# Development of Green Surfactants System for Wettability Alteration for Enhanced Oil Recovery (EOR) Application

by

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15581

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

_____________________
(Dr. Muhammad Ayoub)

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

September 2015

# CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

SITI NUR BALQIS BT FAUZI RAHMAN JAYARAMAN

# ABSTRACT

The study of Chemical Enhanced Oil Recovery (EOR) has started since early 1980's with the similar goal to improve the oil recovery. Recently, chemical injection has become attention in EOR process. The drawback of chemical surfactants technology in the EOR is the high cost and environmental issues. Since there are many gaps to be closed, the research to synthesis surfactants still going on until now. The difference of EOR from the previous recovery techniques is the injection of fluids must be able to reduce the Interfacial Tension (IFT) of the displacing oil and fluid, reducing capillary force and oil viscosity and many more criteria. The main focus of this project is to test Betaine development as green surfactants. The expected results are Betaine could help in reducing the contact angle, IFT value and has high solubility with carbon dioxide, which shows the wettability alteration in reservoir

# ACKNOWLEDGEMENT

Final Year Project has provided me chances to explore new knowledges and experience on different subject matter. It requires intensive research skills and applying the entire subject that has been taught in UTP for the past five years. I am glad I manage to fulfill the requirements with support and help of many individuals.

My deepest gratitude goes to my FYP supervisor, Dr Muhammad Ayoub who is very understanding, helpful and kind throughout these two semesters. A special appreciation dedicated to Mudassar Mumtaz, MSc students for his assistance, acquaintances and support during the research and documentation process. This acknowledgement also goes to FYP 1 Coordinator, Dr Sintaheyu, and FYP 2 Coordinator, Dr Nurul Ekmi for their effort in conduction various seminars, and very useful briefing.

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# TABLE OF CONTENT

## LIST OF ABBREVIATIONS

| | |
|---|---|
| Alpha Olefin Sulfonate | AOS |
| Carbon Dioxide | $CO_2$ |
| Dual-Drop Dual Crystal | DDDC |
| Enhanced Oil Recovery | EOR |
| Interfacial Tension | IFT |
| Methyl Ether Sulfonates | MES |
| Million Tonnes of Oil Equivalent | MTOE |
| Original Oil in Place | OOIP |

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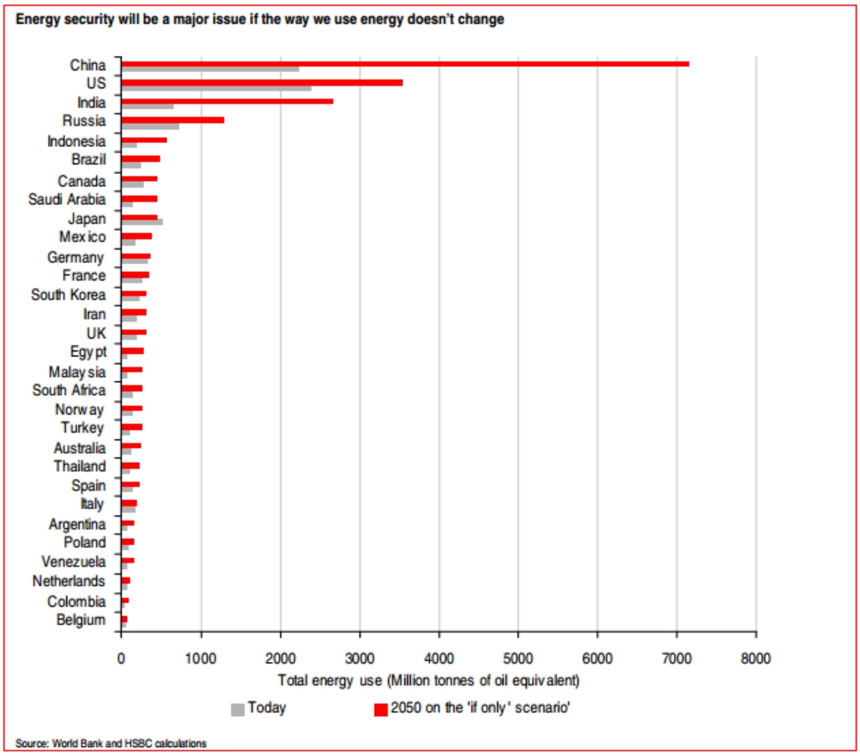
# CHAPTER 1

# INTRODUCTION

## 1.1 Background of Study

Figure 1.1 shows the forecast of economic development for different countries. The grey indicators are the present, while the red indicators are the forecast of total energy use in million tonnes of oil equivalent (MTOE). Every country is facing the new world and the growth rate is increasing for most of the country listed. With respect to the economic growth, oil is still the highest demand compared to renewable energy, coal, nuclear, gas and etc.


Energy security will be a major issue if the way we use energy doesn't change

Source: World Bank and HSBC calculations

Figure 1.1 Forecast Economic Growth Development

In Figure 1.2, it shows that the energy demand is increasing worldwide. The demand arises from the increment of the population and income growth, as reported by the BP Energy Outlook. In 2030, there will be additional of 1.3 billion of the world population compared to present population. There was a report published by the Organization for Economic Co-Operation and Development predict that world population of 9.2 billion by 2050 and thus the world requires 80 % more energy from the current energy available.  Thus, this explains why the graph trends increase drastically.

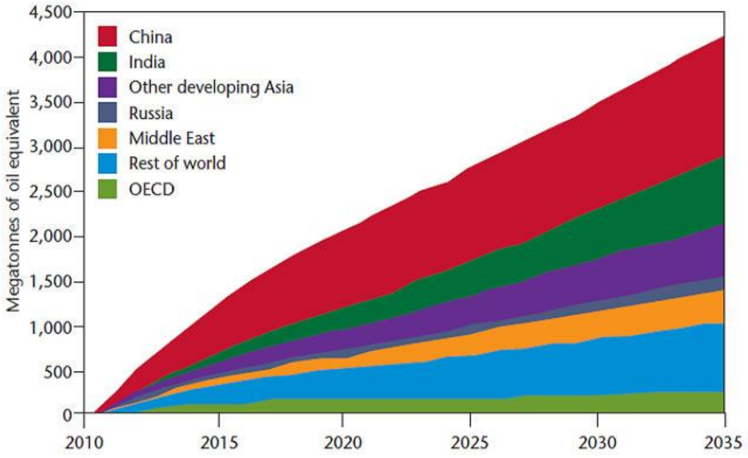


Figure 1.2    Energy Demand Worldwide

For the past few decades, many oil companies are trying to develop new oil recovery method, since it is the fact more than 50% of oil are trapped in the reservoir. The oil has been trapped due to several factors. There are many on-going researches to develop more economically-viable methods to reduce the high cost of recovery. (M.Araujo, 2005). Figure 1.3 shows the mechanism of different types of oil recovery.

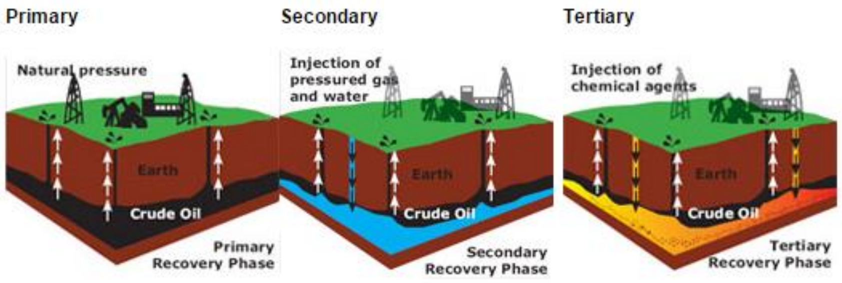


Figure 1.3    Types of Oil Recovery

There are three techniques for oil recovery, primary technique, secondary technique and the third technique is known as enhanced oil recovery (EOR). The methods of each type of oil recovery can be found in Figure 1.4. The first technique which is the primary oil recovery is using natural production mechanism such as solution gas driver reservoir by oil displacement from the reservoir to production wells by liquid expansion. Another methods falls into primary oil recovery are gas-cap drive reservoir, gravity drainage reservoir and combination drive reservoir.

The secondary oil recovery technique is introduced when the underground natural pressure in the reservoir to force out the oil to the surface decreasing. To overcome this situation, external energy is applied by injecting the fluid to increase the reservoir pressure. There are two subdivisions of this technique, which are gas flooding consisting of immiscible gas injection and miscible or high-pressure gas injection and water flooding.

EOR is the enhancement of the secondary oil recovery technique. It has been regarded as the last phase of the oil recovery from the oil field. EOR consist of few techniques, which are thermal recovery, gas injection and chemical injection. In thermal injection, heat is introduced to lower the viscosity of the heavy oil. Gas injection is method of injecting natural gas, nitrogen or carbon dioxide. Oil will be pushed to the surface when the reservoir volume expanded

Chemical injection techniques consist of polymer flooding, microbial injection and liquid carbon dioxide superfluid. The injection of various chemical including surfactants is used to lower the IFT and capillary pressure to enrich the oil recovery. (Ghosh and Li, 2013)

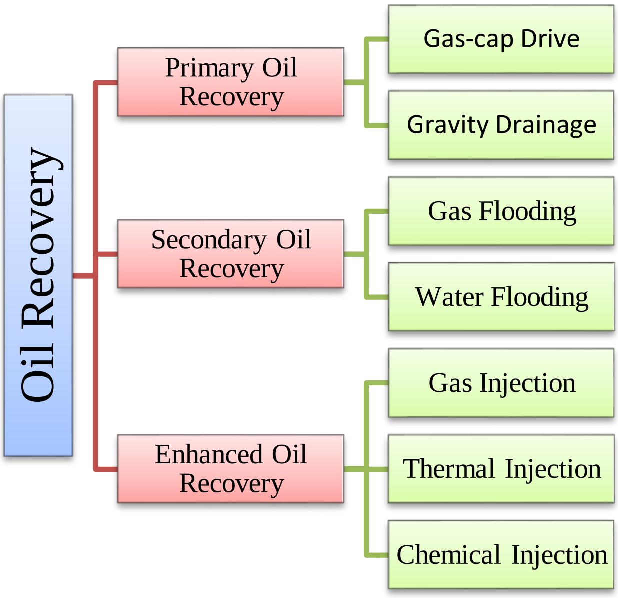


Figure 1.4 Techniques in Oil Recovery

## 1.2 Problem Statement

From the Department of Energy in U.S.A, currently the total oil production worldwide only one third of the total oil available. They claimed that there are 89 billion barrels of additional oil left trapped in the onshore reservoir. From the three stage of oil recovery, EOR has been predicted to produce 30 to 60 percent of the reservoir's oil.

Primary oil recovery only covers 10 percent of OOIP while secondary oil recovery produces 20 to 40 percent of OOIP. In chemical injection, few types of chemical are introduce to reduce the IFT. Polymers in the chemical injection will increase the water viscosity and the sweep efficiency, thus will increase the water/oil mobility.

Chemical injection has a great potential to contribute in EOR. Currently, there are many chemicals used as surfactants to increase the EOR, for example di-tridecyl sulfosuccinic acid ester and alkylpropoxy sulfate sodium salts. However, the progress of the technique is dawdling because the costs of chemical surfactants are high. The chemicals used are not environmental friendly as well.

According to National Petroleum Council, the chemical used in EOR has high potential to affect the biological condition such as loss of aquatic habitat. Biochemical oxygen demand may also increase as well as the quality of the water. Other problems that may arise from EOR are sedimentation, salinity, oil spills and groundwater flows. The available surfactants mostly are chlorinated, fluorinated, and have may functional groups. The long term effects of using chemicals in EOR are the driving force to find green surfactants that more environmental friendly and less harmful to aquatic lives.

Since the chemical injection in EOR has proven to be a success, development of green surfactants is highlight to enhance the process. As an example, Methyl Ether Sulfonates (MES) is produced from the Jatropha Curcas oil to be applied in EOR due is properties that could lower down the IFT. Thus, the author is determined to synthesis a cellulose based surfactant to promote green technology with low production cost.

## 1.3 Objectives

The goal of the project is achieved by following objectives:

- To measure the solubility of Betaine in carbon dioxide
- To measure the contact angle of oil in presence of Betaine surfactants.
- To measure the Interfacial Tension (IFT) of three types of Betaine using pendant drop method.

## 1.4 Scope of Study

The scope of study will only cover the testing of Betaine as cellulose based surfactants to reduce the wettability, for the application of EOR using the available equipment, facilities and other facilities in UTP. Solubility Cell test using carbon dioxide gas are conducted. IFT measurement using pendant drop method and contact angle measurement are carried out to find whether the Betaine are successfully increase the water wettability and which type of Betaine is having better performance.

# CHAPTER 2
# LITERATURE REVIEW

## 2.1 Types of Surfactants

The application of surfactants can mainly be seen in various industries. Since surfactants the degreasing properties, they are used widely in detergent, cleansing agents, pulp and paper manufacturing, paint, cement and textile industries. There must be 3 components for a compound to become surfactants, which are the molecular structure should be composed of polar and non-polar groups, exhibiting surface activity and should form self-assembled (Blackwell, 2008).

In EOR, surfactants function is mainly to reduce the interfacial tension, which eventually will create emulsion between water and oil in the reservoir. The emulsion will flow in continuous phase (Sarkar, 2012).The presence of surfactants will changes the properties of the water at the water/air or water/oil interface. There are four types of main surfactants in industry, anionic surfactants, non-ionic surfactants, cationic surfactants and zwitterion surfactants that will be discussed in this chapter

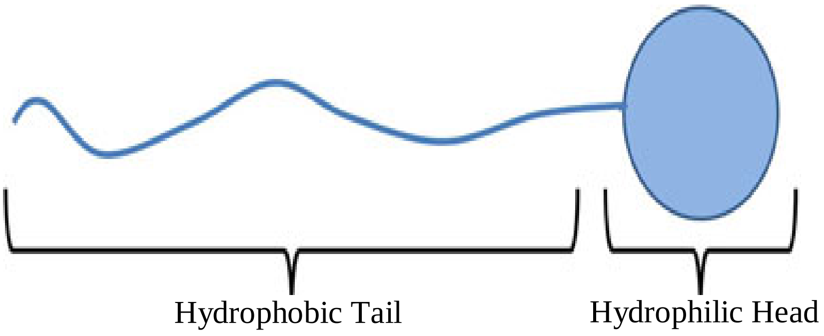


Figure 2.1 Surfactants Configuration

### 2.1.1 Anionic Surfactants

Anionic surfactants are negatively charge and they dissociated in water into amphipilic anion (negatively charge) and cation (positively charge). Anionic surfactants retain few good characteristics which they are less likely to be adsorbed on the reservoir rock, stable in term of forming self-assemble structures, economically feasible of production, and the most vital characteristic is they are very good to lower down the IFT. Anionic surfactants have been used widely in EOR. Some examples of the anionic surfactants are alkylbenzene sulfonates, laury sulfate and lignosulfonates (Sandersen, 2012).

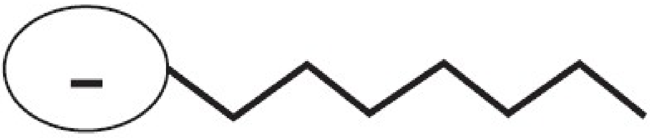


Figure 2.2 Anionic Surfactants

### 2.1.2 Non-ionic Surfactants

According to Gupta and Mohanty, non-ionic surfactants are also being used as co-surfactants to improve the surfactants function in EOR. They have a non-polar head which exhibits non-dissociable properties in aqueous solution. Nonionic surfactants are decent to be used as wetting agents, emulsifier they and they have good foaming properties (Sarkar, 2012). Nonionic surfactants will help the primary surfactants to increase the salt tolerance in the reservoir and accomplishing low IFT during EOR. Examples of surfactants under nonionic category are alcohol, ether, ester and phenol.

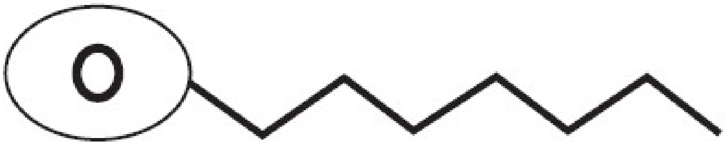


Figure 2.3 Non-Ionic Surfactants

### 2.1.3 Cationic Surfactants

From previous research, Sandersen et al., 2012 cationic surfactants are positively charge and will dissociate in aqueous solution into amphiphilic cation and anion. They cationic surfactants usually are from halogen group, for example Bromide and Chlorine. Thus, they are required to undergo hydrogenation process, which are high cost and make them more expensive compared to other types of surfactants.

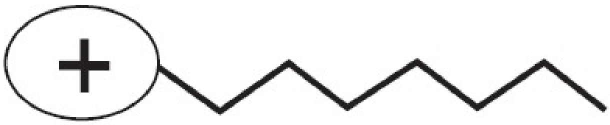


Figure 2.4 Cationic Surfactants

### 2.1.4 Zwitterionic/Amphoteric Surfactants

Zwitterionic (amphoteric) surfactants are unique because they consist of both negative and positive head group attached to the tail. This allow amphoteric surfactants has special properties, where they possessed low toxicity, high foam stability, high resistance to hard water, less effect when there are changes in pH value, temperature, or added electrolytes (Habauka M. Kwaambwa and Fiona M.Nermark, 2013). Since Zwitterionic surfactants has excellent salinity and temperature tolerance compared to the other type of surfactants, many researches on zwitterionic surfactants for oil extraction field have been reported in recent years (Shufeng Guo, 2014).

Figure 2.5 Zwitterionic Surfactants

## 2.2 Wettability Alteration

### 2.2.1 Wettability Definition

The oil and water exist in the reservoir are in immiscible state, where they do not mix. This is due to strong interfacial tension for both fluids that keeps them separated. They will only become miscible at certain temperature, pressure and composition. During normal oil extraction from reservoir, there is some leftover oil trap in between the porous medium.

### 2.2.2 Types of Wettability

Wettability is behaved as a binary switch, where the rock is either water-wet or oil-wet. When the porous medium has strong water wetting properties, the surface prefers to be in contact with water. On a strong oil wetting surface, it favours to be in contact with oil (Abdullah et. al, 2007).

According to (Drummond and Israelachvili, 2004), understanding the wettability of crude oil/brine is vital to determine how it affects the oil recovery. There are two main factors to be considered in order to understand the wettability problem. First is the physical morphology of the core, such as the permeability, connectivity and pore distribution of the reservoir. Second factor are the chemical composition, involving molecular interaction between different phases of materials inside the reservoir.

There three types of wettability in the reservoir, as in Figure 2.6. When the reservoir is water wet, the contact angle is more than 90°. This is where the water preferentially wets the reservoir rock. Mixed wettability case would exist at a contact angle of $90^{o}$. The reservoir is said to be oil wet when the oil tends to stick to the rock, and having contact angle less than 90°. The rocks will be coated with oil; hence the oil recovery rate is low.

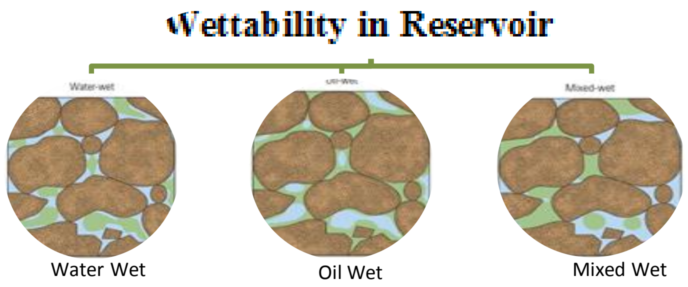


Figure 2.6 Wettability in Reservoir

## 2.3 Wettability Measurement

### 2.3.1 Contact Angle Measurement

The contact angle measurement should involve two immiscible fluids on a solid surface. As an example, if the solid is a core immersed with oil, it will become oil-wet solid surface. If the contact angle is more than 90° , it reflects an oil-wet condition and vice versa. The angle could be from 0° to 180° (Bermudez, 2013). There are two types of common contact angle measurement, which is static contact angle or dynamic contact angle measurement. In Static Sessile drop method, pure liquid drop on a solid surface is measured using angle goniometer with high resolution camera. After capturing the angle between the two interfaces, analysis is done using the computer software (ElMofty, 2012).

For Dynamic sessile drop method, similar steps and arrangement are used. Largest contact angle without increasing the three-phase line are recorded. Then, liquid will be added dynamically. Second steps involving removal of the injected liquid, without reducing the three-phase line too. Measured the smallest angle possible after removal of the liquid and find the difference between them to get contact angle hysteresis. Benefits of using sessile drop methods are the experiment can be conducted at high or low temperature, with different phase of liquid-vapour or liquid-liquid and only small amount were needed for the testing (Bermudez, 2013).

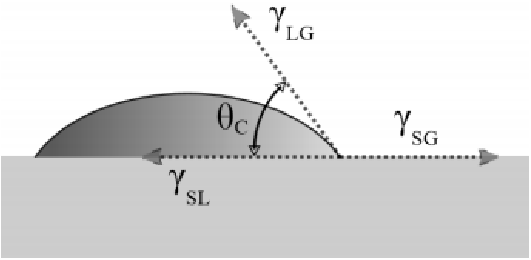


Figure 2.7 Contact Angle Measurements

Wettability is closely related to Young Laplace equation:

$\gamma^{sv} = \gamma^{sl} + \gamma^{lv} \cos\theta$, where

θ is the contact angle between two interface

$\gamma^{sv}$ is the solid interfacial free energy

$\gamma^{sl}$ represent solid/liquid interfacial free energy

### 2.3.2 IFT Measurement

Figure 2.8 shows how surfactants act on oil. Reducing IFT value is the commonly is method used to determine the wettability alteration in enhanced oil recovery. There are many ways of reducing IFT, such as alkaline flooding, surfactants injection and etc. In EOR, IFT reduction is very crucial and plays important roles in oil recovery. When the oil can absorbed the surfactants IFT is reduced and trapped oil recovery can be maximized (Gong et. al., 2016).

The IFT value can be related with the residual oil saturation in function of Capillary numbers, $N_C$:

$$N_C = \frac{u\mu}{\sigma\cos\theta}$$

Where $\sigma$is the IFT value between the two fluids, u represents Darcy Velocity, $\mu$ displacing fluids and $\theta$ is the contact angle. To reduce the Capillary Number, there are few ways which are increasing u, increasing the fluid velocity and reducing IFT. Surfactants can reduce the IFT value up to 1000 times and by lowering IFT, the number of the capillary trap reduced (Sheng, 2015). Hence, the oil flows more easily and the sweep efficiency increases too.

## 2.4 Effects of Surfactants on EOR

Previous researches, (Ayirala et.al., 2006) have conducted a research on beneficial effects of wettability altering surfactants in fractured reservoir measuring Dual-Drop Dual Crystal (DDDC) contact angle of Yates dolomite reservoir fluids. First experiment is conducted by measuring the equilibrium sessile drop to determine the properties of the brine.

The results showed it possess oil-wet properties. Brine containing surfactants are added to the existing brine in the first experiment. After surfactants injection, small amount of crude oil has been seen to float and forming small droplets. The surfactants tend to alter the wettability and it will eventually improve the oil recovery.

Some drawback in the water flooding method, which water goes through the oil instead of sweeping them to the surface. (Kamyabi et. al., 2014) on his research, the authors mentioned that another important factor during oil extraction is the cohesive forces between fluids themselves, the fluids and the rock surface.

By reducing the IFT between the fluids in the reservoir, they will become more stable and suspended emulsion, which eventually improve the oil recovery (Babadagli, 2001; Hirasaki and Zhang, 2004). Addition of surfactants also will increase the Capillary number and change the wettability. Hence, sweep efficiency has increase when the dead end is water wet (Sheng, 2015).

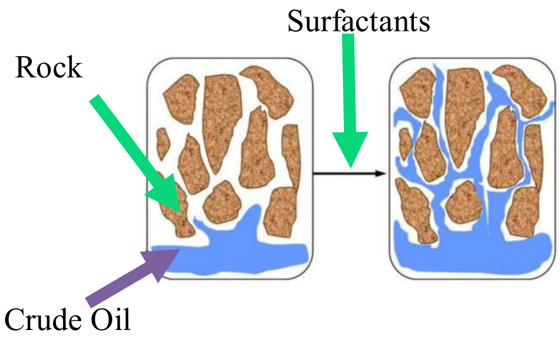


Figure 2.8 Effects of Surfactants on Oil Mobility

Even though the surfactants are less harmful to human, it is affecting the aquatic lives (Mulligan et.al., 2001). Betaine is cellulose surfactant derived from natural source, which is coconut. Some research proves that Betaine is green surfactant which has low toxicity, biodegradable and low costs material (Goursaud et al., 2008). The objective of the study is to determine the suitability of Betaine as surfactants to alter the wettability of the reservoir from oil-wet to water wet condition suits the current need in EOR.

# CHAPTER 3
# METHODOLOGY

## 3.1 Research Methodology

Research methodology encompassed of few stages from the beginning of the project until project completion. The methodology is proposed to achieve the objective the project as well as to show the understanding on the subject matter. The stages of the project are as follows:

1. Project Defining Stage
    a. Identify the project objective
    b. Construct background of studies and problem statement.
    c. Define the scope of study.
    d. Conduct literature review of the project.
    e. Determine the methodology of the research and chemicals required.

2. Research Initiation Stage
    a. Booking of equipment.
    b. Preparation of the samples.
    c. Sample testing and examination.
    d. Perform data collection and recording.

3. Data Analysis and Documentation
    a. Perform data analysis to obtain the result.
    b. Compare the results with the literature
    c. Documentation of research and report preparation.

### 3.1.1 Development of Surfactants system

The surfactants are purchase from the market, which is Cocamidopropyl Betaine S-20, F-50 and C-60, with AOS. The surfactants were diluted according to desired concentration and the Betaine surfactant was then added to the AOS with ratio of 7:3. Total sample prepared are 5 samples.

### 3.1.2 Static Contact Angle Measurement

Contact angle measurement is to identify the wettability of the core. The core plugs were immersed in prepared solution to induced oil-wet surface. It was heated up for 48 hours at 40°C. Next, they were left dried for 24 hours at the same temperature.

### 3.1.3 IFT Measurement using Pendant Drop method

Testing is conducted for different phases, which are oil-brine, surfactant-oil, and air-surfactant at 55°C using different type of prepared surfactants. The results will infer whether the water wettability are increasing or vice versa.

### 3.1.4 Solubility Testing using BP-22

The surfactants solubility in carbon dioxide is measured at 55°C with variation of pressure from 5 bars to 50 bars. The higher solubility rates would indicate better wettability alteration

## 3.2 Project Activities

The project activities are closely related to accomplishment the goals in the Final Year Project. The activities should encompass list of task such as:

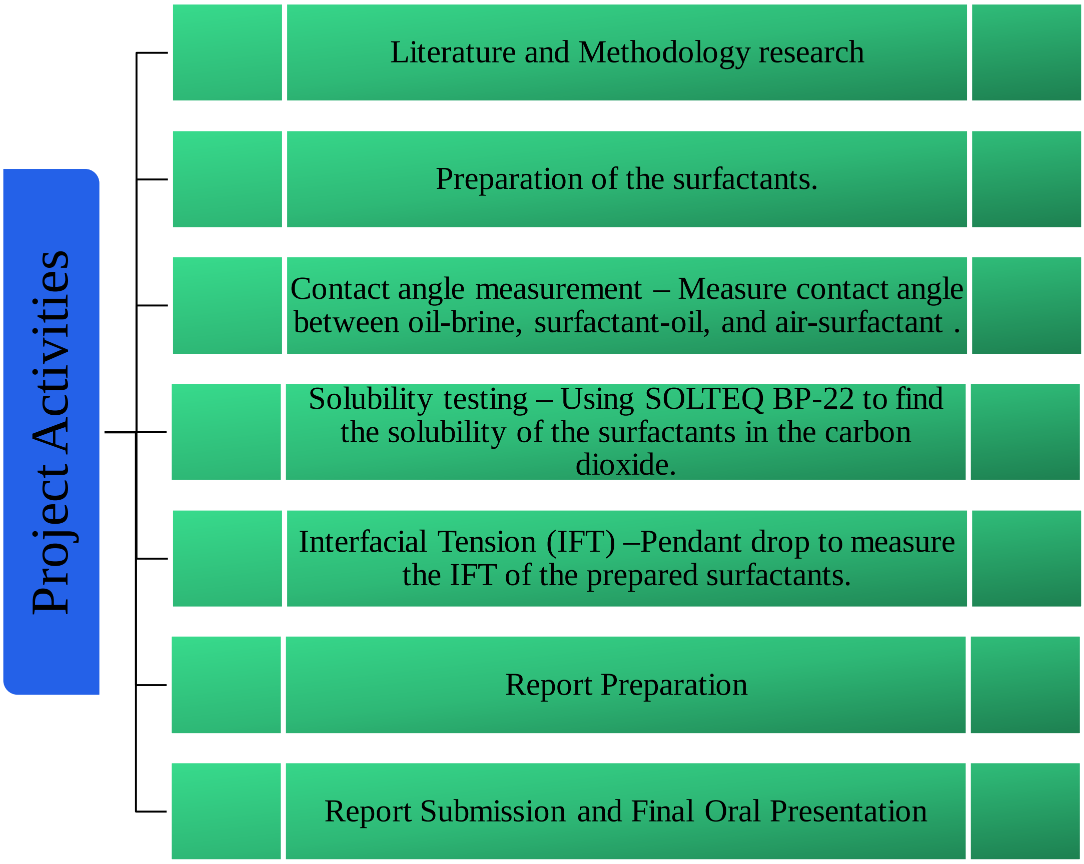
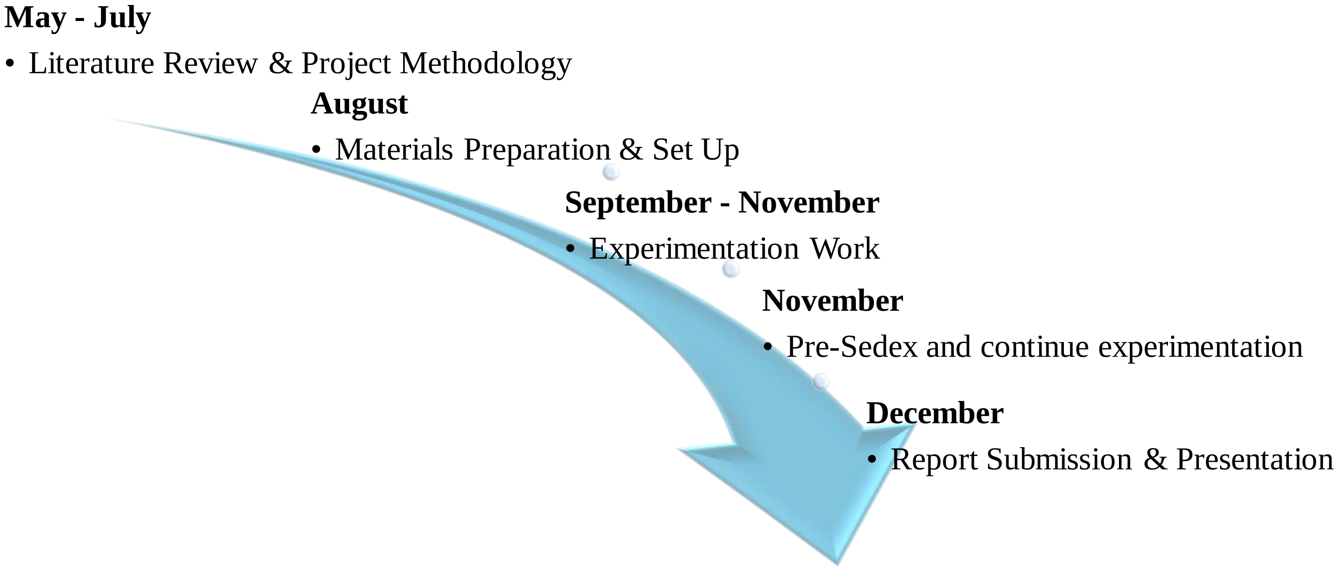


Figure 3.1 Project Activities.

## 3.3 Project Milestone



**May - July**
- Literature Review & Project Methodology

**August**
- Materials Preparation & Set Up

**September - November**
- Experimentation Work

**November**
- Pre-Sedex and continue experimentation

**December**
- Report Submission & Presentation

## 3.4 Gantt chart

Table 3.1 Gantt Chart FYP 1

| ACTIVITY | WEEKS | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Week** | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| **Selection of Project Title** | ■ | ■ | | | | | | | | | | | | |
| **Understanding Project Background** | | ■ | ■ | | | | | | | | | | | |
| **Understanding Fundamental of Wettability** | | | | ■ | | | | | | | | | | |
| **Mini Research on Cellulose** | | | | ■ | | | | | | | | | | |
| **Preparing Methodology of Project** | | | | ■ | ■ | | | | | | | | | |
| **Extended Proposal Preparation and Submission** | | | | | | ■ | ■ | | | | | | | |
| **Proposal Defence** | | | | | | | ■ | ■ | | | | | | |
| **Experimental Work Commence** | | | | | | | | ■ | ■ | ■ | ■ | ■ | | |
| **Submission of Interim Draft Report** | | | | | | | | | | | | ■ | ■ | |
| **Submission of Final Interim Draft Report** | | | | | | | | | | | | | ■ | ■ |

Table 3.2 Gantt Chart FYP 2

| **ACTIVITY** | **WEEKS** | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Week** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** | **12** | **13** | **14** |
| **Preparation of Equipment and Materials** | ▨ | ▨ | | | | | | | | | | | | |
| **Sample Preparation & Testing** | | ▨ | ▨ | ▨ | ▨ | ▨ | | | | | | | | |
| **Progress Report Preparation** | | | ▨ | ▨ | ▨ | ▨ | ▨ | | | | | | | |
| **Submission of Progress Report** | | | | | | | ▨ | | | | | | | |
| **Project Work Continuation** | | | | | | | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | | |
| **Pre-SEDEX Preparation** | | | | | | | | | | ▨ | ▨ | | | |
| **Submission of Draft Report** | | | | | | | | | | ▨ | ▨ | | | |
| **Submission of Dissertation (Soft Bound)** | | | | | | | | | | | | ▨ | | |
| **Submission of Technical Paper** | | | | | | | | | | | | ▨ | | |
| **Viva Presentation** | | | | | | | | | | | | | ▨ | |
| **Submission of Dissertation (Hard Bound)** | | | | | | | | | | | | | | ▨ |

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 Solubility Testing

The solubility cell testing is to measure the solubility of the prepared surfactants in carbon dioxide. The temperature is kept constant at 55°C and the pressure is varied from 5 – 50 bars. For this experiment, 3 types of Betaine surfactants is used, which is Betaine S-20, Betaine F-50 and Betaine C-60. The rate of solubility is to standard AOS surfactants. The equipment use is high pressure solubility cells; model SOLTEQ BP-22.

There are two tank, mixing tank and equilibrium tank. The mixing tank where the pressure was built-up before it's been transferred to the equilibrium cell. The experimental begins by purging the line with Nitrogen,$N_2$.The cell was cleaned up using ethanol and distilled water to remove any tracing cell from previous experiment. Then, the equilibrium cell was vacuum up to 0.5 bars in order to eliminate the trace of nitrogen in the system (Talebian, 2014). The system is heated up to desired temperature. Then, Carbon Dioxide $CO_2$ is introduced into the mixing tank until desired pressure achieved.

After all parameters are satisfied, 10 ml of the sample is injected to the equilibrium cell for each experiment. The connection valve between two tanks is opened for average 30 seconds and closed after the pressure in equilibrium tank stabilizes. The reading is taken using the software with three reading to get consistent data. The calculations to determine the solubility of the surfactants are done with few steps using the equations as follows. (Azmi Mohd Shariff, 2011)

Figure 4.1 SOLTEQ BP-22

Step 1: Calculation of the moles of Carbon Dioxide transferred to the equilibrium cell.

$$n_{CO_2} = \frac{V_T}{RT_a}\left(\frac{P_1}{Z_1} - \frac{P_2}{Z_2}\right) \tag{1}$$

Where; $n_{CO_2} =$ Moles of Carbon Dioxide

$V_T$ = Volume of the mixing tank

$T_a$ = Ambient temperature

$z_1$ = Compressibility of component $P_1$

$z_2$ = Compressibility of component $P_2$

Step 2: Calculate equilibrium pressure of Carbon Dioxide

$$P_{CO_2} = P_T + P_V \tag{2}$$

Where; $P_{CO_2} =$ Equilibrium pressure of Carbon Dioxide

$P_T$ = Total pressure

$P_V$ = Vapour pressure of the solutions

Step 3: Calculate remaining moles of Carbon Dioxide in gas phase

$$n_{CO_2}^{g} = \frac{V_g\, P_{CO_2}}{Z_{CO_2} RT} \tag{3}$$

$V_g$ = Gas volume of the equilibrium cell

$T$ = Operating temperature

Step 4: Calculate moles of Carbon Dioxide in liquid phase

$$n_{CO_2}^{l} = n_{CO_2} + n_{CO_2}^{g} \tag{4}$$

Step 5: Calculate moles of surfactants

$$n_{surf} = \frac{\rho V_1 m_{surf}}{M_{surf}} \tag{5}$$

$\rho$ = density of the surfactants

$V_1$ = Liquid volume of the cell

$m_{surf}$ = Mass fraction of the surfactants

$M_{surf}$ = Molecular weight of the surfactants

Step 6: Calculate the solubility

$$\boldsymbol{a = \frac{n_{CO_2}^{l}}{n_{surf}}} \tag{6}$$

$n_{surf}$ = number of moles of surfactants

The higher solubility of the surfactants in the carbon dioxide indicates better performance. This is because the surfactants will also dissolve in the reservoir, thus create thinning of the crude oil, which reducing viscosity of oil. When the viscosity is reduces, oil will easily flow through the reservoir and this method contributes to 40 percent of the production.(Salwwm Qadir Tunio and Abdul Haque Tunio, 2011) The mobility of oils through the rock is expected to increase. Hence, the rate of oil recovery will improve.

From the tables, it shows that the 2 types of Betaine, which is the S-20 and C-60 solubility increase with the pressure from 5 – 20 bars at 55°C. The same trends apply to the mixed AB surfactants. However, S-20 and AB surfactants show small drop when it is tested at 50 bars. The decreasing trend may be cause by instability of the surfactants at high pressure and high temperature.

Table 4.1 Pressure Measurement Using SOLTEQ BP-22

| Pressure (bar) | AOS | S-20 | C-60 | AB |
|---|---|---|---|---|
| **5** | 0.65 | 1.25 | 0.76 | 1.52 |
| **10** | 0.95 | 2.13 | 0.94 | 2.18 |
| **20** | 1.05 | 2.72 | 1.04 | 2.59 |
| **30** | 1.32 | 3.45 | 1.14 | 3.74 |
| **40** | 1.63 | 3.87 | 2.38 | 3.85 |
| **50** | 2.55 | 4.99 | 2.66 | 3.96 |

From the Figure 4.2, it shows the solubility trends of the surfactants, brine and Tapis Crude oil in Carbon Dioxide. S-20 has the highest solubility among all surfactants. AB also has good performance where it shows higher solubility compared to AOS alone. In AB, percentage of the primary surfactants is less and this show the AB surfactants are greener and less harmful to the environment. When the solubility increases, the brine and crude oil will dissolve better, and the interfacial tension (IFT) between the fluids will reduce, thus increasing the oil recovery. Betaine will give lower IFT values although it is used at low concentration, which is believed to be more economical. (Bataweel, 2011) .

In conclusion, the surfactants solubility in Carbon Dioxide gas at constant temperature rises with the pressure increment. The trends are similar as expected from the previous research from (Talebian et. al., 2014). Higher solubility values also indicate that the wettability has been altered, IFT has been reduced due to higher solubility of surfactants inside oil and $CO_2$ (Talebian et al., 2014). Oil mobility throughout the rocks will increase and more oil recovered shows successful EOR.

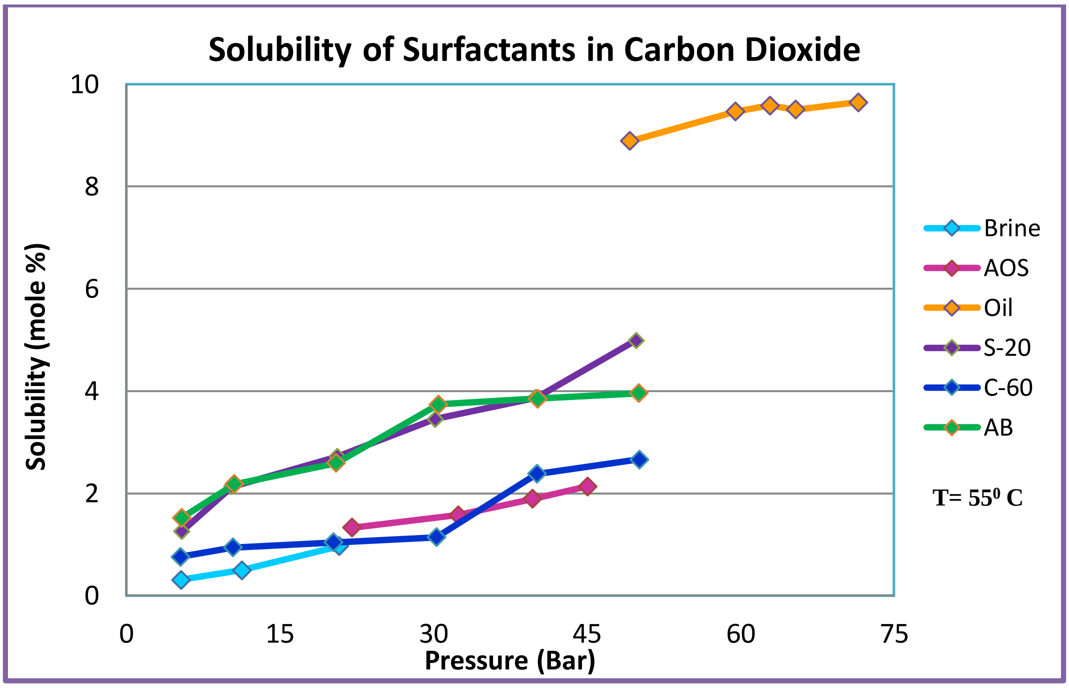


Figure 4.2 Solubility of Surfactants in Carbon Dioxide

## 4.2 IFT Measurement

There are many methods to measure the IFT, such as sessile drop method, spinning drop method, Wilhemly plate method and pendant drop method. The advantages of using pendant drop method are it can be used to measure the IFT value at high pressure and high temperature using Vinci IFT 700.

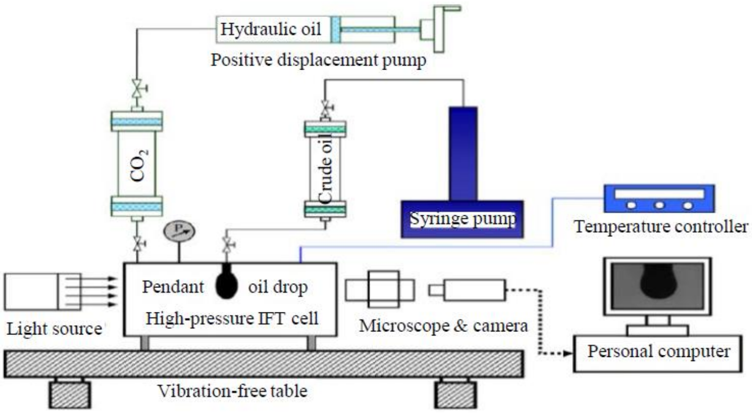


Figure 4.3 Pendant Drop Set up

The temperature is set at 25°C with pressure at 1 bar. Table 4.2 represent the densities of the samples for IFT measurement. Three reading is taken to find the average density.

Table 4.2 Sample Densities

| ***Materials*** | ***Densities at 25°C*** |
|---|---|
| **Air** | 1.2250 |
| **S-20** | 0.9995 |
| **C-60** | 0.9990 |
| **AB** | 0.9991 |

. The drop is expected to be inside the pendant without any external disturbance. Computerize image is use instead of manual analysis, which is believed to be more accurate. The equipment is first cleaned to remove the remaining traces of chemicals and liquid using toluene and water. Next, regulate the temperature of the system. The IFT cell is filled up with first immiscible fluid, for example oil. Gas booster is used to build up the pressure in bulk tank. After the set-point condition satisfied, the sample is injected through the needle and left hanging.

The second liquid is the surfactants. Pendant drop formed after the fluid injected circulated in the measuring cell. When the liquid droplet reached static condition, the gravity and surface force eventually balance and change the shape of the droplet (Adamson, A.W. and Gast, A.P., 1997).

In this case, after the readings are constant, we assume the IFT measurement already reached the thermodynamics equilibrium. 10 consecutive readings are taken to get accurate and consistence result. The pendant drop image is recorded by the camera and the IFT is calculated from the software by solving the algorithm of the Laplace equation. The input required to the software is the gas density, liquid densities, needle size and the address of the image.

The IFT values are represent in the Table 4.3 at 25°C. It shows that the IFT using Betaine S-20 and C-60 surfactants is higher compared to AOS alone. AOS does not alter the wettability very much. However, the IFT value is lower when the mixed surfactants system is tested. Lower IFT values shows that the wettability alteration is successful and AB has a better performance compared to the AOS alone. Oil mobility will also increase when the IFT value decreases, due to injection of surfactants into the system (Xavier, 2011).

Table 4.3 IFT Values

| ***Materials*** | ***IFT Values*** |
|---|---|
| **AOS** | 33.6 |
| **S-20** | 34.3 |
| **C-60** | 34.0 |
| **AB** | 29.5 |

## 4.3 Contact Angle Measurement

Contact angle measurements are conducted to examine the shape and the angle of the surfactants on the rock. It is one of the ways to indicate the wettability alteration in oil recovery mechanism. As mention in the literature, there are three types of wettability of reservoir, and the most preferably in this case is to change the oil-wet system to a more water-wet system. There are few methods that can be used to measure contact angle, for example Captive Bubble, Pendant Drop, Sessile Drop and Spinning Drop.

Sessile Drop method is used. In this experiment, Berea Core was used along with Dulang Crude. The properties of the Tapis Crude are can be referred in Table 4.4. The core was saturated with the oil and experimentation was at conducted at ambient temperature and pressure. The experiment begins with mounted the core on a clean holder. The core slice holder was placed in the chamber. The fluids were injected through the syringe. The reading was taken for 5 seconds and the contact angles image are shown in Table 4.5.

Table 4.4 Tapis Crude Properties

| **Analysis** | **Value** | **Unit** |
|---|---|---|
| Sulphur content | 0.04 | Weight % |
| Water Content | <0.1 | Weight % |
| Density at 15°C | 0.8552 | (g/ml) |
| Adhesion | 8 | (g/$m^3$) |

Table 4.5 is the mean of contact angle for each surfactant in air-surfactants system using Sessile Drop method. The concentration of the surfactants prepared is 1% to avoid the possibility of micelle formation. The contact angle without any surfactants shows reading of 100.12°. When the AOS is added on top of the mixture, the contact angles significantly reduce to 68.87°. The same experiments were repeated using another three types of Betaine.

Table 4.5 Contact Angle Values

| ***Materials*** | ***Contact Angle*** ° |
|---|---|
| **Brine** | 100.12 |
| **AOS** | 68.87 |
| **S-20** | 48.58 |
| **C-60** | 54.2 |
| **AB** | 63.67 |

When contact angle shows less than 90°, it shows that the rock surface preferably to be in contact with that mixture or solution. The injection of Betaine on the mixture also shows that the contact angles have reduce, and S-20 shows best performance in reducing the contact angle. Combination of AOS and Betaine surfactants also shows lower contact angle, compared to pure AOS. This proves that Betaine stands a chance to complement AOS or other primary surfactants to act as their co-surfactants in oil recovery.

The concentration of the surfactants prepared is 1% since there is possibility of micelle formation if the concentration of surfactants is more than 1%. The positive results also indicate that Betaine is able to act as an agent to improve oil recovery because the rock wettability has been altered from oil wet to more water wet. When the rock becomes water-wet, the oil mobility will increase, hence improving the oil recovery. The benefits of wettability alteration also include that the residual oil saturation reduced. In conclusion, further development and modification could be done with Betaine to improve the effectiveness.

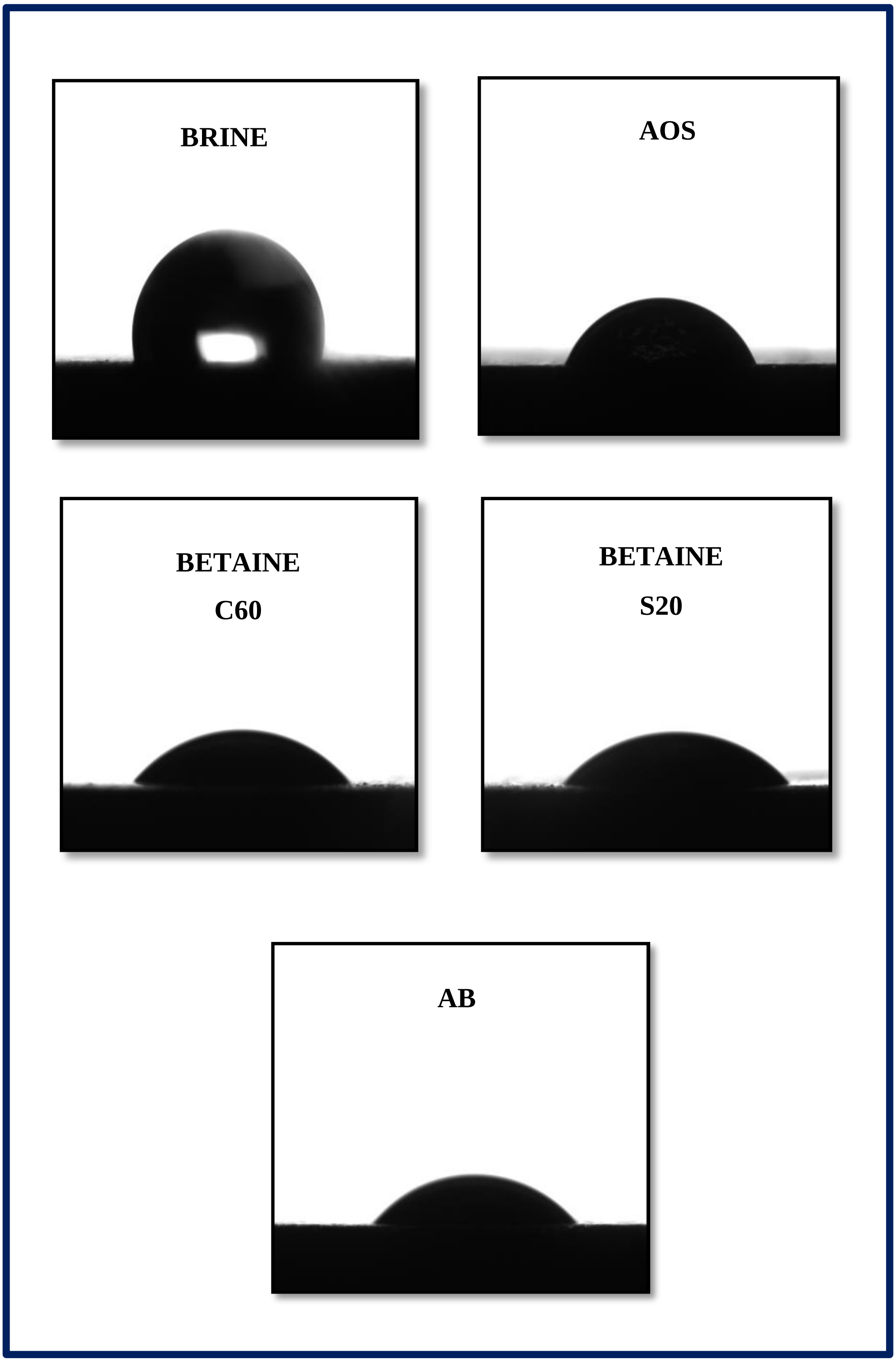


Figure 4.4 Images of Contact Angle

# CHAPTER 5

# CONCLUSION AND RECOMMENDATION

## 5.1 Conclusion

In Solubility Testing, the three types of Betaine have shown positive results, where the solubility of the surfactants in Carbon Dioxide increase with the pressure. This proves that Betaine has progressing base to work as surfactants. The IFT results shows AOS value is 33.6, but the mixed surfactants AB has lower value, which are 29.5. Lowering IFT will helps in improving the oil mobility in EOR. The contact angle testing also shows that the rock has become more water wet, where the contact angle reduced significantly. The ability of Betaine to reduce the amount of primary surfactants will give economic advantages. In conclusion, Betaine has a capability to act as surfactants in EOR. The expectations of this project that the surfactants can alter the wettability of the reservoir and could contribute in EOR research are achieved. Even though Chemical injection in EOR is a promising method, more studies and further enhancement should be made to improve the effectiveness.

## 5.2 Recommendation

Development of the novel surfactants requires further research, since there are many factors to be considered. In this project, we are focusing on the solubility of the surfactants in Carbon Dioxide, to improve the oil mobility, and altering the wettability to be more water wet. For future work, I would recommend the Betaine surfactants to be tested for temperature resistance, salinity tolerance, water hardness and etc.

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