

Prospects of Breaking Crude Oil Emulsions Using Demulsifier Formulated from *Nicotiana tabacum* Seed Oil, Leaf Extracts, and Stalk Ash Extracts

Azuokwu Augustine Azubike*, Eiroboyi Itohan

Department of Petroleum Engineering, Igbinedion University, Okada, Nigeria

Email address:

aazuokwu@gmail.com (A. A. Azubike), ebitoh@yahoo.com (E. Itohan)

*Corresponding author

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Abstract: The presence of crude oil emulsions in oil production and processing systems has been a great concern to industry worldwide. Several methods are available for breaking crude oil emulsions; however, Chemical method is the common demulsification method. Fossil-based materials are mainly used to develop these demulsifiers. Given the recent environmental and sustainability concerns, focus has shifted to the use of bio-based materials like agricultural plant extracts as alternatives to fossil-based demulsifiers. In this study, the prospects of breaking crude oil emulsions using demulsifiers produced from *Nicotiana tabacum* seed oil, leaf extracts, and stalk ash were evaluated. The study is based on the need for local production of demulsifiers in Nigeria, the need for more environmentally friendly and sustainable operations; and the need to put *Nicotiana tabacum* into alternative use due to its associated health hazards when consumed and its massive cultivation. The results of the physiochemical properties of *Nicotiana tabacum* seed oil; the phytochemical analysis of *Nicotiana tabacum* leaf extracts, and the potash concentrations of *Nicotiana tabacum* stalk ash extract showed the presence of hydrophilic and hydrophobic components of demulsifiers. The properties of the formulated demulsifier are similar to those of the commercial demulsifiers. The bottle tests results showed that the formulated demulsifier is capable of breaking medium and high-density crude oil emulsions. Hence, the formulated demulsifier performed comparably to the commercial demulsifiers.

Keywords: Crude Oil Emulsions, Demulsifiers, *Nicotiana tabacum*, Physiochemical, Phytochemical, Bottle Tests

1. Introduction

Hardly does a reservoir yield almost pure crude oil. Crude oil is often produced with water and other contaminants. Typically, crude oil production consisted of 30–90% of oil, 30–70 percent of water, and 2–15 percent of solids by mass [1]. Under production conditions, some portions of water and crude oil can intimately be dispersed throughout one another as small droplets and be stabilized by naturally occurring surface-active molecules such as asphaltene and resins, solids such as clay and waxes [2-5], forming crude oil emulsions.

Crude oil emulsions are classified according to which phase is dispersed and which phase is continuous. According to the

studies carried out by Nalco (2004), Manar El-Sayed Abdel-Raouf (2012), Wong *et al.* (2015), Saad *et al.* (2019), the different types of crude oil emulsions are as follows: [6-9].

- Oil-in-water (O/W) for oil droplets dispersed in water
- Water-in-oil (W/O) for water droplets dispersed in oil
- Multiphase Emulsions - Oil-in-water-in-oil (O/W/O) and Water-in-oil-in-water (W/O/W). That is, both oil-in-water and water-in-oil emulsions occurring simultaneously.

Recent works carried out by Odisu and Salami (2010), Udonne (2012), Falode and Aduroja (2015) Ovuema and Okotie (2015), Saad *et al.* (2019), Sofiah *et al.* (2020), Victory *et al.* (2020), show that Emulsions are undesirable due to the following reasons: [5, 9-14]

- a. Emulsion from sellable crude reduces its commercial value. For this, oil leaving the producing facility has to meet the low water and salt content specifications.
- b. Emulsions cause flow assurance problems. A high level of emulsion in the oil would severely reduce pumping and other transport capacities.
- c. The high salinity of the water would cause corrosion and scaling problems.
- d. Emulsified water in crude oil increases the cost of pumping due to the larger volume and the higher viscosity of the oil resulting in higher oil production costs.
- e. Higher demulsifier and treatment costs.
- f. Emulsions cause productivity decline in wells.
- g. Oil in water disposal /injection system poses environmental concerns.

Hence, the breaking of crude oil emulsion into oil and water phases (demulsification) is, therefore, necessary for oil field production operations. Demulsification can be carried out using chemical, biological, mechanical, thermal, microwave, electrical, ultrasonic, and membrane techniques [15, 16, 9]. However, the chemical technique is the most common demulsification method used in both oil fields and refineries [17-21].

The application of chemicals has great advantages of being able to break an interfacial film effectively, without any need for new equipment or modifications of the existing equipment [22].

The procedures for the formulation of chemical demulsifiers are quite complex. However, emulsifiers and demulsifiers use the same class of chemical substances called “surfactants” [23, 24, 16, 9]. They consist of polymeric surfactants and amine substances such as copolymers, ethylene oxide, propylene oxide, a polymeric chain of EO/PO of alcohols, ethoxylated phenols, nonylphenols, alcohols, amines, resins, and sulphuric acid salts, etc. [25, 11, 12, 5, 26, 27]. Previously, fossil-based materials have been mainly used to develop these demulsifiers [28, 16]. Although, soaps, fatty acids, fatty alcohols, amines, resins obtained from plant materials can be used in the production of demulsifiers [28-32, 25, 16]. Because of the recent environmental and sustainability concerns, the focus has shifted to the use of bio-based materials like agricultural plant extracts as an alternative to fossil-based demulsifiers.

Among the agricultural plants that need to be put into alternative use is *Nicotiana tabacum*, also known as Tobacco, this is due to its associated health hazards when consumed [33-35] and its massive cultivation [35, 36]. *Nicotiana tabacum* is a stout herbaceous plant in the Solanaceae (nightshade family) that is indigenous to the Americas, Australia, South Africa, West Africa, and the South Pacific [37, 38]. Tobacco is a plant product containing mainly nicotine, cellulose, ammonia, protein, and other phytochemicals [37, 39-44, 38, 36].

In this study, the prospects of breaking crude oil emulsions using demulsifier produced from *Nicotiana tabacum* seed oil, leaf extracts and stalk ash were evaluated. The study is based

on the need for local production of demulsifiers in Nigeria [45]; the need for more environmentally friendly and sustainable operations, and the need to put tobacco into alternative use due to its associated consumption and health hazards and it is also based on the fact that it is cultivated massively. Breaking crude oil emulsions using demulsifiers produced in Nigeria will drastically reduce the cost of demulsification as well as improve the economy of Nigeria through the local content initiative. Producing demulsifiers using *Nicotiana tabacum* will provide other alternative uses for the plants, thereby providing an alternative to redirect its human consumption without affecting the income of the farmers. Producing demulsifiers using *Nicotiana tabacum* plant will lead to more environmentally stable and sustainable operations.

2. Materials and Methods

The study encompassed:

- a) Sourcing of *Nicotiana tabacum* plant materials.
- b) Extraction and characterization of *Nicotiana tabacum* seed oil.
- c) *Nicotiana tabacum* leaf extract preparation and phytochemical analysis
- d) *Nicotiana tabacum* stalk ash extract preparation and determination of potash and alkali contents.
- e) Formulation of demulsifiers using *Nicotiana tabacum* leaf extract, seed oil, and stalk ash extract.
- f) Performance evaluation of the formulated demulsifier.

2.1. Sourcing of *Nicotiana tabacum* Plant Materials

Nicotiana tabacum seeds were obtained from Emu Unor in Ndokwa West Local Government Area of Delta State. The seeds were then planted in improvised nursery plastic plant pots in Petroleum Engineering Laboratory, Igbinedion University, Okada. At maturation, the leaves, seeds, and stalks were harvested for the study (Figure 1).



Figure 1. Plant materials (*Nicotiana tabacum* seeds, leaves, and stalks).

2.2. Extraction and Characterization of *Nicotiana tabacum* Seed Oil

Extraction of *Nicotiana tabacum* Seed Oil: Oil from *Nicotiana tabacum* seeds was extracted using the Soxhlet method with hexane as solvent. *Nicotiana tabacum* seeds were air-dried until fully dried. The dried seed was crushed in a mortar and pulverized with the aid of an electric blender. 100 g of the pulverized *Nicotiana tabacum* seeds were packed into a porous thimble and placed in a soxhlet extractor. 500 ml of hexane were placed in a round bottom flask and the soxhlet extractor was assembled. Extraction solvent (hexane) was heated in the bottom flask to 70°C and vaporized into the sample thimble. It condensed in the condenser and dripped back. When the liquid content reached the siphon arm, it emptied into the bottom flask again and the process was continued [46]. The procedures were repeated until all pulverized *Nicotiana tabacum* seeds were used up.

Oil Yields: Oil yields were calculated using equation (1)

$$\text{Yield\%} = \frac{W_1 - W_2}{W_1} \times 100 \quad (1)$$

Where: W_1 =sample weight before extraction and W_2 =sample weight after extraction.

Physiochemical Characterization of the *Nicotiana Tabacum* Seed Oil: The physiochemical properties of *Nicotiana tabacum* seed oil such as specific gravity, viscosity, pH, pour point, flash point, fire points, free fatty acid, acid value, iodine value, peroxide value, and saponification value, etc. were carried out according to standard methods. The specific gravity of the oil was determined at 25°C using a hydrometer. The viscosity of the oil was determined by the Ostwald viscometer. The pH of

the oil was determined by a portable pH Meter (Model: PH-02). The cloud and pour points were determined in accordance to ASTM D2500 (2011) and ASTM D97 (2016) procedures respectively [47, 48]. The flash and fire points of the oil were determined in accordance to ASTM D92-18 (2018) procedures [49]. The chemical properties (free fatty acid value, iodine value, peroxide value, and saponification value, etc.) were determined in accordance to the Association of Official Analytical Chemists (2000) standard [50] as described by Banji *et al.*, (2016) [51]. The color characteristics of the oils were determined by sighting and correlation using colour charts.

2.3. *Nicotiana Tabacum* Leaves Extracts Preparation and Phytochemical Analysis

***Nicotiana Tabacum* Leaves Extracts Preparation:** The soxhlet method of extraction was adopted based on Azwanida (2015) and Gopalasatheeskumar (2018) reports [46, 52]. Mature and healthy leaves of *Nicotiana tabacum* were plucked, washed in dechlorinated water, shade dried, pulverized with the aid of an electric blender, and sieved. 1 kg of the powdered leaves was extracted with two different solvents (methanol and distilled water) to obtain reasonable results from the phytochemical evaluation. The leaf extracts were then stored in airtight amber-colored bottles at 4°C for further usage (phytochemical evaluation and demulsifier formulation).

Phytochemical Analysis of *Nicotiana Tabacum* Extracts: Standard analytical procedures described by Debela (2002), Sahira and Cathrine (2015), Vishnu *et al.* (2019), [53, 54, 55] were used in the phytochemical analysis of methanol and aqueous leaf extracts of *Nicotiana tabacum*. The procedures are presented in Table 1.

Table 1. Procedure for phytochemical tests.

SN	Metabolites	Procedures	Confirmation
1	Alkaloids (Mayer's Test)	To 2 ml of extract, 2 ml of concentrated hydrochloric acid was added. Then a few drops of Mayer's reagent were added.	The presence of green color or white precipitates indicates the presence of alkaloids.
2	Carbohydrates	2 ml of extract was treated with 1 ml of Molisch's reagent and few drops of concentrated sulphuric acid	Formation of purple or reddish color
3	Flavonoids	To 2 ml of extract, 1 ml of 2N sodium hydroxide was added.	The presence of yellow color indicates the presence of flavonoids.
4	Glycosides	To 2 ml of extract, 3ml of chloroform, and 10% ammonia solution were added.	The formation of pink color indicates the presence of glycosides.
5	Oils (Spot test)	A small quantity of extract was pressed between two filter papers	Oil stain on the paper indicates the presence of fixed oils
6	Phenol	2 ml of distilled water followed by a few drops of 10% ferric chloride was added to 1ml of the extract.	The formation of blue or green color indicates the presence of phenols
7	Polypeptides	2 ml of filtrate + 1 drop of 2% copper sulphate solution+ 1 ml of ethanol (95%) + excess of potassium hydroxide pellets	The pink colour ethanolic layer indicates the presence of protein
8	Quinones	To 1 ml of extract, 1 ml of concentrated sulphuric acid was added.	The formation of red color indicates the presence of quinones.
9	Reducing sugars	1ml extract + 5ml HCL + 2ml NaOH	Brick red precipitate
10	Saponins	5ml extract + 5ml H ₂ O + heat 5ml extract + Olive oil (few drops)	Froth appears Emulsion forms
11	Soluble Starch	Few quantities of the extract were boiled with 1 ml of 5% KOH, cooled, and acidified with H ₂ SO ₄ .	A yellow colouration indicates the presence of soluble starch
12	Steroid	2ml extract + 2ml CHCl ₃ + 2ml H ₂ SO ₄ (conc.)	A reddish-brown ring at the junction
13	Tannins (Braymer's Test)	2ml extract + 2ml H ₂ O + 2-3 drops FeCl ₃ (5%).	The formation of dark blue or greenish-black indicates the presence of tannins.
14	Terpenoids	0.5 ml of the extract was treated with 2 ml of chloroform and conc. sulphuric acid.	The formation of red-brown colour at the interface indicates the presence of terpenoids.

2.4. *Nicotiana tabacum* Stalk Ash Extracts Preparation and the Determination of the Potash and Alkali Contents

Stalks of *Nicotiana tabacum* plants were collected and dried to constant weight in an oven (Haier HRDH-71) set at 80°C. The dried stalks were placed in a porcelain crucible and combusted to ash in a muffle furnace. 0.15 Kg of ash was extracted with 2 liters of distilled water until all ashes have been used. The potash and alkali contents of the extracts were determined following the procedures described by Babayemi *et al.* (2010), and Umeh-Idika and Maduakor, (2013) [56, 57]. The *Nicotiana tabacum* stalk ash extracts were kept in bottles at 5°C in the laboratory for the subsequent experimental formulation of demulsifiers.

2.5. Preparation of the Demulsifiers Using *Nicotiana Tabacum* Leaves Extracts, Seed Oil, and Stalk Ash (NTLESESAD)

10 g of the *Nicotiana tabacum* stalk ash extract residues were added to the solution containing 40 g of *Nicotiana tabacum* seed oil and 20 g of *Nicotiana tabacum* leaf extract. The mixtures were placed on the magnetic stirrer- heater at a

regulated temperature of 40°C to dissolve the residues. The mixtures were homogeneously mixed to form the demulsifier and later cooled to room temperature. The physical properties were then determined. The specific gravity of the demulsifier was determined at 25°C using a hydrometer. The viscosity of the demulsifier was determined by the Ostwald viscometer. The pH of the demulsifier was determined by portable pH Meter (Model: PH-02).

2.6. Performance Evaluation of the Formulated Demulsifier (NTLESESAD)

The purpose of the evaluation is to determine the effectiveness of the breaking ability of the formulated demulsifier on crude oil emulsions and to compare the performance with compared to commercially available demulsifiers. The formulated demulsifier was termed the acronym “NTLESESAD”

2.6.1. Sourcing of Commercial Demulsifier

Two common Commercial Demulsifiers were sourced. The properties of the commercial demulsifiers are shown in Table 2.

Table 2. Properties of Commercial Demulsifiers.

S/NO.	Parameter	EO/PO Block Copolymer	SDS (Sodium dodecyl sulphate) solution (10%)
1	Physical State	Liquid	Liquid
2	Appearance / colour	Hazy liquid	Clear, colourless.
3	Specific gravity@60F	1.005 - 1.025	0.9
4	viscosity (cp) or mPa.s	338 @ 40°C	284.3@ 40°C
5	pH	5 - 7 (1% aqueous sol.)	8.7 @ 20°C

2.6.2. Sourcing of Crude Oil Samples

Two crude oil samples were sourced from Nigerian Oil fields designated as Field X and Field Y, Delta State, Nigeria. The Crude oil properties are shown in Table 3.

Table 3. Properties of Crude Oil.

S/NO.	Parameter	Field X	Field Y
1	Appearance/colour	Dark Brownish Liquid	Brownish Liquid
2	Specific gravity@60F	0.929	0.8811
3	API gravity (°API)	20.8	29.1
4	Kinematic viscosity (CST) @60F	76.21	36.4
5	Dynamic viscosity (cp) @60F	70.8	32.07
6	pH	5.4	7.8
7	Resins (wt%)	15.1	13.5
8	Asphaltenes (wt%)	1.6	0.3

2.6.3. Crude Oil Emulsion Preparation

Water in crude oil emulsions was prepared in the laboratory by adding 30 vol% of water containing 0.3% sodium chloride by mass to the oil at room temperature and emulsified by SPAN 80 (Polysorbate 80). The contents were homogeneously mixed in the Hamilton bench mixer at 1200 rpm for 15 minutes.

2.6.4. Bottle Test

The bottle test method was used to evaluate the effectiveness of crude oil emulsion breaking ability of the

formulated demulsifier and to compare the performance with that of the commercially available demulsifiers. Equal concentrations of the formulated demulsifier and the commercial demulsifiers were added to the different bottles. The bottles were placed in a centrifuge and shook for 1 min to ensure thorough mixing of the crude oil emulsions and demulsifiers. The amount of water separated by each of the demulsifiers at 30 minutes intervals was read and recorded.

The demulsifier's efficiency is calculated as follows:

$$\text{Demulsifier's Efficiency} = \text{Water Separation Efficiency} = \frac{\text{Volume of Separated Water (ml)}}{\text{Original Volume of Water in the Crude Oil Emulsion}} \times 100 \quad (2)$$

Demulsifier concentrations of 100 ppm, 200 ppm, and 300 ppm were used to evaluate the effectiveness of the breaking ability of the formulated demulsifier on crude oil emulsions. The performance of the formulated demulsifier was compared with that of the commercial demulsifiers at 300 ppm. Bottle tests were conducted at room temperature (27°C) for 6 hours.

3. Results and Discussions

3.1. Physiochemical Properties of the Extracted *Nicotiana Tabacum* Seed Oil

Table 4 shows the Physiochemical Properties of *Nicotiana tabacum* seed oil extracted. The Physiochemical Properties of *Nicotiana tabacum* seed oil extracted are shown in Table 4. The saponification value (184 mgKOH/g) favoured (demulsifier)

production and soap/ surfactant production. High saponification values are favourable for soap/surfactant production because soaps/surfactants are demulsifiers [16, 9]. In addition, the pH of the oil was not favorable for stable emulsion formation; hence, the oil can easily break the water in the oil emulsion. The oil yield of 32.1% was an added advantage.

3.2. Phytochemicals of the *Nicotiana tabacum* Leaf Extracts

The results of the phytochemical analysis of the *Nicotiana tabacum* leaf extracts are shown in Table 5. Some of the phytochemicals present in the extracts are components of demulsifiers.

Table 5. Phytochemicals of *Nicotiana tabacum* Leaf Extracts.

SN	Metabolites	<i>Nicotiana tabacum</i> Leaf Extracts	
		Methanol	Aqueous
1	Alkaloids (Mayer's Test)	+	+
2	Carbohydrates	+	+
3	Flavonoids	+	+
4	Glycosides	+	+
5	Oils (Spot test)	+	+
6	Phenol	+	-
7	Polypeptides	-	+
8	Quinones	+	-
9	Reducing sugars	+	±
10	Saponins	+	-
11	Soluble Starch	+	+
12	Steroid	+	+
13	Tannins (Braymer's Test)	+	+
14	Terpenoids	+	-

Key: + (Positive); ± (Trace); - (Negative).

3.3. Potash Concentration of the *Nicotiana Tabacum* Stalk Ash Extracts

The potash concentrations of *Nicotiana tabacum* stalk ash extracts are shown in Table 6. The value was lower than plantain peel but higher than that of cassava peel reported by [57]. The *Nicotiana tabacum* stalk ash extracts were alkaline with a pH of 9.6. The concentration of KOH and pH values are shown in Table 6 favouring soap/surfactant (demulsifier) production.

Table 6. Potash Concentration of the *Nicotiana Tabacum* Stalk Ash Extracts.

Samples	Concentration of KOH	pH value
<i>Nicotiana tabacum</i> stalk ash extracts	18.2g/dm ³	9.8

3.4. Properties of Formulated Demulsifier (NTLESEAD) from *Nicotiana Tabacum* Leaves Extracts, Seed Oil, and Stalk Ash

The physiochemical properties of *Nicotiana tabacum* seed oil, the results of the phytochemical analysis of tobacco leaf extract and potash concentrations of *Nicotiana tabacum* stalk ash extract showed the presence of hydrophilic and hydrophobic components of demulsifiers (Tables 4-6).

The properties of the formulated demulsifier are shown in Table 7. The properties are similar to those of the commercial demulsifiers (Table 2). Thus, the formulated demulsifier known as NTLESEAD is favourable for breaking crude oil emulsion.

Table 7. Properties formulated demulsifier (NTLESEAD).

S/NO.	Parameter	Formulated Demulsifier (NTLESEAD)
1	Physical State	Liquid.
2	Appearance / colour	Brownish.
3	Specific gravity@60F	1.02
4	viscosity (cp) or mPa.s	326
5	pH	7

3.5. Performance Evaluation of the Formulated Demulsifier (NTLESESAD)

3.5.1. Effectiveness of the Breaking Ability of the Formulated Demulsifier on Crude Oil Emulsions

Figure 2 and Figure 3 showed the effects of the formulated demulsifier (NTLESESAD) on Field X and Field Y crude oil emulsion samples. The results showed that the formulated demulsifier is capable of breaking the two crude oil emulsions. However, the demulsifier is more effective on Field Y's crude oil emulsion samples. The emulsion breaking performance of a demulsifier is a function of the crude oil emulsion stability and the demulsifier's properties [58, 13]. The stability of crude oil emulsions depends on the physicochemical properties of the crude constituents, their interrelationships, and interactions with each other [59, 19, 60, 13].

The crude oil of Field X has higher specific gravity, viscosity, resin, and asphaltene but lower pH compared to the crude oil of Field Y (Table 2).

- (a) *Influence of density*: The density difference between oil and water may affect the rate of flocculation and demulsification [13]. The higher the density of the crude oil emulsion, the more the difficulty encountered in breaking the emulsion. Consequently, the formulated demulsifier (NTLESESAD) was more active on Field Y's crude oil emulsion with lower density (Table 2 and Figures 2-3)
- (b) *Influence of viscosity*: Higher crude viscosity causes low crude oil emulsion separation. The higher the viscosity of the continuous phase, the lower the diffusion coefficient and collision frequency of the drops. While the decreased in the continuous phase (oil) viscosity enhanced the kinetic motion of the dispersed water droplets, causing increased bombardment, resulting in film relaxation, film rupture, and coalescence. [61] stated that crude oil with higher viscosity and higher asphaltene/ resin contents

negatively reduces the diffusion coefficient of the demulsifier molecules, thus inhibiting the demulsification process. Consequently, as shown in Table 2 and Figures 2-3, the formulated demulsifier (NTLESESAD) is less efficient on Field X's crude oil emulsion with higher viscosity.

- (c) *Influence of pH*: pH strongly affects the interfacial properties of asphaltene at the oil/water interface. At high or low pH, asphaltene's functional groups become charged, enhancing its surface activity and thereby increasing the stability of the crude oil emulsion [62]. That is, water-in-oil emulsion becomes more stable at very high and at very low pH [63, 18]. As a result, the formulated demulsifier (NTLESESAD) is more efficient in Field Y's crude oil emulsion with suitable pH (Table 2 and Figures 2-3).
- (d) *Influence of asphaltene and resins*: Asphaltenes and resins pose problems in oil-water separation. At a given pH, the higher the amounts of resin and asphaltene, the more stable the crude oil emulsion [62]. Higher Asphaltene/ Resin contents negatively decrease the diffusion coefficient of the demulsifier molecules, thereby decreasing the demulsification efficiency (Table 2 and Figures 2-3). Consequently, as shown in Table 2 and Figures 1-2, the formulated demulsifier (NTLESESAD) is less efficient on crude oil emulsion in Field X with higher Asphaltene / Resin contents (Table 2 and Figures 2-3).
- (e) *Effect of demulsifier concentration*: Demulsifier concentration is one of the major variables that can either decrease or improve emulsion stability, and thus the demulsification efficiency [9, 64]. In this study, an increase in demulsifier concentration increased the demulsification efficiency (Figures 2-3).

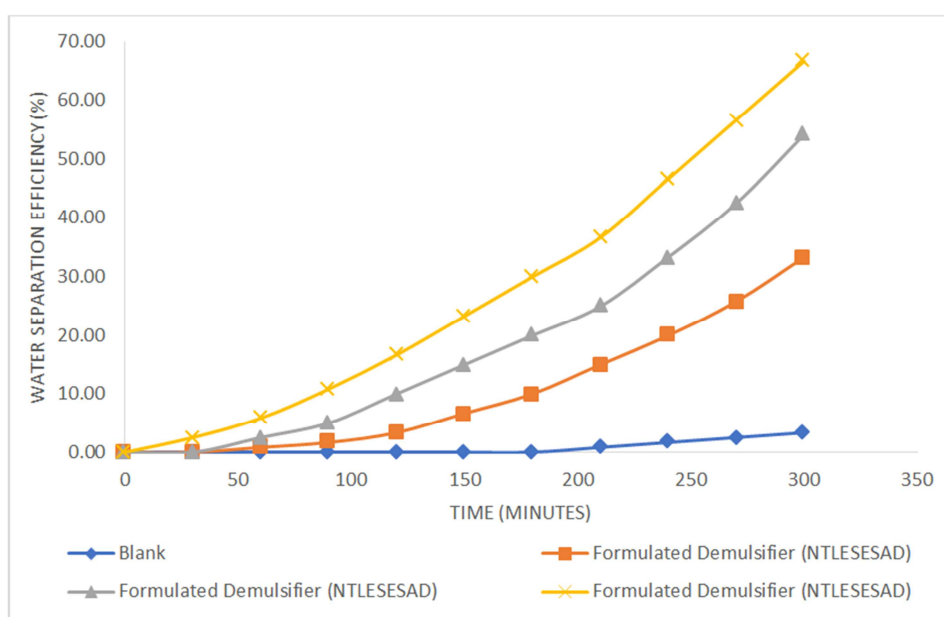


Figure 2. The effect of the formulated demulsifier (NTLESESAD) on Field X crude oil emulsion sample.

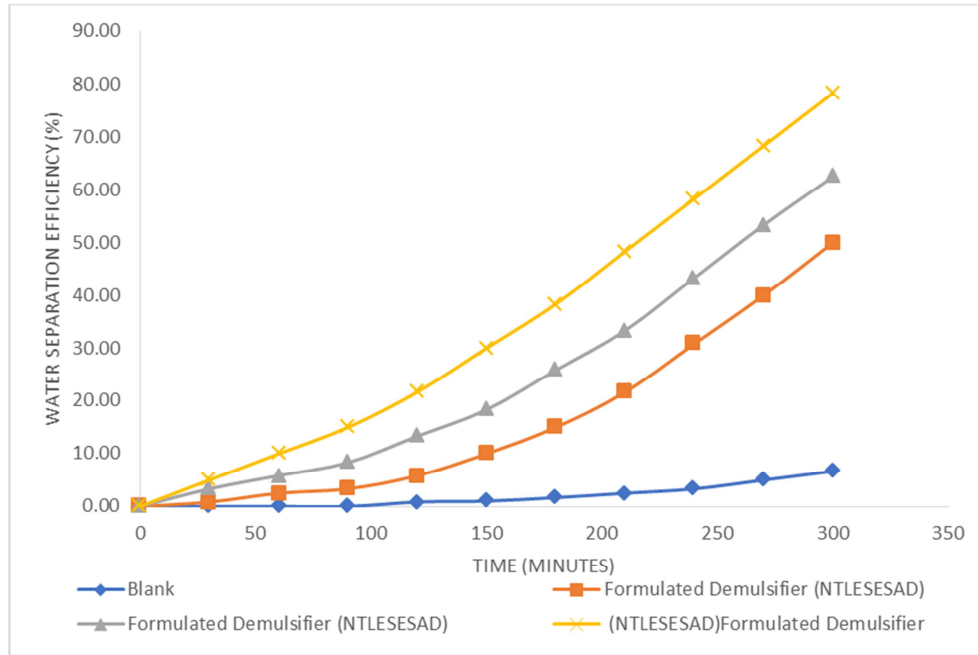


Figure 3. The effect of the formulated demulsifier (NTLESESAD) on Field Y crude oil emulsion sample.

3.5.2. Comparison of the Performances of the Formulated Demulsifier (NTLESESAD) and the Commercially Demulsifiers

The emulsion breaking performance of a demulsifier is a function of the stability of the crude oil emulsion and the properties of the demulsifiers [58, 13]. The properties of the formulated demulsifier (Table 7) are similar to those of the commercial demulsifiers (Table 2).

The bottle test results (Figures 4-5) showed that the formulated demulsifier performed comparably to the

commercial demulsifiers (EO/PO Block Copolymer and Sodium dodecyl sulphate). The six hours demulsification efficiency of the crude oil emulsion from Field X was 66.67% for NTLESESAD, 73.33% for EO/PO Block Copolymer, and 61.67% for Sodium dodecyl sulphate. While the six hours demulsification efficiency of crude oil emulsion from Field Y was 78.33% for NTLESESAD, 86.67% for EO/PO Block Copolymer, and 65.83% for Sodium dodecyl sulphate. This implies that the formulated demulsifier (NTLESESAD) is better than Sodium dodecyl sulphate.

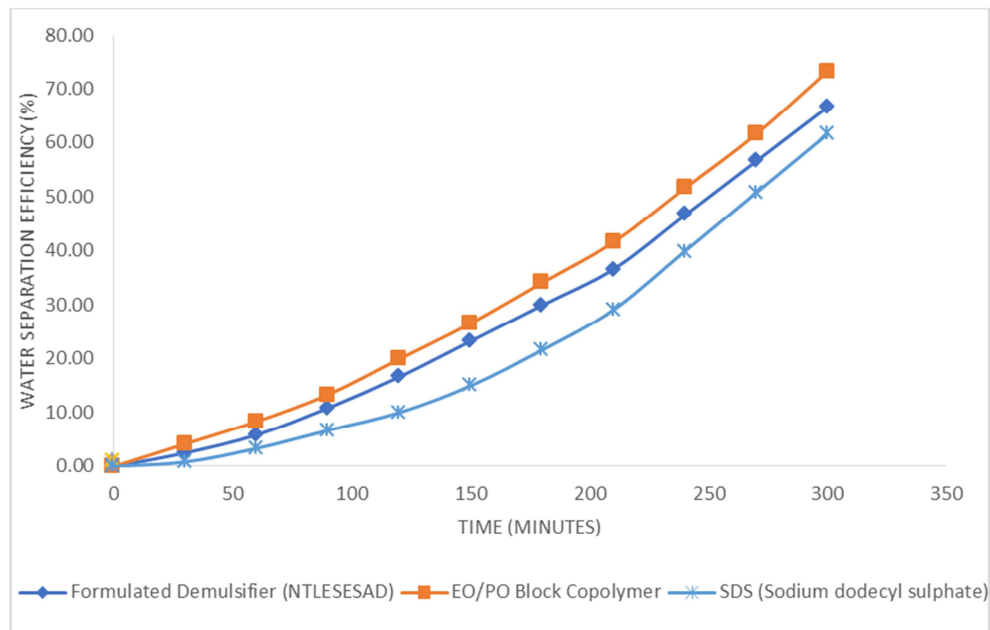


Figure 4. Comparison of the performances of the formulated demulsifier (NTLESESAD) and the commercial demulsifiers on Field X crude oil emulsion sample.

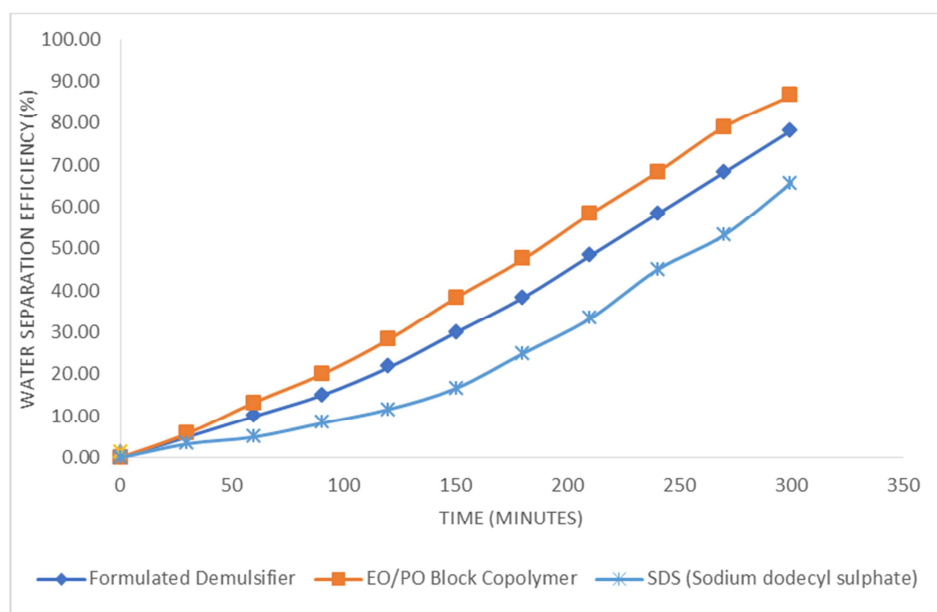


Figure 5. Comparison of the performances of the formulated demulsifier (NTLESESAD) and the commercial demulsifiers on Field Y crude oil emulsion sample.

4. Conclusions

Based on the results of the study, the following conclusions were drawn:

- The results of the physiochemical properties of *Nicotiana tabacum* seed oil; the phytochemical analysis of tobacco leaf extracts, and the potash concentrations of *Nicotiana tabacum* stalk ash extract showed the presence of hydrophilic and hydrophobic, components of demulsifiers.
- The properties of the formulated demulsifier (NTLESESAD) are similar to those of the commercial demulsifiers.
- The bottle tests results showed that the formulated demulsifier is capable of breaking medium and high-density crude oil emulsions.
- The emulsion breaking performance of the demulsifier is a function of the physicochemical properties of the crude oil emulsion constituents, their inter-relationships, and interactions with each other.
- The bottle tests showed that the formulated demulsifier performed comparably to the commercial demulsifiers.
- Optimum demulsification conditions should be evaluated based on the field conditions.

Declaration of Competing Interests

The authors declare that there are no competing interests (financial or personal influencing the work reported in this paper).

Nomenclature

Demulsifier formulated from *Nicotiana Tabacum* Leaves

Extracts, Seed Oil, and Stalk Ash.

References

- [1] Zhang J., Li J., Thring R. W., Hu X., Song X. (2012): "Oil recovery from refinery oily sludge via ultrasound and freeze/thaw". *J. Hazard. Material*, 203, pp. 195-203.
- [2] Bhattacharyya, B. R. (1992): "Water Soluble Polymer as Water-in-Oil De-emulsifiers". (US Patent 5,100,582).
- [3] Sjöblom J. (2001): "Encyclopedic Handbook of Emulsion Technology". CRC Press, Hoboken.
- [4] Yang, X., Verruto, V. J., and Kilpatrick, P. K., (2007); "Dynamic Asphaltene-Resin Exchange at the Oil/Water Interface: TimeDependent W/O Emulsion Stability for Asphaltene/Resin Model Oils". *Energy Fuels* 21: 1343–1349.
- [5] Ovuema, A., Okotie S., (2015): "Emulsion Treatment in the Oil Industry". A case study of Oredo Field Crude Oil Emulsion. Society of Petroleum Engineers: SPE-178381-MS.
- [6] Nalco (2004), "Crude Oil Emulsion", Oil Field Chemicals Training Manual; Nalco Company.
- [7] Manar El-Sayed Abdel-Raouf (2012): "Crude Oil Emulsions – Composition Stability and Characterization" InTech, ISBN 978-953-51-0220-5; page 183-185.
- [8] Wong S. F., Lim J. S., Dol S. S. (2015): "Crude oil emulsion: A review on formation, classification and stability of water-in-oil emulsions", *Journal of Petroleum Science and Engineering*, Volume 135, Pages 498-504, ISSN 0920-4105, <https://doi.org/10.1016/j.petrol.2015.10.006>.
- [9] Saad M. A., Mohammed Kamil, Abdurahman N. H., Rosli Mohd Yunus and Omar I. Awad (2019): "An Overview of Recent Advances in State-of-the-Art Techniques in the Demulsification of Crude Oil Emulsions". *Processes*, 7, 470; doi: 10.3390/pr7070470 www.mdpi.com/journal/processes

- [10] Odisu, Teddy and Salami, Deborah. O. (2010): "Formulation and Production of Crude Oil Demulsifiers from Locally Sourced Materials"; *Journal of Physical Sciences and Innovation*; Volume 2.
- [11] Udonne J. D. (2012): "Chemical treatment of emulsion problem in crude oil production". *Journal of Petroleum and Gas Engineering* Vol. 3 (7), pp. 135-141.
- [12] Falode Olugbenga Adebajo, Aduroja, Opeyemi Christy (2015): "Development of Local Demulsifier for Water - In-Oil Emulsion Treatment". *International Journal of Sciences: Basic and Applied Research (IJSBAR)* (2015) Volume 24, No 1, pp 301-320.
- [13] Sofia Atirah Raya, Ismail Mohd Saaid, Abdelazim Abbas Ahmed, Abubakar Abubakar Umar (2020): "A critical review of development and demulsification mechanisms of crude oil emulsion in the petroleum industry". *Journal of Petroleum Exploration and Production Technology*, 10: 1711–1728, <https://doi.org/10.1007/s13202-020-00830-7>
- [14] Victory Ikechi Okwe, Bright Bariakpo Kinete, Ifeanyi Samson Nwankwo (2020): "Performance Evaluation of Surfactant and Demulsifier in Crude Oil Emulsion Treatment" *International Journal of Recent Engineering Science* 7.222-26.
- [15] Gafonova, O. V. (2000): "Role of Asphaltenes and Resins in the Stabilization of Water- in-Hydrocarbon Emulsions". M. Sc Thesis, University of Calgary.
- [16] Ojinnaka C. M., Ajenka J. A., Abayeh O. J., Osuji L. C., Duru R. U. (2016): "Formulation of best-fit hydrophilic/lipophile balance-dielectric permittivity demulsifiers for treatment of crude oil Onyegbado, CO; Iyagba, ET; Offor, OJ (2002): "Solid soap production using plantain peels ash as source of alkali". *Journal of Applied Science and Environmental Management*. 6 (1): 73–77. emulsions". *Egyptian Journal of Petroleum* (2016) 25, 565–574.
- [17] Grace, R. (1992): "Commercial Emulsion Breaking". American Chemical Society, Washington DC. 313-338.
- [18] Emmanuel J. Ekott, Ubong I. Etukudo (2014): "Studies on pH Variations in Crude Oil Demulsification". *International Journal of Engineering and Technical Research (IJETR)* ISSN: 2321-0869, Volume-2, Issue-10.
- [19] Razi, M.; Rahimpour, M. R.; Jahanmiri, A.; Azad, F. (2011): "Effect of a different formulation of demulsifiers on the efficiency of chemical demulsification of heavy crude oil". *J. Chem. Eng. Data*, 56, 2936–2945.
- [20] Nikkha, M.; Tohidian, T.; Rahimpour, M. R.; Jahanmiri, A. (2015): "Efficient demulsification of water-in-oil emulsion by a novel nano-titanium modified chemical demulsifier". *Chem. Eng. Res. Des.* 94, 164–172.
- [21] Igwilo K. C., Ogbudu R. E., Okolie S. T. A., Ohia Princewill, Okolie Nnanna (2017): "Experimental Analysis of Chemical De-Emulsification Using Polymerization and Sulfonation Methods on Niger Delta Crude Oil". *International Journal of Petroleum and Gas Engineering Research* Vol. 1, No. 1, pp. 1-8.
- [22] Amir Mosayebi, Reza Abedini (2013): "Using Demulsifiers for Phase Breaking of Water/Oil Emulsion". *Petroleum and Coal* 55 (1) 26-30.
- [23] Lee R. F., (1999): "Porphyrins from crude oil tested as emulsifying agents of W/O emulsions". *Spill Sci. Technol. Bull.* 5 (2).117–126.
- [24] Jan C. J. Bart; Emanuele Gucciardi; Stefano Cavallaro (2016): "Biolubricants: science and technology". Oxford: Woodhead Publishing.
- [25] Fink J. K. (2012): "Petroleum engineer's guide to oil field chemicals and fluids". Elsevier, Amsterdam.
- [26] Abullah M. M. S., Al-Lohedan H. A and Attah A. M. (2016): "Synthesis and application of amphiphilic ionic liquid based on acrylate copolymers as demulsifier and oil spill dispersant." *Journal of Molecular Liquids* 219: 54–62.
- [27] Murtada Mohammed Abdulredha, Siti Aslina Hussain, Luqman Chuah Abdullah (2020)". "Overview on petroleum emulsions, formation, influence and demulsification treatment techniques". *Arabian Journal of Chemistry* (2020) 13, 3403–3428.
- [28] Ahmed M. Al-Sabagh, Nadia G. Kandile & Mahmoud R. Noor El-Din (2011): "Functions of Demulsifiers in the Petroleum Industry", *Separation Science and Technology*, 46: 7, 1144-1163.
- [29] Dalmazzone C. and Noik C. (2001): "Development of new "green" demulsifiers for oil production, in: SPE International Symposium on Oilfield Chemistry, Society of Petroleum Engineers.
- [30] Al-Sabag A. M., Noor El-Din M. R., Abo-El Fotouh S., Nasser N. M. (2009): Investigation of the Demulsification Efficiency of Some Ethoxylated Polyalkylphenol Formaldehydes Based on Locally Obtained Materials to Resolve Water-in-Oil Emulsions, *Journal of Dispersion Science and Technology*, 30: 2, 267-276.
- [31] Nuraini M., Abdurahman H. N, Kholijah A. M. S. (2011): "Effect of chemical breaking agents on water-in crude oil emulsion system". *International Journal of Chemical and Environmental Engineering*.
- [32] Emuchay D., Onyekonwu M. O., Ogolo N. A., Ubani C. (2013): "Breaking of emulsions using locally formulated demulsifiers". SPE Nigeria Annual International Conference and Exhibition, Society of Petroleum Engineers, August 2013.
- [33] Wilkinson C. A., Weeks W. W. (1994): "Alkaloid Analysis in Flue-Cured Tobacco. In: Linskens H. F., Jackson J. F. (eds) *Alkaloids. Modern Methods of Plant Analysis*", vol 15. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-84226-9_5
- [34] HHS (Department of Health and Human Services) (2014): "The health consequences of smoking—50 years of progress": A report of the Surgeon General. Atlanta, GA: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Center for Chronic Disease Prevention and Health Promotion, Office on Smoking and Health; 2014.
- [35] Cadmus Eniola Ajayi, Tumi Iken, Tomi Japkor, Phillip Oluwafemi, Akinbode Adebisi Akindele. (2018). "The reality of tobacco farmers exploitation in a region in Nigeria. Tobacco Induced Diseases". 16. 10.18332/tid/84202.
- [36] Shahbandeh M. (2021): "Tobacco production worldwide 2019, by country". <https://www.statista.com/statistics/261173/leading-countries-in-tobacco-production/>

- [37] Chinnadurai Vajjiram, Vanitha A. and Kalimuthu K. (2017): "FTIR and GC-MS Analysis of Bioactive Compounds in Ethanol Extract of Tobacco Callus (*Nicotiana Tabacum* L.)". World Journal of Pharmaceutical Research, Volume 6, Issue 14, 530-545. DOI: 10.20959/wjpr201714-9918.
- [38] Kheawfu, K., Kaewpinta, A., Chanmahasathien, W., Rachtanapun, P., & Jantrawut, P. (2021). Extraction of Nicotine from Tobacco Leaves and Development of Fast Dissolving Nicotine Extract Film. *Membranes*, 11 (6), 403. MDPI AG. Retrieved from <http://dx.doi.org/10.3390/membranes11060403>
- [39] Jones Nádia M. Bernardo-Gil M. Gabriela, Lourenço M. Graça. (2001): "Comparison of Methods for Extraction of Tobacco Alkaloids". Journal of Aoac International Vol. 84, No. 2, 309.
- [40] Peter Machado (2008): "Feasibility of Extracting Solanesol from Tobacco Biomass as a Byproduct following Protein Recovery". Thesis submitted to the Faculty of the Graduate School of the University of Maryland, College Park.
- [41] Xie Z, Whent M, Lutterodt H, Niu Y, Slavin M, Kratochvil R, Yu L. L. (2011): "Phytochemical, antioxidant, and antiproliferative properties of seed oil and flour extracts of Maryland-grown tobacco cultivars". J Agric Food Chem. 2011 Sep 28; 59 (18): 9877-84. doi: 10.1021/jf202069g. Epub 2011 Sep 1. PMID: 21827135.
- [42] Anyiam Ngozi Donald (2020): "Extraction and Estimation of the Amount of Nicotine in a Tobacco Leaf". International Journal of Creative Research Thoughts (IJCRT) | Volume 8, Issue 8| ISSN: 2320-2882.
- [43] Min Wei, Fu Yang, Xuyan Song, Ran Li, Xi Pan, Qiang Gao, Yunlu He, Mingqiao Ye, and Hongyun Hu (2020): "Extraction of Nitrogen Compounds from Tobacco Waste via Thermal Treatment". Energies, 13, 4619; doi: 10.3390/en13184619 www.mdpi.com/journal/energies
- [44] Venelina Todorova Popova, Tanya A. Ivanova, Albenia S. Stoyanova, Violeta V. Nikolova, Docheva M., Tzvetia H. Hristeva, Stanka Todorova Damyanova, Nikolay P. Nikolov (2020). "Chemical constituents in leaves and aroma products of *Nicotiana rustica* L. tobacco". International Journal of Food Studies. 9. 10.7455/ijfs/9.1. 2020.a2.
- [45] Sulaiman A. D, Abdulsalam S. and Francis A. O. (2015): "Formulation of Demulsifiers from Locally Sourced Raw Materials for Treatment of a Typical Nigerian Crude Oil Emulsion". Paper presented at the SPE Nigeria Annual International Conference and Exhibition, Lagos, Nigeria, August 2015. Paper Number: SPE-178377-MS, <https://doi.org/10.2118/178377-MS>
- [46] Azwanida N. N. (2015): "A Review on the Extraction Methods Use in Medicinal Plants, Principle, Strength, and Limitation". Med Aromat Plants 4: 196. doi: 10.4172/2167-0412.1000196.
- [47] ASTM D 2500 (2011): "Standard Test Method for Cloud point of Petroleum Products". ASTM International, West Conshohocken, PA. 5.02.
- [48] ASTM D 97 (2016). "Standard Test Method for Pour point of Petroleum Products". ASTM International, West Conshohocken, PA. 5.01.
- [49] ASTM D 92-18 (2018): "Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester", ASTM International, West Conshohocken, PA, www.astm.org; DOI: 10.1520/D0092-18.
- [50] AOAC (2000): "Official Methods of Analysis of the Association of Official Analytical Chemists". 17th ed., Washington DC, pp. 500-540.
- [51] Banji Adaramola, Adebayo Onigbinde and Oluwatosin Shokunbi (2016): "Physiochemical properties and antioxidant potential of *Persea Americana* seed oil". Chemistry International 2 (3) (168-175.
- [52] Gopalasatheeskumar K. (2018): "Significant Role of Soxhlet Extraction Process in Phytochemical Research". Mintage journal of Pharmaceutical & Medical Sciences Vol 7, Suppl 1, 2ISSN: 2320-3315 | 43-47.
- [53] Debela, A. (2002): "Manual for Phytochemical Screening of Medicinal Plants". Ethiopian Health and Nutrition Research Institute, Addis Ababa, Ethiopia, 35-47
- [54] Sahira Banu K. B and Cathrine L. (2015): "General Techniques Involved in Phytochemical Analysis". *International Journal of Advanced Research in Chemical Science (IJARCS) Volume 2, Issue 4, PP 25-32 ISSN 2349-039X (Print) & ISSN 2349-0403 (Online) www.arcjournals.org*
- [55] Vishnu Balamurugan, Sheerin Fatima. M. A, Sreenithi Velurajan (2019): "A Guide to Phytochemical Analysis". *JARIE-ISSN (O)-2395-4396, Vol-5 Issue-1*.
- [56] Babayemi J. O., Dauda K. T., Nwude D. O. and Kayode A. A. A., (2010): "Evaluation of the Composition and Chemistry of Ash and Potash from Various Plant Materials-A Review". *Journal of Applied Sciences*, 10: 1820-1824.
- [57] Umeh-Idika Adaku and Maduakor Melody (2013): "Soap Production Using Waste Materials of Cassava Peel and Plantain Peel Ash as an Alternative Active Ingredient, Implication for Entrepreneurship". *IOSR Journal of VLSI and Signal Processing (IOSR-JVSP) Volume 3, Issue 3 (Sep. – Oct. 2013), PP 01-05 e-ISSN: 2319 – 4200, p-ISSN No.: 2319 – 4197 www.iosrjournals.org*
- [58] Kokal S., Aramco S. (2005): "Crude oil emulsions: a state-of-the-art review". SPE Prod Facil 20 (December 2004): 5–13. <https://doi.org/10.2118/77497-PA>
- [59] Mikula R. and Munoz V. (2000): "Characterization of demulsifiers". Cambridge University Press: Cambridge.
- [60] Abed S. M., Abdurahman N. H., Yunus R. M., Abdulbari H. A., Akbari S. (2019): "Oil Emulsions and the Different Recent Demulsification Techniques in the Petroleum Industry - A Review". doi: 10.1088/1757-899X/702/1/012060.
- [61] Al-Sabagh A. M., Nasser N. M., Khamis E. A., Abd-El-Raouf M. (2015): "Resolution of Water in Crude Oil Emulsion by Some Novel Aromatic Amine Polyesters". Egyptian Journal of Petroleum; 24, 363–374.
- [62] Sandrine Poteau and Jean-François Argillier (2005): "Influence of pH on Stability and Dynamic Properties of Asphaltenes and Other Amphiphilic Molecules at the Oil-Water Interface". *Energy & Fuels*, 19, 1337-1341.
- [63] Mortada Daaou, Dalila Bendedouch (2012): "Water pH and surfactant addition effects on the stability of an Algerian crude oil emulsion". Journal of Saudi Chemical Society.
- [64] Saad M. A., Abdurahman N. H, Rosli Mohd Yunus (2021): "Synthesis, characterization, and demulsification of water in crude oil emulsion via a corn oil-based demulsifier". Materials Today: Proceedings 42 (2021) 251–258.