Effect of Microbial Lipase Enzymes on Wettability, Interfacial Tension and Adhesion of Crude oil/brine/solid Interactions

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Abstract *LPE1 and LPE2 are lipase enzymes produced from crude oil contaminated soil isolates: Verticillium sp. and Penicillum sp. respectively. The enzymes were produced in broth medium using standard microbiological technique. The influence of the produced enzymes on wettability, interfacial tension and adhesion behavior of crude oil/brine/solid system were investigated. These properties were evaluated using standard methods. The experimental result reveal that the produced lipases changed the wettability nature of oil/brine/solid system to a water wet by the contact angle measurement. The microbial lipases also changed the adhesion behavior of the oil on glass slide from adhesive behavior to non-adhesion. In the case of interfacial tension, no significant change was observed when the lipase enzymes were introduced into the system. These findings suggest the possible application of the microbial lipases for enhanced oil recovery.*

Keywords: *LPE; lipase enzymes; wettability; interfacial tension, adhesion, oil/brine/solid system.*

Abbreviations

HCl	Hydrogen Chloride
IFT	Interfacial tension
LPE	Lipase enzyme
NaOH	Sodium Hydroxide
θ_{Ref}	Contact angle measured with a brine phase without adding enzymes
θ_{Enzyme}	Contact angle measured with a brine phase with different concentrations of enzymes
$\Delta\theta$	Change in contact angle between θ_{Ref} and θ_{Enzyme}
γ_{os}	Oil-solid interfacial tension
γ_{ow}	Oil-water interfacial tension
γ_{ws}	Water-solid interfacial tension

I. INTRODUCTION

In the oil and gas industry, the use of enzymes has been recently suggested for several applications [1]. A robust of enzymes has been provided for tolerating oil reservoir condition by the modern biotechnology industry. Some applications of enzymes in the oil and gas company have been reported [1]. Such application includes; biodegradation of petroleum derived effluents, breaking of gel in drilling operation to avoid filter cake formation, removal of Sulphur in hydrocarbon, production of “enzyme-based acid” which is used for the purpose of treating formation damage and matrix-acidizing of carbonate, pre-treatment of biopolymers using enzyme to improve the handling characteristics of biopolymer.

As we know, the reservoir rock wettability is one of the most controlling properties for oil recovery. Therefore, the need for studying the wettability of the reservoir rock is necessary. To measure the reservoir rock wettability is not an easy task because of the oil/water/rock interaction. Anderson, 1986 provided a review of various methods of measuring tools for wettability. The various measuring tools for wettability measures the alteration of wettability from different perspectives. The following wettability measuring tools includes; contact angle, spontaneous imbibition, surface imaging tests and zeta potential measurement.

The contact angle method for measuring wettability is the widely used method for measuring the wettability of a liquid/solid system. Wettability is an oil/water/rock interaction which can be explained by contact angle of a drop of liquid for example water on a solid surface [3].

Young’s Equation is used to explain the relationship that exist between the contact angle and the surface energies. The Young’s equation is expressed as:

$$\gamma_{ow}\cos\theta = \gamma_{os} - \gamma_{ws} \qquad 2.1$$

Where γ_{ow}, $\gamma_{os,}$ and γ_{ws} represent the oil-water, oil-solid, and water-solid interfacial tensions respectively and θ is the contact angle.

Measurement of contact angle passes through a denser medium (fluid), so for a water/oil/rock system, the angle of contact is measured through the water.

The angle of contacts is measured in degrees and if contact angle (θ) 0^o and less than 90^o it is referred to water-wet, but if θ is between 90^o and 180^o, it is classified as oil-wet, and 90^o contact angle is classified as the neutral-wet [2].

Crude oil/water/solid system interactions depend on several properties such as oil and water composition and chemical and physical properties of the solid body. The brine composition of the interaction severely affects the charge at the interface [4]. The chemical properties of the oil which is useful in the interaction at the interface plays a crucial role in crude oil/water/solid system [5].

Adhesion test was introduced in 1989 by Buckley [6]. The essence was to characterize the interaction between a crude oil/brine of varying composition. During the test for adhesion behavior, it produces an indication of water film stability in crude oil/brine/solid interaction. From Buckley's [6] computation, it was observed that adhesion test can behave in three different ways, which includes adhesion behavior, non-adhesion behavior and temporary adhesion behavior.

In the crude oil-water interface reaction, the number of active interfacial sites cannot be directly measured [4], but can be measured by interfacial properties changes in interfacial tension (IFT) and electrophoretic mobility [7]. IFT decrease in the case of acidic oil and increases with increasing pH in the case of basic oil. When the pH of the brine phase is very low or very high, the basic and acidic functional groups of the crude components will react leading to in-situ generation of catalytic enzymes. These catalytic enzymes further change the IFT with a function of time [8].

II. MATERIALS AND METHOD

A. Materials

The materials used in these experiments were; glass slides of 28×48 square inch were used in the experiments to measure the contact angle, micro syringe and a KSV camera 200. Two types of crude oil, X1 and X2 (Table 1) from two oil reservoirs in the Niger Delta region were used in the static experiments. Both oils were filtered through a 0.5 µm filter to remove any coarse particles prior to use as reported by Osuoha [9]. Sea water was used in all experiments as the brine, the composition of the brine solution is shown in Table 2.

B. Methods

Wettability Test

A KSV camera 200 was used in the measurement of enzyme-water-oil contact angle on a solid surface which technique is based on sessile drop. A Hamilton micrometer syringe were used to deposit droplets on the glass slides and all the experiment were performed under ambient condition.

Different concentrations of the enzymes which ranges from 0 to 2 wt % were used in this experiment as the heavier (aqueous) phase and crude oil A and B as the lighter (oleic) phase. A micro syringe was used to deposit a droplet of crude oil on the glass slide which are surrounded with the enzymes, the droplet of crude oil displaces the enzyme from the surface of the slide giving rise to dynamic water receding condition.

The second phase of the experiment was conducted on aged slide. The glass slides were soaked in crude oil for 15 days at a temperature of 80^oC, after the 15^{th} day they were then removed from the crude oil and rinsed off the crude oil stains using toluene. Afterwards, it was soaked in decant for about 2 minutes and finally rinsed with distilled water [10]. The slides were used as the solid surface for this experiment.

The dimensionless term for the wettability calculation $\Delta\theta/\theta_{Ref}$ was defined, where θ_{Ref} is the contact angle values measured at reference point where enzymes are not added to the brine solution and Δθ is the difference in contact angle measured at reference point and at the point where enzymes were added to the brine solution ($\theta_{Ref} - \theta_{Enzyme}$). The results obtained from this experiment are then presented in the subsequent section.

Interfacial Tension (IFT) Measurement

Selected enzymes (LPE1 and LPE2) were added to the brine phase with different concentrations in contact with crude oil to observe the effect of enzymes on interfacial activity between aqueous and oleic phase.

The aqueous and oleic phase were equilibrated at a 1:1 volume ratio and were allow for 72 hours after agitating to stabilize. KSV camera 200 pendant drop instrument were then used in measuring the IFT between the interface of aqueous and oleic phase. The IFT values were determine by analyzing the shape of the oil drop hanging from the tip of a syringe. The measurement was done by fitting of the Young-Laplace Equation to the drop image. The drop shape of the solution is related to the Hansen and Rodsrud [11] equation.

Adhesion Test

A micro syringe with inverted needle were used to collect a volume of the crude oil and then was disperse to form a drop of oil under the brine solution with the selected enzymes. As the oil droplet is submerged into the brine solution, is then allow to contact a smooth solid surface (glass slide). After 2 minutes of the drop, the oil droplet was withdrawn back into the needle. Three different behaviors were established at that stage; adhesion behavior, non-adhesion and temporary adhesion behaviors.

This experiment was conducted on a clean and aged solid surface. The aged solid surface was soaked for 15 days at a temperature 80^oC. A KSV camera 200 were use in the experiment for easier observation on the oil drop-water-solid surface contacts. NaOH and HCl were the two salt used in adjusting the pH of the aqueous solution.

The precision of the method was determined in terms of repeatability or reproducibility and intermediate precision studies [12].

III. RESULTS

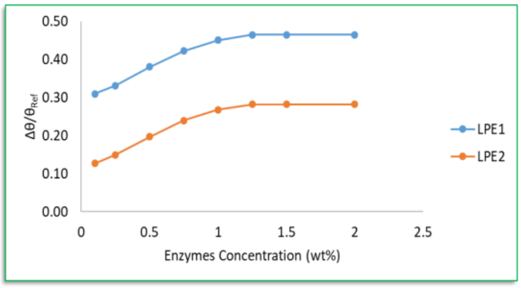

Fig 1 Plot of $\Delta\theta/\theta_{Ref}$ against LPE1 and LPE2 concentration when the solid surface used is without aging and the crude oil X1 as the oleic phase

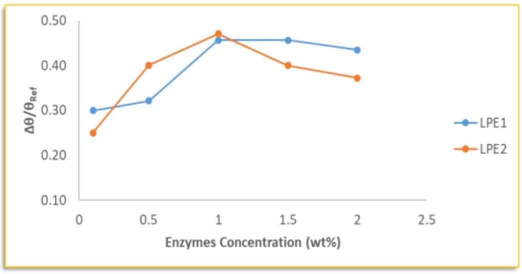

Fig 2 Plot of $\Delta\theta/\theta_{Ref}$ against LPE1 and LPE2 concentration when the solid surface used is aged at 80^{o}C and crude oil X1 is the oleic phase

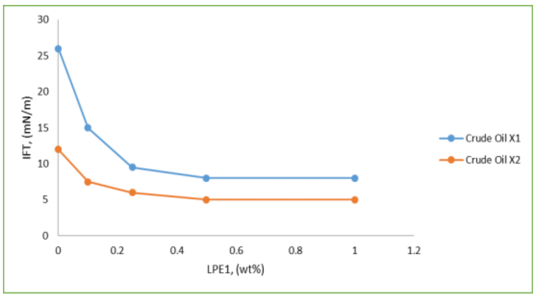

Fig 3 IFT for different concentration of LPE1-brine for crude oil X1 and X2

Table 1: Characteristics of the Crude Oil

Crude Oil ID	Density at 20^{o}C (g/ml)	Viscosity (cP)	Acid number (mg KOH/g oil)	Base number (mg KOH/g oil)
X1	0.8436	34	0.13	1.1
X2	0.8784	1.3	3.25	0.9

Table 2: Composition of Brine

Chemical compound	Na^+	Ca^{2+}	Cl^-	HCO_3^-	K^+	SO_4^{2-}
Concentration of ions (ppm)	11000	524	22300	124	3022	289

IV. DISCUSSION

Contact angle measurement for crude oil X1 without aging the glass slide and with aging the glass slide and brine solution with different enzymes (LPE1 and LPE2) concentrations as the aqueous phase were measured. As shown clearly from the result, contact angle difference when enzyme was not added and when enzyme was added shows about 33^o differences in some cases which is quite significant. From the result it is observed that the change in contact angle ($\Delta\theta$) is more visible as enzyme concentration increases and the fraction $\Delta\theta/\theta_{Ref}$ increases on till it reaches a plateau for the case of glass slide without aging (Figure 1 and 2).

Interfacial tension result between crude oil X1 and crude oil X2 is shown in Figure 3. The IFT was measured at different concentration of LPE1 enzyme when added to the brine solution. IFT values of crude oil X1 and X2 were measured without addition of enzyme to be 26 and 12 mN/m respectively. But as LPE1 enzyme was added, the result showed that with increase in the concentration of LPE1 enzyme for the two crude oil system, IFT decreases.

Enzyme effect on adhesion behavior was examined using crude oil X2. From the experimental result of the adhesion test, it is observed that the addition of LPE1 enzyme leads to a shift of crude oil X2/pH 4 and salt concentration of 0.5 M for the brine-enzyme solution/glass slide interaction from adhesion to a non-adhesion behavior (Table 3). The microbial isolates *Verticillium* sp. and *Penicillum* sp were also reported by Osuoha [1] to be potent producers of tyrosinase enzyme.

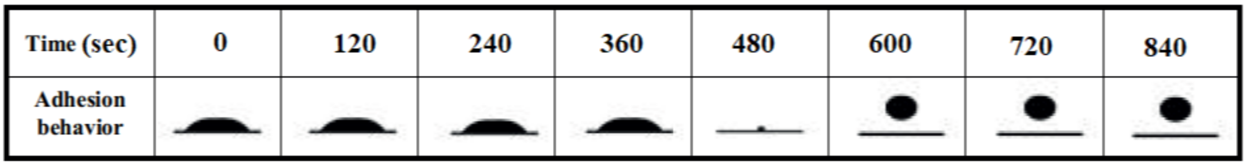

Fig 4: Adhesion Behavior of Crude Oil X2 at pH 4 and 0.5M Salt Concentration by LPE1 Enzyme Introduction

V. CONCLUSIONS

Contact angle measurements showed a more water-wet system with in the presence of the microbial lipase enzymes especially the LPE1 enzyme. The interfacial tension (IFT) measured between crude oil and brine solution that contains enzymes showed a lower value when compared with the untreated brine, therefore, the addition of enzymes in the brine solution did not have any effect on the viscosity brine. From the adhesion test, enzyme addition to brine solution showed a three different behaviors moving from adhesion behavior to a non-adhesion behavior.

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