IMPROVED MEASUREMENT TECHNIQUE FOR STUDYING THE EFFECT OF BACTERIAL SOLUTION ON IFT AND CONTACT ANGLES

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ABSTRACT

A number of interfacial tension and contact angle measurements were carried out with a goniometer in order to understand the active mechanisms causing the additional oil recovery in a Microbial Improved Oil Recovery (MIOR) process. A synthetic hydrocarbon as the drop and bacteria suspended in brine as the continuous phase were employed in a static and dynamic condition. The measurements in the static condition show that by using bacteria, IFT was lowered and the contact angle changed slightly. However, our hypothesis is that the bacteria are capable of forming very stable emulsions of oil in brine and the real IFT value is probably much lower and the contact angle might be changed significantly. In the static condition the observation times were short and the bacteria in the small water drop was probably depleted in nutrients and oxygen during the observation period, and this might have stopped the metabolic activities that lead to reduction of interfacial tension. Therefore, the main objective of the current work was to address the limitations of goniometer measurements for the MIOR process. A dynamic system was introduced in the medium and therefore a constant flow of fresh bacterial suspension with enough nutrients and oxygen was ensured. The IFT and the contact angle values obtained from the new method are presented and compared with the static results. The results show that the reduction in the interfacial tension in the case of continuous flow of fresh bacteria is greater than the IFT reduction in the case without a flow system. It was also observed that the contact angle was lower in the dynamic system compared to the static system. The new experimental procedure is more relevant for investigation of IFT mechanisms in MIOR processes.

INTRODUCTION

An interfacial tension between two liquids indicates the existence of a thermodynamic equilibrium between the two phases. When two immiscible fluids contact a solid surface, one of them tends to spread or adhere to it more so than the other, hereby wettability of a reservoir rock-fluid system is defined. Wettability plays an important role in the flow processes in the reservoir rock influencing the amount of residual oil in a reservoir and its ease of recovery. Several standard texts and reviews discuss the various methods which are in use for interfacial tension and contact angle measurements. Techniques such as the du Nouy ring, Wilhelmy plate and spinning drop methods were traditionally used to measure static tensions. None of them has satisfied the IFT and contact angle measurements in reactive systems, such as those involved in Microbial Improved Oil Recovery. In the MIOR process, bacterial growth is stimulated in the porous space so that bacteria and their bioproducts can help mobilize additional oil from the reservoir. A well recognized method for measurement of IFT is the use of static pendant drop. Due to the fact that interfacial tension exhibits a decrease with increasing time in the MIOR system, pendant drop is an important practical technique and it permits continuous study of interfacial and contact angle phenomena without mechanical interference that occurs when other techniques are used.

EXPERIMENTAL WORK

Previous publications by Crescente et al. (2006) and the author et al. (2008) on numerous core flood experiments, they reported that NSPB and SPB have positive effects on the final oil recovery. Subsequent studies have been done in order to understand the active mechanisms that probably are causing the additional oil recovery. Possible mechanisms enabled by bacteria include interfacial tension reduction, wettability changes and selective pore blocking. Therefore the present paper is a continuation of a series of laboratory experiments and consists of interfacial tension and contact angle measurements by an automated pendant drop goniometer.

Goniometer apparatus:

The goniometer is a computer controlled and user programmable instrument and consists of mainly a light source, an adjustable sample stage, a video camera, lens and an image capturing system. A circulation system was added to the goniometer by introducing an inlet at the top and an outlet at the bottom of the cuvette or chamber. Flow was initiated by using two pumps and two long needles to inject and extract the continuous phase at a constant rate of 3 ml/hr. Figure 1 shows a schematic drawing of the goniometer and the circulation system used to do the experiment at dynamic conditions.

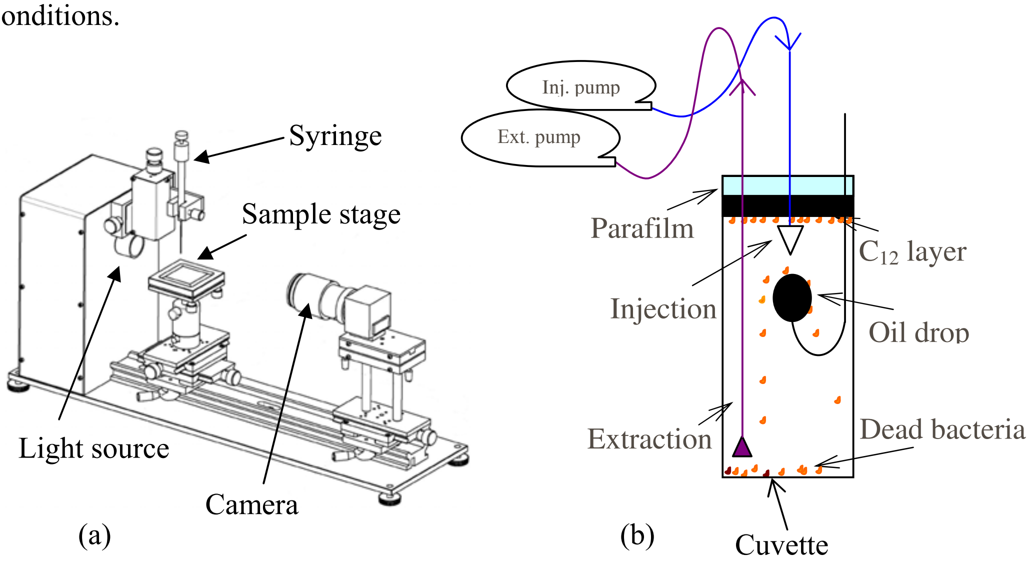

Figure 1: The schematic picture of (a) Goniometer apparatus and (b) Circulation system

Materials:

Synthetic reservoir brine and a model hydrocarbon, n-Dodecane (C_{12}) were used as the water phase and as the oil phase respectively. This brine was also used to cultivate the bacteria. The studied bacterium, *Rhodococcus* sp 094, was an alkane oxidizing bacterium. *Rhodococcus* sp. 094 is forming very stable crude oil in water emulsions and is thoroughly characterized by Bredholt et al. (1998). Two different variants of the bacteria were tested; cells of surfactant-producing bacteria (SPB) cultivated on dodecane and cells of non-surfactant-producing bacteria (NSPB) with acetate as carbon source. Quartz plate samples were prepared for the contact angle experiments.

Some initially water-wet plates were chemically treated to obtain oil-wet properties in order to evaluate the contact angle changes on quartz plates with different initial wettabilities. In this work, a mixture with 3 volume part of *SurfaSil*^{TM} and 7 volume parts of Pentane solution was used for the wettability alteration process.

Experimental procedure:
Both IFT and contact angle experiments were conducted either in a static or in a dynamic condition. The static system means that a constant volume of the surrounding phase is used while the dynamic system is referred to the status where fresh bacteria are always present due to the circulation system. The temperature was kept at 30°C in all cases. Each experiment has also been repeated at least once to try to confirm the result. The experimental steps are summarized as follows:

Cleaning procedure- Before each experiment, all equipments such as syringe, needle and other parts were cleaned with cycles of methanol, toluene and distilled water.

IFT measurement- Pendant drop experiments were conducted using a hooked needle with a syringe containing dodecane as a less dense liquid and a cuvette containing the medium or culture as a high dense phase. After placing the syringe filled with dodecane and the cuvette on their locations, the height was adjusted for the cuvette to be visible in the picture. The cuvette has a small volume of 5ml; therefore parafilm was used to keep the volume as constant as possible inside the cuvette and to avoid evaporation. Ideal drop size varies with different applications but generally larger drops are desirable. An appropriate drop size of 9µl was used in all cases. As the experiment is started the apparatus starts taking pictures. After the picture sequence was done, software is used to process all of the images and gives IFT values versus time. For any pendant drop where the densities of the two fluids in contact are known, the surface tension may be measured based on the Young-Laplace equation.

Contact angle- Measuring wettability in form of contact angle experiments is a difficult type of measurement since it is so sensitive to the surrounding environment. In addition measurements are sensitive to the production of sessile drops. In this type of experiment a drop of liquid is resting below the plane surface of a solid where brine or bacteria culture is the surrounding phase. After the quartz plate was placed on screws, the hooked needle was adjusted until its tip was visible in the screen. An appropriate drop size of 12µl was generated and detached from the syringe tip. The drop should be attached to the quartz surface as carefully and slowly as possible to minimize the spreading and subsequent recoil after contact. Enlarged photos of the drop were taken, and the program determined the contact angles between the tangent to the drop profile and the surface. The angle between the droplet and the surface can be used to declare whether the system is water-wet, oil-wet or intermediate wet.

RESULTS AND DISCUSSION

Two variants of *Rhodococcus* sp. 094 bacteria have been tested for interfacial tension reduction and contact angle changes due to bacteria exposure. Bacterial solution with a constant concentration of 10^7 CFU/ml (Colony Forming Unit/ml) was prepared in high strictly sterile condition in our biotechnology department every week. CFU is a measure of viable bacterial numbers. The results of the present work are giving important supplementary knowledge for evaluation of previous results on rock samples.

IFT reduction:

Field (Deng et al. 1999) and laboratory (Herd et al. 1992) investigations report IFT reductions by bacteria. Therefore a number of experiments have been conducted with a goniometer to measure interfacial tension of dodecane pendant drops in Brine, SPB and NSPB. It should be mentioned that during the experimental time IFT values are steadily decreasing until a stabilized value is reached. This stabilized value indicates the IFT between the oil droplet and the brine/culture. Table 1 gives the stabilized IFT values and the time spent for the different media and conditions.

Table 1: Interfacial tension results

System	**Static condition**			**Dynamic condition**		
	Drop Size, µl	IFT (mN/m)	Time	Drop Size, µl	IFT (mN/m)	Time
Brine-C_{12}	9	18.3	3 h	8.5	18.3	3 h
NSPB-C_{12}	9	13.6	5.5 h	8.5	5.2	38 h
SPB-C_{12}	9	10.4	6 h	8.5	4.8	36 h

Measuring interfacial tension with bacteria was a time consuming process. Kowalewski et al. (2005) reported IFT reductions from 38 to 0,006 mN/m over a two weeks period for a different bacteria species. In our cases, a short time of around 6 hours was used for the static condition while in the dynamic system the duration was around two days for each experiment. Ideally the experiments should have been conducted for the same period of time as the corefloods. But it seems that it is almost impossible to do the experiments for a very long period because the small amount of liquid in the cuvette might vaporize and the bacterial metabolisms could not be activated for so long period. Looking at the IFT measurements from the Table 1 it is clear that there is a significant change in the interfacial tension between two variants of the bacteria for the short observation period. The reduction of interfacial tension is more significant with SPB than with NSPB. The result for NSPB cells is close to 13.6 mN/m and for SPB seems to be around 10.4 mN/m. On the other hand there are only small differences in the results when the time is long and the final result is more or less the same. The result for both variants seems to be between 4.8-5.2 mN/m in the dynamic condition. The reason is related to the fact that the bacteria are aerobic, so they need nutrients and oxygen during their metabolic activities. The bacteria in the small water drop may be depleted in nutrients and oxygen during the static observation period, and this may stop the metabolic activities that lead to reduction of interfacial tension. Therefore to get lower IFT, the dynamic status was introduced to ensure a continuous growth of the bacteria around the hydrocarbon droplet. This setup could support the metabolic activity for a longer time to reduce the IFT. This method was used in bacterial suspension/hydrocarbon systems, where long times were required to measure changes in IFT. Another fact is that some activation time is needed for the bacteria to adjust to the new conditions. Bredholt et al. (1998) reported that a few hours had to pass before most of the cells in a culture attached to the oil phase. The most intensive emulsification took place when the cells attacked to the oil phase as a carbon source. Biosurfactants are produced as a byproduct of metabolism. These chemicals lower the IFT at the oil-water interface. Capillary trapped residual oil is reduced by lowering IFT and this leads to displacement of oil that can not be displaced by water alone. NSPB cells need more time than SPB cells to produce the biomass which leads to the creation of an emulsification phase between oil and water. Therefore the SPB cells are quickly adapted to metabolize on dodecane, while NSPB needs some time to attach to the dodecane and to be able to produce surfactant. Despite these differences, after this adaptation has occurred NSPB will behave as SPB.

Contact angle changes:

The contact angle experiments were implemented for measuring wettability changes during the bacteria application. Reported changes both towards more water wet (Mu et al. 2002) and towards more oil wet (Polson et al. 2002) conditions can have a positive effect on recovery. Initial water wet and oil wet quartz plates were used in the measurement of wettability in this work because the Berea sandstone used in the core floods mainly consists of quartz. The stabilized contact angles given in Table 2 indicate wettability properties as a result of interaction of the forces existing between three oil/brine or culture /quartz interfaces.

Table 2: Contact angle results

Contact angle (degree)	**Initial oil wet Quartz**		**Initial water wet Quartz**	
	Static	Dynamic	Static	Dynamic
NSPB-Quartz-C12	120.5	117.7	35.5	28.8
Brine-Quartz-C12	124.5	124.5	39.5	39.5
SPB-Quartz-C12	125.2	121.8	47.8	40.2

The contact angles measured with the bacteria are compared with the results obtained with the brine. The contact angle with brine indicates the initial wettability status of the plates. Wettability status in the case of the treated plate shows that chemical alteration was successful to reach the oil wet property. The results show that NSPB and SPB have different behaviours regarding the change of wettability. These results are consistent with the results from Shabani et al. (2008). It is clear that the NSPB in comparison to the brine indicates more water-wet characteristics while the SPB shows less water-wet characteristics. This trend is similar for all static conditions and for both initially water-wet and initially oil-wet quartz samples. While the contact angles for the bacteria systems in the dynamic system are quite different, even though both indicate a water-wet system. Another point is that changes in wettability for initially water-wet cases are greater for initially oil-wet cases. By comparing dynamic results with the results for the static system it is obvious that the decrease over long time for both variants are large and it seems that NSPB and SPB cultures have the same trend regarding change of wettability. However it does not look like there is a strong effect on the wettability changes. There might be many explanations on why the results are different in the two systems. One reason, and the most likely one, is that in the dynamic measurement the brine containing bacteria are able to carry more bacteria in the system and they all try to reach the small oil drop, thus reducing IFT. The reduction in IFT results in wettability properties. Another reason may be that bacterial mass are in contact with the solid surfaces before the oil drop is attached to the plate surface and the bacteria may cover the surface as a thin film. This thin film of bacterial solution may contribute to the change of wettability of the surface. One of the problems of biosurfactant flooding might be the adsorption of bioproducts on the surface in the reservoir rock. This decreases the concentrations of bacteria below that required to perform the task. This problem could be compensated by injecting continuously bacterial solution. The different behaviour of NSPB and SPB regarding change of wettability in the case of static situation may be due to their characteristics and amount of the nutrients and oxygen. SPB is originally hydrophobic while NSPB is hydrophilic. The activation time for the bacteria and the short duration for the experiment are also important aspects.

CONCLUSION

The most important conclusions from this work are summarized in the following:

- A modified pendant drop goniometer was successfully used to measure the IFT and contact angle between oil and brine/bacteria.
- Reduction in interfacial tension was observed for both static and dynamic condition when exposed to SPB and NSPB. The reduction was larger with the dynamic system than the static system.
- Changes in wettability were obtained with both SPB and NSPB. The magnitude of the wettability changes in the dynamic condition was larger than in the static condition. For the static condition, the change in wettability was insignificant.
- No big difference was observed between NSPB and SPB regarding change of wettability and reduction of IFT in the late stage of the experiments.
- The IFT reduction and wettability changes indicate that they are possible recovery mechanisms. That means that they have effects on other mechanisms that may influence the overall recovery.

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