Volume 2022, 9 pages
Article ID: ASTE-2211032112821
Applied Science and Technology Express
https://www.htpub.org/Applied-Science-And-Technology-Express/

Fenugreek surfactant: Extraction, Synthesis and Evaluation of Foam Properties for Application in Enhanced Oil Recovery

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Article

Article history:
Received
Received in revised form
Accepted

Keywords:
Oil industries, Plant, Foam stability, EOR

Abstract

With the decline in oil discoveries during the last few decades, enhanced oil recovery (EOR) technologies play significant roles to meet the growing energy demand. Foam flooding, commonly known as foam assisted water alternating gas (FAWAG), has been recognized among the effective techniques in EOR. In this study, seeds of *Fenugreek* plant were used to extract oil through solvent extraction technique. Subsequently, the oil was used to chemically synthesize a surfactant and characterized using FTIR spectroscopy. Dynamic foam stability ($t_{1/2}$) was investigated using Ross miles method to establish synergy actions between the surfactant and brine using a response surface methodology tool. Furthermore, a $t_{1/2}$ numerical model was developed after establishing the optimized stability condition. At this condition, foam morphology was characterized by microscopic analysis to observe changes in bubble size and distribution in decay profile. The results revealed that by utilizing 25 g of the seed materials, about 7 % of the oil yield was obtained which has resulted to the synthesis of about 13.86 g of surfactant. The surfactant was confirmed by the FTIR analysis due to the appearance of many important characteristic functional groups. The surfactant foam demonstrates appreciable stability (maximum; 152.66 s and optimized; 52.3 s) in relation to its good morphology (bubble size and distribution) observed. The study further established that the $t_{1/2}$ is due to synergy between the surfactant and brine in the model. The findings of the paper have provided sufficient preliminary investigations and recommend suitable applications of plant derived surfactants in EOR foam technology.

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1. Introduction

Crude oil demand is endless because of the unprecedented domestic and industrial needs [1, 2]. Essentially, is one of the most important fuel sources and has significantly contributed to the world's energy consumption [3]. The goal of many oil companies in today's world is to maintain a profitable economic oil rate and maximize oil recovery factor. Maximizing the recovery factor in a cost-efficient way is becoming more important, as oil experts now believe that new recoverable oil fields will begin to decline sharply [1]. Several oil extraction methods have been in practice such as the primary and secondary methods [4], however, today, enhanced oil recovery (EOR) is the most advanced method and has been receiving unprecedented attention in oil industries [5, 6]. The EOR is also called a tertiary recovery method which can extract 30-60 % more of reservoir's oil compared to 20- 40 % using the primary and secondary recovery. This method was developed to further increase oil production after exhausting primary and secondary methods [7-9]. It involves injection of any foreign fluid intended to further extract the residual oil [10-13]. Water and gas can be injected alternatively as Water Alternating Gas (WAG), or sometimes depending on the conditions causing gas escaping, surfactant in this case can replace water so that the gas could be enclosed as a foam bubble. This is mainly to address the issue of high gas mobility and minimize production of gas cap in order to improve sweep efficiency; this technology is known as Foam Assisted Water Alternating Gas (FAWAG) injection [14, 15]. The FAWAG method is the only method that employs the use of foam to trap gas and reduce its mobility. Foam can also be used in EOR method to minimize the gravity overriding, viscous fingering and channeling problem. FAWAG also provides good mobility control of gas flow by delaying early gas breakthroughs and has emerged as a new method for well flow improvement [16].

However, foam behavior and its stability remained one of the prevailing challenges in oil fields, as a result, understanding foam behavior and stability is important [12] [17]. Surfactants from natural sources exhibited efficient and successful applications in various industries due to their low toxicity, high biodegradability, multi-functionality, environmental capability and resource availability [18]. Thus, this study seeks to investigate the foam stability properties derived from *Fenugreek* seeds for application in EOR method.

2. Materials and methods

2.1. Collection, preparation, and analysis of plant materials

Matured *Fenugreek* seeds were obtained from kurmi market, Kano State, Nigeria and were taken to Plant Science Department, Bayero University Kano for identification. The seeds were air dried in the laboratory for 3 days and were then mechanically crushed to smaller particulates to obtain larger surface areas, weighed, and kept airtight in a container for further analysis. The moisture analysis was obtained using Eq. 1 [19].

$$Moisture\ content\ (\%) = \frac{initial\ seeds\ mass - dried\ seeds\ mass}{dried\ seeds\ mass}\ x\ 100 \quad (1)$$

The acid value was determined by weighing exactly 5 g of seeds sample and placed in a 250 ml flask. Thereafter, equal mixture of ethanol and ether were combined to make up 50 ml and neutralized by KOH (0.5 N). The resulting mixture was heated for 10 minutes for complete sample dissolution, upon cooling, 1 ml of phenolphthalein indicator was added and shaked vigorously. The resulting mixture was titrated with KOH (0.5 N) until a pink color was observed and persisted for about 15 seconds. The entire procedure was repeated without the sample to serve as a control (blank). Subsequently, Eq. 2 was used to calculate the acid value [19].

$$Acid\ value = \frac{TD\ x\ N\ x\ 56.1}{m} \quad (2)$$

Where, TD; titre difference (B-S), m; sample mass (g), B; blank titre value, S; sample titre value and N is the normality of titrating solution (KOH used herein).

For saponification value, exactly, 2 g of sample was placed in a 250 ml flask and about 25 ml equal mixture of ethanol and KOH was added. The mixture was then heated in a water bath for 30 minutes with continuous stirring. Upon cooling, 1 ml of phenolphthalein indicator was added, and the resulting mixture was titrated with 0.5 N HCl. The entire procedure was repeated without the sample (blank). The saponification value was calculated using the same Eq. 2 [19].

2.2. Extraction Procedure

Exactly, 25 g of *fenugreek* seeds was weighed and placed in the Soxhlet extractor's thimble, 200 ml of n-hexane was transferred into a 500 ml capacity round bottom flask of the Soxhlet extractor. The apparatus was operated at 60^{o} C and the condenser unit was connected to water source to condense the solvent vapor. The extraction process was repeated severally for about 9 refluxes in 3 hours after which the extraction process was completed. Subsequently, the oil extract was separated from the solvent and the yield was calculated using Eq. 3. The procedure was adopted from [19] with modification.

$$Percent\ yield\ (\%) = \frac{mass\ of\ extrated\ oil}{mass\ of\ seeds\ materials}\ x\ 100 \quad (3)$$

2.3. Synthesis of surfactant

Exactly 10 ml of oil was heated at 80-90^{o} C for 15 minutes to simmer the oil. Thereafter, 5 g NaOH was added, and the resulting mixture was continuously heated at 80^{o} C for about 3 hours until a dark solid product was obtained. To ensure completion of the reaction, a small amount of the solid product was dissolved in distilled water until a clear and homogeneous solution was obtained. Furthermore, the material was analyzed using FTIR spectroscopy.

2.4. Foam stability Studies

Design Expert Software (DOE, V7) was used to develop surfactant/brine systems at various concentration ratios. The surfactant and brine concentrations were kept from 0.1-0.5 % and 1.0-3.0 %, respectively. The central composite design (CCD) was applied which enabled the formation of 13 experimental formulations shown in Table 1 with 5 centre points at 0.3/2.0 % (surfactant/brine) to serve as central replicates according to the CCD.

Thereafter, Ross-Miles method was employed to generate foams in order to assess the foam stabilities of the formulations developed. For each of the formulations, exactly 4 ml was introduced into the standardized burette which later was allowed to pass and dropped into the receiver vessel (measuring cylinder). As a result, turbulence was created which enabled foam generation. The maximum foams heights were measured immediately, and foams half-lives ($t_{1/2}$) were observed with respect to foams decay rates. It is important to note that the burette and the measuring cylinder were kept at a constant distance throughout the experiments, and the foam height measurements were taken above the water drainage. All the experiments were performed in replicates and the average foam heights and stabilities were recorded.

Table 1. Design of experimental formulation for foam generation and stability.

Experiment	Surfactant (%)	Brine (NaCl) (%)
1	0.30	2.00
2	0.30	3.00
3	0.30	1.00
4	0.50	1.00
5	0.30	2.00

6	0.10	1.00
7	0.10	3.00
8	0.30	2.00
9	0.30	2.00
10	0.50	2.00
11	0.30	2.00
12	0.10	2.00
13	0.50	3.00

Subsequently, all the stabilities data obtained were subjected to analysis of variance (ANOVA) and the maximum criteria for foam stability was set as a goal to obtain an optimum condition. The response surface methodology tool was used to establish the relationship between the effect of surfactant and brine concentrations on foam stabilities. The highest order polynomial with the significant terms was considered by taking cognizance of the model that is not aliased.

Thereafter, the optimized condition recommended by the software analysis with respect to concentrations of surfactant/brine system was further experimented to compare with the modeling.

2.5. Foam morphology

The optimized foam generated was used to study the foam morphology i.e., bubble size, lamella division, and relative bubble distribution. The foam microstructures were observed using a high-resolution microscopy. The changes in bubbles size, lamella division and distribution were monitored at different time (0, 5 and 10 min.) to observe the bubble coalescence, and the mean values were recorded.

3. Results and discussion

3.1 Physico-chemical Analysis

The results obtained from the various physico-chemical analyses on the extracted *fenugreek* seed oil and synthesized surfactant have been presented in Table 2. *Fenugreek* seeds can be seen to possess 7 % oil yield which is higher considering only 25 g of the sample was used, this also corresponds with the low moisture content (11.3 %) obtained. This indicates that *Fenugreek* seeds could be suitable resources for oil extraction. However, the high saponification value of 189.14 mg/g is also an indicator that the *fenugreek* seeds oil extract contains sufficient acid functional groups which could serve as a precursor suitable for surfactant synthesis.

Table 2. Physico chemical analyses.

Parameters	Results
Seed materials	
Acid value (mg/g)	2.34
Saponification value (mg/g)	189.14
Moisture (%)	11.3
Oil	
Physical state	Yellowish liquid
Yield (%)	7.0
Surfactant	
Physical state	Black solid
Mass (g)	13.9
Active conc. (g/100mL)	0.139

From the FTIR spectra presented in Fig. 1, the synthesis of surfactant has been established due to the appearance of the characteristic peaks corresponding to the broad absorption band at 3365cm^{-1} as assigned to O-H stretching vibration due to absorbed water molecule. The strong absorption peaks at 2851.61-3007.86 cm^{-1} are assigned to both symmetric and asymmetric stretching of methyl (-CH_3) and methylene (-CH_2) groups which can be attributed to the existence of fatty acids and their methyl esters within the carboxyl groups (COOH). Based on the FTIR spectra result obtained, different functional groups existed in surfactant of *fenugreek* seed oil such as carboxyl, fats, amides and esters. The physical states of the surfactant have been presented in Table 2.

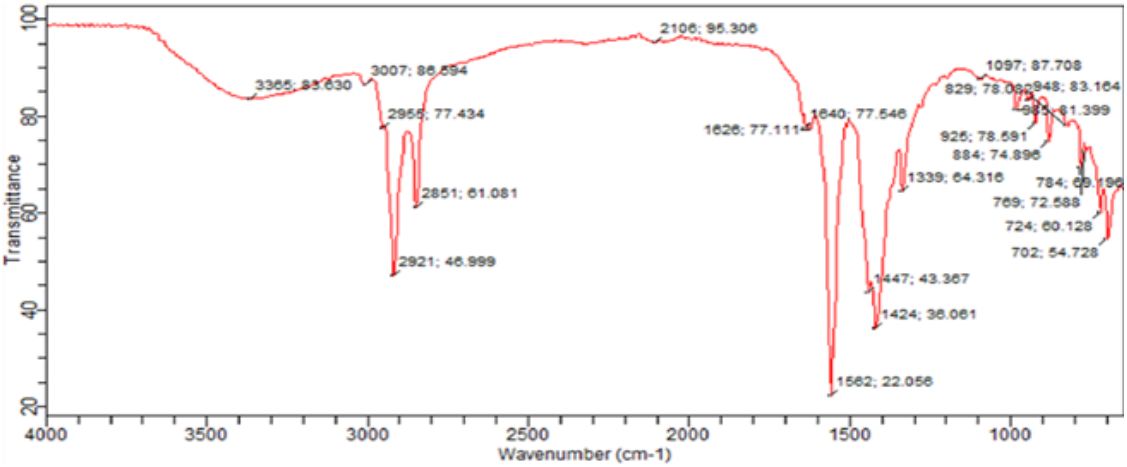

Figure 1. Result of FTIR analysis of synthesized bio surfactant

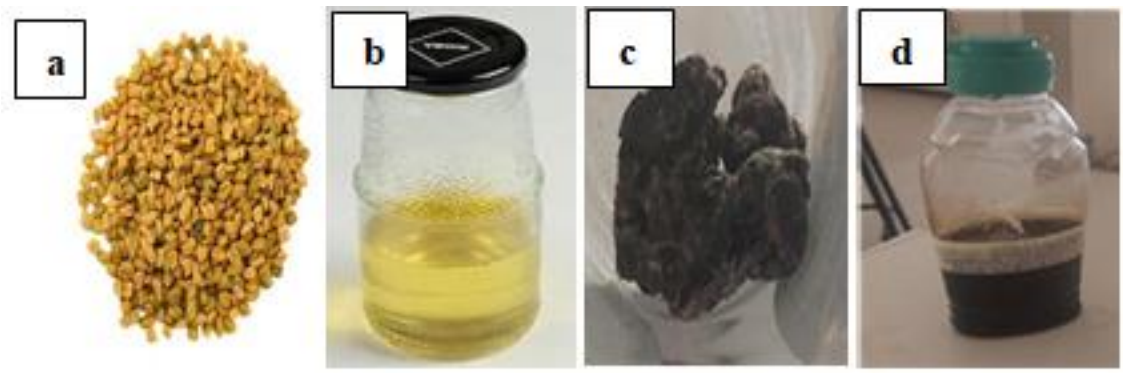

Figure 2. (a) *Fenugreek* seeds (b) Extracted oil (c) Synthesized surfactant (d) surfactant con. (%)

3.2 Foam stability

The foam stability ANOVA results data have been presented in Table 3. From the table, the prob. > F was found to be less than 0.0500, indicating that the model is significant. Similarly, the F value of 5.53 is adequately describing that the model chosen (cubic model) has well fitted. Furthermore, the R square value is used to assess data fitness if the model R is near 1.00 [20, 21]. Consequently, the R square of 0.85 in this study has revealed that the model is appreciable and further confirmed that the difference (0.08) between the predicted (0.77) and the adjusted (0.69) R square values are within the acceptable range of < 0.2 [20-22].

Table 3. ANOVA response for foam stability.

Model	F value	R square	P- value Prob.> F	
Cubic	5.53	0.85	0.0282	significant

Accordingly, the plot illustrated in figure 3 shows the correlation between the predicted and experimental data at which the correlations best fitted within the normal probability which further confirms the fitness of the model.

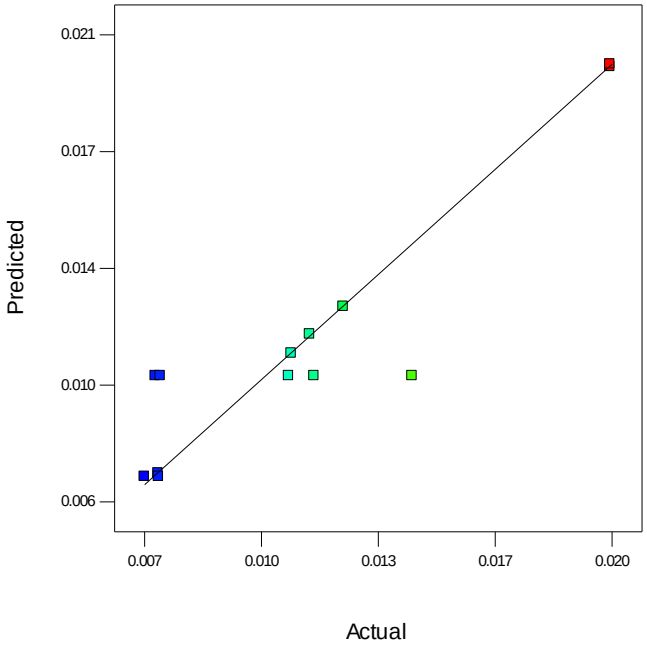

Figure 3. Correlation plot of the predicted versus actual foam stability

Consequently, equation 4 shows the final model equation that describes the quantitative contributions of the input materials (brine and surfactant) with respect to foam stability.

$$\textbf{\textit{Foam stability}} = 99.5575+230.5483*[Brine]-346.2700*[Surfactant*Brine]-309.1155*[Surfactant^2] + 176.3113*[Brine^2]-296.4450*[Surfactant^2*Brine]-274.7441*[Surfactant*Brine^2] \quad (4)$$

Furthermore, Fig. 4 shows the 3-D plot of foam stability, it can be seen that as the concentration of brine increases, the relative foam stability of the surfactant-brine hybrid increased until it reached a maximum stability. However, surfactant alone has little influence on foam stability except when in synergy with the brine.

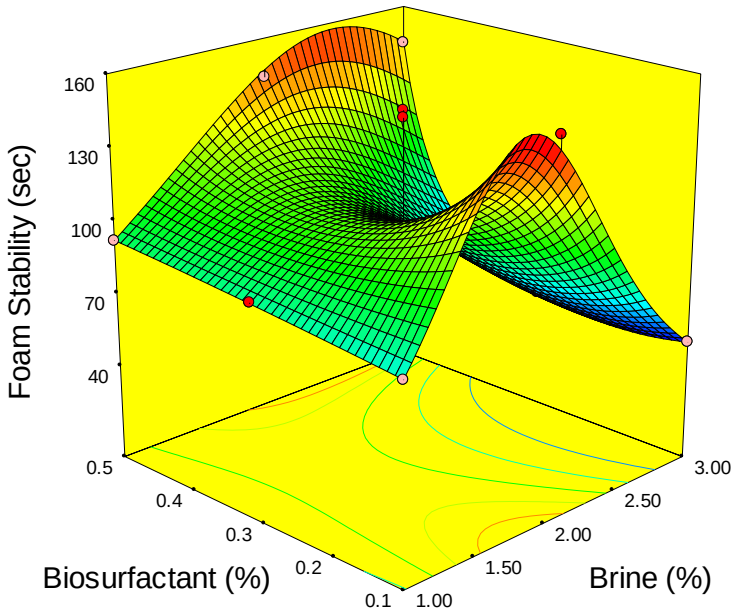

Figure 4. Three-Dimensional plot of foam stability showing the synergic interaction of brine with surfactant

The optimum condition had been achieved after the establishment of the foam stability behavior. The maximum value of foam stability was set as a criteria goal. Out of 20 optimum conditions generated, Table 4 shows the recommended optimum condition based on desirability which describes the extent to which goal criteria chosen to achieve optimal conditions is 1.0. Subsequently, the accuracy of the model developed was evaluated by observing good agreement between the model predicated and experiment values with error reported as 0.07.

Table 4. Optimized conditions of surfactant-brine formulation.

Input variables		**Desirability**	**Model predicted**	**Experimental**	**Error**
Surfactant (%)	Brine (%)		Foam $t_{1/2}$ (s)	Foam $t_{1/2}$ (s)	
0.22	2.94	1.00	48.70	52.30	0.07

3.3 Foam morphology

The plot of bubble size with decay time has been provided in Fig. 5 and the foam microstructures showed in Fig. 6. As the foam decay time increases, the average bubble size increases which describes the foam rupture behavior. Smaller bubble sizes were observed to be dominant at initial time and were more stable than the bigger bubble. However, as time increases, small bubble size coalesced due to the water volume fraction overcome the lamella strength leading to its thinning, breakage, and joining to become bigger bubbles. Similarly, the bubble distribution can also be seen in the micrographs.

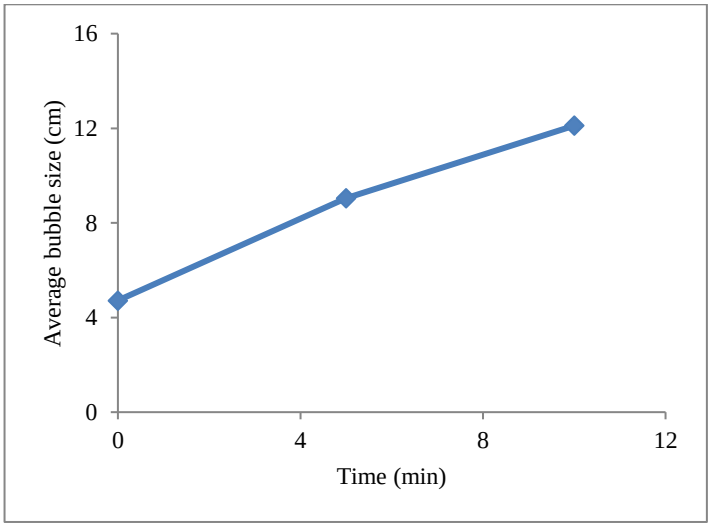

Figure 5. The plot of bubble size distribution

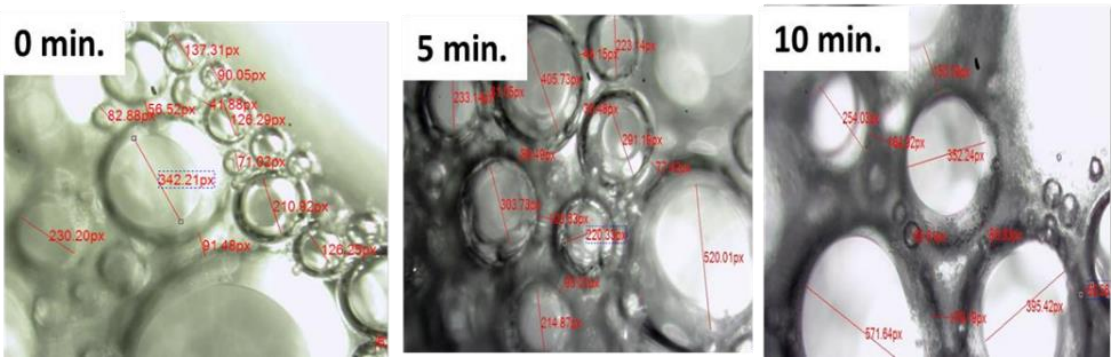

Figure 6. Shows the bubble size distribution at various times (0 min, 5 min and 10 min)

4. Conclusions

This study validates the possibility of using plant derived organic surfactant to generate EOR foams which could have potential application in oil industries. Further investigations should be carried out to evaluate foam stability using foam scan equipment and mobility reduction factor (MRF) using Coreflood equipment at reservoir conditions.

Acknowledgements

The authors of this paper acknowledged the Department of Pure & Industrial Chemistry for providing with the reagents & glassware used, Faculty of Science Multipurpose lab for providing facility to carry out the synthesis, and lastly the Centre for Biotechnology, Bayero University Kano for providing the Microscopy for bubble analysis.

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