# Mechanism of Alkaline Flooding in Low Acid Number Crude

by

Maziah binti Abu Mukhtar

Dissertation submitted in partial fulfillment of
the requirement for the
Bachelor of Engineering (Hons)
(Petroleum Engineering)

DECEMBER 2012

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

# CERTIFICATE OF APPROVAL

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Approved By,

Mr Iskandar Dzulkarnain

# 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.

MAZIAH BINTI ABU MUKHTAR

# ABSTRACT

Alkaline flooding is capable to mobilize and recover a part of residual oil remaining after waterflood. It is an enhanced oil recovery technique which involved the injection of alkaline chemical such as sodium hydroxide or sodium carbonate during waterflooding operations. The reaction that takes place between alkaline chemical and certain types of oil leads to surfactant generation in situ. It will eventually lead to reduction of interfacial tension (IFT) hence improve the oil recovery. In numerous literatures, alkaline flooding is mostly done on high acid number crude. However, there are also cases of successful alkaline flooding in low acid number crude. In addition, there is no exact theory that relates acid number with oil recovery. In this study, the mechanisms of alkaline water flooding in low acid number crude are investigated. The improvement of oil recovery in alkaline flooding does not only depend on the acid number. Emulsification contributes to improvement of oil recovery. In addition, the formation of Winsor Type III microemulsion shows the desirable condition during EOR. This project is carried out by experimental work and simulation using UTHCHEM software.

# ACKNOWLEDGEMENT

The great pleasure to His Almighty, the author has successfully complete his research project within the time given.

The author would like to express deepest gratitude to the supervising lecturer, Mr Iskandar Dzulkarnain from Geoscience and Petroleum Engineering Department for his support, advice, guidance, and patience. The author appreciates the way he has taught to approach, analyze and solve the problems; these invaluable gifts will be carried in future career and life.

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# 1. INTRODUCTION

Alkaline flooding is one of the ways to improve the oil displacement efficiency. It is capable to mobilize and recover a part of residual oil remaining after waterflood. Alkaline agents such as sodium hydroxide could react with naturally occurring organic acids in crude oil hence results in soaps at water-oil interface. Surfactants generated in situ reduce the interfacial tensions (IFT) between water and oil that increases the production. The effectiveness of alkaline flooding is attributed to a number of mechanisms. There are four most important mechanisms, emulsification and entrainment, wettability reversal-oil-wet to water-wet, wettability reversal-water-wet to oil-wet, and emulsification and entrapment. The first mechanism, emulsification and entrainment, results from reduction of the IFT and the formation of an emulsion in which oil is entrained. If the emulsion is mobile, the oil saturation will decrease and oil will move through the reservoir. Injection of alkaline chemicals can also cause a reversal of wettability from either oil-wet to water-wet or vice versa. The change in wettability and subsequent readjustment of fluids within the pores favorably affects the relative permeability to the oil phase. Discontinuous residual oil can be reconnected and caused to flow. When this wettability reversal is coupled with IFT reduction, the waterflood residual oil saturation can significantly decrease (Johnson, 1976).

### 1.1 Background Study

A measure of the potential of a crude oil to form surfactants is given by the acid number (sometimes called total acid number or TAN). Total acid number is the mass of potassium hydroxide (KOH) in milligrams required to neutralize one gram of crude oil. The factors influencing alkaline flooding in oil reservoirs are oil acid number, alkali concentration and type, brine salinity, and test temperature.

### 1.2 Problem Statement

In numerous literatures, alkaline flooding is mostly done on high acid number crude. However, there are also cases of successful alkaline flooding in low acid number crude. This study will investigate how possible it is in low acid number and the mechanism involved.

### 1.3 Objectives and Scope of Study

The objectives are to:

- Identify emulsification as mechanism for alkaline flooding in low acid number crude oil
- Examine microemulsion in low acid number crude

Scope of study:

- Emulsification mechanism in alkaline flooding using low acid number crude
- Three types of microemulsion
- IFT in Winsor Type III microemulsion
- Increment of oil recovery using this EOR method

The scope of study is feasible for the project to be completed within time frame.

# 2. LITERATURE REVIEW AND THEORY

## 2.1 Oil Recovery Stages

Traditionally, oil recovery operations have been divided into three stages: primary, secondary and tertiary. The stages described the production stage in chronological sense. Primary production resulted from the displacement energy naturally existing in a reservoir. The second stage of operation which is secondary recovery usually was implemented after primary production declined. Traditional secondary recovery processes are waterflooding, pressure maintenance and gas injection. This stage followed by tertiary stage which used miscible gases, chemicals or thermal energy to displace additional oil once the secondary recovery process become uneconomical. Many reservoir production operations are not conducted in specified order. Some secondary stages are not applicable to the reservoirs hence directly applied tertiary stage for recovery. Because of such situations, the term “enhanced oil recovery” (EOR) became more accepted instead of “tertiary recovery”. (Green & Willhite 1998)

EOR processes involve the injection of a fluid or fluids or some type into a reservoir. The injected fluids and injection processes supplement the natural energy present in the reservoir to displace oil to a producing well. The interaction between injected fluids with the reservoir rock/ oil system creates favorable condition for oil recovery. These interactions result in lower IFT’s, oil swelling, oil viscosity reduction, wettability modification, or favorable phase behavior. (Green & Willhite 1998)

EOR processes can be classified into five categories: mobility-control, chemical, miscible, thermal, and other processes such as microbial EOR. Among the chemical methods, alkaline flooding is a process in which injected alkaline chemicals react with certain components in the oil to generate a surfactant in situ. (Green & Willhite 1998)

## 2.2 Microscopic Displacement

The effectiveness of process fluids in removing oil from the rock pores is an important aspect of any EOR. Phase trapping and mobilization of fluids in porous media governed by capillary and viscous forces. It is very significant in microscopic displacement. Thus, to understand the recovery mechanism in EOR processes, an understanding of these forces is vital. Besides, interfacial tension (IFT), rock wettability, and capillary pressure also contribute in microscopic displacement.

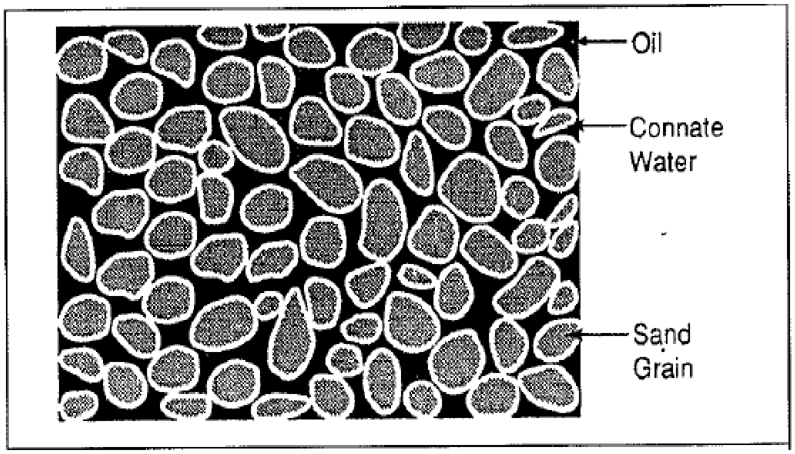


**Figure 1: Closeup of oil and water between grains of rock**

Water coexists with oil in reservoir even when the reservoir has not been waterflooded or flooded by a natural waterdrive. Although in this case water may be immobile, interfacial forces can still influence performance of subsequence flow processes. If a reservoir has been flooded, water saturations will be high and the water phase will be mobile.

Surface tension is where a force, F is acting normal to a liquid surface of length, L. It is related to the work needed to create new surface area, usually expressed in dynes/cm. “Surface tension” term is used for surface between a liquid and its vapor or air, while “interfacial tension” for the surface between two different liquids, or between liquid and a solid.

Wettability is the tendency of one fluid to spread on or adhere to a solid surface in the presence of a second fluid. When two immiscible phases are in contact with a solid surface, one phase usually attracted to the solid stronger than other phase. The stronger attracted phase is called the wetting phase. The figure shows residual oil saturations in a strongly water-wet and a strongly oil-wet rock.

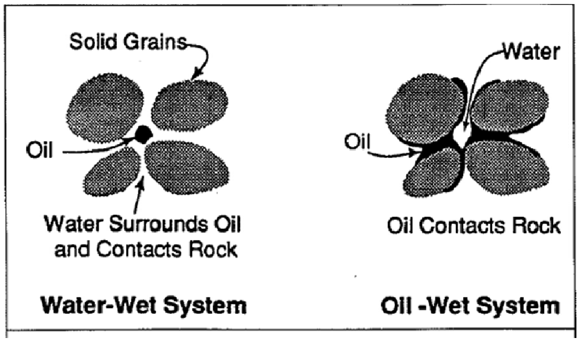


**Figure 2: Effect of wettability on saturation**

Wettability can be measured quantitatively by examining the IFT between two immiscible fluids that are in contact with solid.

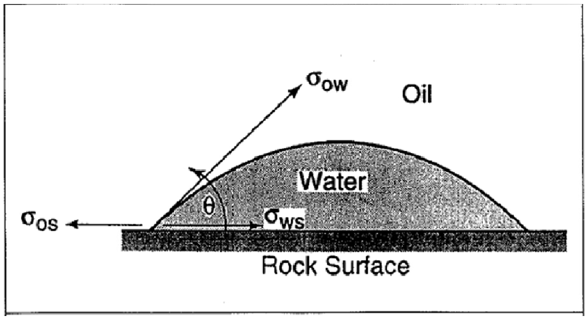


**Figure 3: Interfacial forces at an interface between two immiscible fluids and a solid**

Not all saponifiable components that may form surfactant are petroleum acids. Several mechanism including reduction of IFT, contribute to increased oil displacement efficiency due to formation of surfactant.

## 2.3 Chemicals Used and In-Situ Formation of Surfactants

The most widely used alkaline agents are sodium hydroxide, sodium orthosilicate and sodium carbonate. The process is dependent on alkali reacting with petroleum acid, “napthenic acid” in a crude oil to form surfactant in situ.

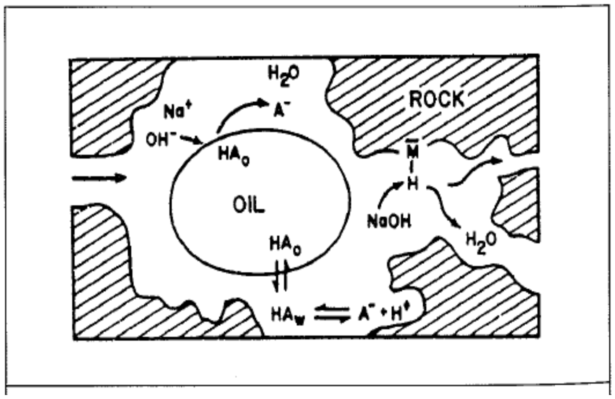


**Figure 4: Schematic of alkali recovery process**

A measure of potential of a crude oil to form surfactants is given by acid number. This is the amount of KOH, usually given in milligrams, required to neutralize 1g of naphtenic acid.

## 2.4 Recovery Mechanisms

There are several mechanisms involved regarding oil displacement by alkaline flooding. There are four different mechanisms based on oil emulsification and wettability reversal (Johson, 1976). *Emulsification and entrainment* is the mechanism where oil-in-water emulsion formed is entrained by the fluid flow and can then be produced. *Wettability reversal* is when the alkaline agent changes the injection water pH and the rock wettability is reversed from oil-wet to water-wet. This displacement takes place in oil-wet reservoir. *Wettability reversal* also occurs in water-wet reservoir (Cooke et al, 1974). Besides that, *emulsification and entrapment* explains that additional oil could be produced because of the oil emulsion droplets by small pores. (Jennings et al, 1974). The principal mechanism considered in alkaline flooding is the reduction of the oil-water IFT although other displacement mechanisms have been identified.

## 2.5 Application of Alkaline Flooding to Low Acid Oil

Various literatures show the successful of alkaline flooding in high acid number crude. However, there is few studies show the possibility of successful alkaline flooding in low acid number crude. Paper written by T.R. French and C.B. Josephson on topic Surfactant-Enhanced Alkaline Flooding with Weak Alkali proved that surfactant-enhanced alkaline flooding is applicable in oils with low acid content.

IFT experiments were performed with crude oil from Kansas. The oil has total acid number (TAN) that is nearly zero (0.01 mg KOH/ g oil). From the experiment, the aim was to separate the effect of weak alkali and IFT reduction when using very low TAN crude. The experiment was performed with an anionic surfactant (Petrostep B-100).

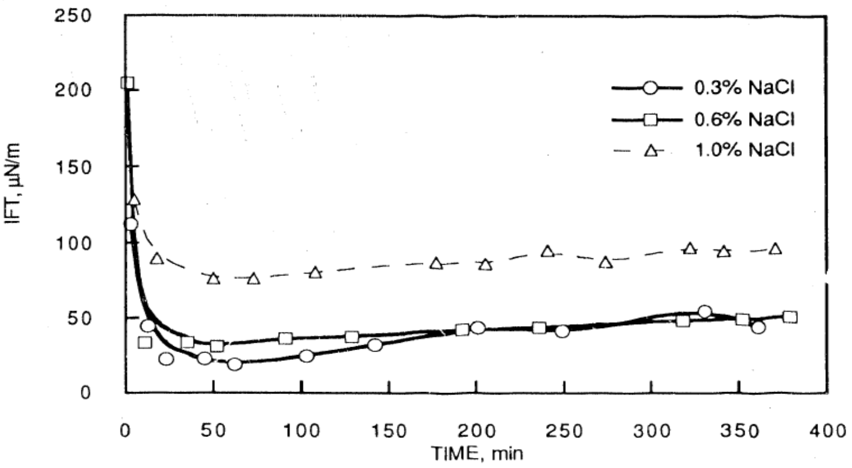


**Figure 5: IFT of Allen Co. (KS) crude oil and 0.1% Petrostep B-100 surfactant, pH 9.5, 52 degree C**

The figure above shows the IFT reduction of the experiment. Although in this experiment was done using additional of surfactant, it showed that alkaline flooding can work also in low acid number crude. Acid number does not always correlate with oil recovery.

Besides, another case study that involved low acid number crude was written by Jill S. Buckley and Tianguang Fan in their paper, Crude Oil/ Brine Interfacial Tensions. IFT between crude oil and brine is an important variable in water/ oil and water/ oil/ gas displacements. IFT affects capillary pressure, capillary number, adhesion tension, and the dimensionless time for imbibitions. In the paper, the authors presented the study of IFT for few types of crude oil sample including high and low acid number crude.

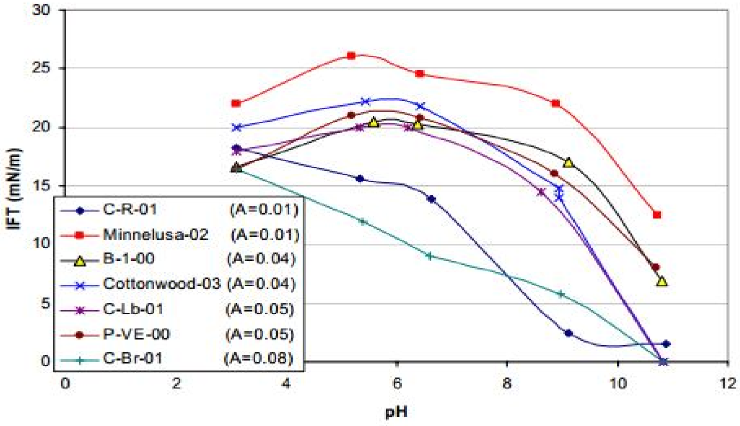


Figure 6: Low acid number oils

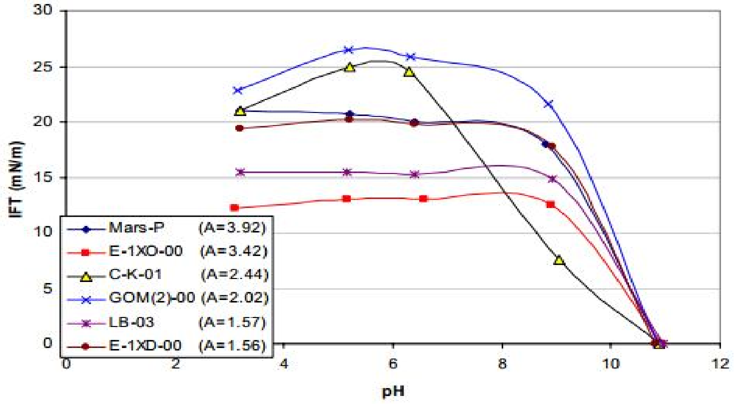


Figure 7: High acid number oils

Two of the low acid-number samples have IFTs that decrease continuously with increasing pH and four have measurable IFTs at the highest pH tested, about 11. All of the high-acid-number also exhibits a maximum IFT value at low to intermediate pH; in the highest pH tests, IFTs are all below measurable level. No distinctions were found between high or low acid oil.

This project is significant to examine the mechanism involved in alkaline flooding in low acid number crude since there are still few studies about it.

## 2.6 Microemulsion

A microemulsion is a system of water, oil and amphiphile which is a single optically isotropic and thermodynamically stable liquid solution (Danielsson and Lindman). In some respects, microemulsions can be considered as small-scale versions of emulsions, for example droplet types dispersions either of oil-in-water (o/w) or of water-in-oil (w/o). Such a description, however, lacks precision since there are emulsions (or macroemulsions). In particular, in emulsions the average drop size grows continuously with time so that phase separation ultimately occurs under gravitational force. For microemulsions, once the conditions are right, spontaneous formation occurs. As for simple aqueous system, microemulsion formation is dependent on surfactant type and structure. If the surfactant is ionic and contains a single hydrocarbon chain, microemulsions are only formed if a co-surfactant are also present. With double chain ionics and some non-ionic surfactants a co-surfactant is not necessary. This results from one of the most fundamental properties of microemulsions, that is, an ultra-low interfacial tension between the oil and water phases. The main role of surfactant is to reduce IFT between oil and water phase sufficiently.

A well-known classification of microemulsions is that of Winsor who identified four general types of phase equilibria:

- Type I: the surfactant is preferentially soluble in water and oil-in-water (o/w) microemulsions form (Winsor I). The surfactant is only present as monomers at small concentration.
- Type II: the surfactant is mainly in the oil phase and water-in-oil (w/o) microemulsions form. The surfactant-rich oil phase coexists with the surfactant-poor aqueous phase (Winsor II).
- Type III: a three-phase system where a surfactant-rich middle-phase coexists with both excess water and oil surfactant-poor phases (Winsor III or middle-phase microemulsion).
- Type IV: a single-phase (isotropic) micellar solution, that forms upon addition of a sufficient quantity of amphiphile (surfactant plus alcohol). Depending on

surfactant type and sample environment, types I, II, III or IV form preferentially, the dominant type being related to the molecular arrangement at the interface.

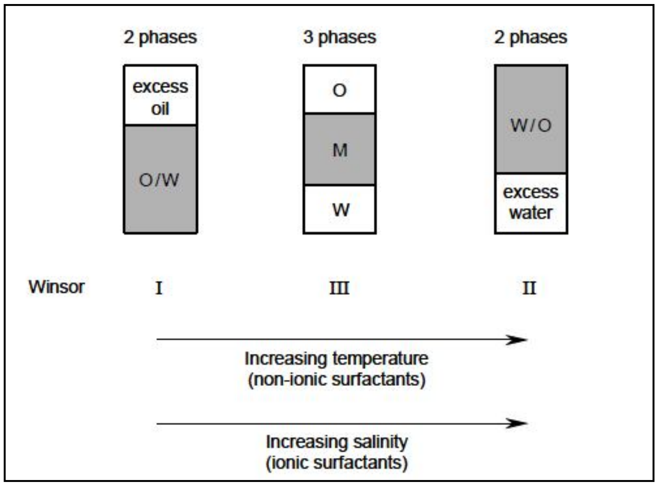


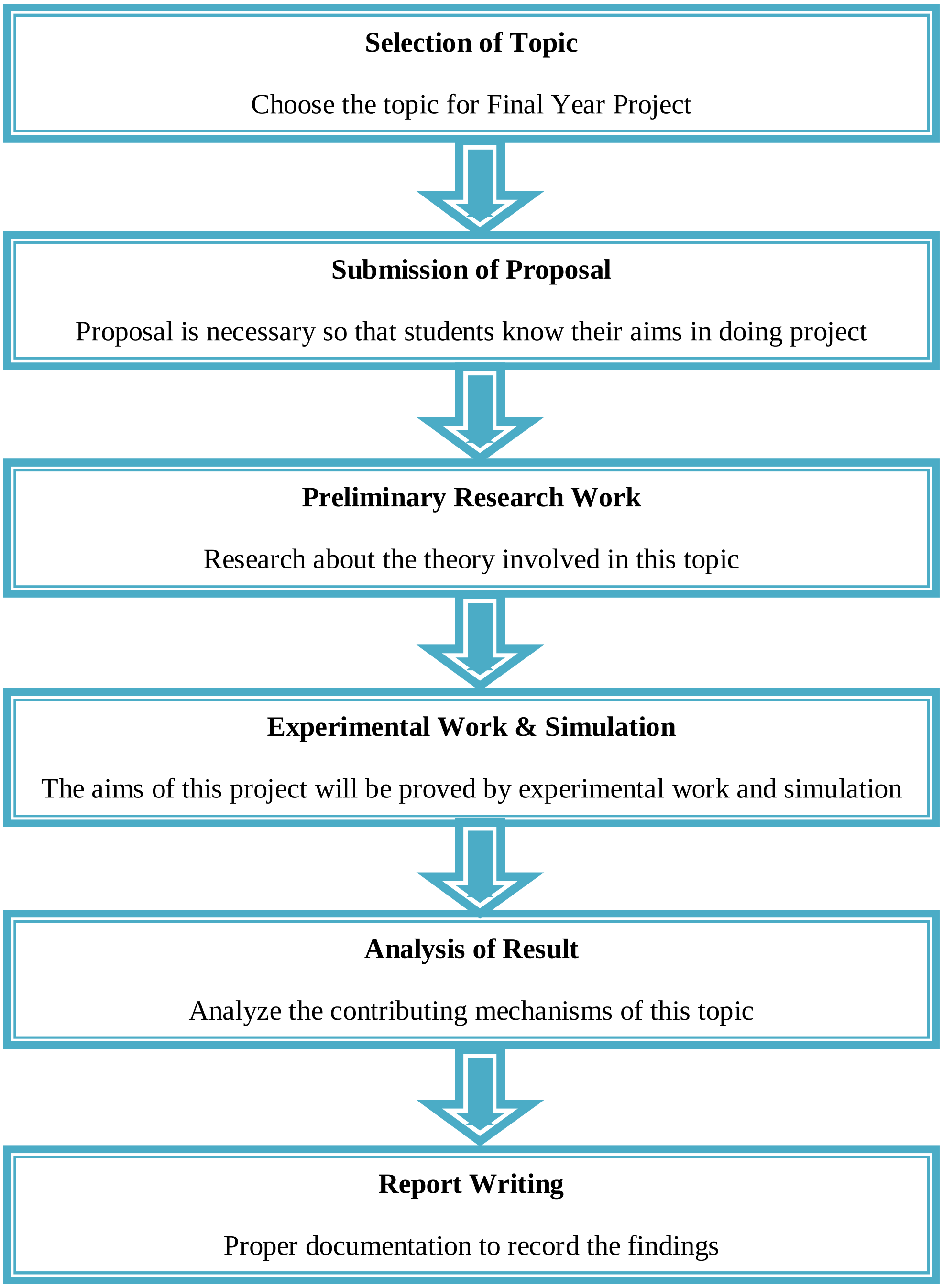
**Figure 8: Winsor classification and phase sequence of microemulsions**

Winsor classification and phase sequence of microemulsions encountered as temperature or salinity is scanned for non-ionic and ionic surfactant respectively. Most of the surfactant resides in the shaded area. In the three-phase system the middle-phase microemulsion (M) is equilibrium with both excess oil (O) and water (W).

Throughout this study, only these three types of microemulsion will be discussed.

# 3. METHODOLOGY/ PROJECT WORK

## 3.1 Project Activities



**Selection of Topic**

Choose the topic for Final Year Project

**Submission of Proposal**

Proposal is necessary so that students know their aims in doing project

**Preliminary Research Work**

Research about the theory involved in this topic

**Experimental Work & Simulation**

The aims of this project will be proved by experimental work and simulation

**Analysis of Result**

Analyze the contributing mechanisms of this topic

**Report Writing**

Proper documentation to record the findings

## 3.2 Research Methodology

- Understand the basic theory and literature review on alkaline flooding in low acid number crude
- Identify the mechanism involved in alkaline flooding in general
- Study the contributing paramaters in alkaline flooding
- Narrow the scope on emulsification as mechanism to be studied
- Frequent meeting with supervisor to make sure the study is on the right track

## 3.3 Gantt Chart

**Table 1: First Semester**

| No | Detail/ Week | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Topic Selection/ Proposal | ■ | ■ |  |  |  |  | midsem |  |  |  |  |  |  |  |
| 2 | Preliminary Research Work |  | ■ | ■ | ■ | ■ | ■ |  |  |  |  |  |  |  |  |
| 3 | Submission of Proposal Defense Report |  |  |  |  |  |  |  | ■ |  |  |  |  |  |  |
| 4 | Proposal Defense (Oral Presentation) |  |  |  |  |  |  |  |  | ■ | ■ | ■ |  |  |  |
| 5 | Literature Review Studies |  |  |  |  |  |  |  |  | ■ | ■ | ■ | ■ | ■ |  |
| 6 | Experimental Setup Studies |  |  |  |  |  |  |  |  |  |  | ■ | ■ | ■ |  |
| 7 | Submission of Interim Draft Report |  |  |  |  |  |  |  |  |  |  |  | ■ |  |  |
| 8 | Submission of Interim Report |  |  |  |  |  |  |  |  |  |  |  |  | ■ |  |

**Table 2: Second Semester**

| No | Detail/ Week | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Acid Extraction Experiment | ■ | ■ |  |  |  |  | midsem |  |  |  |  |  |  |  |
| 2 | Acid Number Measurement |  | ■ |  |  |  |  |  |  |  |  |  |  |  |  |
| 3 | Compatibility Test Experiment |  |  | ■ | ■ |  |  |  |  |  |  |  |  |  |  |
| 4 | Phase Behavior Test |  |  |  |  | ■ | ■ |  | ■ |  |  |  |  |  |  |
| 5 | Simulation of EOR |  |  |  |  |  |  |  | ■ | ■ | ■ | ■ |  |  |  |
| 6 | IFT Determination |  |  |  |  |  |  |  |  | ■ |  |  |  |  |  |
| 7 | Result Analysis |  |  |  |  |  |  |  | ■ | ■ | ■ |  |  |  |  |
| 8 | Result Discussion |  |  |  |  |  |  |  | ■ | ■ | ■ |  |  |  |  |
| 9 | Report Writing |  |  |  |  |  |  |  |  |  |  | ■ | ■ |  |  |

## 3.4 Experiments

**Table 3: Experiments and parameter needed**

| Experiment | Materials | Equipment | Parameter |
|---|---|---|---|
| Acid Extraction | 2-Ethylimidazole, Ethanol, crude oil | Stirrer, thermometer, separating funnel, weighing scale, retort stand | Low acid number crude |
| Acid Number Determination | Ethanol, Potassium Hydroxide, carboxylic acid | Burette, cylinder, weighing scale, retort stand, beaker, pH-indicator | Acid number in crude oil |
| Compatibility Test of Alkali Solution | Sodium Hydroxide, Sodium Chloride, distilled water | Test tube, cylinder, weighing scale | Optimum concentration of alkali and brine solution |
| Phase Behavior Test | Sodium Hydroxide, Sodium Chloride, distilled water, crude oil | Test tube, cylinder, weighing scale | Microemulsion |

## 3.5 Experimental Work

Before starting the experiment, it is required to remove the acid number from Dulang crude oil first in order to obtain nearly zero acid number oil. Besides, compatibility test is done to find the optimum alkali and brine concentration to be used in the experiment.

### 3.5.1 Acid Extraction

- Materials: 2-Ethylimidazole, Ethanol, crude oil
- Apparatus: Beaker, stirrer, thermometer, separating funnel, retort stand, weighing scale
- Procedure:

Extraction solvents reagent was created by mixing 1L of Ethanol with 200g of 2-Ethylimidazole. 500g of crude oil was weighed and poured to the 200g reagent mixture. The mixture was stirred for 10 minutes. The mixture was put into separating funnel for 30 minutes at room temperature.

### 3.5.2 Acid Number Determination

- Materials: Ethanol, Potassium Hydroxide, carboxylic acid
- Apparatus: burette, cylinder, weighing scale, retort stand, beaker
- Procedure:

0.1 mole of KOH was dissolved into ethanol. 500ml solvent for crude oil was prepared by adding 250ml tolune, 225ml ethanol, 25ml distilled water. Titration with 0.1M KOH alcoholic solution was done. 10g of sample was weighed and added into 100ml of the solvent in the beaker. After completely swirled, titration was done to determine the amount of KOH solution needed to neutralize the acid in the crude oil. Titration was stopped when the pH-indicator displayed neutral colour. The pH and acid number were recorded in a table.

### 3.5.3 Compatibility Test

- Materials: Sodium Hydroxide, Sodium Chloride, Distilled water
- Apparatus: Test tube, cylinder, weighing scale
- Procedure:

The mass of sodium hydroxide and sodium chloride needed for preparing solution was calculated using the fomula below and weighed.

$$\boxed{\text{Mass} = (\text{volume x mass percentage}) / 100}$$

Solution of 1.5% NaOH, 0.5 % NaCl, 1.0 % NaCl, 1.5% NaCl and 4% NaCl was prepared. 10ml of 1.5% NaOH solution was poured to 4 test tubes (10ml each test tube). Then, 10ml of solution with different salinity were added to the respective test tubes. The test tubes were swirled and put in the oven at temperature of 70 degree Celcius for a few days.

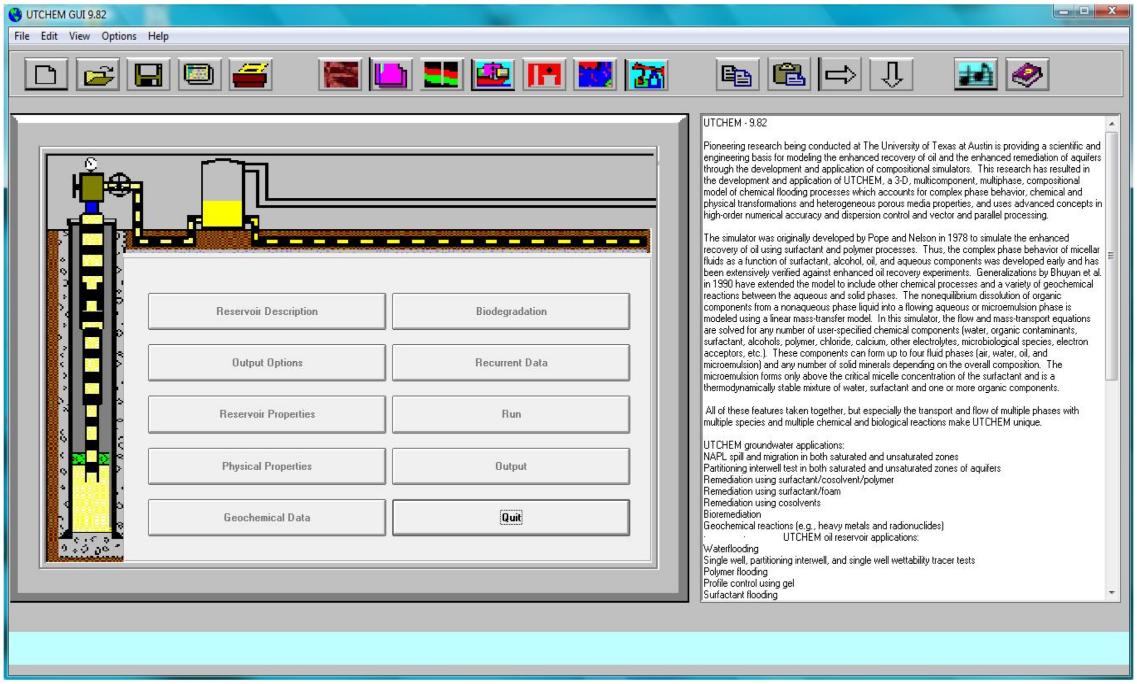
Besides, solution of 0.5% NaOH, 0.5% NaCl, 1.0% NaCl, 1.5% NaCl and 2.0% NaCl was prepared. 10ml of 0.5% NaOH solution was poured to 4 test tubes (10ml each test tube). Then, 10ml of solution with different salinity we added to the respective test tubes. This time, Calcium was added to the test tubes. The test tubes were swirled and put in the oven at temperature of 70 degree Celcius for a few days.

### 3.5.4 Phase Behavior Test

- Materials: Sodium Hydroxide, Sodium Chloride, Distilled water, crude oil
- Apparatus: Test tube, cylinder, weighing scale
- Procedure:

Once compatibility test was done, 5ml of the acid-alkali mixture was taken and mixed with 5ml of low acid and acidic crude oil. The test tubes was swirled gently and put in the oven at temperature of 70 degree Celcius. The test tubes were left for 10 to 20 days.

## 3.6 Simulation using UTCHEM Software



UTCHEM - 9.82

Pioneering research being conducted at The University of Texas at Austin is providing a scientific and engineering basis for modeling the enhanced recovery of oil and the enhanced remediation of aquifers through the development and application of compositional simulators. This research has resulted in the development and application of UTCHEM, a 3-D, multicomponent, multiphase, compositional model of chemical flooding processes which accounts for complex phase behavior, chemical and physical transformations and heterogeneous porous media properties, and uses advanced concepts in high-order numerical accuracy and dispersion control and vector and parallel processing.

The simulator was originally developed by Pope and Nelson in 1978 to simulate the enhanced recovery of oil using surfactant and polymer processes. Thus, the complex phase behavior of micellar fluids as a function of surfactant, alcohol, oil, and aqueous components was developed early and has been extensively verified against enhanced oil recovery experiments. Generalizations by Bhuyan et al. in 1990 have extended the model to include other chemical processes and a variety of geochemical reactions between the aqueous and solid phases. The nonequilibrium dissolution of organic components from a nonaqueous phase liquid into a flowing aqueous or microemulsion phase is modeled using a linear mass-transfer model. In this simulator, the flow and mass-transport equations are solved for any number of user-specified chemical components (water, organic contaminants, surfactant, alcohols, polymer, chloride, calcium, other electrolytes, microbiological species, electron acceptors, etc.). These components can form up to four fluid phases (air, water, oil, and microemulsion) and any number of solid minerals depending on the overall composition. The microemulsion forms only above the critical micelle concentration of the surfactant and is a thermodynamically stable mixture of water, surfactant and one or more organic components.

All of these features taken together, but especially the transport and flow of multiple phases with multiple species and multiple chemical and biological reactions make UTCHEM unique.

UTCHEM groundwater applications:
NAPL spill and migration in both saturated and unsaturated zones
Partitioning interwell test in both saturated and unsaturated zones of aquifers
Remediation using surfactant/cosolvent/polymer
Remediation using surfactant/foam
Remediation using cosolvents
Bioremediation
Geochemical reactions (e.g., heavy metals and radionuclides)
UTCHEM oil reservoir applications:
Waterflooding
Single well, partitioning interwell, and single well wettability tracer tests
Polymer flooding
Profile control using gel
Surfactant flooding

**Figure 9: UTCHEM software interface.**

### 3.6.1 Background of UTCHEM Software

UTCHEM is a three-dimensional chemical flooding compositional simulator. The simulator takes into account aqueous species such as water, electrolytes (anions and cations), chemical species such as surfactant, polymer, tracers, and oleic species such as crude oil. These components may form up to three liquid phases -aqueous, oleic, and microemulsion- depending on the amount and effective salinity of the phase environment.

Surfactant phase behavior (Pope and Nelson, 1978; Satoh, 1984; Prouvost et al., 1985; Camilleri et al., 1987), three phase relative permeability (Delshad et al.,1987; 1989), oil desaturation (Delshad et al., 1986; Delshad, 1990), well models (Saad, 1989), shear-thinning polymer viscosity (Wreath et al., 1990), cation exchange with clays and micelles (Hirasaki, 1982; Bhuyan et al., 1990), tracer partitioning (Jin et al. 1995), geochemical reactions (Bhuyan et al., 1990; 1991, Wu, 1990) are included in UTCHEM.

Following are the basic assumptions made in the development of the mathematical models of the simulator:

1. Fluids and rock are slightly compressible.
2. The solid phase is immobile.
3. Darcy’s law applies.
4. Dispersion follows a generalization of Fick’s law to multiphase flow in porous media.
5. Ideal mixing holds
6. Surfactant and polymer are treated as monospecies with molecular weight distribution
7. Polymer, electrolytes, and tracers do not occupy any pore space
8. The fluid phase behavior is independent of reservoir pressure

### 3.6.2 Simulation of Project

Simulation of alkaline flooding is very difficult due to complex chemical reactions. These complexities include reaction between alkali and acidic components of crude oil to generate soap in situ, reaction of injected alkali reaction with formation brine and minerals, effects of reaction products on other transport phenomena, and interactions with surfactant and polymer if they are injected.

Before running the simulation in UTCHEM, input for reservoir description was determined. The components present are water, oil, chloride and calcium. For reservoir properties, the input porosity is 20%, the permeability is 100 mD with initial reservoir pressure of 1800 psi. The input for physical properties such as IFT is taken from calculated result in phase behaviour test.

# 4. RESULT AND DISCUSSION

## 4.1 Acid Extraction

Acid extraction experiment was done based on “Removing of Naphthenic Acid from Beijiang Crude Oil” paper. The experiment was successful and de-acidified crude oil was obtained.

**Figure 10: Gravity separation**

The figure above shows the gravity separation process using separating funnel. The de-acidified oil is at the top. This is because the density of oil is lower.

## 4.2 Acid Number Determination

For acid number determination, the titration with 0.1M KOH was done successfully by using pH-indicator to measure the pH.

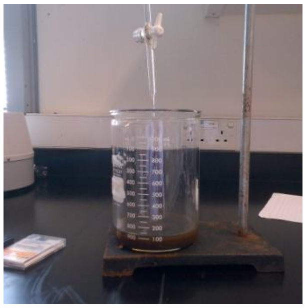


**Figure 11: Titration to measure acid number**

In this experiment, while doing titration, pH indicator was used to read the pH. Once neutral pH achieved, titration was stop.

**Figure 12: pH indicator**

The formula below was used to calculate the acid number.

$$\boxed{\text{Acid number (mg KOH/g)} = 56.10\ M\ (A-B)/\ W}$$

M: molarity

A: the amount of KOH required to titrate the sample (ml)

B: the amount of KOH required to titrate the blank solvent (ml)

W: the weight of sample (g)

**Table 4: Acid number**

| Crude Oil | Crude Oil Weight (gram) | Volume of titration alcoholic KOH (ml) | pH value before titration | pH value after titration | Acid number (mg KOH/ g oil) |
|---|---|---|---|---|---|
| Dulang | 10 | 1.65 | 5 | 7 | 0.93 |
| De-acidified | 10 | 0.1 | 6 | 8 | 0.0056 |
| Acidic | 10 | 7 | 4 | 7 | 3.93 |

Some literatures mention the range of low acid number crude is below 1.00 mg KOH/ g oil. Based on the acid measurement in this experiment, the acid number for Dulang crude oil is already low because it is less than 1.00 mg KOH/ g oil. However, extraction of the crude oil is still needed to obtain nearly zero acid number in order to get better result for low acid number crude.

## 4.3 Compatibility Test

This experiment was done in order to get the optimum brine and alkaline solution used for alkaline flooding. The mixture that becomes cloudy indicates the brine and alkaline is not compatible.

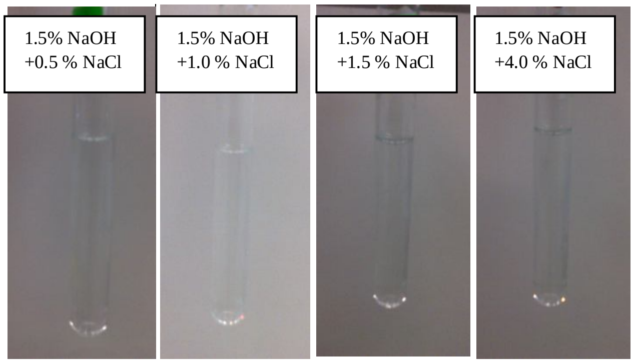


**Figure 13: Compatibility test without Ca**

From this experiment, the mixture from all test tubes shows clear colour. No precipitate or cloudy mixture was seen. In this experiment, only alkaline and brine were used. One of the reasons there is no precipitate formed was due to the absence of Ca dan Mg ion. Both two chemicals were not added in this experiment.

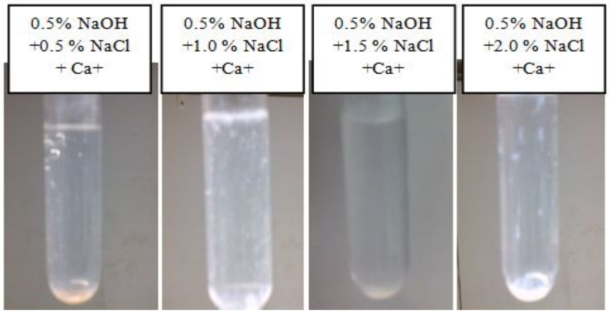


**Figure 14: Compatibility test with Ca**

From the figure above, it is clearly seen that every test tubes possessed precipitate except the mixture of 0.5% NaOH, 1.5% NaCl and Ca. The presence of Ca leads to precipitation. The mixture that has no precipitate or less is compatible.

## 4.4 Phase Behavior Test

The mixture from compatibility test was used. Phase behavior test was done for 0.5% NaOH and 1.5% NaOH by using different salinity and type of oil. 5ml mixture of alkaline and brine solution was mixed with 5ml of de-acidified crude oil. The figure below shows the observation once the crude oil was added into the test tube and swirled.

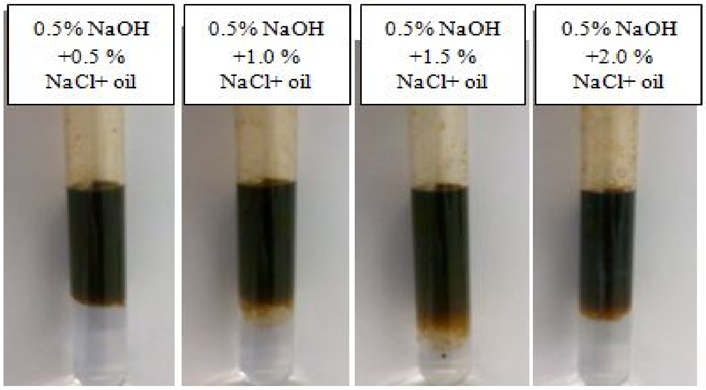


**Figure 15: Phase behavior test for 0.5% NaOH and de-acidified oil**

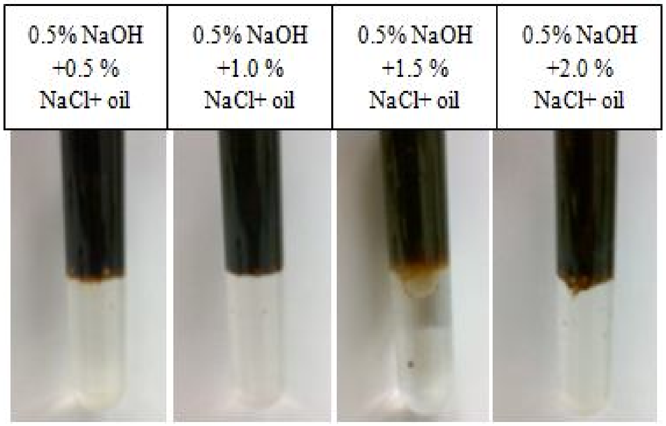


**Figure 16: Phase behavior test for 0.5% NaOH and de-acidified oil after 7 days**

Microemulsion started to form in the mixture of 0.5% NaOH, 1.5% NaCl and de-acidified crude oil. It shows that the concentration should be used during injection if alkaline flooding was carried out.

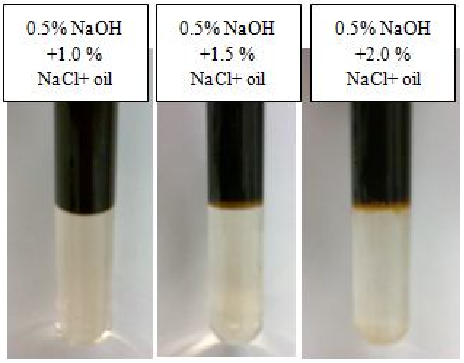


**Figure 17: Phase behavior test for 0.5% NaOH and acidic oil after 7 days**

Different from de-acidified crude, the acidic oil in that mixed in 0.5% NaOH and 2.0% NaCl start to form three layers. The middle layer might increase more if it is left for some more time.

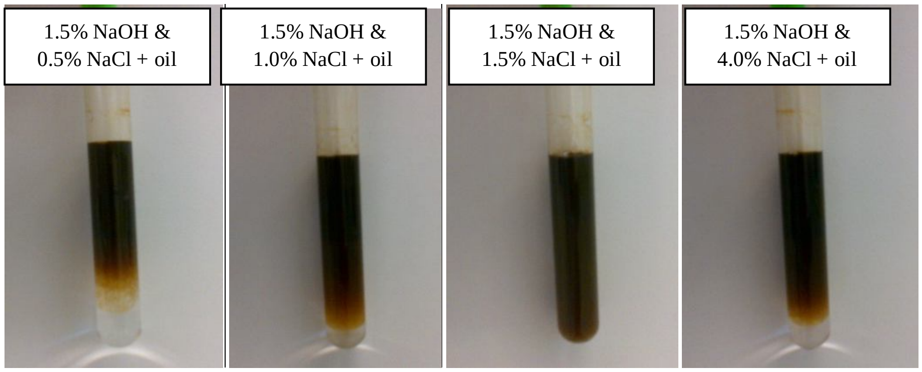


**Figure 18: Phase behavior test for 1.5% NaOH and de-acidified oil**

The mixture of 1.5% NaOH + 1.5% NaCl with de-acidified crude oil display different result compared to other mixture.

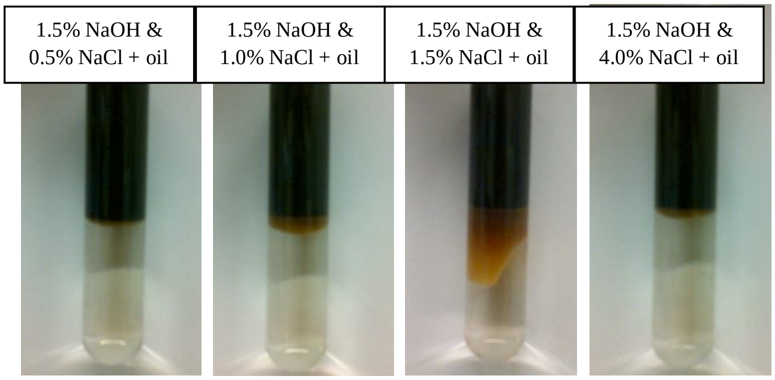


**Figure 19: Phase behavior test for 1.5% NaOH and de-acidified oil after 10 days**

The mixture was left in the oven for 10 days. The mixture of 1.5% NaOH + 1.5% NaCl with de-acidified crude oil possessed middle phase microemulsion (Winsor Type III).

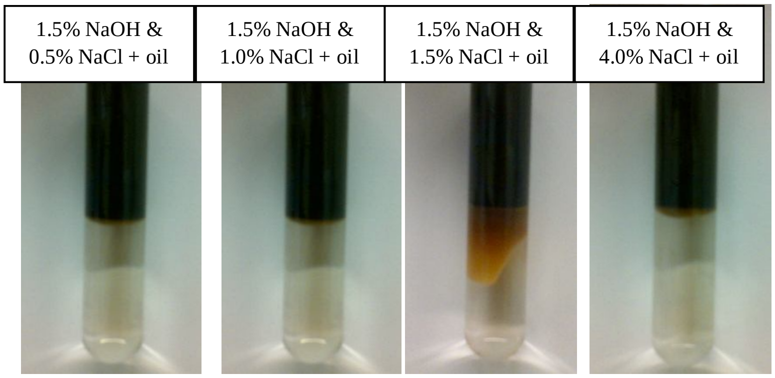


**Figure 20: Phase behavior test after 20 days**

The mixture of 1.5% NaOH + 1.5% NaCl with de-acidified showed the same result even after 20 days. The three phases or layer in the test tube considered as Winsor Type III. Type III microemulsion is unique and favorable because both interfaces have equal volumes and low IFT.

A thermodynamically stable phase, called a microemulsion is formed under certain conditions when oil, water, and surfactant are mixed (Bourrel and Schechter, 1988). A microemulsion is a distinct surfactant-rich phase consisting of surfactant, oil, water and often a co-solvent.

Winsor (1954) classified oil/water/surfactant microemulsions as Type I, Type II and Type III. A transition in microemulsion phase behavior is caused by variables such as salinity, temperature, pressure, surfactant and co-surfactant structure, and equivalent alkane carbon number (EACN) of the oil (Austad and Milter, 1998; Bourrel and Schechter, 1988; Green and Willhite, 1998). For anionic surfactants, the classical transition from Type I to Type III to Type II is shown by an increase in salinity. Healy et al. (1976) presented the concept of optimum salinity and optimum solubilization ratio (volume of oil/water divided by volume of surfactant in the microemulsion). A theoretical relationship between solubilization ratios and IFT was derived by Huh (1979). His theory predicts IFT to be inversely proportional to the square of the solubilization ratio.

Thus, a quick and accurate way to estimate IFT is to measure the solubilization ratio after equilibration and use the Chun Huh equation to calculate IFT. This approach enables us to quickly determine the optimum salinity among other important characteristics of the microemulsion such as viscosity.

Winsor Type I has oil-in-water micromeulsion. At this condition, surfactant stays in the same phase. It is difficult to achieve ultra-low IFT.

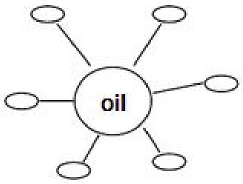


**Figure 21: Winsor Type I - Oil in water micromemulsion**

Winsor Type II has water-in-oil microemulsion. Surfactant lost to the oil and observed as surfactant. This condition should be avoided in EOR.

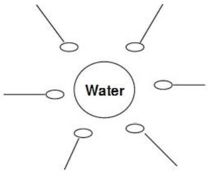


Figure 22: Winsor Type II: Water in oil microemulsion

Winsor Type III is favorable condition in EOR. Surfactants with an equal attraction to the oil and water are optimum.

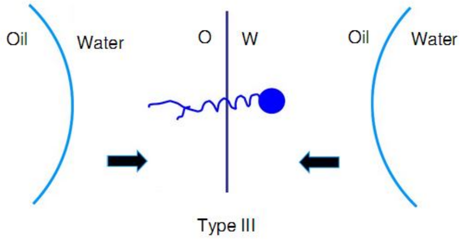


Figure 23: Winsor Type III

The figure below shows the surfactant phase behavior from Type I until Type III.

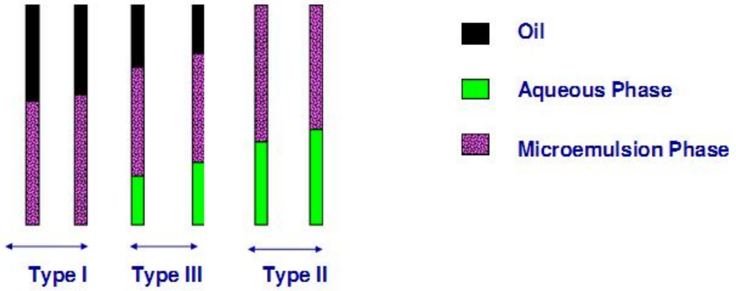


Figure 24: Surfactant phase behavior

Further action of this experiment was doing the IFT calculation.

$$\sigma_o = \frac{V_o}{V_s} \qquad \sigma_w = \frac{V_w}{V_s}$$

$\sigma_o$ = oil solubilization ratio
$V_o$ = volume of oil solubilized
$V_s$ = volume of surfactant
$V_w$ = volume of water solubilized

**Figure 25: Solubilization ratio formula**

The above formula was used to get the solubalization ratio.

$$\boxed{3.3/2.1 = 1.57}$$

The value obtained will be put in the Chun Huh equation below in order to get the IFT.

$$\gamma = \frac{C}{\sigma^2}$$

**Figure 26: Chun Huh equation**

$$\boxed{0.3/\ 1.57^\wedge 2 = 0.12 \text{ dynes/ cm}}$$

The calculated IFT is important to be input in the software for simulation.

## 4.5 Simulation using UTCHEM Software

As mentioned earlier, simulation of alkaline flooding is very difficult because of complex chemical reactions. The following assumptions have been made in developing the reaction equilibrium model in UTCHEM.

1. All reactions attain thermodynamic equilibrium
2. The molar activity coefficients of all reactive species are unity so that molar concentrations replace activities in reaction equilibrium calculations.
3. No redox reactions are present.
4. The reservoir is isothermal. Temperature changes resulting from chemical reactions are negligibly small.
5. Pressure and volume changes resulting from chemical reactions are negligibly small.
6. The water present in any phase has the same chemical composition and is in equilibrium with matrix minerals.
7. The active acid species in the crude oil can be represented collectively by a single pseudo acid component, HA. HA is highly soluble in oil and
8. Supersaturation of aqueous species is not allowed.

The author tried the best to understand the reactions that take into account behind the software. EQBATCH is based on the framework established by Bhuyan in 1989. In this program, local thermodynamic equilibrium is assumed. It is used to estimate the initial equilibrium state of the reservoir. EQBATCH estimates the initial equilibrium based on the formation and water composition, the acid number of crude oil, as well as water and oil saturations. The initial equilibrium data is vital since it will become the input into a UTCHEM alkaline model.

Two graphs were generated in this simulation:

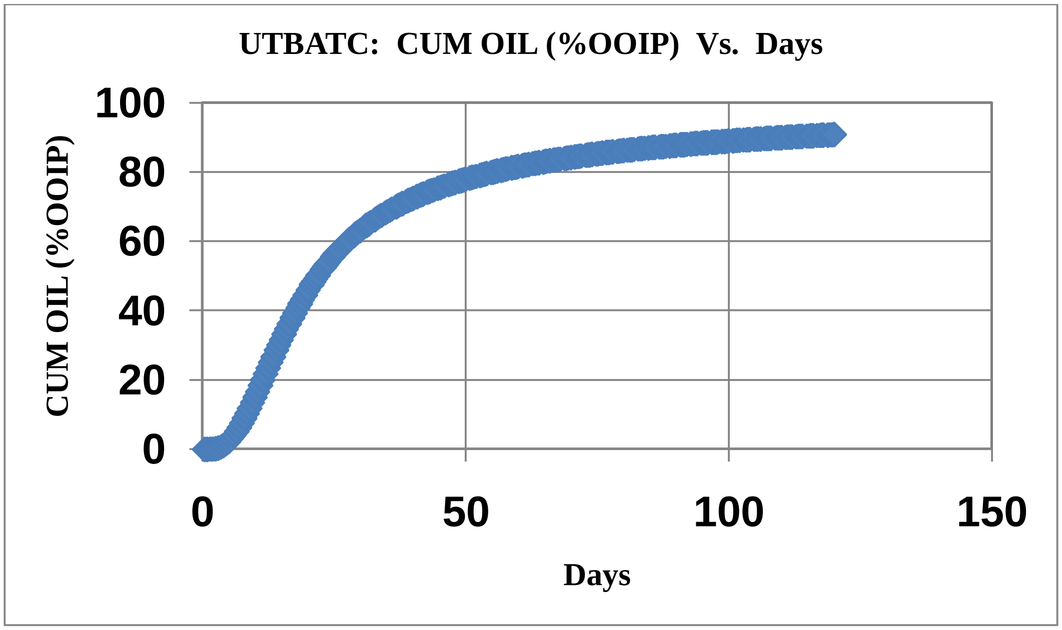


**Figure 27: Cumulative Oil (OOIP) vs Days**

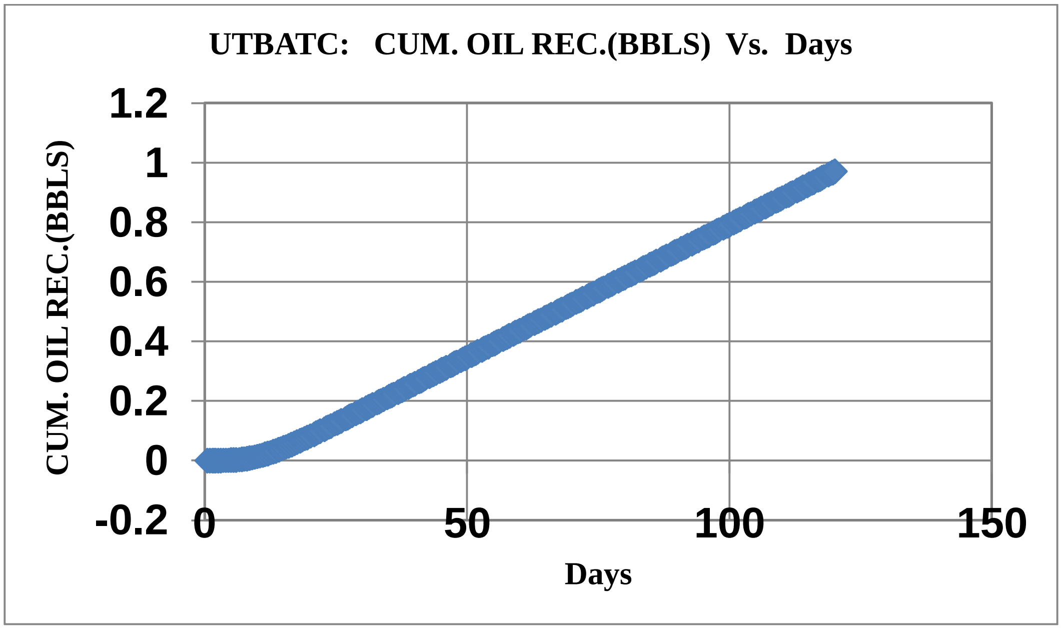


**Figure 28: Cumulative Oil Recovery**

Based on the graph above, cumulative oil and cumulative oil recovery increased. It shows that the alkaline flooding helps to improve oil recovery.

# 5. CONCLUSION AND RECOMMENDATION

## 5.1 Conclusion

The low acid number was obtained with the value nearly to zero. The acid number measurement of de-acidified oil is 0.0056 mg KOH/ g oil. Compatibility test was carried out using the same concentration of NaOH and variation of brine concentration. All of the mixture shows clear colour. None of the mixture in the test tubes shows cloudy or precipitate in the absence of Ca. However, when the alkaline and brine solution is mixed with Ca, precipitates formed except in the mixture of 0.5% NaOH, 1.5% NaCl and Ca. Further experiment was carried out. Phase behavior test was carried out using de-acidified and acidic crude oil. The mixture of 1.5% NaOH + 1.5% NaCl with de-acidified crude oil possessed middle phase microemulsion (Winsor Type III). It is favorable condition in EOR. Surfactants with an equal attraction to the oil and water are optimum.It is known that Winsor Type III has low IFT. Thus, to prove it, solubalization ratio was calculated. A theoretical relationship between solubilization ratios and IFT was derived by Huh (1979). His theory predicts IFT to be inversely proportional to the square of the solubilization ratio. Thus, a quick and accurate way to estimate IFT is to measure the solubilization ratio after equilibration and use the Chun Huh equation to calculate IFT. This approach enables us to quickly determine the optimum salinity among other important characteristics of the microemulsion. By using Chun Huh equation, the value of IFT calculated was 0.12 dynes/cm.

The value of IFT is input in the UTCHEM simulator. Form the oil recovery graph, it showed that the oil recovery is improving day by day. This indicates the successful of the EOR method.

## 5.2 Recommendation

There are four mechanisms that contribute to the successful of alkaline flooding. However, in this project, only emulsification is discussed and analyzed further as mechanism that involved in this EOR method. During the study of this project, the author unable to use RPM machine for core flooding experiment. Due to this problem, only phase behavior test was able to be carried out and able to achieve Winsor Type III microemulsion that possess low IFT. The research was done further by using EOR simulator. The IFT calculated from phase behavior test was put in the UTCHEM software to simulate the flooding. It is suggested that, for future, core flooding should be run so that further study on the other mechanism such as end-point relative permeability change and wettability reversal can be investigated experimentally. Besides, deeper understanding to use the simulator is necessary so that the simulation done has better quality.

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