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Assessment of *Coconut Surfactant's* Foam Properties for Enhanced Oil Recovery

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Abstract

The application of surfactant's foam in Foam Assisted Water Alternating Gas (FAWAG) is one of the progresses recorded in Enhanced Oil Recovery (EOR) strategies. This study is aimed at synthesizing a bio-surfactant from the coconut oil extract and investigating the foam properties such as stability and bubbles size. The Ross-miles approach, supported by response surface methodology, was utilized to investigate the foam stability. The morphology of the foam was characterized by microscopic analysis to ascertain the foam size distribution and lamella division. According to the results, about 15.8 g of the surfactant was synthesized and key functional groups were identified by FTIR. Analysis of variance (ANOVA) for foam stability indicates a p-value of 0.0008 which establishes the model's significancy. Furthermore, the model's acceptable accuracy was demonstrated by the adjusted R^2 of 0.87, which was highly consistent with the model R^2 value of 0.93. The Foam was found to reach its maximum stability up to 55 second, demonstrating synergy between surfactant and brine. The stability was strongly influenced by brine concentration more than the impact of surfactant concentration. Thus, this foam could find application in EOR.

Keywords: *Coconut oil; Surfactant; EOR; Foam; Ross-Miles.*

1. Introduction

The need for energy has risen significantly in recent years despite the expedite development of alternative energy sources. Global energy consumption has increased largely due to the necessity of crude oil as a fuel source [1]. Several oil recovery methods such as primary and secondary methods have been used to bring the oil to the surface [2]. About 60 to 70 percent of oil remains under the ground following primary and secondary recovery operations due to the trapping effect as a result of capillary forces and other rock-fluid factors [3-4]. Consequently, residual oil is recovered using tertiary recovery method known as Enhanced oil recovery (EOR), which is used to recover oil beyond the capacity of primary and secondary recoveries [5-7].

EOR injections consist of steam flooding, surfactants, polymers, and microbes [8]. Foam flooding has been recognized as one of these techniques with tremendous potential to address numerous issues that arise at different stages of the hydrocarbon recovery process [9-10]. Since foam lowers gas mobility, it is well known to be an efficient tool for EOR [11]. The process entails the injection of gas into the lower area of the formation and surfactant solution into the higher region [12]. Foam is used in the foam-assisted water alternating gas (FAWAG) method to improve the production rate in the producer well, reduce the gas-oil ratio (GOR), and boost sweep efficiency during a gas injection [13]. Surfactants can be employed as flocculation and wetting agents [14], oil recovery enhancement [15], emulsion stabilization [16], and foam formation [17] because of their ability to reduce interfacial tension (IFT) [18]. One of the

difficulties faced in foam-assisted EOR is the stability of foam in porous media. Stability is the capacity of foam to maintain its original characteristics, especially its quality. The primary physical processes that cause the foam to become unstable are foam irrigation, clumping, and bubble coarsening [19-20]. Organic natural surfactants are degradable, safe for formation, and environmentally friendly compared to synthetic surfactants [21]. Therefore, natural plants such as coconuts contains oil which is a renewable resource that has been found to be converted into surfactants and used for foaming applications. Coconut surfactants have been known to exhibit excellent foaming properties due to their unique chemical composition. They contain fatty acids which are essential and precursor to synthesize surfactants. The foam properties can be evaluated using various techniques such as foam height tests, stability tests, and bubble size analysis.

2. Experimental

2.1. Sample selection, collection and preparation

Fresh coconuts (*Cocos nucifera*) were procured from the Yar Kasuwa market in Kumbotso Local Government Area of Kano state, Nigeria (Figure 1a). The varieties of coconuts used were mature, West African Tall green coconuts. The coconuts were dehusked and deshelled to remove the kernel. The coconuts were rinsed and shredded into smaller particles to improve surface area for efficient and successful extraction (Figure 1b).

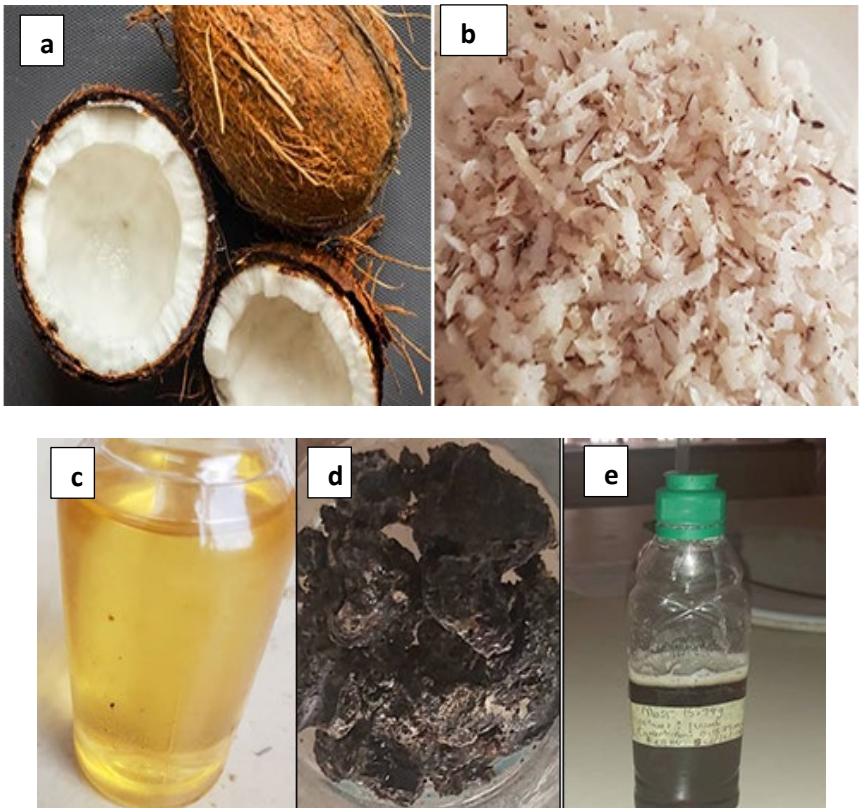


Figure 1. (a) Coconut sources (b) Coconut flakes (c) Coconut oil (d) Coconut surfactant (e) Active concentration.

2.2. Physicochemical analysis

2.2.1. Percentage moisture content

The weight of the freshly collected sample was recorded. The sample was set to air dry for 3 days and its dried weight was noted. The moisture content was determined using the formula;

$$\%\ moisture\ content = \frac{A - B}{A}\ x\ 100 \qquad (1)$$

where, A is the mass of the fresh sample (g); B is the mass of the dry sample (g).

2.2.2. Acid value of the oil

An equal amount of ethanol and petroleum ether was used to dissolve 5.0g of the sample, and the mixture was then neutralized with 0.5N KOH in a 250mL conical flask to measure the oil's acid value. The sample was dissolved by heating the resulting mixture for 10 minutes. Exactly 5 drops of phenolphthalein indicator solution were added, and after cooling, the contents were shaken vigorously. With 0.5N KOH, the mixture was titrated until the endpoint (colorless to pink) was noticed for 15 seconds. The procedure was run once using a blank sample, and the volume was recorded. The Acid value was calculated using the formula,

$$Acid\ value = \frac{\text{Vx Nx } 56.1}{\text{W}} \qquad (2)$$

where, V represents the volume of KOH solution in milliliters (mL) (Titre difference) (B-S). The parameters B and S are blank titre value (mL) and sample titre value (mL). Whereas, N and W are normality of KOH solution and weight of the sample(g) respectively.

2.3. Saponification value of the oil

A 2.0g portion of the sample was dissolved in 25 ml of 1:1 combination of ethanol and KOH in a 250 mL conical flask to ascertain the oil's saponification value. After heating in a water bath attached to a reflux condenser from the Soxhlet extractor, the mixture was continuously spun for thirty minutes. After the oil was fully dissolved, precisely, five drops of phenolphthalein indicator were added to the mixture. The liquid was then titrated with 0.5N HCl until the endpoint (pink to colorless) was observed.

The entire process was carried out again using the same amount of KOH solution at the same time and condition but without the sample (blank) and the volume was recorded. The following formula was used to determine the saponification value.

$$Saponification\ value = \frac{\text{Vx Nx } 56.1}{\text{W}} \qquad (3)$$

where, V is the volume of HCl solution in mL (Titre difference) (B-S). The parameters B and S are blank titre value (mL) and sample titre value (mL). Whereas, N and W are normality of HCL solution and weight of the sample(g) respectively.

2.4. Extraction procedure

Soxhlet extraction was the method of extraction employed in this study. A filter paper was used to weigh the sample, which was then placed into the extractor's thimble at a precise weight of 25g. Exactly 200mL of solvent (n-hexane) were put into a round-bottom flask with a capacity of 500mL. The solvent vapor was condensed using a reflux condenser that was mounted on the top of the extractor and linked to the water reservoir. To vaporize the n-hexane, a heating mantle was positioned below the round-bottom flask and set to 60^{o}C. A colorless condensate and no trace of oil were noticed after each extraction procedure was run for 9 refluxes within 3 hours. The solvent siphoned over the barrel, and the condenser was disconnected. The sample was taken out after cooling, and oil was obtained by complete solvent evaporation (Figure 1c).

2.4.1 Percentage yield of oil

Prior to and after the extraction process, the sample's weights were recorded. Furthermore, the weight of the extracted oil was noted. The following formula was used to calculate the percentage yield:

$$Percent\ yield\ (\%) = \frac{\text{mass of oil extracted}}{mass\ of\ sample}\ \text{X } 100 \qquad (4)$$

2.5. Synthesis of surfactant

Exactly 10mL of coconut oil was weighed and simmered for 15 minutes at 80-90^{o}C. Exactly 5g of NaOH was added and heated continuously for two (2) and half hours at 80^{o}C while

stirring continuously until a solid black product was formed (Figure 1d and e). A large amount of foam was formed when the product was dissolved in distilled water to ensure completion of the reaction.

2.6. Foam stability studies

Using Design-Expert Software (DOE), the concentrations of surfactants and brine were investigated through the use of the response surface methodology (RSM) in conjunction with Central Composite Design (CCD) [22]. As indicated in Table 1, a total of 13 runs (each with four center points at 0.3 and 2.0 %) were conducted.

Table 1. Brine and surfactant % optimization through experimental design.

Run	Surfactant (%)	Brine (%)	Run	Surfactant (%)	Brine (%)
1	0.5	1.0	8	0.3	3.0
2	0.3	2.0	9	0.1	3.0
3	0.5	2.0	10	0.3	2.0
4	0.1	2.0	11	0.5	3.0
5	0.3	2.0	12	0.1	1.0
6	0.3	2.0	13	0.3	1.0
7	0.3	2.0			

The Ross-Miles method was used for measuring the stability of foam produced in which the foam forming solution was presented in a burette of 50cm^3 volume capacity onto a 10cm^3 measuring cylinder. The foam stability and foam height of different surfactant concentrations were measured and recorded. The foam height was taken at the top of the foam column only while the foam stability was determined in terms of half-life. The half-life is the time taken for a foam to decay (collapse to half of its original height). All measurements were performed in triplicates to obtain maximum volume in the graduate cylinder.

2.7. Foam morphology

The lamella division, bubble morphologies and size distribution of foam were identified by image analysis. The microstructures of the surfactant foam were examined using a scanning electron microscope. The foam images were recorded immediately after the foam was generated and viewed at different time interval.

3. Results and discussion

3.1. Physicochemical analysis

Table 2 presents the physicochemical analysis, the dry coconut extract with a moisture content of 0.62%, well below acceptable levels.

Table 2. Physicochemical analysis of oil

S/N	Analysis parameter	Composition
1	Moisture content (%)	0.62
2	Oil yield (%)	23.12
3	Acid Value (mgKOH/g)	1.82
4	Saponification value (mgKOH/g)	187.55
5	Color	Pale yellow
6	Mass (g)	15.8
7	Active concentration (%wt)	0.158

Low moisture content is preferred because it extends shelf life and makes foods resistant to fungus attack, whereas high moisture can lead to hydrolytic rancidity of fats and oils [23]. Low acid value corresponds to a moisture content of 1.82, which is also preferred since it promotes low moisture content. This parameter serves as an indicator of oil edibility, with lower

values correlating with the higher storage quality [24]. Utilizing the n-hexane as a non-polar solvent, coupled with heating at 80°C, resulted in the extraction of 23.12%. The measured saponification value of 187.55mg KOH/g suggests the presence of short and medium-chain triglycerides coconut oil [25]. Oil with low saponification value are suitable for surfactant synthesis [26]. The soap appeared dark brown solid that results from the chemical interaction between the oil and NaOH.

3.2. FTIR analysis

Coconut oil is commonly dominated with saturated lauric acid and traces of linoleic and oleic unsaturated acids. After the synthesis, the FTIR spectra of the synthesized surfactant is shown in Figure 2. The weak broad peak with a wavenumber of 3409cm^{-1} corresponds to the O-H stretching of an absorbed water molecule. Additionally, peaks at 2958, 2851, and 2821cm^{-1} indicate sp^2 and sp^3 C-H aliphatic stretching present in the fatty acids (likely hypsochromic shift occurs). Strong peak near 1600 cm^{-1} signifies C=O stretching, while weak peaks at region of 1200 cm^{-1} are due to C-O which serves as active reaction sides in surfactant formation (-C-O$^-$Na$^+$). At finger print region, peaks near 1400 cm^{-1} indicate -CH_3 & -CH_2 bending vibrations and 702 cm^{-1} demonstrates long chain hydrocarbon, respectively.

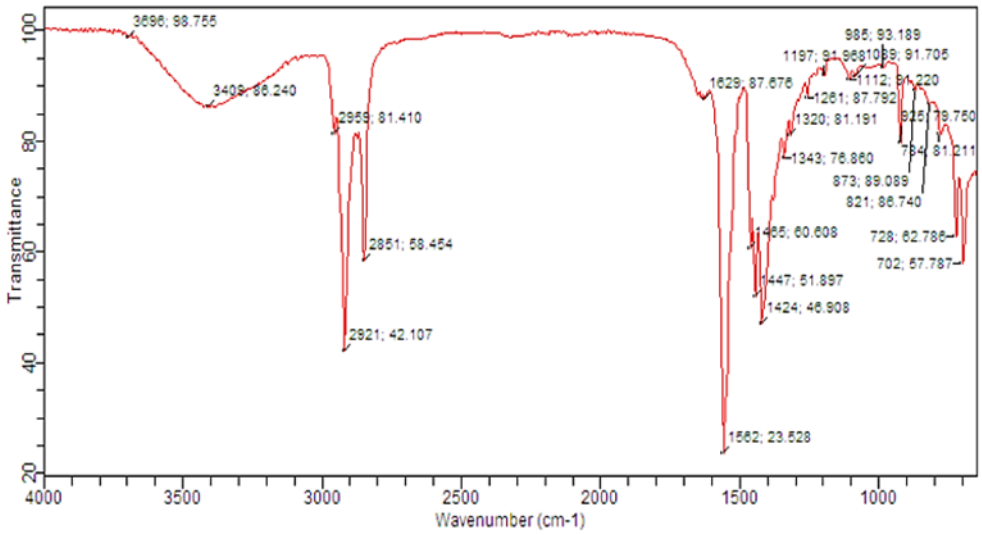


Figure 2. FTIR analysis of bio surfactant synthesized from coconut.

3.3. Foam stability

Table 3 presents the analysis of variance (ANOVA) results for foam stability. A p-value (prob> F) of 0.0008, less than 0.05 indicates the significance of the model.

Table 3. ANOVA analysis

Source	Sum of squares	df	Mean square	F Value	p-value Prob > F	results
Model	1948.52	5	389.70	17.51	0.0008	*significant*
A-biosurfactant	17.20	1	17.20	0.77	0.41	
B-brine	1683.71	1	1683.71	75.65	<0.0001	
AB	2.50	1	2.50	0.11	0.7475	
A^2	23.42	1	23.42	1.05	0.3391	
B^2	243.67	1	243.67	10.95	0.0130	
Residual	155.80	7	22.26	-	-	
Lack of fit	51.19	3	17.06	0.65	0.6220	*not significant*
Pure Error	104.61	4	26.15	-	-	
Cor Total	2104.32	12	-	-	-	

As indicated by Table 3, the model's acceptable accuracy was demonstrated by the adjusted R^2 of 0.8731, which was highly consistent with the calculated R^2 value of 0.93. The calculated R^2 value helps in estimating the agreement of data, and a value near 1.00 indicates good data fitness [27-28]. Adequate precision, measuring the signal-to-noise ratio, yielded a ratio of 12.137, exceeding the desirable threshold of 4. This high ratio indicates an accurate signal, affirming the model's reliability [29]. With the precision ratio of 12.137, model proves effective for navigating the design space, offering valuable insights into foam stability.

Figure 3 compares the actual (experimental) foam stability values, to those predicted by the response surface method. A high degree of precision between the experimental data and the model is indicated by the foam stability R^2, which was found to be 0.93. This strong correlation enhances the reliability of the response surface method in predicting foam stability values.

Foam stability = *17.63 + 60.05*(surfactant) - 19.64*(brine) - 3.95*(surfactant)*(brine) - 72.80*(surfactant^2) + 9.39*(brine^2)*

The three-dimensional (3D) response surface plot used to examine foam stability is shown in Figure 4. The plot shows that as brine concentration increases, the relative foam stability. Notably, surfactants exhibit minimal impact on foam stability unless there is an interaction with brine.

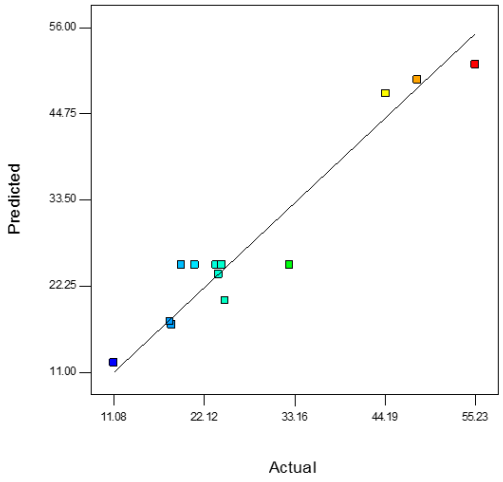


Figure 3. Scatter plot of predicted response vs. actual response from RSM design.

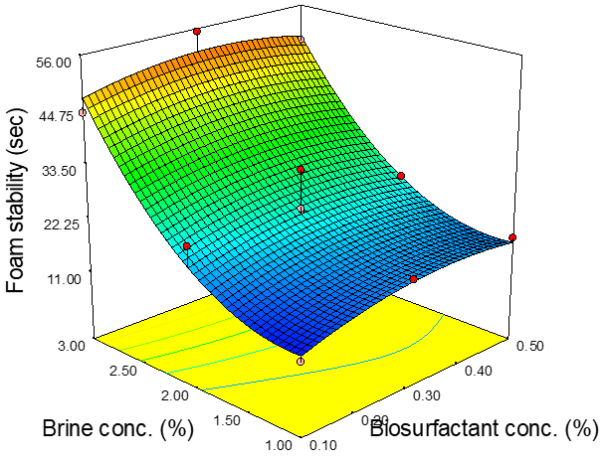


Figure. 4. Response Surface plot of Foam stability showing the interaction between surfactant and brine.

3.4. Optimization and validation of reaction

The optimal variable values are presented in Table 4. Optimization was carried out by determining the percentage error. A mere 7.8% error was calculated upon model evaluation indicating a concordance between the predicted and experimental values.

Table 4. Optimal conditions derived by RSM for surfactant-brine formulations.

Optimal Conditions		Desirability	Experimental	Predicted	Error (%)
Surfactant (%)	Brine (%)		Foam t1/2 (s)	Foam t1/2 (s)	
0.33	3.00	0.91	55.23	51.24	7.8

3.5. Foam morphology and bubble size distribution

The morphology of the foam was examined using a microscope. Figure 5 illustrates a linear relationship between bubble size and decay time, highlighting a noteworthy observation. The graph indicates that bubble size increases with time. This insight, derived from the image

analysis, contributes to a comprehensive understanding of foam morphology and size distribution dynamics.

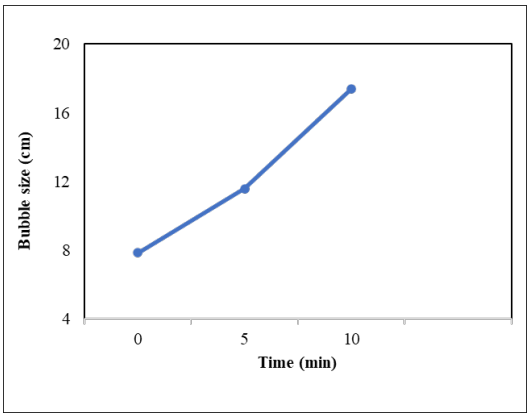
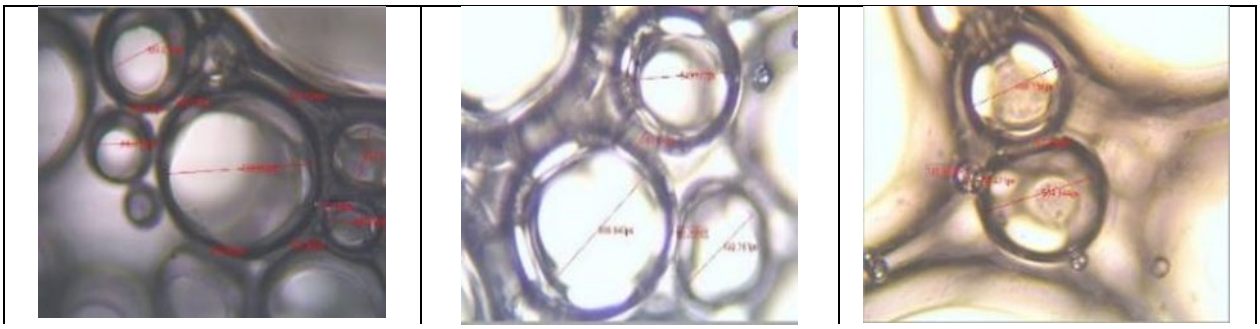


Figure 5. Graph of bubble size against time.

Figure 6 shows the shape of optimized surfactant (foam with bubble size) viewed under a microscope with the aid of a computer at different time. The longer the time, the shapes of bubble size changes from spherical to ellipsoidal and finally the foam breaks. The best foam shape employed in the industry for EOR is the spherical shape because it is stable.



O minute 5 minutes 10 minutes

Figure 6. Images of bubble size distribution at different time

4. Conclusion

In conclusion, this study successfully created a bio-surfactant from coconut extract for EOR. The surfactant proved to be a viable alternative to synthetic surfactant for foam-based EOR. Response Surface Methodology (RSM) optimized the foam stability with a low error rate of 7.8%. Microstructural analysis presents smaller bubbles. Future research is recommended to further evaluate the surfactant's performance under reservoir conditions for broader understanding.

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Nomenclature

EOR	*Enhanced oil recovery*
RSM	*Response surface methodology*
CCD	*Central composite design*
FAWAG	*Foam assisted water alternative gas*
ANOVA	*Analysis of variance*
GOR	*Gas oil ratio*
DOE	*Design of experiment*

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