

Experimental Investigation of the Impact of Biosurfactants on Residual-Oil Recovery

S. V. Ukwungwu, A. J. Abbas, G. G. Nasr

Abstract—The increasing high price of natural gas and oil with attendant increase in energy demand on world markets in recent years has stimulated interest in recovering residual oil saturation across the globe. In order to meet the energy security, efforts have been made in developing new technologies of enhancing the recovery of oil and gas, utilizing techniques like CO₂ flooding, water injection, hydraulic fracturing, surfactant flooding etc. Surfactant flooding however optimizes production but poses risk to the environment due to their toxic nature. Amongst proven records that have utilized other type of bacterial in producing biosurfactants for enhancing oil recovery, this research uses a technique to combine biosurfactants that will achieve a scale of EOR through lowering interfacial tension/contact angle. In this study, three biosurfactants were produced from three *Bacillus* species from freeze dried cultures using sucrose 3 % (w/v) as their carbon source. Two of these produced biosurfactants were screened with the TEMCO Pendant Drop Image Analysis for reduction in IFT and contact angle. Interfacial tension was greatly reduced from 56.95 mN.m⁻¹ to 1.41 mN.m⁻¹ when biosurfactants in cell-free culture (*Bacillus licheniformis*) were used compared to 4.83 mN.m⁻¹ cell-free culture of *Bacillus subtilis*. As a result, cell-free culture of (*Bacillus licheniformis*) changes the wettability of the biosurfactant treatment for contact angle measurement to more water-wet as the angle decreased from 130.75° to 65.17°. The influence of microbial treatment on crushed rock samples was also observed by qualitative wettability experiments. Treated samples with biosurfactants remained in the aqueous phase, indicating a water-wet system. These results could prove that biosurfactants can effectively change the chemistry of the wetting conditions against diverse surfaces, providing a desirable condition for efficient oil transport in this way serving as a mechanism for EOR. The environmental friendly effect of biosurfactants applications for industrial purposes play important advantages over chemically synthesized surfactants, with various possible structures, low toxicity, eco-friendly and biodegradability.

Keywords—Bacillus, biosurfactant, enhanced oil recovery, residual oil, wettability.

I. INTRODUCTION

EXPLOITATION of oil resources in mature reservoirs is Essential for meeting future energy demands. The implementation of the three primary EOR techniques for recovering the crude oil that is left behind in oil wells includes; gas injection, thermal flooding and chemical injection which consists of polymer flooding, CO₂ injection

and microbial injection. Microbial Enhanced Oil Recovery (MEOR) is an important tertiary oil recovery method which is cost-effective and eco-friendly technology to drive the residual oil trapped in the reservoirs [1]-[3]. The potential of microorganisms to degrade heavy crude oil to reduce viscosity is considered to be very effective in MEOR. Since thermophilic spore-forming bacteria can thrive in very extreme conditions in oil reservoirs, they are the most suitable organisms for this purpose [4], [5]. Surfactants of microbial origin in recent time have become of great interest because of their advantages over their chemical counterparts which include low toxicity, biodegradability, effectiveness in adverse environmental conditions, ability to produce from renewable resources and environmental compatibility [3]. These benefits of metabolic products can be explored in solving many problems often encountered during oil production in respect to improving the recovery of crude oil from reservoir rocks [6]. It is therefore very necessary to protect the environment by utilizing microbial flooding technique for EOR processes and the products of microbial fermentation of carbohydrates.

The fundamental cause for leaving oil behind is economics. In general, the process of recovering oil from any conventional reservoir requires (a) a pathway which connects oil in the pore space of a reservoir to the surface and (b) sufficient energy in the reservoir to drive the oil to the surface. Lack of these requirements in the environment results in oil getting left behind [7]. The chemicals used for EOR must be compatible with the physical and chemical environments of oil reservoirs. The varying permeability of petroleum reservoirs is also a major concern in EOR processes. When water is injected to displace the oil, it preferentially flows through areas of highest permeability and bypasses much of the oil [8].

In *in situ* MEOR method, bacteria inoculated with water in to the well will progress into high permeability zones at first. Then at a later stage will grow and occlude those zones due to their size and the negative charge on their cell surface. This eventually helps to increase the sweep efficiency, and thus a more efficient oil transport can be achieved [7], [9]. Oil advancement through porous media is expedited by modifying the interfacial properties of the oil-water minerals. In such a system, microbial activity alters fluidity (viscosity reduction, miscible flooding); displacement efficiency (decrease of interfacial tension, increase of permeability); sweep efficiency (mobility control, selective plugging); and driving force (reservoir pressure). The second principle is known as upgrading. In this case, the degradation of heavy oils into lighter ones occurs by microbial activity. Instead, it can also aid in the removal of sulphur from heavy oils as well as the

Sunday. V. Ukwungwu, graduate student, is with the department of Petroleum and Gas Engineering, The University of Salford, Manchester (phone: +44 (0) 791 855 4877, e-mail: s.v.ukwungwu@edu.salford.ac.uk).

Abubakar. J. Abbas is a Lecturer in Petroleum and Gas Engineering Lecturer with The University of Salford, Manchester (phone: +44 (0) 161 295 3170, email: a.j.abbas@salford.ac.uk).

Ghasem G. Nasr is the Director of Spray and Petroleum Research groups with The University of Salford Manchester (phone: +44 (0) 161 295 5213, fax: +44 (0) 161 295 5575, e-mail: G.G.Nasr@salford.ac.uk).

removal of heavy metals [10]-[12]. Microorganisms can synthesize useful products by fermenting low-cost substrates or raw materials. Therefore, MEOR can substitute chemical enhanced oil recovery (CEOR), which is a very pricey technology [6], [13]. In MEOR, the chosen microbial strains are used to synthesize compounds analogous to those used in CEOR processes which are very expensive [6], to increase the recovery of oil from depleted and marginal reservoirs.

II. MATERIALS AND METHODS

As all oil reservoirs are essentially devoid of oxygen, anaerobic bacteria are generally preferred in field applications. *Bacillus* are aerobic or facultative anaerobic and can grow on nutrient agar. The reference strains were used as negative and positive controls for PCR amplifications and gram stain which includes; *B. subtilis* (DSM 3256), *B. licheniformis* (DSM 1913), *Paenibacillus polymyxa* (DSM 740). Sufactants were cultured using specified media that matches with formation water of the proposed reservoir.

Minimal salt medium: Sucrose (30 g L⁻¹), KNO₃ (5 g L⁻¹), KH₂PO₄·2H₂O (1 g L⁻¹), K₂HPO₄·2H₂O (1 g L⁻¹), NaCl (3 g L⁻¹), MgSO₄·7H₂O (0.2 g L⁻¹), CaCl₂·2H₂O (0.2 g L⁻¹), was stirred in a glass bottle of distilled water for 30 minutes and pH was adjusted to 7.0. The medium was filter sterilized using a 0.22µm filters and delivered into ninety six (96) viles (broths) to a volume of 13 mL each, using an electronic stripette. The nutrient agar; beef extract (3 g L⁻¹), peptone (5 g L⁻¹), with or without agar (15 g L⁻¹) was prepared in a 1 litre bottle and stirred for 30 minutes. Autoclaved at 125 °C and 1.6 bar for 45 minutes and after cooling poured into 20 petri dishes and allowed to set before storing upside down to prevent condensation.

The isolation of pure cultures was retrieved in the fume cupboard to prevent any external contamination. Freeze dried strains were carefully removed from glass tubes and 1000µL of prepared media was added to each to dissolve the strains. The strains were plated and inoculated separately and further incubated at temperatures of 30 °C and 37 °C for 48 hours, and then analysed for growth, biosurfactant production and interfacial tension/contact angle experiment. An extensive laboratory study was conducted for the measurement of the interfacial tension between crude oil and biosurfactant and formation water covering the ranges of (0.05 to 12.41) MPa pressure, (26 to 75) °C temperature. The laboratory experiments were conducted using the TEMCO pendant drop method combined with the solution of the Laplace equation for capillarity for the profile of the oil drop in the oil-brine equilibrium environment. For the droplet phase, n-dodecane was selected from the list and for the external phase, in this case formation water, brine (5%) was selected and lastly the solid phase which is steel (the needle) was selected. Measurements were made for each set of temperature and water salinity for pressures of (0.05, 3, 5.7, 10.34 and 12.41) MPa for a total of 110 IFT (mN/m) measurements.

III. RESULT AND DISCUSSION

The control experiment for crude oil/distilled water system was conducted to show the expected decreasing trend of interfacial tension (from 56.95mN/m at 26 °C to 14.13mN/m at 60 °C) for raw crude oil/distilled water system as shown in Fig. 1. A similar trend was also reported by [14] for 0.005M SA in n-decane/water system. IFT measurements are shown to be lower at higher pressure of 12.41MPa, with values of 17.51 mN/m, 15.23 mN/m, 14.13 mN/m. In this study, interfacial activity was reported for oil/distilled water at 42 °C and 0.05 MPa to be 45.25 mN/m can be compared with the value of 46.8 mN/m reported by [15], with n-octane/distilled water at 40 °C and 1.38 MPa. The effect of temperature on the pure grade hydrocarbon he used, gave in most cases a linear decreasing trend in IFT with increasing temperature over the investigated range.

TABLE I
EXPERIMENTAL IFT DATA FOR DISTILLED WATER AND OIL SAMPLE AT
VARYING TEMPERATURE AND PRESSURE

T/°C	P/MPa				
	0.05	3.00	5.70	10.34	12.41
26	56.95	37.57	28.89	19.32	17.51
42	45.25	32.37	23.43	17.68	15.23
60	43.74	29.47	19.36	15.98	14.13

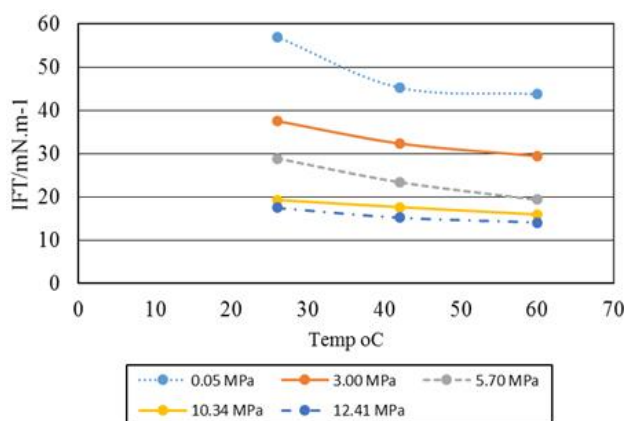


Fig. 1 Variation of IFT with Temperature and Pressure for crude oil/distilled water system

The experimental results of the variation of IFT with pressure and temperature for *Bacillus licheniformis* cells mixed with formation water/crude oil system, shows that IFT steeply decreases with increasing pressure with an asymptotic trend towards a constant value at higher temperatures as illustrated in Fig. 2.

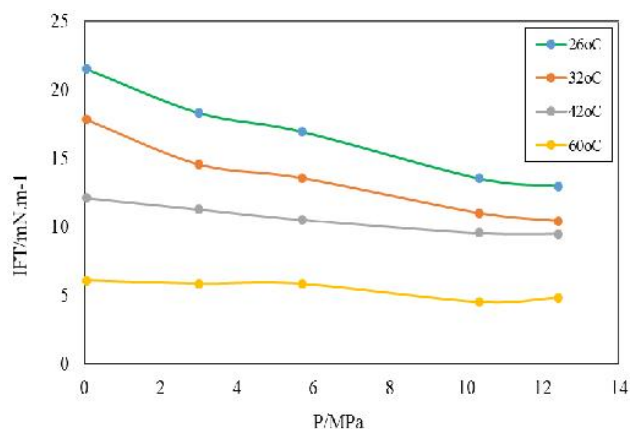


Fig. 2 Variation of IFT data with Pressure and Temperature for *B. licheniformis* cells

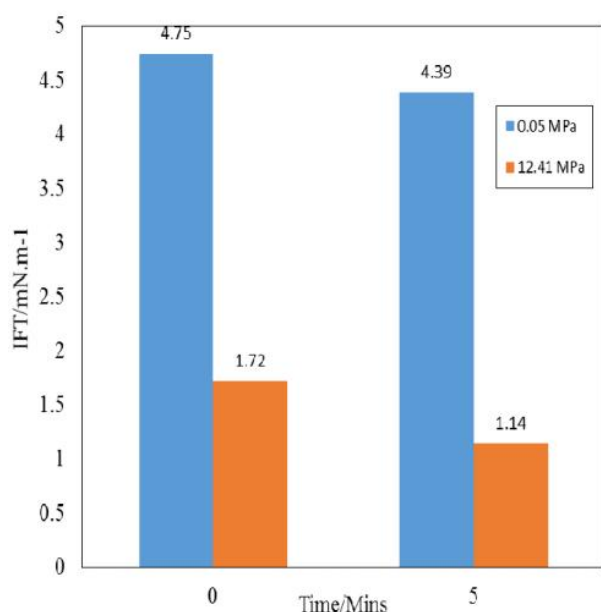


Fig. 3 Variation of IFT with Time and Pressure for *Bacillus licheniformis* (cell-free) at 42 °C

Cell-free biosurfactant of *Bacillus licheniformis* gave the greatest reduction values of IFT as shown in Fig. 3. Measurements were taken after a five minutes' time duration to observe the effect of the biosurfactant concentration. It was assumed that equilibrium between the liquids was reached after five minutes of forming the oil film. This is in conformity with reports of [16] where oil drops were equilibrated for five minutes in order to get reliable results. At 42 °C IFT value of 1.14mN/m was lowest at a constant pressure of 12.41 MPa as compared to 60 °C where the IFT value rose to 3.06 mN/m at the same pressure as seen in Fig. 4. This is an evidence to demonstrate the importance of screening biosurfactants to isolate the most profitable and versatile amphilic surface compounds to be used for EOR applications, since environmentally friendly biosurfactants of

the same family have different surface active strength behaviours.

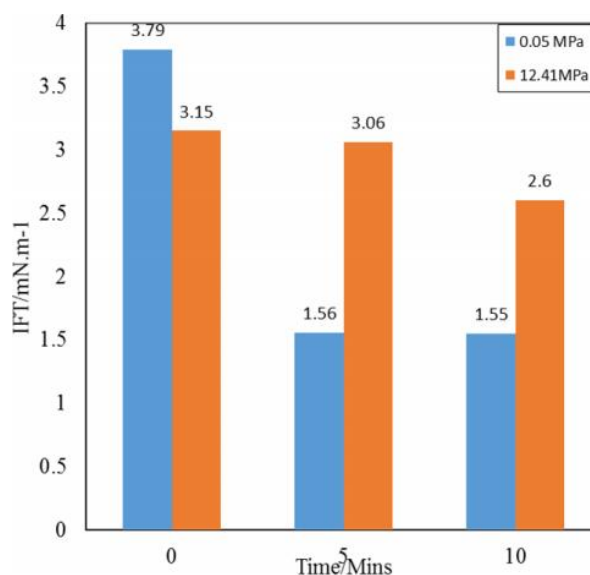


Fig. 4 Variation of IFT with Time and Pressure for *Bacillus licheniformis* (cell-free) at 60 °C

The effect of varying IFT with time and temperature was clearly observed for *B. subtilis* (cell-free) at a constant pressure of 0.05 MPa. Fig. 5 indicates that the biosurfactant concentration approached its critical point, thus lowering the free energy of the system. The CMC can be clearly seen as the IFT decreases to 10.31 mN/m and 5.58 mN/m after five minutes at 42 °C and 60 °C respectively, and continued decreasing with a lower slope to 4.83 mN/m after twenty-five minutes at a temperature of 60 °C. The effect of increasing time of IFT reduction between oil/biosurfactant with formation water followed the trend investigated by [17], following the isolation of biosurfactant strains for the purpose of anti-fungal of fusarium head blight virus with wheat.

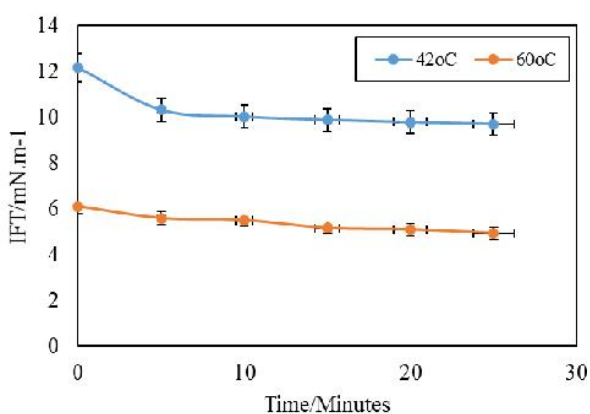


Fig. 5 Variation of IFT data with Time and Temperature for *B. subtilis* (cell-free) at 0.05 M/Pa

Fig. 6 (A) shows the effect of pressure on IFT with time. It was found that interfacial tension values decrease more at lower pressures and the aging effect was observed more at a lesser time before reaching the CMC at 0.05 MPa (10.31 mN/m), 3 MPa (9.03 mN/m) and 5.70 MPa (8.85 mN/m). An uncommon phenomenon was observed in Fig. 6 (B), where an undulating IFT effect was seen to occur at pressures of 10.34 MPa and 12.41 MPa. The sudden increasing and decreasing of IFT with time may be the result of mutual solubility changes of the system with pressure. However, no literature was found to support this unusual effect.

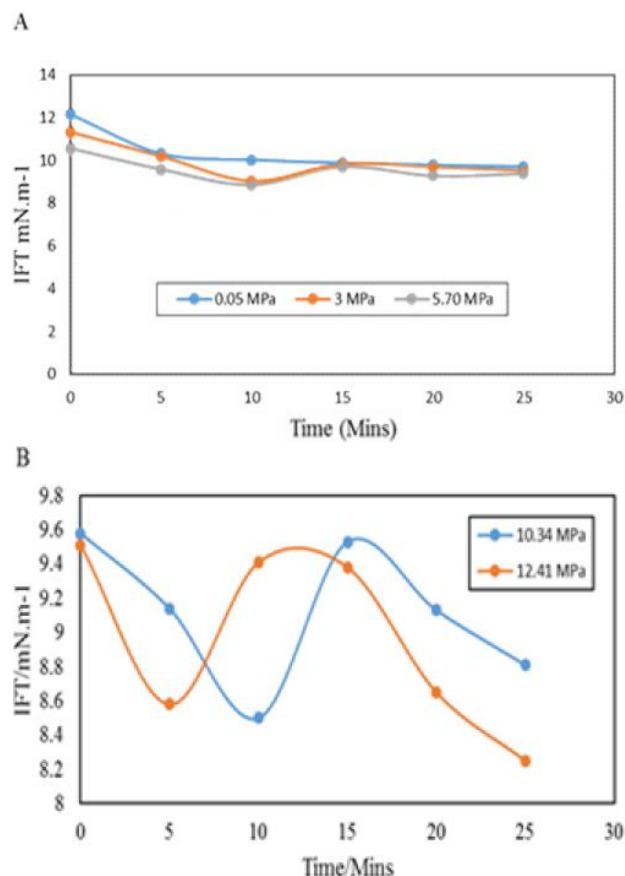


Fig. 6 (A), (B) Variation of IFT with Time and Pressure for *Bacillus subtilis* with cells at 42 °C

IV. CONCLUSION

The effect of the critical micelle concentration that was observed in this study may have resulted due to increasing temperatures (between 42 and 60 °C). Since the growth of the biosurfactants produced in this study were observed to survive at 37 °C for a 2-week period before the death phase began, it can be assumed that in this study when the CMC was reached in a less time of twenty-five minutes, the activity of the biosurfactants declined and possibly the microbes began to die as a result of high temperature. And not necessarily that the nutrients were totally consumed, sporulation is thought to have begun at this point. Further studies are required in combining

the three produced biosurfactants to observe the effect on IFT/contact angle reduction on crude oil sample and to measure steady state relative permeability by core flooding to determine the amount of oil recovery. Lipopeptide biosurfactant from *Bacillus* species were selected for use in this study to reduce the costs of biosurfactant production in high yields and to optimize large scale fermentation and recovery system conditions.

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