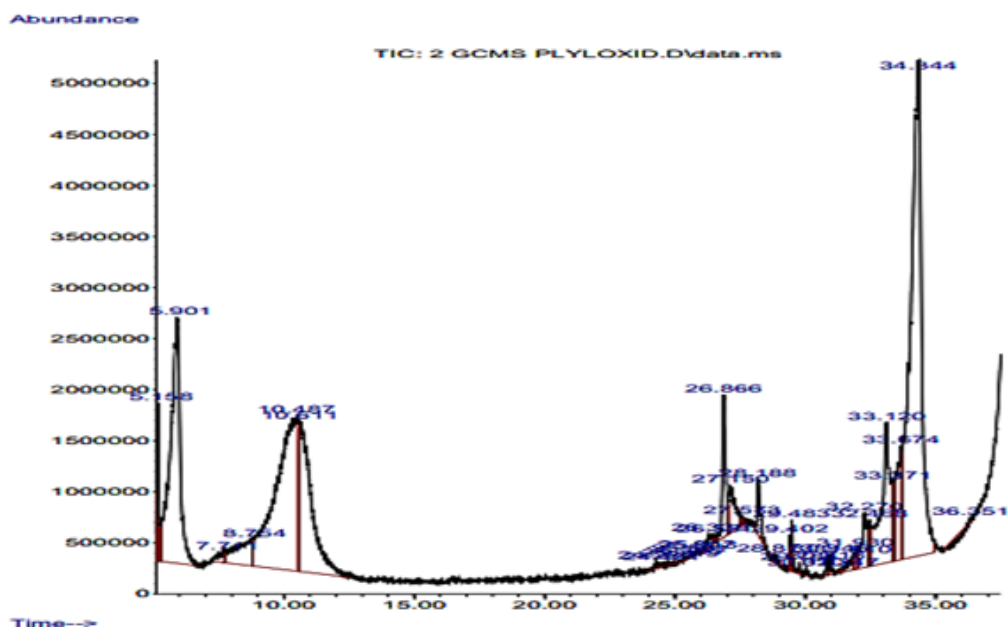


Plate 4.2: Gas Chromatography-Mass Spectrometry (GC-MS) of soursop seed oil

Plate 4.2 shows gas chromatography-mass spectrometry (GC-MS) of soursop seed oil. From GC-MS results, it can be seen that the soursop seed oil compose predominantly of 9-Octadecenoic acid, oleic acid ($C_{18}H_{34}O_2$) with 30.72% percentage composition. Followed by 3-Trifluoroacetoxypentadecane ($C_{17}H_{31}F_3O_2$) with percentage composition of 19.0%. Cycloeicosane ($C_{20}H_{40}$) with percentage composition of 13.54%, n-Propyl11-octadecenoate ($C_{21}H_{40}O_2$) is 10.71%, Oleic acid ($C_{18}H_{34}O_2$) is 8.35%, and all other compounds are were found to be small in percentages.

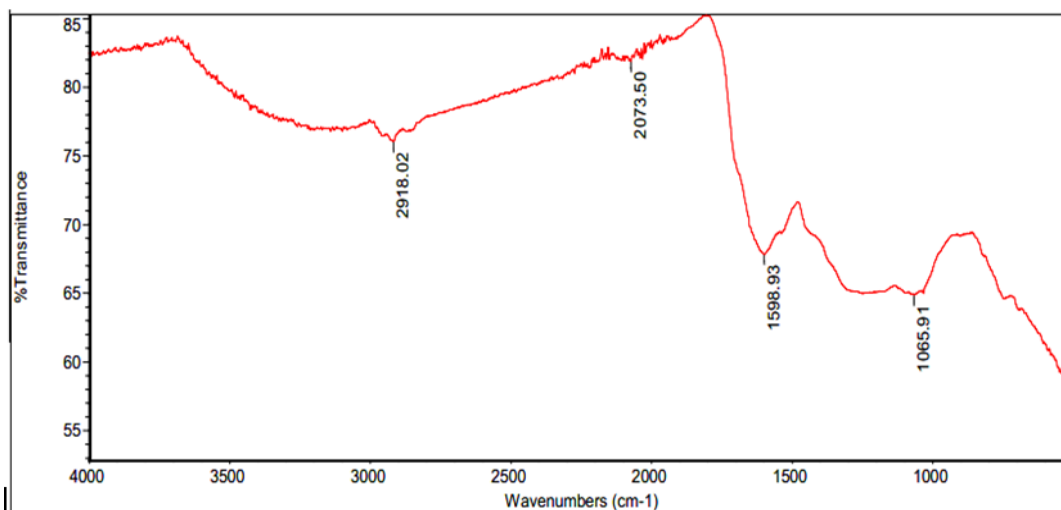


Plate 4.3: Fourier transform infrared (FTIR) spectrophotometer of functional groups of Formulated type A demulsifier.

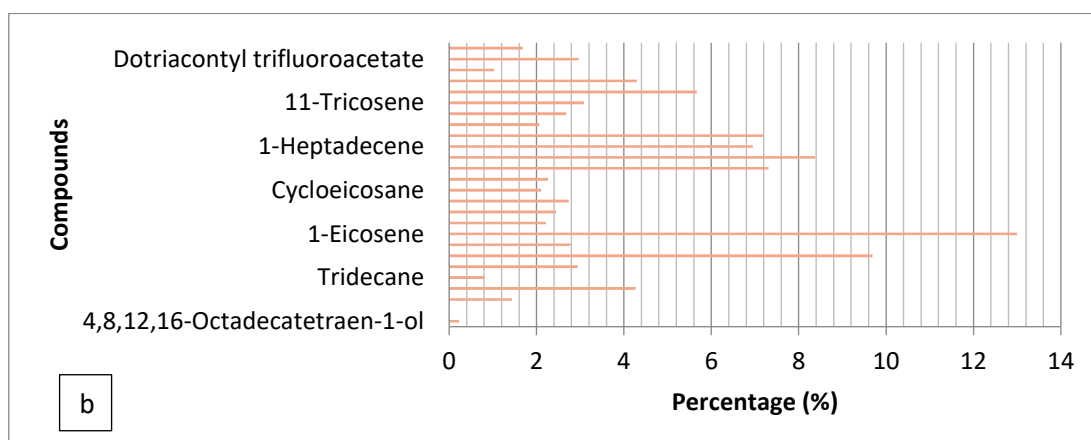


Plate 4.4: Gas Chromatography-Mass Spectrometry (GC-MS) of Formulated type A (a) in terms of peak area (b) in terms of percentage composition

Plate 4.4 illustrates that 1-Eicosene ($C_{20}H_{40}$) has the highest percentage composition of 13%, followed by dotriacontyl pentafluoropropionate ($C_{35}H_{65}F_5O_2$) with 9.7%, Henicos-1-ene ($C_{21}H_{42}$) with 8.4%, 1-Docosene ($C_{22}H_{44}$) with 7.3% and 9-Octadecenal ($C_{18}H_{34}O$) with 7.2%. All other components were less in percentage. 1-docosene is considered to be a hydrocarbon lipid molecule. It is a very hydrophobic molecule, practically insoluble (in water), and relatively neutral. It has a role as a human metabolite. 1-Docosene is a natural product found in *Azadirachta indica*, *Daphne odora*, and other organisms. 9-Octadecenal belongs to the class of organic compounds known as fatty aldehydes. These are long chain aldehydes with a chain of at least 12 carbon atoms. Thus, 9-octadecenal is considered to be a fatty aldehyde.

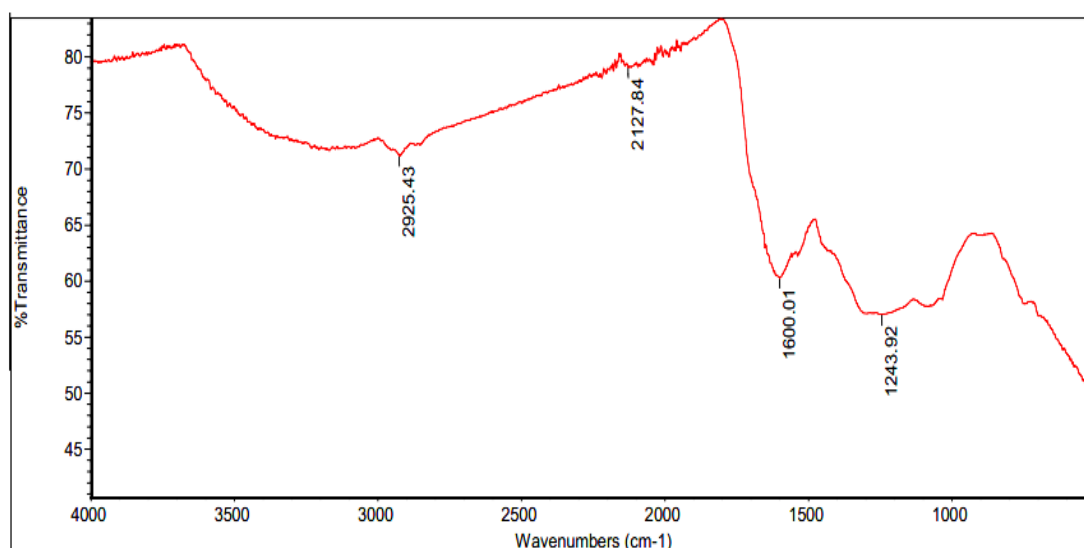
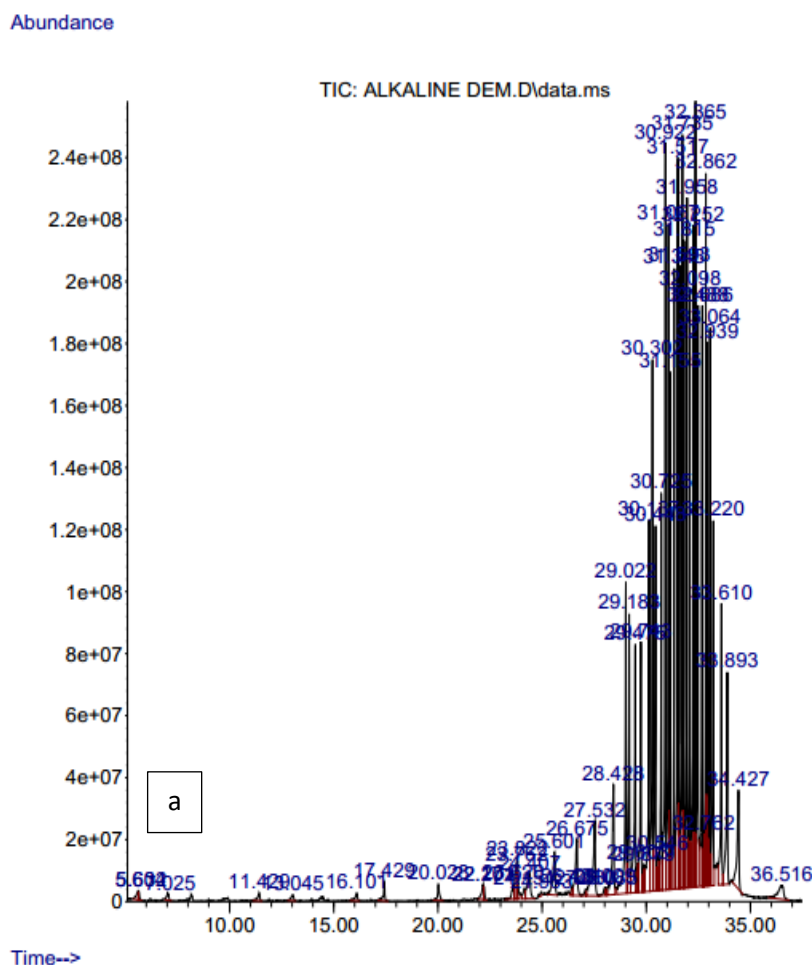


Plate 4.5: Fourier transform infrared (FTIR) spectrophotometer of functional groups of Formulated type B demulsifier.

Plate 4.5 shows Fourier transform infrared (FTIR) spectrophotometer of functional groups of Formulated type B demulsifier. The peak at 1243.92 (1250-1000) cm^{-1} are assigned to Amine N-H (1° -amine), 2 bands, N-H (2° -amine). The peak at 1243.92 (1275-1200) cm^{-1} is attributed to C-O stretching with strong vibration belonging to alky aryl ether. C-N stretching with medium vibration belonging to the amine compounds is observed at 1250-1020 cm^{-1} . Vinyl ether and aromatic ester, observed at 1250-1020 and 1225-1200 cm^{-1} are all attributed to C-O stretching with strong vibration. O-H bending with medium vibration belonging to carboxylic acid is observed at 1440-1393 cm^{-1} , while C=C stretching with medium belonging to cyclic alkene is observed at 1650-1566 cm^{-1} .

The peak at 1600.01 (1650-1600) cm^{-1} is assigned to C=C stretching with medium belonging to conjugated alkene. The peak at 2127.84 (2145-2120) cm^{-1} is attributed to C=C stretching with medium vibration belonging to conjugated alkene. An α , β -unsaturated ester and conjugated anhydride observed at 1730-1715 and 1800-1770 cm^{-1} respectively are all assigned to C=O stretching with strong vibration. The peak at 2925.43 (3000-2840) cm^{-1} is attributed C-H stretching with medium vibration alkane.

Plate 4.6 shows gas chromatography-mass spectrometry (GC-MS) of Formulated type B demulsifier (a) in terms of peak area (b) in terms of percentage composition. Plate 4.6 illustrate that, 1-Nonadecene ($\text{C}_{19}\text{H}_{38}$) has the highest percentage composition of 15.9 %, followed by 1- Docosene ($\text{C}_{22}\text{H}_{44}$) with 12.8 %, dotriacontyl pentafluoropropionate ($\text{C}_{35}\text{H}_{65}\text{F}_5\text{O}_2$), 9-Tricosene ($\text{C}_{23}\text{H}_{46}$) with 7.4%, and Octatriacontyl trifluoroacetate ($\text{C}_{40}\text{H}_{77}\text{F}_3\text{O}_2$) with 7.2%. All other components were less in percentage.



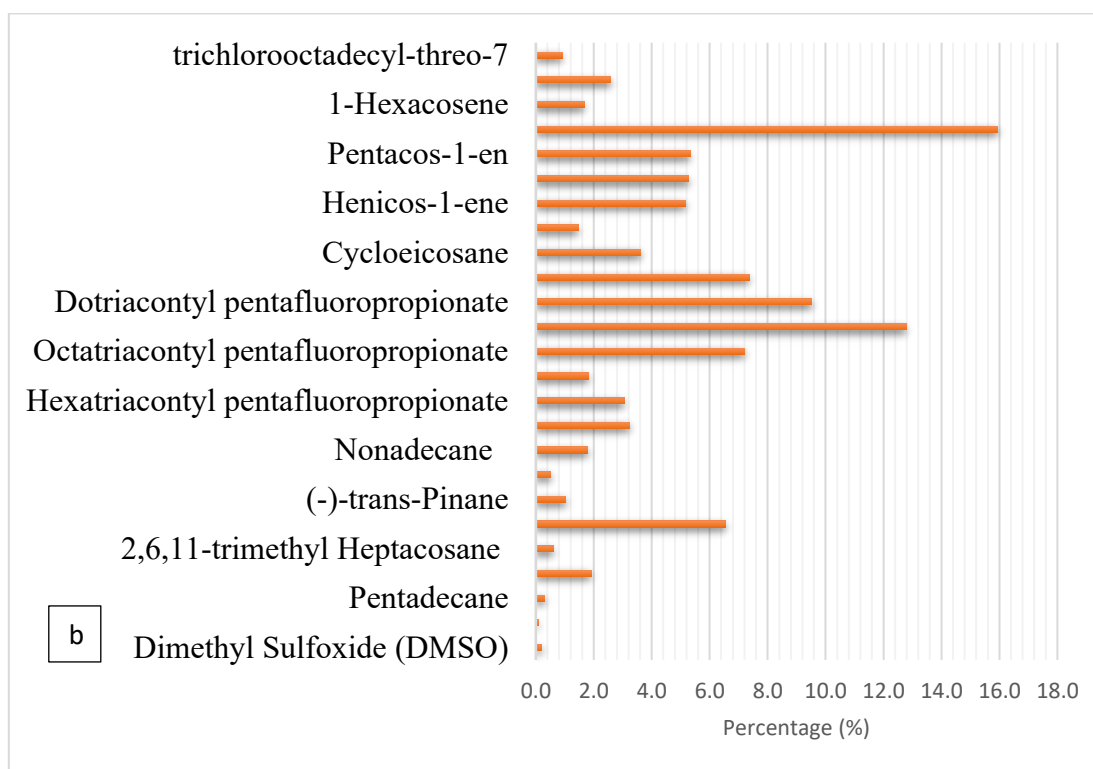


Plate 4.6: Gas Chromatography-Mass Spectrometry (GC-MS) of Formulated type B demulsifier (a) in terms of peak area (b) in terms of percentage composition 1-Nonadecene is an unbranched alkene composed of nineteen carbon atoms with a double bond. It finds extensive use in scientific research, serving as a valuable model compound for investigating the characteristics of alkanes. Additionally, it acts as a versatile substrate for synthesizing various compounds. 1-Nonadecene has played a pivotal role in studying the reactivity and solubility of alkanes in different solvents, providing insights into their properties. Moreover, it serves as a fundamental building block for the synthesis of diverse compounds, including fatty acids and esters.

1-docosene belongs to the class of organic compounds known as unsaturated aliphatic hydrocarbons. These are aliphatic hydrocarbons that contains one or more unsaturated carbon atoms. These compounds contain one or more double or triple bonds. Thus, 1-docosene is considered to be a hydrocarbon lipid molecule. 1-docosene is a very hydrophobic molecule, practically insoluble (in water), and relatively neutral. It has a role as a human metabolite. 1-Docosene is a natural product found in *Azadirachta indica*, *Daphne odora*, and other organisms. 9-Tricosene, known as muscalure, is an insect pheromone found in dipteran flies such as the housefly. Females produce it to attract males to mate. It is used as pesticide. Pentacos-1-ene is an alkene that is pentacosane which has been dehydrogenated to introduce a double bond at the 1-2 position. It has a role as an animal metabolite. It derives from a hydrid

of a pentacosane. 1-Pentacosene is a natural product found in *Nelumbo lutea*, *Vanilla planifolia*, and other organisms.

Table 3: Hydrophilic-lipophilic balance of both formulated and existing market type demulsifiers with that of crude oil samples.

S/N	SAMPLES	VISCOSITY (mPaS)	ACID VALUE (mgKOH/gOil) CRUDE OIL	SAPONIFICATION (mgKOH/gOil)	HLB-20 (1-S/A)
1	16AU	22.3	9.34	327.12	19.428955
2	219	219	12.3	376.22	19.346
3	343	21.7	9.21	320.44	19.425
4.	445	34.4	9.13	351.28	19.48
5.	Mixblend	33.2	9.42	348.21	19.4589
DEMULSIFIERS					
1	Form A	8.7	6.732	224.4	19.4
2	Form B	9.3	5.8905	211.7775	19.4437
3	Existing Marketing Type A	13.1	2.5245	134.64	19.625
4	Existing Market Type B	14.6	2.244	151.47	19.7037

Table 3 shows hydrophilic-lipophilic balance of both formulated and existing market type demulsifiers with that of crude oil samples. From the Table 3, for the experimental results obtained, hydrophilic-lipophilic balance values here for all demulsifiers and emulsion samples are greater than 10. Fundamentally, natural emulsifiers that stabilize a water-in-oil (W/O) emulsion exhibit an HLB value in the range of 3 to 8, hence demulsifiers with a high HLB value will destabilize these emulsions (Castro, 2001). For acid value and saponification, the commercial type A/B demulsifier results exceeded that obtained from the individual wells and the mixblend and therefore cannot separate crude oil emulsions effectively.

Results obtained for Formulated type B demulsifier with value 19.4437 may be able to separate effectively for both individual Wells and Mixblend as they possess relatively close values except for Well 219 with HLB of 19.346. HLB calculated results obtained from the Formulated type A demulsifier with 19.4 will best separate both all the individual wells and their mixblend, because its value is not far from the HLB result of Well 219, which is 19.346 and is within the range of other individual wells and their mix blends.

Table 4: Dielectric constant formulated demulsifiers, commercial demulsifiers and crude oil emulsion with their pH and specific gravity.

S/N	SAMPLES	DIELECTRIC CONSTANT (YD)	pH	SPECIFIC GRAVITY
CRUDE OIL EMULSION				
1	16AU	2.3	6.7	0.92
2	219	2.53	6.6	1.018
3	343	2.46	6.6	0.92

S/N	SAMPLES	DIELECTRIC CONSTANT (YD)	pH	SPECIFIC GRAVITY
4	445	2.48	6.4	0.95
5	MIXBLEND	2.49	6.2	1.016
DEMULSIFIERS				
1	FORMULATED TYPE A	8.34	5.7	0.9012
2	FORMULATED TYPE B	8.12	8.6	0.9019
3	EXT MARK TYPE A	2.3	7.2	0.9126
4	EXT MARK TYPE B	2.8	6.7	0.9133

Table 4 shows dielectric constant formulated demulsifiers, commercial demulsifiers and crude oil emulsion with their pH and specific gravity. Dielectric constant (k) of a substance is the ratio of the capacitance of the substance to that of air. Ajiienka *et al.* (1993) listed dielectric constant of diatomic and polyatomic materials at room temperature (25°C) for hydrocarbon to be (2-6) and that of water to be (78.5-80). Therefore, dielectric constant (k) of emulsions must be between these two limits of oil and water, depending on the nature of the emulsifying agent. However, dielectric constant value increases as water volume fraction increase (Mohammed & Mohammed, 2013). Hence, demulsifiers from this experiment with increased dielectric constant value poses high affinity to water.

Conclusion

The resolution of oilfield emulsions using locally-available biodegradable raw material have been presented in this study. This study involves the formulation of demulsifiers from non-edible and biodegradable soursop seeds oil. The performance of these demulsifiers with existing type market demulsifiers were also compared utilizing key indicators like hydrophilic-lipophilic balance (HLB) and dielectric constant. This study hereby utilized key indicators like hydrophilic lipophilic balance (HLB) and dielectric constant to select best fit demulsifiers to demulsify water-in-oil type emulsions of various crude oil samples and their blends. Experimental data presented for HLB and dielectric constant showed that formulated type demulsifiers possess a good performance on the experimented water-in-oil type emulsion. However, utilizing the breaker test, the existing type market demulsifiers (commercial demulsifiers) gave a better efficiency with the relative rate of water break out.

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