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Preparation and Characterization of Different Bio-Based Demulsifier from Corncob for Crude Oil Emulsion Management

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Abstract

The search for innovative technology or materials that will reduce the challenges of demulsification of emulsions for better efficiency is intensively ongoing in the petroleum industry. It is therefore pertinent to develop innovative materials to achieve the effective separation of emulsions. In this work, two different methods of acid-hydrolyzed process (microwaved and furnace) at different temperatures (180 and 250 ℃) were evaluated for the preparation of environmentally friendly biodemulsifier: microwaved ash (MVA) and furnace-based ash (FBA) demulsifiers from corncob. The eco-friendly demulsifiers were characterized by Fourier transform infrared spectroscopy (FT-IR), Gas chromatographic-mass spectroscopic (GC-MS) and Scanning electron microscopy (SEM) and their chemical content and physico-chemical properties compared with a commercial chemical demulsifier (Phase treat). The SEM analysis reveal distinct variation in the morphology of the hydrolyzed ashes, attributed to differences in the hydrolysis conditions, specifically temperature and heating method. The FT-IR spectra of the biodemulsifiers were found to contain functional groups such as OH, C=O and C-O similar to that of the chemical demulsifier. The GC-MS results reveal the presence of amphiphilic compounds in both biodemulsifiers with the ability to break the water-in-oil emulsion as observed in the chemical demulsifier. In the bottle test analysis carried out to determine the efficacy of the biodemulsifiers, it was observed that the MW-based demulsifier performed better with a separation efficiency of 72 % when compared to 60 % and 39% for the chemical demulsifier and FBA -based demulsifier respectively. This work not only promote the efficient utilization of agricultural waste (corncob), but also provides an insight into the exploration of new demulsifying materials with excellent performance.

Keywords: *Bio-based demulsifiers; Corncob; Crude oil; Demulsification; Emulsion management.*

1. Introduction

The petroleum industry faces a challenging problem as a result of the fast-growing oil and gas sectors' high oil production and emulsion formation. The process of oil production (also known as oil recovery) produces the emulsion. Powerful and efficient demulsifiers are required for use in the enhanced oil recovery (EOR) process [1]. Applying surfactants which are surface-active substance helps in reducing the interfacial tension between the two phases and create stability in the emulsion mixture [2-3]. Several petroleum related researches have taken keen interest in the durability of oil-in-water emulsions in order to advance the effectiveness and related approaches for oil-in-water separation. Oil-in-water emulsions have been treated with several techniques such as; thermal, chemical, electrical or combination of those methods [4-6]. However, the economic viability and efficiency of separation as well as the treatment resource is what determines the treatment method that would be utilized in the emulsion separation process [7]. According to Mohyaldinn *et al*. [8], temperatures are insufficient to significantly increase the solubility of a certain crude oil in water.

The importance of the demulsifiers and the demulsification process has increased as demand for oil with better quality (light and sulfur free crude oil) increases. The development of

the demulsification processes of oil/water (O/W) emulsions is also necessary to obtain significant oil recovery. The chemical demulsification (CD) process has been used in a number of demulsification processes which more popular among researchers than other procedures for demulsifying crude oil emulsions due to its higher and quicker efficiency [9-10]. Additionally, the chemical used in the demulsification operations can be created using various nonionic surfactant mixes. These demulsifiers have a two-part chemical structure: a hydrophobic portion made up of amide, alkyl fatty esters, polyoxypropylene, and alkyl phenol formaldehyde ethers, and a hydrophilic portion made up of polyoxyethylene. Because the currently utilized chemicals have various drawbacks, such as being expensive and polluting, it is necessary to build new demulsifiers that are both affordable and environmentally benign [11].

Many technologies such as cellulose/nanocellulose, lignosulfonates, nano-particles, and vegetable oils have been developed and utilize for demulsification of O/W emulsions [12-15]. Currently, nanocellulose such as cellulose nanocrystal (CNC) and cellulose nanofibril (CNF) are utilized as potential EOR agents and surfactants in solving challenges in the oilfield because traditional oilfield chemicals have been found to be unstable, environmental and economical unfriendly as well as causing damages to the formations [14,16]. The abundance of hydrophilic hydroxyl groups and hydrophobic alkyl-group containing β crystalline edges on the surface of CNCs gave it surfactant characteristics in addition to its degradability, low density, renewable, less damage to formations, controllable structure and environmentally friendly thus, offering it an inherent advantages and broad applicability in oilfield operations [14,17]. For instance, the amphiphilic property facilitates nanocellulose adsorption at the water-oil interface, where the hydrophobic domain aligns with the oil phase, and the hydrophilic domains are exposed to water for effective demulsification [12].

Lignosulfonates are utilized in a multiplicity of applications, including formulations as plasticizers, dispersants, and stabilizers, because of their amphiphilic nature. Their behavioral pattern in aqueous solution, at surfaces, as well as interfaces are constrained by their chemical composition which determines their function and performance [2]. The behavior of lignosulfonates in surfaces, interfaces and aqueous solutions such as reducing the interfacial tension (ITF) in crude oil reservoirs during core flooding enhances oil recovery (EOR) from the reservoir [3].

The hydrophobicity-hydrophilicity of lignosulfonates also play critical role as dispersant or surfactant in emulsion management, where fractions with higher molecular weight, lower charge density and increased hydrophobicity is collected [18]. Demulsifiers have been produced from vegetable oil-base like; soybean oil [19], palm oil [20], castor oil [21] and calabash seed oil [22] all presenting good demulsification capacities.

As the development of demulsification process continues, it is necessary therefore to produce an eco-friendly and effective demulsifying agent because conventional demulsifiers used for emulsion treatment are frequently expensive and hazardous. Therefore, the research is aimed to prepare and characterization of different bio-based demulsifier (MWA and FBA) from corncob for crude oil emulsion management. The prepare demulsifiers were compared with a commercial demulsifier for efficiency.

2. Materials and methods

2.1. Materials

Fresh corn was acquired from the local market, the seeds were removed and the cob was cut into smaller sizes, dried in the oven and milled. The chemicals used were obtained from Nile University Chemistry Laboratory and they are all of analytical grade. A commercial chemical demulsifier Phase treat (code: 42172) obtained from University of Port-Harcourt was used as a reference standard in comparison to the bio-based formulated demulsifiers.

2.2. Ash preparation and acidification process

2.2.1. Furnace burner ash (FBA) preparation of the corn cob

The FBA was prepared by modifying the method of Yuan, *et al*., [23] which is a simple one-step hydrothermal method using corncob as raw materials, 50g of the milled corncob was

placed in a furnace burner and heated at 250°C for six hours which produced 31g of burnt ash. Furthermore, 15g of the ash was agitated at 500 rpm with a mixture of 30 mL of 0.5M H_2SO_4 for 30 min to acidify the ash. It was then washed to neutral pH, filtered and allowed to dry for 2 days at room temperature.

2.2.2. Microwave ash (MWA) preparation of the corn cob

The MWA was prepared by modifying the method of Yuan, *et al*., [23] which is simple one-step hydrothermal method using corncob as raw materials. 50g of the milled corncob was added to 100 mL of 0.5M H_2SO_4 and agitated with a magnetic stirrer at 500rpm for an hour. The mixture was then transferred into the microwave and heated for three hours at 180°C. After that, the ash was rinsed to a neutral pH before drying at room temperature.

2.3. Demulsifier preparation process

2.3.1. Formulation of demulsifier using FBA and MWA

The method of Yuan *et al*., [23] was used to formulate the ethanol based demulsifier. Then 2g of the acidified FBA and MWA each was transferred into a measuring cylinder and then 5mL of ethanol was added to form a biodemulsifier. After thorough shaking, it was stored for further analysis.

2.4. Emulsion preparation

The method of Yuan, *et al*,[23] was used for emulsion management. 400mL of distilled water was mixed with 140mL of crude oil in an 800 mL beaker, and the mixture was heated at 70°C for about 20 min. Then, it was stirred for 20 min at the rate of 11000 rpm with a magnetic mixing machine. The stirring process was repeated twice to obtain a stable oil–water emulsion. The emulsion was kept stable at least one week at ambient temperature.

2.5. Bottle testing

The crude oil emulsion breaking capacity of the developed biodemulsifier was assessed using the bottle test method according to Yuan, *et al*, [23] and compare with a commercial chemical demulsifier: phase treat. To each bottle of emulsion, 5 ml of the prepared demulsifier was added. To ensure that, the emulsions and demulsifiers were thoroughly mixed, the bottles were placed under observation to record the separation at 5-minute interval.

$$\text{Water separation efficiency} = \frac{volume\ of\ water\ seperated}{original\ volume\ of\ water\ in\ the\ crude\ oil\ emulsion} * (100) \qquad (1)$$

2.6. Scanning electron microscopy (SEM) analysis

SEM analysis was used to examine the surface structure of the starch samples at magnifications of 8000x, 9000x, and 10000x on a scanning electron microscope (JEOL-JSM-7600F-USA). The starch samples were covered with platinum coating after being double-stick tape attached on aluminum stubs. At a 15kV accelerating potential, the materials were examined and photographed.

2.7. Fourier transform infrared spectroscopy (FTIR) analysis

The FTIR analysis was carried out using Nicolet iS10 FTIR Spectrometer. The spectral frequency was within the range of 4000 and 350 cm^{-1} with a spectral resolution of 4 cm^{-1}. The IR spectra were analyzed using spectroscopic software Win-IR Pro Version with a peak sensitivity of 2 cm^{-1}.

2.8. Gas chromatographic-mass spectroscopic (GC-MS) analysis

GC-MS analysis was carried out on a Perkin Elmer Turbo mass spectrometer (Norwalk, CTO6859, USA). Which includes a Parkin Elmer Auto Sampler XLGC. The column used was Elite -5 capillary column measuring 30m x 0.25mm with a thickness of 0.25 mm composed of dimethyl polysiloxans.

3. Result and discussion

3.1. Result for GC-MS analysis

In recent years, researchers have made use of bio-polymers such as cellulose and lignosulfonates in treating emulsions and enhanced oil recovery (EOR) but more materials and technologies are still sourced for to enhance their performance [13-14,24]. Presently, nanocellulose (cellulose nanocrystal and cellulose nanofibril) are used as potential EOR agents and surfactants in solving oilfield problems because traditional oilfield chemicals are unstable, environmental unfriendly and expensive [14,16]. The amphiphilic property of nanocellulose gave its surface characteristics and enhances its adsorption at the water-oil interface, where the hydrophobic domain aligns with the oil phase, and the hydrophilic domains are exposed to water for effective demulsification [12].

The result of the GC-MS analysis for microwave ash demulsifier (MWA Figure 1 and Table 1) showed that there were nine compounds detected between retention times ranging from 7-19 seconds. Among this nine compounds tetra(chloro)decanoic acid at RT 15.11 and percentage abundance of 272%, 1-oxaspiro-chlorophenyl at RT 12.57 and percentage of 265% and tetrachloropentane at RT 7.45 and percentage of 208% were detected as the highest and most important compounds in the sample. The presence of C=O, O-H and C-O functional groups that produces the hydrophilic and lipophilic characteristics in demulsifiers found confirms that the sample can be used as a demulsifier. Although there is limited research specifically on microwave ash demulsifiers, Adewunmi & Kamal. [25] evaluated the potential of fly ash, obtained through microwave-assisted ashing, as a demulsifier for crude oil emulsions. The results indicated its promising demulsification performance.

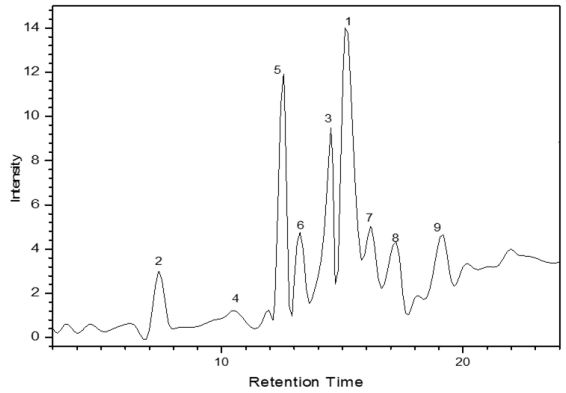

Figure 1. GC-MS spectrum of microwave ash (MWA) demulsifier.

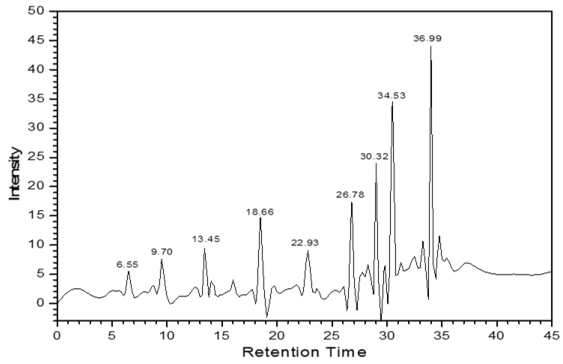

Figure 2. GC-MS spectrum of furnace ash (FBA) demulsifier.

Table 1. Profiles of the microwave ash demulsifier (MWA).

S/No	Retention time	Compound names	Molecular formula	Conc. %
1.	15.11	Tetra(chloro)decanoic acid	$C_{10}H_{28}O_2Cl$	272
2.	7.45	Dichloromethylclopropyl	$C_9H_{16}Cl_2$	195
3.	14.62	Tetrachloropentane	$C_5H_8Cl_4$	208
4.	10.41	3 Chloro 2 nitrobenzyl alcohol	$C_7H_6ClNO_3$	188
5.	12.57	1-oxaspiro-chlorophenyl	$C_{15}H_{17}ClO_2$	265
6.	13.33	Cyclohexane-limonene	$C_{10}H_{16}O_2$	135
7.	16.20	Cyclohexanol-acetate	$C_{12}H_{20}O_2$	196
8.	17.45	1,4 cyclohexadiene	$C_{10}H_{16}$	136
9.	19.20	3-Cyclohexen –I-ol	$C_{12}H_{20}O_2$	195

There were 9 composites in the GC-MS analysis of FBA demulsifier (Figure 2). Table 2 displays the detected constituents together with their retention time from 6-40(min) and percentage concentration. Among the 9 compounds, 1-hydroxyl 2-proanone, 1-propenol, terpenoids, O-Ethyl phenol and dodecanoic acid with percentage abundance of 26.50, 21.80, 17.07, 13.27 and 11.31% respectively are the most occurring compounds. The result exhibits a hydrophilic character due to the presence of the carboxylic groups, esters, phenolic group and elatol (Table 2). Elatol is a halogenated sesquiterpene in the chamiqrene natural product family. A two-ring cyclic unsaturated compound with O-H, Cl and Br attached at the 1,2 and 6 carbon atoms. It has been reported to play important roles in ecological interactions such as anti-herbivores activity and potential defense against infection by microorganisms [26]. Previous studies have reported that the development and effectiveness of cellulose-based materials as surfactant for emulsion separation [27-28].

Table 2. Profiles of the furnace ash demulsifier (FBA).

S/N	RT	Compound name	% Conc
1	6.55	Comphene	0.4
2	9.70	Halogenated compounds	1.52
3	13.45	Acetic acid-methylester	5.34
4	18.66	Dodecanoic acid	11.32
5	22.93	Elatol	2.73
6	26.93	O-Ethylphenol	13.27
7	30.37	Terpenoids	17.07
8	34.53	1-Propenol	21.8
9	36.99	1-hydroxyl 2-proanone	26.5

There were 19 composites in the GC-MS spectrum of the commercial chemical demulsifier (Figure 3). The commercial chemical demulsifier contain two major constituents (and their relative peak) of acetic acid (27.28%) and 1-hydroxy-2-propanone (16.40) (Table 3). The minor components present are acetic acid methyl ester (3.65%), 2,3-dihydro-benzofuran (3.65%) and phenol (3.05%). The presence of C=O, O-H and C-O functional groups that produces the hydrophilic and lipophilic characteristics in demulsifiers found confirms that the sample is a demulsifier. Previous studies have also shown the successful application of chemical demulsifiers in crude oil emulsion treatment [29-30].

Hence, the results obtained from the formulated eco-friendly demulsifiers demonstrated that they contain the compounds with the ability to break an oil-in-water or water-in-oil emulsions. It also agrees with works in literature on the use of biomaterials for effective emulsion management.

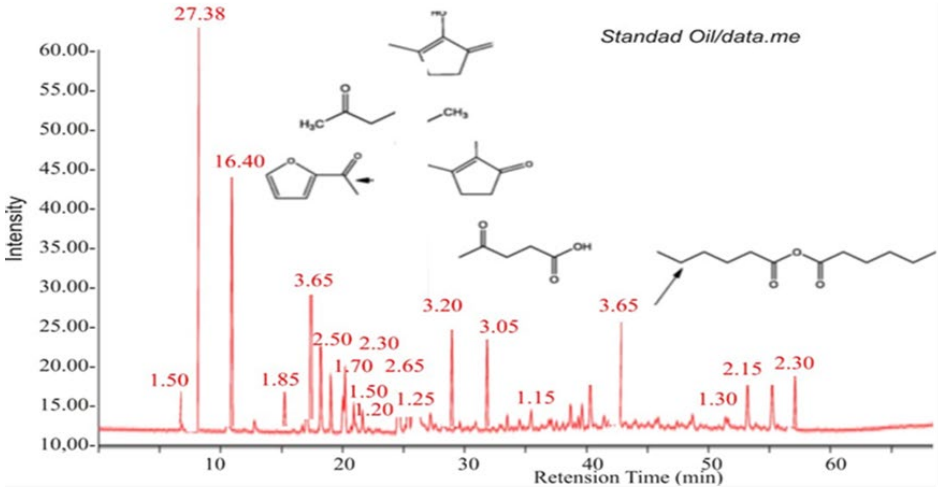

Figure 3. GC-MS spectrum of the chemical demulsifier.

Table 3. Profiles of the standard chemical demulsifier.

S/No.	RT (mins)	Compound name	Area %
1.	8.20	2-amino 1,3-propanediol	1.50
2.	9.40	Acetic acid	27.38
3.	10.95	1-hydroxyl 2-proanone	16.40
4.	15.60	1-hydroxyl 2-butanone	1.85
5.	15.85	Acetic acid-methylester	3.65
6.	18.05	Butanedial	2.55
7.	18.80	2-cyclopentane-1-one	1.70
8.	18.60	Furfural	2.30
9.	20.85	2,2,4-trimethyl1,3dioxolane	1.50
10.	21.65	1,2propanone	2.65
11.	22.05	2-butanone	1.20
12.	26.95	2,3-dimethyl-cyclopentane	1.25
13.	27.80	2-furanone	1.15
14.	29.70	3methyl 1,2cyclopentanedione	3.20
15.	31.50	Phenol	3.05
16.	35.70	4-methyl-phenol	1.30
17.	39.70	4-ethyl-phenol	2.15
18.	43.62	2,3-dihydro-benzofura	3.65
19.	59.95	Glucosandi-one	2.30

3.2. Result for FT-IR analysis

FTIR spectra of the samples are shown in Figure 4. The spectra reveal the presence of different functional groups such as the alcohols (-OH), carbonyl (-C=O), ether (C-O-C), ethylene (C=C) and the alkyls (C-H).

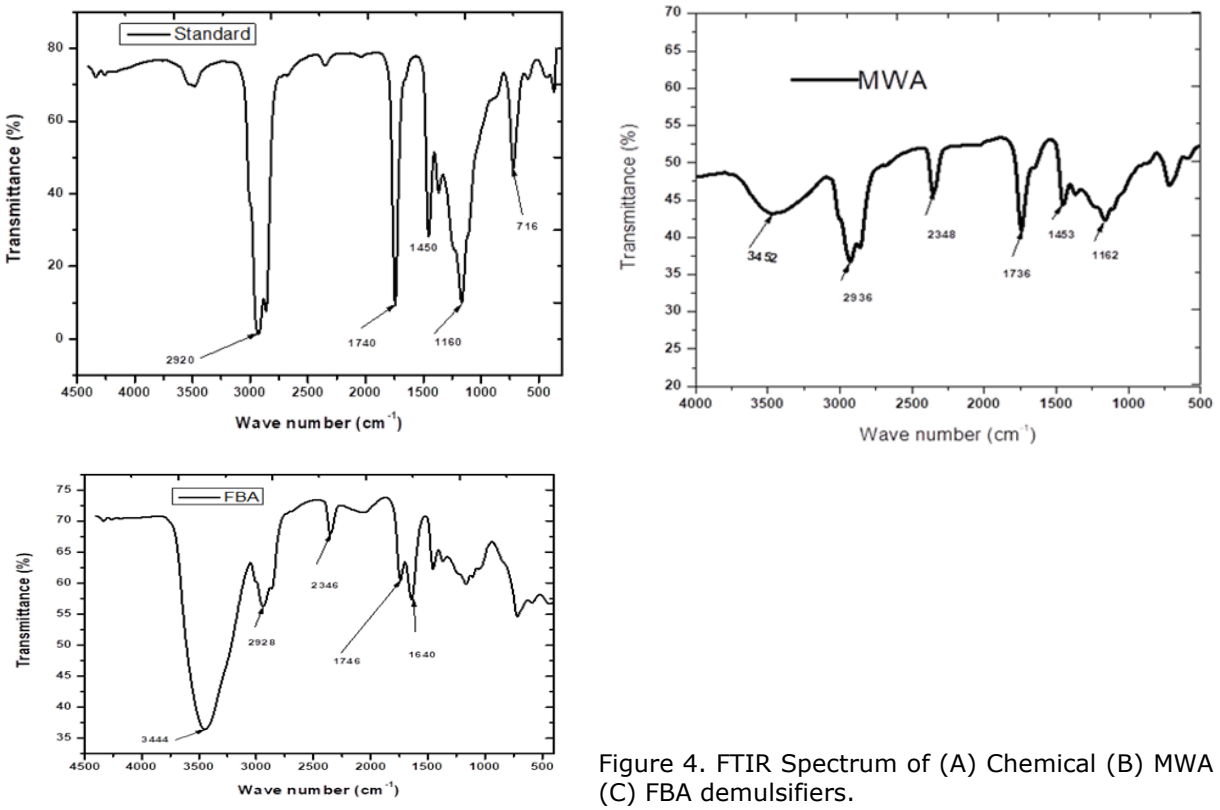

Figure 4. FTIR Spectrum of (A) Chemical (B) MWA (C) FBA demulsifiers.

In all the samples, the sharp absorption peaks at 3007.19–2852.08 cm^{-1} are given to both symmetrical and asymmetrical alkane stretching ($-CH_3$) and alkenes ($=CH_2$) within the aliphatic hydrocarbon groups [31]. The spectrum (Fig 4A) of the chemical demulsifier (Phase

treat) revealed the presence of various characteristic vibrational peaks when compared the spectra of other bio-based demulsifiers. The spectrum reveals the presence of a low intensity peak at 3440 cm^{-1} which is characteristic of O-H stretching vibration for the chemical demulsifier whereas, the bio-based samples showed strong O-H peaks especially FBA demulsifier. The low intensity demonstrated that the O-H group are less abundant in the chemical demulsifier. The vibrational peaks around 1740-1750 cm^{-1} characteristic to the carbonyl functional groups (C=O) was found to be present in all samples though of low intensity in FBA-based demulsifier. All the samples show similarity in the vibrational peak in the range of 1200-1000 cm^{-1} which is characteristic of the C-O stretching vibration, [32] thereby confirming the presence of compounds such as alcohols, phenols, acids, esters, ethers which have been found present in the GC-MS analysis.

Therefore, the functional group identified in the spectra of the different formulated demulsifiers confirms that the compounds present in the demulsifiers contain amphiphilic characteristics and thus, have the ability to break down the attractive forces and enhances emulsion separation.

3.3. SEM analysis

The SEM analysis was conducted to examine the morphological characteristics of two hydrolyzed corncob samples. The first sample was hydrolyzed at 250°C using a furnace heater, while the second sample was microwaved at 180°C. The SEM images (Figure 5-6) revealed distinct differences in the surface morphology of the different samples [32-33].

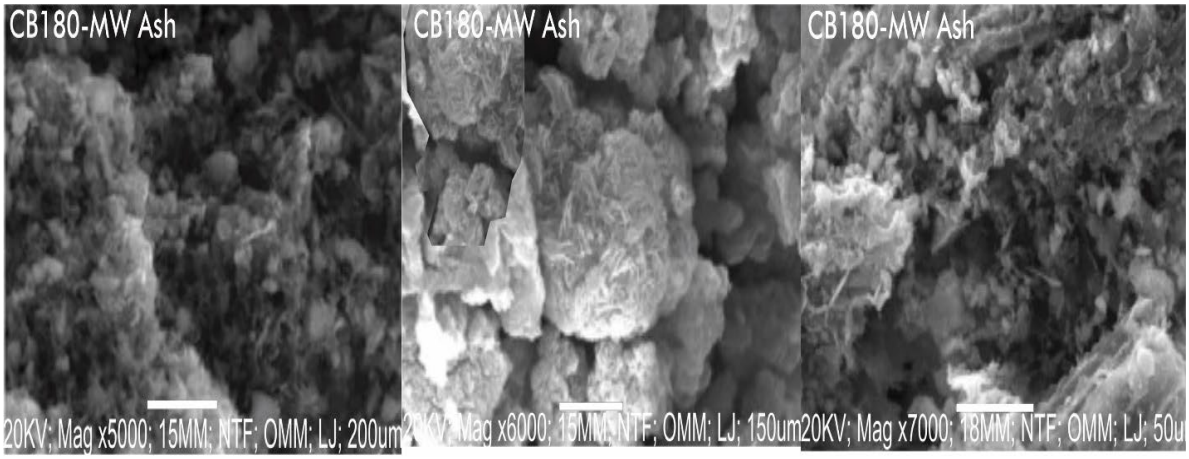

Figure 5. SEM analysis of microwave ash CB180-MW.

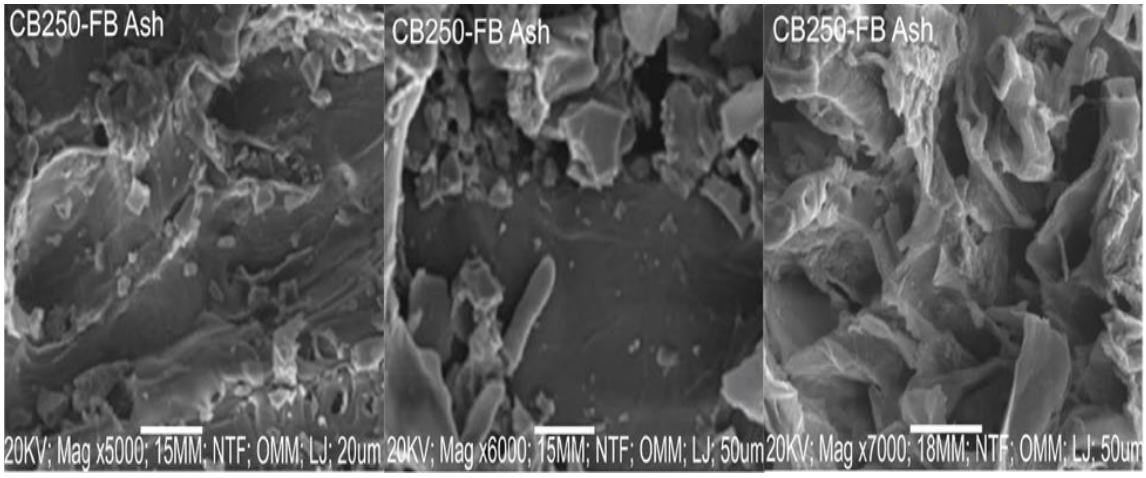

Figure 6. SEM analysis of furnace burn ash.

In the SEM image of the corncob sample hydrolyzed using a furnace heater at 250°C (Figure 6), it can be observed that the surface appears relatively rough, non-uniformed in size and contains large number of interstitial holes. The ash particles are well-distributed with no significant agglomeration or clustering. This suggests that the hydrolysis process at higher temperature in a controlled environment resulted in complete combustion and uniform ash formation [34]. On the other hand, the SEM image of the corncob sample microwaved at 180°C (Figure 5) shows a different morphology. The surface appears smooth and small sized, some areas exhibit agglomeration and clustering of ash particles, indicating incomplete combustion and non-uniform ash formation. The acid hydrolysis of the corncob at this temperature created a nanocellulose like structure that is in small particle form. Research have shown that acid hydrolysis of lignocellulose biomaterials has been extensively used for the production of cellulose nanocrystals (CNCs) by enabling the cleavage of the glycosidic bond within the cellulose microfibrils [35-36].

These differences in morphology between the two hydrolyzed corncob samples can be attributed to variations in the hydrolysis conditions, specifically temperature and heating method. The higher temperature and controlled environment of the furnace hydrolysis process likely facilitated more complete combustion and irregular ash formation. In contrast, the lower temperature and rapid heating of the microwave hydrolysis process may have resulted in incomplete combustion and uniformity in ash formation [37].

3.4. Bottle test

3.4. Bottle test for all demulsifier

The bottle test results (Figure 7) demonstrated that the chemical demulsifier exhibited a fast demulsification time, rapidly breaking down the emulsion and facilitating the separation of the oil and water phases at 40 mins while it showed a lower efficiency when compared to the MWA demulsifier which demonstrated the best separation efficiency (Figure 8). The furnace ash demulsifier exhibited the least demulsification efficiency in the bottle test. Therefore, the trend in terms of efficiency is MVA (72 %) > chemical (60 %) > FBA (39 %).

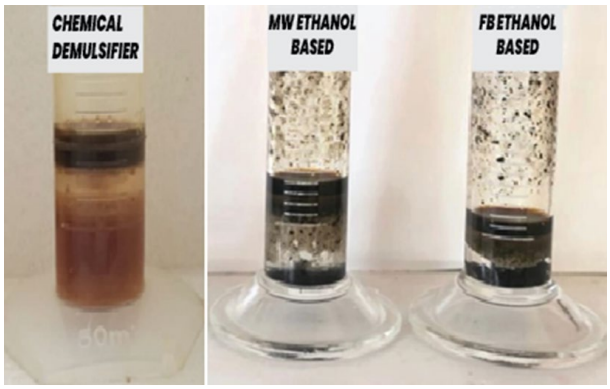

Figure 7. Bottle test analysis of the demulsifier.

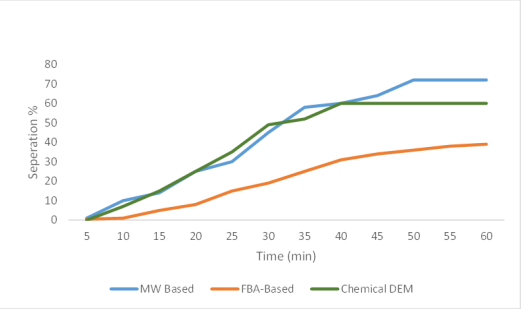

Fig. 8. Time and separation efficiency of the demulsifier.

Though the microwave ash demulsifier exhibited best demulsification efficiency when compared to other demulsifiers, it required up to 60 mins to achieve better separation thereby giving the chemical demulsifier an edge in terms of separation time. In respective of time of separation, the trend is Chemical (40 mins) > MWA (60 mins) > FBA (> 60 mins because maximum efficiency is not yet attained as at 60 mins).

4. Conclusion

The results obtained from the bottle test demonstrated that both biodemulsifiers showed promising demulsification capabilities, as evidenced by the significant reduction in water content and faster separation of oil and water phases especially MWA demulsifier. This indicates their potential for application in emulsion management within the petroleum industry. In the SEM result, the differences in morphology between the two hydrolyzed corncob samples was attributed to variations in the hydrolysis conditions, specifically temperature and heating method. The higher temperature and controlled environment of the furnace hydrolysis process likely facilitated more complete combustion and irregular ash formation. In contrast, the lower temperature and rapid heating of the microwave hydrolysis process may have resulted in incomplete combustion and uniformity in ash formation

Furthermore, the GC-MS analysis provided valuable information about the chemical composition of the demulsifiers. The results show cased the presence of compounds with amphiphilic characteristics These unique characteristics contribute to the demulsification process by destabilizing the emulsion and promoting phase separation. The FT-IR analysis confirmed the presence of the functional groups such as the hydroxyl, carbonyl and ether which poses these amphiphilic characteristics required in the demulsifiers. The similarities in the GC-MS and FT-IR of the FBA, MWA and standard chemical demulsifier showed that corncob is a potential biomaterial for the production of efficient demulsifiers. Thus, it can be concluded that the development and characterization of nanoparticle-based demulsifiers, particularly the use of corn cob as a biodemulsifier, holds great potential for improving emulsion management in the petroleum industry. The utilization of these demulsifiers can lead to enhanced separation efficiency, reduced production costs, and improved environmental sustainability.

Based on the results and discussions, it can be concluded that the development and characterization of bio-based demulsifiers, particularly the use of corn cob as a biodemulsifier, holds great potential for improving emulsion management in the petroleum industry. The utilization of these demulsifiers can lead to enhanced separation efficiency, reduced production costs, and improved environmental sustainability.

Data availability: *The data that has been used is confidential.*

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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