ALKALINE FLOODING OF LOW ACID NUMBER CRUDE OIL

By

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CERTIFICATION OF APPROVAL

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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.

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ABSTRACT

Alkaline flooding is the earliest chemical flooding method reported. Its usage was in the beginning limited to reservoirs with high acid numbers because of the assumption that recovery is due to in situ surfactant that is formed from alkali-acidic components reactions. Alkaline flooding while succeeded in increasing microscopic sweep did not reduce the mobility ratio. Consequently, the macroscopic sweep was not improved. Later work proved that improvement in recovery was not dependent on high acid number. This work aims to relate the increase in recovery by alkaline flooding due to end-points relative permeability changes and formation of IFT reducing components that do not depend on acids.

Dulang crude, Waxy crude and Sodium Hydroxide as the alkaline solution were tested. Removals of acids from the crudes were effected by adding 2-Ethylimidazole in Ethanol with the crudes. The extracted and un-extracted crudes were used in alkaline flooding using Berea sandstone cores with initial water flooding; End-points relative permeability changes and incremental recoveries from alkaline flooding were measured from the displacement tests for comparisons. Core properties after displacements were also inspected for any effective porosity and permeability alterations. Effluents from the displacement test were tested for alcohol formation which was expected to be a major Interfacial Tension (IFT) reducing component.

Synthetically mixed crude oil (n-Heptanes/ Butanol/ Oleic Acid) were tested with alkaline solution to identify component which affected the IFT the most. Emulsion stability test was also conducted using Dulang crude with alkaline solution to quantify the Interfacial Viscosity (IFV) which could play a major role in improving the volumetric efficiency.

Incremental recoveries from alkaline flooding for un-extracted crude were around 7 – 10 % whereas for the extracted crude 5 – 6% incremental. End-points relative permeability to the displacing fluid, Krw' was reduced to around 30 - 50% in alkaline flooding compared to water flooding in all the displacement tests, thus leads to a lower Mobility Ratio of 0.5 – 0.7 in the case for alkaline flooding. pH detection of more than 0.5 indicates a high possibility of alcohol formation from the effluents of the displacement runs. Effective permeability of the core sample prior to flooding increased after the displacement test with an increase of around 0.2 – 13% increment from all cases.

From all the synthetic crude mixture, Butanol as one of the type of alcohol, lead to the greatest IFT reduction of 0.14 Dynes/cm at 5% wt concentration. This confirmed that even if very small amount of alcohol was formed, it can lead to a very low IFT. From emulsion stability test, at 2 % wt concentration of alkaline, the emulsion formed was the most stable giving the longest time for separation of around 33 minutes. This explained the stability of emulsion droplets formed in alkaline flooding which improved the volumetric efficiency thus leading to a higher oil recovery.

Alkaline flooding still offers a cheap alternative to other interfacial tension (IFT) reducing chemical process. Well defined relationships between the recovery improvements to key mechanisms in alkali flooding can be valuable in designing flooding processes using alkali as part of alkali polymer or alkali-surfactant-polymer flooding.

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Nomenclatures

E – Overall Recovery Efficiency
E_v – Volumetric Displacement Efficiency
E_d – Microscopic Displacement Efficiency
N_C – Capillary Number
V – Fluid Velocity
M – Mobility Ratio
Kro – Oil Relative Permeability
Krw – Water Relative Permeability
Krw' – End-point Water Relative Permeability
Kro' – End-point Oil Relative Permeability
μo – Viscosity Oil
μw – Viscosity Water
Swc – Critical Water Saturation
Sro – Residual Oil Saturation
Q – Flow Rate
Qw – Water Flow Rate
dP – Pressure Difference of Outlet and Inlet
L – Length of Core Sample

CHAPTER 1

1. INTRODUCTION

1.1. Project Background

Alkaline or caustic flooding is one of the methods by which oil displacement efficiency can be improved. Alkaline flooding is an Enhanced Oil Recovery (EOR) process where the pH of the injection water is increased by the addition of relatively inexpensive alkaline agents such as sodium carbonate, sodium silicate, sodium hydroxide and potassium hydroxide in an effort towards improving oil recovery [1].

As what being classified by Cooke *et al.* [2] and Ehrlich R. *et al.* [3], the principal theory of the process is the flooded alkaline solution will react with the acidic component in the crude oil inside the reservoir to form in situ surfactant which leads to the lowering of water-oil interfacial tension [4], spontaneous emulsification of oil and water [5], and wettability alteration [6].

However, Mayer *et al.* [7] reported from the pilot testing on various field utilizing alkaline flooding, it was discovered that even in reservoirs with very low acid number; the performance of alkaline flooding somehow equals with reservoirs with higher acid number, and in some cases performs better and this opposed the general theory for alkaline flooding.

This observed phenomenon requires better understanding of the displacement mechanism by considering other factors besides the conventional theory of enhanced recovery from alkaline flooding.

1.2. Problem Statement and Project Significance

1.2.1. *Problem Identification*

It was believed in the past that the application of alkaline flooding is limited only to high acid number crude oil; presence of acids in the crude oil in early studies [3] shows the minimum acid numbers ranging from 0.5 to 1.5 mg KOH/gram oil have been suggested for a successful alkaline flooding [2][4]. However there is no direct correlation been observed between acid number (AN) of the crude, interfacial activity and the incremental oil recovery [3][8]. Mayer *et al.* [7][9] summarized that even in reservoirs with very low acid number of 0.2-0.22 AN, the incremental recovery was 5-7% PV (Pore Volume) compared to a high acid number reservoirs of 0.6 AN which achieved <1% PV increment. This shows even reservoirs with low acid number, the success of alkaline flooding is equal and sometimes better than high acid number reservoirs. The problem identified from these is that other displacement mechanisms beside acid-alkaline reaction to generate in-situ surfactant must be investigated to explain the incremental recovery in low acid number crude oil.

1.2.2. *Significance of the Project*

To be able to describe the displacement mechanisms of alkaline flooding in low acid number crude oil will greatly enhanced the prospect of implementing alkaline flooding since the method is one of the low-cost alternatives in EOR. To explain the phenomena of the increase in recovery of alkaline flooding for low acid number crude oil, three (3) key solutions were devised; (i) Better understanding of existing displacement theory of reduction in IFT and wettability alteration by quantifying the changes in relative permeability end-points, (ii) formation of alcohol elements in the effluents, and (iii) rock properties alteration after displacements experiments.

1.3. Objectives and Scope of Studies

1.3.1. *Objectives*

a. **To examine and illustrate the changes of relative permeability end-points for alkaline flooding for low acid number crude oil**

Alkaline solution cause wettability changes of rock from oil-wet to water-wet and emulsion can be formed through the reduction of IFT. Relative permeability describes the ability of fluid to flow and the reduction of fluid saturations. Incremental recovery can be obtained from relative permeability analysis through residual saturations values for displaced phase and end-points relative permeability of displacing phase measurements which mobility ratio can be calculated in order to quantify the dependency on acid number towards the recovery.

b. **To identify the formation of alcohol elements in the effluents while investigating the components in crude oil composition which most affects IFT reduction and recovery**

In low acid number crude, it is believe that acid constituent plays a smaller role in reducing IFT which could leads to better oil recovery. Thus, components in crude sample will be examined to identify which affects the IFT the most. This would establish that alkaline flooding in low acid number crude does not depend on the acid content. Alcohol leads to ultra-low IFT reduction in oil-water system, thus if formation of alcohol can be confirmed, it will be vital in explaining the increase of recovery in alkaline flooding.

c. **To quantify the effect of dissolution/precipitation of rock minerals**

Physical properties of the reservoir rock will be altered due to interaction between alkaline solutions with the rock surface. Exchanges of ion and minerals during alkaline flooding will be explained based on proven literature review. Alteration of the porosity and permeability before and after displacement runs will be examined.

1.3.2. *Scope of Studies*

- Acid Number measurement of the oil sample for core flooding, IFT measurement.
- Removal of acidic components (Naphthenic Acid) for neutralization of crude oil using Ionic Liquids.
- Core Flooding experiments to measure the End-Points Relative Permeability and Mobility Ratio using Dulang and Waxy crude oil (Acidic and De-Acidified).
- Post-evaluation after core displacements of effluents for Alcohol formation and core properties
- Interfacial Tension (IFT) measurement of the oil and alkaline solution sample mixed with either Alcohol, n-Heptane, or Oleic Acid.
- Emulsion stability test of alkaline with different concentrations mixed with Dulang crude oil.

1.4. Relevance of the Project

The findings from this research will enhance the applicability of alkaline flooding in EOR process for reservoirs with low acid numbers. Through lab experiments, it is hope that the prospect of alkaline flooding will not just be limited to reservoirs with high acid number of 0.5 to 1.5 AN [2][4], but also to low acid number reservoirs (below 0.5 AN) which is very common throughout Malaysian field. The research is relevant in providing explanation on why it was observed that even reservoirs with low acid number, alkaline flooding has been quite successful in EOR project.

1.5. Feasibility of the Project within Scope and Time Frame

With careful planning and full dedication in conducting this research, all the experimental works were managed to be completed in time. All the materials and equipments to conduct the experiments were readily available; and with the assistance of the technicians in operating the equipments, all data has been successfully recorded and all the objectives set for this research has been achieved.

CHAPTER 2

2. LITERATURE REVIEW

2.1. Enhanced Oil Recovery Concept

In Enhanced Oil Recovery (EOR), the overall recovery efficiency E of any fluid displacement process is given by the product of the macroscopic, or volumetric displacement, efficiency E_v and the microscopic displacement efficiency, E_d[1]

$$E=E_vE_d \qquad (1)$$

Macroscopic displacement efficiency is a measure of how well the displacing fluid has contacted the oil-bearing parts of the reservoir. The macroscopic displacement efficiency is made up of two other terms: the areal sweep efficiency, E_s and the vertical efficiency, E_i.

Macroscopic displacement is affected by the following factors: properties of injected fluids, properties of displaced fluids, properties and geological characteristics of reservoir rock, and geometry of injection and production well pattern

Microscopic displacement efficiency is a measure of how well the displacing fluid mobilizes the residual oil once the fluid has contacted the oil. For the purpose of this research, we are mainly concerned with interfacial tension (IFT), wettability, relative permeability, and mobility ratio.

2.1.1. *Interfacial Tension*

Interfacial tensions or surface tension can be referred as forces per unit length acting at the fluid-fluid and rock-fluid interfaces. Interfacial tension between two fluids represents the amount of work required to create a new unit of surface area at the interface. In oil recovery, a low interfacial tension between oil-water is preferred to mobilize the residual oil.

2.1.2. *Rock Wettability*

Wettability is the tendency of a rock to prefer one fluid over another, by being either oil-wet or water-wet. Wettability is a function of the chemical composition of both the fluids and the rock.

2.1.3. *Capillary Number*

Residual oil saturation always depends on the dimensionless ratio of viscous to capillary forces defined as the capillary number,

$$N_C = \frac{v\mu}{\sigma\phi} \qquad (2)$$

Based on the equation, it is preferable to have low interfacial tension between oil-water and viscosity of the displacing fluid must be reduced to give a higher capillary number thus lower residual oil.

2.1.4. *Mobility Ratio*

The mobility ratio describes the displacement efficiency of our injected fluid. A mobility ratio of less than 1 is preferable based on the equation below

$$M = \frac{\frac{k_{rw}}{\mu_w}}{\frac{k_{ro}}{\mu_o}} \qquad (3)$$

Mobility ratio effects stability of a displacement process, with flow becoming unstable (non-uniform displacement front) when M>1.0 called viscous fingering. In displacement, a more stable (M <1.0) is more preferable.

2.1.5. *Relative Permeability*

Relative permeability is the ratio of effective permeability of a particular fluid at a particular saturation to absolute permeability of that fluid at total saturation.

The relative permeability curve will explain how is the displacement efficiency is going to be based on the end-points of the relative permeability of each fluid phases as well as the incremental recovery based on the residual saturation points.

2.2. Alkaline Flooding

Alkaline agents have an appeal for enhanced oil recovery because of their low cost and favourable performance in laboratory test. Alkaline agents mobilize oil efficiently through several mechanisms.

However, careful screening and preliminary studies must be conducted before any EOR method including alkaline flooding can be implemented.

2.2.1. Screening Criteria

In determining the feasibility of alkaline flooding, previous detailed studies of alkaline field projects have been conducted since 1960. Screening parameters were identified from a detailed study of alkaline field projects, and summarize by French *et al.* [10]

Screening Parameters	Explanation
Gypsum	Reservoirs with gypsum (anhydrite) content greater that 0.1 percent should be rejected as it consumes alkali agent, with 1% gypsum can consume 10 PV of a 1% solution of $NaHCO_3$
Kaolinite	Reservoir with kaolinite only injected alkali with low pH, because kaolinite can deter flooding with high pH alkali
Montmorillonite	The mineral can consume much of the injected alkali by adverse precipitation due to its large surface area and very high cation exchange capacity.
Sandstone	Highly preferred for alkaline flooding
Acid number	Important for oil to have high acid number to achieve low IFT. But, even with crude oil with a low acid number, alkaline flooding can be successful due to other mechanism. Detailed study of alkaline project shows no correlation between oil acid number and project success.
CO2	Reservoirs with high C02, mole fraction of C02 (in produced gas) higher than 0.01, or a pH less than 6.5 are not good candidates.

Table 1: Alkaline Flooding Screening Criteria

2.3. Alkaline Flooding Displacement Mechanism

Alkaline flooding is an EOR process where the pH of the injection water is increased by the addition of relatively inexpensive alkaline agents such as sodium carbonate, sodium hydroxide and potassium hydroxide in an effort towards improving oil recovery. The alkali reacts with the acidic constituents in the crude oil leading to lower water-oil interfacial tension, emulsification of oil and water. Also, alkali may react with the rock grain surfaces, leading to wettability alteration.

Johnson *et al.* [11] provides a brief overview of the mechanism that will improve the oil recovery from alkaline flooding:

2.3.1. Emulsification and Entrainment

Increase capillary number by reacting with organic acids in crude oil to form emulsifying soaps. The soap/surfactant emulsifies oil and water and reduces IFT by two to three orders of magnitude. The oil-in-water emulsion formed is entrained by the fluid flow can then be produced.

2.3.2. Wettability Reversal

When displacement processes occur in oil-wet reservoir, residual oil is the continuous phase. Injection water changes rock wettability to water-wet. As a result, water-oil relative permeability and water-oil mobility ratio are lowered [13].

Even in water-wet reservoir, the discontinuous non wetting residual oil can be changed to continuous wetting phase if proper conditions of reservoir temperature, pH, and salinity of alkaline solution are met [2]. Presence of water droplet in the continuous oil-wet phase raises the pressure gradient of the flow. Capillary pressures are overcome and residual oil saturation is reduced.

2.3.3. Emulsification and Entrapment

Additional oil could be produced due to entrapment of oil emulsion droplets by small pores. Since the flow is diverted into poorly swept or un-swept areas, volumetric sweep efficiency is improved.

2.4. Basic Chemical Model for Alkali/ Oil Chemistry

Addition of the alkali chemicals results in a high pH because of the dissociation in the aqueous phase. For example using NaOH, it dissociates to yield [OH⁻] as follows [13]:

$$NaOH \rightleftarrows Na^{+} + OH^{-} \tag{4}$$

Equilibrium dissociation of water is given by

$$K = \frac{[OH^{-}][H^{+}]}{[H_2O]} \tag{5}$$

Where brackets indicate molar concentrations and an increase in [OH⁻] causes a decrease in [H⁺]. Water concentration is essentially constant.

The hydroxide ion must react with a petroleum acid from the crude oil to form a surfactant. Some of the petroleum acid in the crude oil partitions into the aqueous phase according to the solubility expression:

$$K_D = \frac{[HA_o]}{[HA_w]} \tag{6}$$

Where K_D is the distribution or partition coefficient and HA_O and HA_W denote petroleum acid in the oil and water phase.

The petroleum acid dissociates in aqueous phase according to the expression

$$HA_W \rightleftarrows H^{+} + A^{-} \tag{7}$$

The dissociation is governed by the equilibrium relationship

$$K_A = \frac{[H^{+}][A^{-}]}{[HA_W]} \tag{8}$$

The species A^- is an anionic surface-active agent. Thus, recalling the hydroxide ion being dissociates in the aqueous solution, caustic reaction will occur

$$HA_W + OH^{-} \rightleftarrows A^{-} + H_2O \tag{9}$$

A measure of the potential of a crude oil to form surfactants is given by the acid number. Theoretically, higher the acid number, more surfactants can be formed thus better oil recovery. But this is not so since acid number does not always correlate with oil recovery due other recovery mechanisms due to the alkaline solutions.

2.5. Rock/Fluid Interactions and Loss of Alkaline Chemical

Usually due to alkaline reactive minerals, alkaline chemical is consumed during a displacement process [7]. Only a small amount of the chemical is used in the reaction with petroleum acids to form in situ surfactants. Hydroxide can interact with reservoir rock in several manner depends on the rock mineralogy. Thus, irreversible dissolution of silica and anhydrite can occur, and Base exchanges of divalent ions followed by precipitation of insoluble hydroxides can take place [13].

One caustic/rock interaction that is important in alkaline flooding is the reversible sodium/hydrogen base exchange;

$$\bar{M}H + Na^+ + OH^- \rightleftarrows \bar{M}Na + H_2O \qquad (10)$$

Where $\bar{M}$ denotes a mineral-base exchange site. The exchange reaction indicates that both sodium and hydroxyl ions are involved in the Base exchanges. For every hydrogen mineral site exchanged, both a sodium and hydroxyl elements are lost. It was observed that the exchange process delay the breakthrough which can be significant in oil recovery.

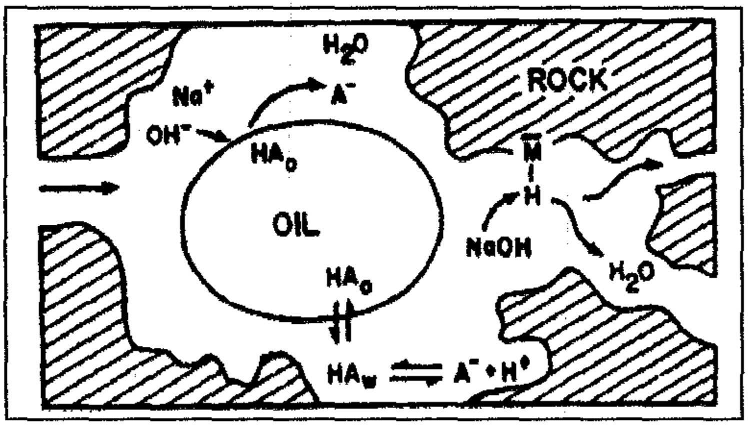


Figure 1: Schematic Diagram of Ions Exchanges between Alkaline-Oil-Rock

Besides that, alkali will react with Ca^{2+} and Mg^{2+} and can precipitate. This reaction can be advantageous as it is sometime used in chemical flooding to soften the brine. Pre-flushing with alkaline chemicals is common, but the reaction results in loss of alkaline chemicals. At the right temperature (above 70°C) and pressure (above 1000 Psia), the precipitated minerals can be flushed out, thus improving the overall transmissibility of fluid as the grain surfaces are dissolved in the displacing fluid.

2.6. Removal of Naphthenic Acids using Ionic Liquid

A common method of removing the acidic components of which the crude is "washed" with alkaline solution to produce neutralized salt from the acid-alkaline reaction has major problems which are:

- The forming of tight emulsion where it is almost impossible to separate the crude and the alkaline solution
- Neutralized salt which is formed are usually in liquid state and miscible with the crude sample thus difficult to be extracted

From the work of Lijuan *et al.* [14], ionic liquids were used to remove the acid constituents and it overcomes the problems faced from the above method.

2.6.1. *Imidazole Derivatives in Solvents as Ionic Liquid*

Imidazole and its derivatives are five-membered heterocyclic compounds containing two nitrogen atoms, in which one is pyrrole-N and the other is pyridine-N. Pyrrole-N participates in the conjugated system, while pyridine-N, which does not participate in the conjugated system, has strong alkalinity and can easily combine with H+ to form an imidazole-cation, which is a common cation of ionic liquid.

Naphthenic acid is a weak acid; therefore, the stronger the alkalescence of imidazole derivatives, the easier the reaction of them. It was considered that alkalescence of 2-Methylimidazole was the strongest.

Lijuan *et al.* [14] found that the usages of pure polar polar solvents to extract acid were tremendously improved with the addition of Imidazole mixture. It was seen that the acid-removal rates of ethanol, *n*-propyl alcohol, *n*-butanol, and isopropanol were better with the Imidazole derivative solutions gave a larger increase to the acid-removal rates compared to the pure solvents.

Polar solvents that were selected have different alkyl alcohol carbon number. The increase of the alkyl alcohol carbon number would result in the mixture become more miscible. It is because alkyl alcohol with fewer carbon numbers had a stronger polarity and weak solubility in crude oil. The polarity of alcohol weakened with the carbon number increasing; therefore led to the decrease in the amount of oil that can be yield from the neutralization reaction as more oil solubilised in the reagents.

From the literature [14], it was found that by using Imidazole derivatives in Ethanol, it provides the highest oil yield rate from the neutralization reaction, with Acid Number of the crude sample is greatly reduced to almost below 0.001 AN.

2.7. Interfacial Rheological Properties

Wasan *et al.* [15] first studied the effect of alkaline materials on interfacial rheological properties of oil/water system. The rheological properties of a liquid are dominant features that can be quantified to characterize its behaviour, and the response of a liquid to a forced shearing flow is the basis for determining the specific rheological properties of a given liquid.

Interfacial viscosity significantly decreases in the presence of sodium hydroxide. Similarly, the rapid coalescence of oil droplets and poor stability of emulsions were traced back to ultra low interfacial viscosity. The phenomena were attributed to estherification and soapanifiation of natural surfactants adsorbed at the interface from the oil phase.

From the research, it was observed:

- Alkaline materials may decrease the interfacial viscosity by orders of magnitude and the average values are usually less than 0.1 Mn s/m. The greatest effect was found in the case of hydroxides, particularly sodium hydroxides.
- Effect of temperature on interfacial rheological properties is dominant only at low alkali concentrations and long contact times. But, at high alkali content and particularly at low shear rate, the effect of temperature is negligible.

From the research, it is explainable why alkali-containing systems readily from emulsions which then break also very rapidly indicating the instability of the emulsion. Apparently, what is often being reported in alkaline flooding experiments is that the in-situ formation of stable emulsion is not a contradiction to the findings from the research. These might the alkali concentration is too low (< 2% wt) or the dynamic force are high enough to re-emulsify permanently the liquid system thus leading to a better recovery through mobile emulsion of oil droplets. This could explain the improved recovery for low acid crude system.

2.8. Alcohol Formation in Crude Oil

Chemical reactions that occurred between the interactions of alkaline solution with acid components of crude oil may possibly generate other chemical residues beside soap or in situ surfactants.

Due to the presence of unstable hydroxide ion in the alkaline solution, theoretically, it could react with the carbon chain in the crude oil to formed alcohol. Catalyst for this reaction could be the high temperature and pressure along with Ca/Mg/Fe/Al elements coming from the rock minerals. The possibility of the generation of alcohol is due to the fact that chemical industry produced alcohol based on if not the same approach, with almost similar condition. Usually, preparation of alcohol is due to substitution reaction. Primary alkyl halides react with aqueous NaOH or KOH mainly to primary alcohols in Nucleophilic Aliphatic substitution.

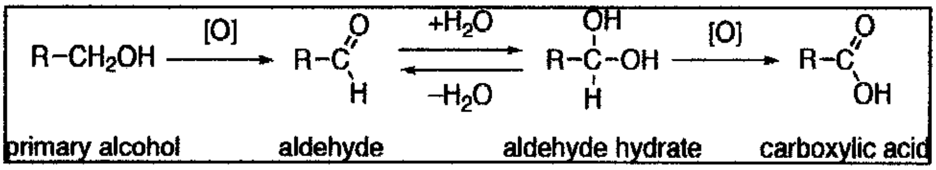


Figure 2: Oxidation of Alcohol to form Carboxylic Acid

Alcohol can be directly oxidized to form weak carboxylic acid. Potassium Permanganate is usually used as the reagents to promote the formation of the acid.

A reason why formation of alcohol is important in oil-water system is because it will promote ultra low IFT [2] as it increases the contact angle high enough to emulsify the oil droplets such that it will mobilize the residual oil.

2.9. Acid Number Definition

Total Acid Number (TAN) or **Acid Number (AN)** is the amount of potassium hydroxide in milligrams that is needed to neutralize the acids in one gram of oil. The acid number is a measure of the amount of carboxylic acid groups in a chemical compound, such as a fatty acid, or in a mixture of compounds. In a typical procedure, a known amount of sample dissolved in organic solvent is titrated with a solution of potassium hydroxide with known concentration and with phenolphthalein as a colour indicator.

Acid Number value can be deduced by a couple of different methods, commonly are potentiometric titrations or by colour indicator titration:

- **Potentiometric titration**: The sample is normally dissolved in Toluene and Propanol with a little water and titrated with alcoholic potassium hydroxide (if sample is acidic). A glass electrode and reference electrode is immersed in the sample and connected to a voltmeter/potentiometer. The meter reading (in mill volts) is plotted against the volume of titrant. The end point is taken at the distinct inflection of the resulting titration curve corresponding to the basic buffer solution.
- **Colour indicating titration**: An appropriate pH colour indicator e.g. phenolphthalein, is used. Titrant is added to the sample by means of a burette. The volume of titrant used to cause a permanent colour change in the sample is recorded and used to calculate the TAN value.

CHAPTER 3

3. RESEARCH METHODOLOGIES

Six main phases in the research work were completed: (1) Acid Number Measurement, (2) Acid Extraction, (3) Core Flooding, (4) Post-Flooding Evaluation, (5) IFT Measurement, and (6) Emulsion Stability Test.

3.1. Acid Number Measurement

The measurements (colour titration) were carried out with reference to American Standard Testing Measurement 974 (ASTM 974). The un-extracted crude and extracted crude for both Dulang and Waxy crude sample are measured using the method stated above.

Chemicals and Apparatus:

Erlenmeyer 250ml, Graduated Cylinder 100ml, Buret 5ml (0.01ml subdivision), Weighting Scale (accurate to 0.01g), Ethanol, Potassium Hydroxide (0.1M), Bromothymol Blue Indicator Solution.

Procedure:

- Alkaline solution was prepared by weighting out 0.1 mole of KOH (= 5.611 g), which later be dissolved it in water, and water was added to make the total volume equal to exactly 1 litre as it will give 0.1N KOH solution.
- Then 50 ml of ethanol denatured was added into a 250 ml Erlenmeyer flask. 3 to 4 drops of bromothymol blue indicator solution was mixed and titrated with 0.1N KOH aqueous solution.
- Accurately 60g of sample was weighted and mixed into neutralized ethanol. The sample was swirled completely until dissolved by the solvent with constant heat supplied at 40 °C.
- Then immediately it was titrated with 0.1N KOH aqueous solution at room temperature, using a 5 ml buret. The solution was stirred vigorously and the KOH aqueous solution was added along, dropwise when approaching the end point. By using a pH meter, the titration was stopped when the pH read zero, to indicate the solution had been neutralized completely.
- The volume of KOH required to neutralize the sample was recorded to calculate the acid number of the crude oil sample.

3.2. Acid Extraction and Neutralization

Two extraction methods were adopted as the first method that will be described below produced significant errors in the extraction process. Nevertheless, both methods will be discussed for research purposes.

Method I

Wang *et al.* [16] proposed a method to remove naphthenic acid in crude oil through reaction of an ammonia solution of ethylene glycol with the oil sample. It was reported almost 90% of the acid components can be removed through the reaction.

Chemicals and Apparatus:

Beaker, Three-neck flask, magnetic stirrer, electric stirrer, temperature controller.

Reagents: Ammonia Solution (25% v/v in water), Ethylene Glycol

Procedure:

- Solution consists of ammonia solution of 3 wt% with ethylene glycol was prepared by mixing it in a beaker, constantly stirred using magnetic stirrer.
- Then the oil sample was put into the three-neck flask with an electric stirrer and temperature controller.
- Constant stirring was employed during the extraction. Extraction temperature was in the range 50-60 °C, and the extraction time was after 30 minutes.
- After extraction, the mixture was put into a separating funnel for 1 hour at 70 °C to gravity separate the solvent with the acid compounds from the oil.
- Bottom of the funnel will be the ammonia solution of ethylene glycol and naphthenic acid ammonia salt, and at the top of the funnel is the de-acidified oil.

Method II

Lijuan *et al* [25] in her work, proposed a method to extract Naphthenic Acids from crude oil sample using Ionic Liquid as the medium of extraction. This method was adopted for this research it overcomes the problems in method I and the results obtained were up to satisfaction.

Chemicals and Apparatus:

Beaker, Conical Flask, Magnetic Stirrer, Thermometer, Separating Funnel + Ring-O holder

Reagents: 2-Ethylimidazole, Ethanol (99% Pure)

Procedure:

- 1 litre of Ethanol was measured and mixed together with 227.5 of 2-Ethylimidazole powder, and later dissolved it with Ethanol. Magnetic stirrer was used to stir the mixture together.
- 500g of crude oil sample was weighted. Then 200g of the reagent mixture is mixed with the crude sample in a 1L conical flask. This gave a ratio of reagent: oil to 0.4:1.
- During the extraction, it was heated at a constant 30°C and constantly stirred using magnetic stirrer. This process was conducted for 20 minutes.
- After the extraction, the mixture was put into a separating funnel for 30 minutes at room temperature to gravity separate the reagent with the acid compounds extracted from the crude oil.
- In the top of the funnel was the reagent with ionic liquid and in the bottom was mainly the de-acidified crude oil. The weight of the extracted crude oil should not be more than 500g to indicate that the reagent mixture had completely been separated

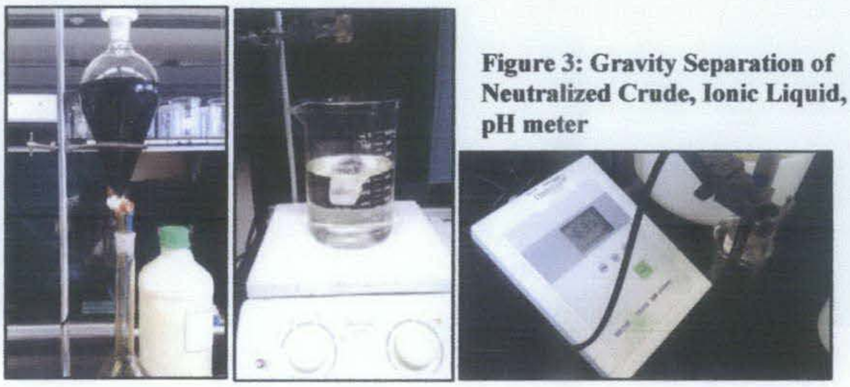


Figure 3: Gravity Separation of Neutralized Crude, Ionic Liquid, pH meter

3.3. Core Cleaning

Before displacement test can be carried out, the core samples were properly cleaned and saturated to ensure each runs are not affected by any impurities inside the core sample.

Chemicals and Apparatus:

Soxhlet Extractor

Toluene

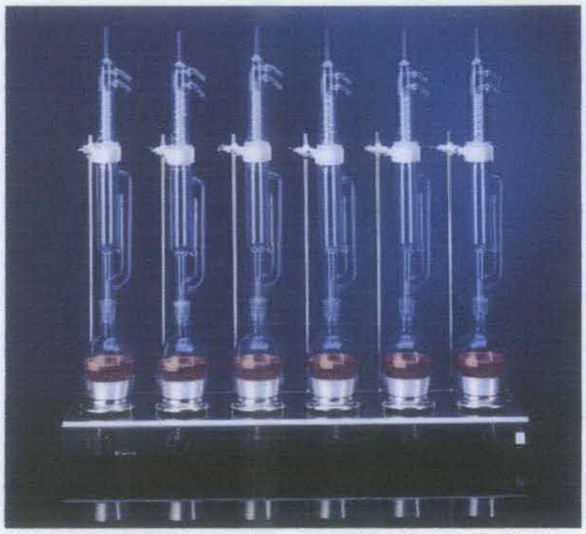


Figure 4: Soxhlet Extractor for Core Cleaning

Procedure:

- The Soxhlet distillation extraction method was used to dissolve and extract oil and brine from rock core sample by using solvents.
- The cleanliness of the sample was determined from the colour of the solvent that siphons periodically from the extractor which must be clear. The samples were placed in the extractor and cleaned by refluxing solvent.
- The solvent was heated and vaporized in boiling flasks and cooled at the top by condenser. The cooled solvent liquid falls into the sample chamber. The cleaned solvent fills the chamber and soaks the core sample.
- When the chamber is full, the dirty solvent which was used to clean the core siphons were absorbed back into the boiling flask and was redistilled.

3.4. Dry Core Properties

Chemicals and Apparatus:

Oven, Poro-Perm System

Nitrogen gas

Figure 5: Poro-Perm Measurement System

Procedure:

- After the cleaning process, the core samples were put into oven to dry any residues of toluene which might be entrapped in the pore spaces.
- Using Porosimeter, nitrogen gas was filled into the core chamber to completely saturate the sample.
- Using suitable confined pressure of 1200 Psia and setting up the pressure steps for reading purposes, stabilize air porosity and absolute permeability values were obtained.
- The permeability obtained are gas permeability, thus it was corrected using the built-in software to correct the values using Klikenberg correction method.

3.5. Core Flooding

Saturating the Core

Chemicals and Apparatus:

Relative Permeability System
Brine Water (5% wt NaCl), Crude Oil Sample, Alkaline Solution (2% wt NaOH)

Figure 6: Relative Permeability System

Procedure:

- The core samples underwent two saturating stages, firstly with normal brine water as pre-flush. The core permeability to brine was measured using a constant rate pump.
- Assuming the core is 100% saturated with water, initial volume of water should be equal to the pore volume.
- Then it was flooded again with crude oil until both samples were at the state of irreducible water saturation. Original oil in place was determined based on the amount of displaced water.
- Following this, the cores were aged for 24 hours. It was believed that this aging period was sufficient for the crude oil, brine, and core material to at least approach wetting equilibrium.

Flooding the Core

Procedure:

- After aging, brine of 5% Sodium Chloride content was used to flood and displaced the oil. The process was conducted until a stable residual oil was established. This is when only water is being produced at the outlet.
- Then continuously flooding of the alkaline solution to remove the residual oil. Volume of the additional oil produced was recorded.
- Incremental recoveries and end-points relative permeability of each runs were calculated for data discussions.

3.6. Post Flooding Evaluation

After each displacement run, the effluents from each runs were analyzed for alcohol formation, and the core properties were again measured to find any alterations that have been made to porosity and permeability.

3.6.1. Rock Properties

Alkaline solutions react with certain minerals in the rocks. The hydroxide ions in the alkaline solutions may react to dissolve the grains and form new minerals due to high temperature and pressure. This reaction may alter the physical properties of our reservoir rock in terms of porosity and absolute permeability.

The core samples were basically cleaned and dried using method described in 3.3 – 3.4. The new properties of each core samples were then compared against its initial properties.

3.6.2. Alcohol Traces Detection

Oxidation method was adopted to detect the alcohol formation. The oxidation process promoted the alcohol elements to form weak carboxylic acid in the effluents due to the chemical reactions which will be further described in the discussion sections.

Figure 7: pH meter for Basic-Acid Deflection

Five (5) gram of Potassium Permanganate (KMnO4) was mixed with the effluents sample to directly oxidized if any, alcohol elements in our solution through heating and constant stirring. pH of the solution was measured again to indicate if any acidic compounds has been formed due to the oxidization of the alcohol.

3.7. IFT Measurements

In determining the IFT reduction from various mixtures of components for the crude sample with alkaline solution, Sessile Drop Method is adopted using IFT 700 equipment.

Chemicals and Apparatus

IFT 700 Equipment
Dulang Crude Oil Sample, Alkaline Solution (2% wt NaOH), n-Heptane/ Oleic Acid/ Butanol (1 – 30% wt)

Figure 8: IFT 700 Systems

Procedure:

- Synthetic oils were prepared by mixing Dulang crude with different components (Butanol, n-Heptane, and Oleic Acid).
- The chamber cell where the mixed oil droplets with alkaline solution were cleaned to remove any impurities using a degreaser and air-blower.
- The cell was then pressurized to 1000 Psia at constant temperature of 70°C to resemble the core flooding conditions which were set in the previous experiments.
- A single Dulang crude oil droplet was formed in the pressure cell by carefully controlling the inlet/ outlet pressure of the oil tank. A microscope camera was used to capture the digital images of the oil droplets to ensure the oil droplet was stable.
- The chamber which was filled with the Dulang oil droplet was then filled with alkaline solution by slowly adjusting the inlet/ outlet pressure of alkaline tank.
- IFT was then measured once the systems were at equilibrium as alkaline made contact with the crude oil.
- The processes were repeated to measure IFT for every synthetic mixture being prepared.

3.8. Emulsion Stability Test

The stability of emulsion formed when different concentration of alkaline solutions mixed with Dulang crude were quantified based on the time taken for the two phases to separate after stirring and heating process.

Chemicals and Apparatus

Beaker, Magnetic Stirrer

Dulang Crude Oil Sample, Alkaline Solution

Procedure:

- Alkaline solution with different concentration Solution (1%, 5%, 10% wt NaOH) was mixed with the Dulang Crude oil
- Ratios of mixture of 40:60 with 40 % volume to alkaline, 60% volume to oil were used for every case.
- The mixtures were carefully stirred and heated until emulsions were formed for 30 minutes.
- After that, time was recorded to measure the time taken where the two phase to be separated again completely.
- The separation process was conducted at normal ambient condition (room temperature).

Figure 9: Emulsion Stability Measurement

3.9. Viscosity and Density Measurement

Basic properties of fluid being used in the displacement runs and IFT measurement are measured beforehand. Viscosities of each fluid were measured using Rolling Viscometer and density using Densitometer.

Viscosity Measurement

Chemicals and Apparatus

Rolling Viscometer

Crude Oil Sample, Alkaline Solution, Brine Water

Figure 10: Rolling Viscometer

Procedure:

- The equipment first was calibrated by rotating the visco-spindle filling normal tap water into the cup container. The spindle for measurement was tightened to ensure the rotations of needle were correctly in place.
- Sample to be measured were filled inside the container at the specific height before measurement.
- Measurements started using spindle Class-1 at RPM 100. Accuracy of measurement was based on calibration values displayed on the screen. Values above 20% were considered correct thus viscosity reading at that value were recorded.
- Multiple measurements were conducted using different needle class (Class-2 and Class-3) to ensure the viscosity values were correctly measured and to ensure consistencies in the reading were achieved.
- Highest calibration values were obtained if the right spindle class and the right RPM was used for measurement.

Density Measurement

Chemicals and Apparatus

Densitometer

Crude Oil Sample (Acidic, De-Acidified, Synthetic), Alkaline Solution

Figure 11: Densitometer System

Procedure:

- The desired fluid sample to be measured was injected slowly into the air tube.
- The fluid was injected continuously until the tube was full and no air bubble was formed between the fluid samples in the tube.
- Air bubble will affect the density measurement as it will give erroneous values.
- Once this was achieved, temperature of 70°C was set, and the tube was heated up until at a stabilized pre-set temperature.
- Then the option to start recording the density was selected. The equipment provided the density value once the reading had stabilized.

3.10. Tools, Materials, and Equipments

Below is the summary of the utilized chemicals and the equipments throughout the research work.

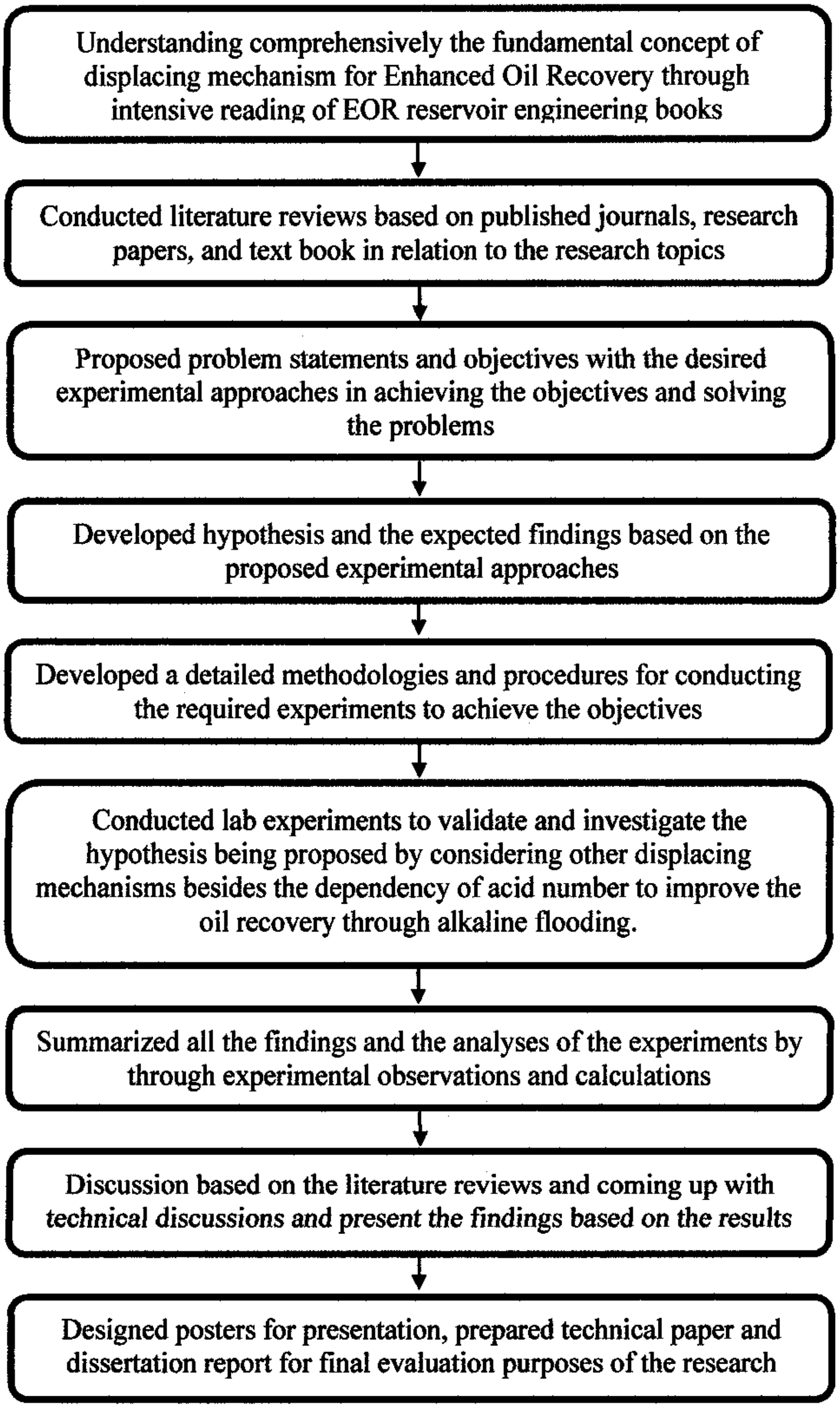
Chemicals/ Materials	Experiment
Dulang Crude Oil	Core Flooding/ IFT/ Emulsion Stability
Waxy Crude Oil	Core Flooding/ IFT
Sodium Hydroxide	Core Flooding/IFT/ Emulsion Stability
Sodium Chloride	Core Flooding
Potasium Permanganate	Alcohol Oxidation
2-Ethylimidazole	Neutralization of Acid
Ethanol	Neutralization of Acid/ Acid Number Measurement
Ethylene Glycol	Neutralization of Acid
Ammonium Solution	Neutralization of Acid
Bromothymol Blue Indicator Solution	Acid Number Measurement
Potassium Hydroxide	Acid Number Measurement
n-Heptanes	IFT Measurement
Butanol	IFT Measurement
Oleic Acid	IFT Measurement
Distilled Water	Core Treatment
Toluene	Core Treatment (Soxhlet Extractor)

Table 2: List of Chemicals

Main equipment used for each experimental work:

- Sohxlet Extractor
- Air Forced Drying Oven
- Interfacial Tension Meter
- PoroPerm System
- Relative Permeability Test System
- pH Meter / pH Indicator

3.11. Project Activities



Understanding comprehensively the fundamental concept of displacing mechanism for Enhanced Oil Recovery through intensive reading of EOR reservoir engineering books

Conducted literature reviews based on published journals, research papers, and text book in relation to the research topics

Proposed problem statements and objectives with the desired experimental approaches in achieving the objectives and solving the problems

Developed hypothesis and the expected findings based on the proposed experimental approaches

Developed a detailed methodologies and procedures for conducting the required experiments to achieve the objectives

Conducted lab experiments to validate and investigate the hypothesis being proposed by considering other displacing mechanisms besides the dependency of acid number to improve the oil recovery through alkaline flooding.

Summarized all the findings and the analyses of the experiments by through experimental observations and calculations

Discussion based on the literature reviews and coming up with *technical discussions and present the findings based on the results*

Designed posters for presentation, prepared technical paper and dissertation report for final evaluation purposes of the research

Figure 12: Completed project activities for the research work

Gantt charts are included in Appendix 1 and 2 for the detailed schedule of each experimental work.

CHAPTER 4

4. RESULTS AND DATA GATHERING

Below are the summaries of the results obtained from each experimental phases. Detailed results from each experiment are presented in the Appendix for references.

4.1. Table 3: Crude Oil Properties For Displacement Runs at 70°C

Crude Sample	Dulang	Dulang De-Acidified	Waxy	Waxy De-Acidified	Dulang Acid Added
Density (g/cc)	0.792	0.784	0.761	0.755	0.793
Specific Gravity (SG)	0.810	0.802	0.779	0.772	0.811
Viscosity (cP)	4.260	3.930	2.212	1.923	4.150
Acid Number (AN)	0.110	0.0012	0.0026	0.0013	1.21

4.2. Table 4: Acid Neutralization

		Before Extraction	After Extraction	Acid Removal Rate (%)	Added Acid
Dulang Crude	Acid Number	0.11	0.0012	98.9	1.21
	pH Value	6.34	7.14		5.81
Waxy Crude	Acid Number	0.0026	0.0013	50.0	
	pH Value	6.86	7.823		

4.3. Core Displacement Test

Injection Rate (ml/min)	
Alkaline Solution	0.5
Brine Water	1.0
Inlet Pressure (Psia)	1000
Core Temperature (Celcius)	70
Overburden Pressure (Psia)	1500

Table 5: Displacement Operating Conditions

	Water Flooding (%)	Alkaline Flooding (%)	Incremental Recovery (%)
Run 1 (Dulang)	**74.35**	**85.21**	**10.86**
Run 2 (Dulang De-Acidified)	**74.51**	**86.51**	**6.20**
Run 3(Waxy)	**76.70**	**83.70**	**7.00**
Run 4 (Waxy De-Acidified)	**78.69**	**83.33**	**4.61**
Run 5 (Dulang Acid Added)	**76.49**	**92.00**	**15.50**

Table 6: Recovery Calculation from Displacement Test

	Critical Water Saturation, Swc	Residual Oil from Waterflooding, Sor	End-point Water Relative Permeability Krw'	Residual Oil from Alkaline Flooding, Sor	End-point Alkaline Water Relative Permeability, Krwa'
Run 1 (Dulang)	0.286	0.231	0.255	0.122	0.153
Run 2 (Dulang De-Acidified)	0.275	0.255	0.32	0.193	0.152
Run 3 (Waxy)	0.273	0.233	0.542	0.163	0.431
Run 4 (Waxy De-Acidified)	0.283	0.213	0.492	0.167	0.322
Run 5 (Dulang Acid Added)	0.279	0. 235	0.287	0.080	0.212

Table 7: Relative Permeability End-Points

	Difference of End-Points Relative Permeability (%)	Mobility Ratio Water	Mobility Ratio Alkaline
Run 1 (Dulang)	40.00	1.0755	0.5387
Run 2 (Dulang De-Acidified)	52.50	1.2451	0.4937
Run 3 (Waxy)	20.48	1.1870	0.7879
Run 4 (Waxy De-Acidified)	34.55	0.9367	0.5117
Run 5 (Dulang Acid Added)	26.13	1.2247	0.7551

Table 8: Mobility Ratio of Water Flooding and Alkaline Flooding

4.4. Post Flooding Evaluation

		Porosity (%)	Difference %	Permeability (mD)	Difference %	Grain Volume (cc)
RUN 1	Before Displacement	18.37	+ 0.27	79.48	+ 10.30	68.31
	After Displacement	18.42		87.67		68.26
RUN 2	Before Displacement	18.38	+ 0.71	75.32	+ 13.13	68.29
	After Displacement	18.51		85.21		68.19
RUN 3	Before Displacement	18.33	+ 0.22	151.55	+ 2.42	69.77
	After Displacement	18.37		155.21		69.73
RUN 4	Before Displacement	18.37	+ 0.11	139.11	+ 0.22	69.73
	After Displacement	18.39		139.41		69.68
RUN 5	Before Displacement	18.35	+ 0.054	82.12	+ 4.14	68.32
	After Displacement	18.36		85.52		68.31

Table 9: Rock Properties Measurement

	Dulang	Dulang De-Acidified	Waxy	Waxy De-Acidified
pH Before	7.13	7.23	7.11	7. 23
pH After	6.73	6.68	6.43	6.52
ph Difference	0.4	0.55	0.68	0.71

Table 10: pH detection for alcohol traces from oxidation

4.5. Synthetic Oil Density at 70°C

Synthetic Mixture	Density (g/cc)	API
Crude + n-Heptanes (5%)	0.891	27.31
Crude + n-Heptanes (10%)	0.893	26.95
Crude + n-Heptanes (35%)	0.899	25.90
Crude + Alcohol (0.5%)	0.793	46.94
Crude + Alcohol (1%)	0.795	46.49
Crude + Alcohol (5%)	0.798	45.82
Crude + Oleic Acid (0.5%)	0.791	47.39
Crude + Oleic Acid (1%)	0.796	46.26
Crude + Oleic Acid (5%)	0.81	43.19

Table 11: Density Measurement for Synthetic Mixture

4.6. IFT Measurement

Solution	Added Synthetic Concentration (% wt)	IFT (Dynes/cm)
Alkaline + Crude Oil (Acidic)	2	2.24
Alkaline + Crude Oil (De-Acidified)	2	4.15
Alkaline + Crude Oil (Added n-Heptanes)	5	5.47
	10	7.05
	35	7.14
Butanol+ Alkaline + Crude Oil	0.5	1.45
	1	0.92
	5	0.14
Alkaline + Crude Oil (Oleic Acid Added)	1	4.89
	3	3.51
	5	0.24

Table 12: IFT Measurement for different synthetic Dulang crude oil mixture

4.7. Emulsion Stability Test

	Alkaline Concentration (% wt)	Time for Separation (Mins)
Dulang Crude	1	33.45
	2	31.12
	10	27.23

Table 13: Emulsion Stability Test by measuring the time taken for separation

CHAPTER 5

5. DATA ANALYSES AND DISCUSSIONS

5.1. Acid Neutralization

From Lijuan *et al.* [14], ionic liquids are used to remove the acid constituents as it overcomes the problems discussed in the literature review which happened when the first extraction method were tested. The ionic liquids that have larger polar differences with the crude oil can be quickly separated from crude oil. There is no water in this process; therefore, the emulsification problem associated with the common aqueous solution will be overcome.

Naphthenic acid is a weak acid; therefore, the stronger the alkalescence of Imidazole derivatives, the easier the reaction of them. Usages of pure polar polar solvents like Ethanol to extract acid were tremendously improved with the addition of Imidazole mixture to create the Ionic Liquid.

Dulang Crude achieved almost 95% acid removal rate whereas Waxy around 50% based on its Acid Number before and after extraction. Originally it was determined that Dulang initially had 0.11 AN and Waxy 0.0012 AN from ASTM 974 measurement procedures. After extraction, Dulang crude Acid Number goes down to 0.0012 AN, and Waxy to 0.0013 AN.

Difference in the acid removal rate depends on the original acid content of the crude. If the crude initially contains a reasonably high amount of acid constituents, there will be more neutralization from the alkaline-acid reaction, thus more acid is neutralized giving rise to removal rate.

5.2. Core Displacement Tests with Water and Alkaline Flooding

Before displacement tests were conducted, porosity and permeability of the cores along with the viscosity of the crude sample at flooding temperature were recorded as data input for the displacement runs.

From the 5 displacement runs that were conducted, the recovery factors are calculated based on the volume of crude oil that has been produced at the outlet of the core after water flooding and alkaline flooding. In general, recovery factor by water flooding for all cases are almost identical but Waxy Crude showed slightly higher recovery from water flooding.

This was mainly due to the viscosity of Waxy Crude (Acidic: 2.212 cP, De-Acidified: 1.923 cP), which was lower than Dulang Crude (Acidic: 4.26 cP, De-Acidified: 3.93 cP). Commonly in water flooding process, macroscopic displacement efficiency affects the recovery greater compared to microscopic efficiency. Mobility ratios for water flooding to displace Waxy Crude were slightly lower compared Dulang Crude based on the end-points of the relative permeability Krw@Sor and Kro@Swc. Assuming the viscosity is constant for the water and oil, the mobility ratio to displace Waxy Crude is around 0.95 – 1.187 whereas for Dulang Crude is around 1.08 – 1.245 for both before and after de-acidification process. This observation correlates with the definition of mobility ratio, the lower the mobility; the more stable the displacement process which prevents any viscous fingering affect that leads to a higher oil recovery. In water flooding, we are not concerned with the microscopic efficiency as the water does not alter the properties of the crude oil and the rock surfaces. However in any EOR application, both microscopic and macroscopic efficiency must be thoroughly analyzed to describe the displacement mechanism and to ensure a successful EOR application can be implemented.

As for alkaline flooding, overall the recovery is higher by 5-10% incremental compared to water flooding for all crude samples. Incremental recovery for Dulang Crude before acid removal showed higher recovery of 10.86% compared to De-Acidified Dulang Crude of which only 6.20%. Whereas for Waxy Crude, incremental recovery before acid removal showed higher recovery of 7.00% compared to De-Acidified Waxy Crude of which only 4.61%. From various studies of alkaline flooding, in-situ surfactant is generated by the reaction of alkaline elements with the acid constituents which leads to higher recovery based on principal displacement mechanism in alkaline flooding. However, as what being obtained from the displacement test, the difference in alkaline flooding recoveries for non-removed acid crude compared to De-acidified crude is not that much, and it is still acceptable. However for Dulang Added Acid sample which acid was added to crude to increase the Acid Number, the recovery is higher of 15.50% incremental compared to all other runs. This is actually prove that alkaline flooding performs best where there is significant acid constituents in the crude oil to have significant lowering of IFT, wettability alteration, and emulsification of the residual oil. But, as what being observed even in low acid number crude oil (less than 0.0015 AN) where there is almost non-existence of the acid components, the recovery is still up to satisfaction. Thus, this leads to further discussions on other displacement mechanism that leads to this phenomena based on the data gathered and experimental observation.

5.3. Macroscopic Displacement Efficiency

Macroscopic displacement efficiency is a measure of how well the displacing fluid has contacted the oil-bearing parts of the reservoir. In general, macroscopic displacement is affected by the following factors: properties of injected fluids, properties of displaced fluids, properties and geological characteristics of reservoir rock, and geometry of injection and production well pattern. In linear core displacement runs, the basis of explaining the efficiency will be more on the properties of the injected fluid and the reservoir rock, which in this case are the core samples

5.3.1. *End-Points Relative Permeability*

End-points relative permeability for water and oil, Krw@Sor and Kro@Swc are determined from the displacement test at terminal conditions. Residual oil saturation is when there is no more oil being displaced by either water of alkaline flooding. For all the displacement cases, the end-points for water relative permeability were reduced from 20 to 50% from its original value when alkaline flooding is implemented. This observation corresponds to lower residual oil value for alkaline flooding compared to water flooding.

Lower end-points relative permeability for alkaline solution indicates the flow favours the displacement of oil, as it reduced the by-passing of the displacing fluid which in this case the alkaline solution. In terms of wettability, this indicates that the core samples in alkaline flooding becomes more water-wet as the water prefers to adhere to the rock surfaces, higher resistance to flow which leads to the mobilization of residual oil which initially occupies the surfaces of the rock. Wettability alteration is due to the lowering of IFT from alcohol formation and in-situ surfactant formed, which mobilized the residual oil to form oil droplets which previously is wetting the rock surfaces.

5.3.2. *Improved Mobility Ratio*

The introduction of alkaline into water does not just increase the pH of the solution to 11-15 pH, but also gives a slight rise to the viscosity of the water from 1.00 cP to 1.21 cP, 21% increase.

Water Flooding (%)	Alkaline Flooding (%)	End-point Water Relative Permeability, Krw	End-point Alkaline Water Relative Permeability, Krwa	Mobility Ratio Water	Mobility Ratio Alkaline
74.35	85.21	0.255	0.153	1.0755	0.5387
74.51	80.71	0.32	0.152	1.2451	0.4937
76.7	83.7	0.542	0.431	1.1870	0.7879
78.69	83.33	0.492	0.322	0.9367	0.5117
76.49	92	0.287	0.212	1.2247	0.7551

Table 14: Recovery with end-points relative permeability and mobility ratio

As what being discussed previously in the case of mobility ratio for water flooding, with the reduction of end-points relative permeability and the increase of viscosity for the displacing fluids, the mobility ratio will be lowered. Mobility ratio for water flooding of all displacement cases showed a mobility of around 0.9 to 1.2 whereas for alkaline the mobility is reduced to a value of around 0.5 to 0.7, almost 20 to 50% reduction in mobility value. This leads to a better and stable sweeping efficiency as Mobility < 1 promotes a piston-like displacement to displace the oil in the reservoir.

5.3.3. *Rock Properties Alteration*

Porosity describes the pore spaces that are either inter-connected or isolated that can possibly stores hydrocarbon. Permeability which describes the ability for the fluid to flow, affects the recovery of oil as it governs the movement of the oil inside the rock. Alkaline flooding apparently altered the physical properties of the core in terms of porosity and absolute permeability as from the experiment it shows an increase in both properties. The dissolution of minerals had enlarged some of the pore spaces and throats, promoting better transmissibility for the fluid to flow between the pores spaces. An increment of 0.05 to 0.7% porosity and 0.2 to 13% permeability were observed for all the core properties after each displacement runs.

Alkaline solutions react with certain minerals in the rocks during displacements. The hydroxide ions in the alkaline solutions may have reacted to the grain surfaces to dissolve the grains and due to high temperature and pressure within the core samples and may have been flushed out by the displacing fluid along with the crude oil during displacements. . Due to equipment limitation, the actual amount of Ca^{2+}, Mg^{2+}, or any other minerals which is flushed and mixed together with the effluents cannot be determined. However, for future work it is recommended to analyse the composition of the effluents using any chemical reagents to force precipitation of these mineral ions to visible salt/ solid.

5.4. Microscopic Displacement Efficiency

5.4.1. *Lowering of Interfacial Tension (IFT)*

From Talash *et al.* [17], alkaline flooding has been well known to reduce IFT leading to a better oil recovery, and a behaviour model on the relative permeability curve due to IFT reduction and wettability changes. When the system's IFT is reduced to low or ultra-low, the curve tends to approach crossed lines of 45°. This means that the oil is mobilized due to emulsification or wettability alteration of the rock surface as the value of water saturation from intersection between the water and oil relative permeability curve will be more than 0.5 [17]; more water-wet.

However in low acid number crude oil, the dynamic behaviour of IFT reduction by the in-situ surfactant generated from the alkaline-acid reaction is not significant as shown from IFT reduction comparison between Dulang Crude and De-Acidified Dulang Crude, where it is 2.24 dynes/cm and the later to be 4.15 dynes/cm. This behaviour indicates that with low acid number, the surface activities between alkaline and solution is less thus leading to higher IFT compared to oil with higher acid number where the IFT is greatly reduced. Thus this leads to investigation if other surface additives were generated to reduce the IFT which does not depend on the alkaline-acid reaction.

It is well known that the addition of alcohol in the displacing fluid will promote the reduction of IFT which in turns mobilize the residual oil by forming emulsions [18]. However, adding alcohol in the displacing fluid involves higher cost, different operating procedures, and health concerns in actual process. Thus, this leads to the objectives to investigate if there is any in-situ formation of alcohol from alkaline flooding.

Due to the presence of unstable hydroxide ion in the alkaline solution, theoretically, it could react with the carbon chain in the crude oil (Alkanes) to formed alcohol components. Catalyst for this reaction could be the high temperature and pressure along with Ca/Mg/Fe/Al elements coming from the rock minerals. The possibility of the generation of alcohol is due to the fact that chemical industry produced alcohol based on if not the same phenomena, with almost similar condition with the temperature and pressure.

The effluents from displacement runs were tested for alcohol trace. The oxidation process of alcohol will lead to the formation of weak carboxylic acid. Effluents from the displacement runs initially have pH around 7.21 – 7.45, due to the fact some of the alkaline elements may have been miscible into the crude oil. After the oxidation process which involves the reaction of the crude oil with Potassium Permanganate (KMnO4), the pH is again measured for any deflection. From the 4 displacement runs, it had shown a slight lowering value of the pH to around 6.4 to 6.7, indicating a slightly acidic solution. Thus from these findings, there is possibility that in-situ alcohol elements had been formed.

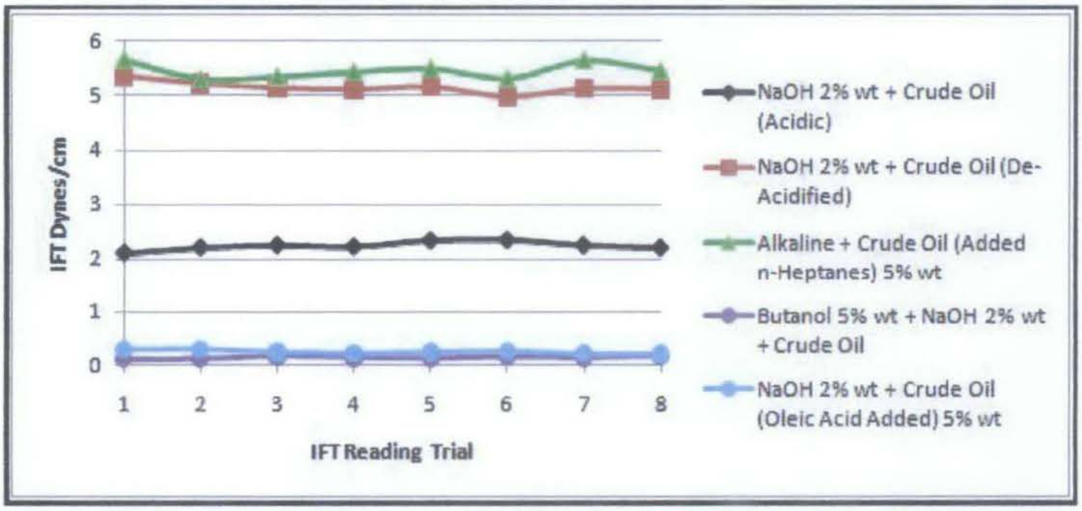


Figure 13: IFT Measurement for different Synthetic Oil mixtures

An additional test were conducted by creating synthetic mixture of Dulang Crude by mixing with Butanol, n-Heptane, and Oleic Acid. Referring to

Figure 13, when alcohol was mixed into the oil-water-alkaline system, the lowest IFT achieved was 0.14 dynes/cm at Butanol concentration of 5 wt%. It was observed that as we increased the amount of Butanol, the IFT is reduced further to ultra-low IFT (near to 0.01 dynes/cm). This prove the significance of the formation of in-situ alcohol in the oil-water reservoir system; alcohol reduce the IFT to mobilize the residual oil thus increase the recovery.

However, it was observed when the crude oil becomes heavier; the effect of IFT reduction becomes less. n-Heptane was used to represent the heavy components of the crude oil. At 35% wt of n-Heptane added to the crude oil, the IFT was at 7.15 dynes/cm, comparing to when at 5% of n-Heptane, the IFT was lower at 5.47 dynes/cm. Thus this shown that alkaline flooding might not be successful in reducing the IFT in crude oil with more heavier components in it.

5.4.2. *Higher Interfacial Viscosity (IFV)*

Wasan *et al.* [15] first studied the effect of alkaline materials on interfacial rheological properties of oil/water system. The rheological properties of a liquid are dominant features that can be quantified to characterize its behaviour, and the response of a liquid to a forced shearing flow is the basis for determining the specific rheological properties of a given liquid. In other words, it describes the stability of a fluid to be in continuous phase when external shear forces are applied. In our scenario, it describes the stability of emulsion being formed.

In actual, interfacial viscosity (IFV) significantly decreases in the increase of presence of sodium hydroxide. Similarly, the rapid coalescence of oil droplets and poor stability of emulsions were traced back to ultra low IFV.

However in cases where the alkaline concentration is low where in this case alkaline flooding having around 1 to 2 wt% alkaline concentration, the interfacial viscosity is still high enough to re-emulsify permanently the liquid system thus leading to a better recovery through continuous oil phase.

To quantify these, emulsion stability test were conducted by estimating the time taken for emulsion being formed to be separated when the alkaline concentration is steadily mixed with Dulang Crude at temperature of 70^{O}C. It was observed that at low concentration of alkaline at 1% wt, the time taken was around 33 minutes for both emulsion to be separated at room temperature and pressure. However as the concentration of alkaline increases at 10% wt, the time taken for the separation becomes shorter to around 27 minutes. This shows that at a very high concentration of alkaline (above 1% wt NaOH); the continuous oil phase in the emulsion is not that stable compared to lower concentration (below 1% wt NaOH). This could explain the increase in recovery of alkaline flooding for low acid number crude oil or even in high acid number crude oil. A continuous oil phase in the emulsion will promote greater recovery provided there is enough energy from behind the flooding front to push the mobilize oil to the production outlet. The stability of the emulsion formed does not depend on the acid number regardless if it is low or high, but instead depend on the concentration of alkaline used.

CHAPTER 6

6. CONCLUSIONS AND RECOMMENDATIONS

6.1. CONCLUSIONS

Incremental recovery from alkaline flooding in low acid number crude oil is not only due to of alkaline-acid reaction to generate in-situ surfactant, but also depends on other displacement mechanisms. To conclude the research work,

- End-points displacing fluid relative permeability is lowered indicating better displacement efficiency, delayed breakthrough, and better sweeping of the residual oil
- Dissolution of rock grain promotes higher rock absolute permeability, thus better fluid transmissibility between pore spaces for recovery
- Improved Mobility ratio as alkaline solution with higher viscosity (1.2 – 1.5 cP) than water (0.9 - 1 cP) produce a more stable displacement, thus reducing the affect of viscous fingering.
- Detection of in-situ formation of alcohol from alkaline flooding in the crude oil system lowers the interfacial tension (IFT) to around 0.01 – 0.14 dynes/cm helped to mobilize the residual oil.
- High interfacial viscosity (IFV) due to the low concentration of alkaline solution (1 – 2% wt NaOH) promotes a more stable emulsion to be formed thus further aid the increase in recovery.

6.2. RECOMMENDATIONS

The results from this research work can later be improved and expanded to better strengthen the findings and further justify the objectives that have been achieved.

- Core displacement test should be conducted in core samples where the native wettability and reservoir fluids are still intact and at its initial state to ensure the results are representative of the reservoir conditions.
- Wider range of crude oil with different properties, different alkaline types and concentration should be used in measuring the reduction of IFT and recoveries from displacement test so that results found from this research can be applied to various types of crude oil system.
- Specific equipments and new experimental design should be used to better prove the existence of alcohol and rock minerals in the effluents.

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APPENDIXES

Appendix 1: FYP 1 Gantt chart

No.	Activities	Week														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Selection of FYP topic		▨					**Mid-Semester Break**								**Final Examination Week**
2	Preliminary Research Work			▨	▨											
3	Preliminary Report Submission						🟥									
4	Literature Review				▨	▨	▨		▨							
5	Seminar 1 (Optional)					🟥										
6	Progress Report Submission									🟥						
7	Research Work Continues								▨	▨	▨	▨	▨			
8	Submission of Interim Report													🟥		
9	Oral Presentation														🟥	

Appendix 2: FYP II Gantt chart

No	Activities		Jan			Feb				Mar				Apr				May			
			2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
1	Chemical Solution Preparation		■									Progress Report		Pre-EDX (Poster & Final Report Draft Submission)	EDX	Oral Presentation	Final Report Submission	Hardbound Submission			
2	Acid Extraction & Acid Number Measurement			■																	
3	Core Preparation				■																
4	IFT Measurement									■	■										
5	Emulsion Stability Test												■								
6	Core Flooding & Effluents Testing	Dulang				■															
		Dulang De-Acidified					■														
		Waxy						■													
		Waxy De-Acidified							■												
		Dulang Acid Added								■											

Appendix 3: Initial Core Properties

Run 1 Core Name	K-4
Porosity (%)	18.37
Permeability (air,mD)	102.68
Permeability (infinite,mD)	79.48
Diameter, cm	3.81
Length, cm	7.33
Volume Bulk, cc	83.68
Volume Pore, cc	15.37
Volume Grain, cc	68.31
Grain Density, g/cc	2.55
Bulk Density, g/cc	2.08
Dry Weight, gm	174.36

Run 2 Core Name	K-4
Porosity (%)	18.38
Permeability (air,mD)	98.23
Permeability (infinite,mD)	75.32
Diameter, cm	3.81
Length, cm	7.33
Volume Bulk, cc	83.68
Volume Pore, cc	15.38
Volume Grain, cc	68.30
Grain Density, g/cc	2.55
Bulk Density, g/cc	2.08
Dry Weight, gm	174.36

Run 3 Core Name	K-2
Porosity (%)	18.33
Permeability (air,mD)	169.98
Permeability (infinite,mD)	151.55
Diameter, cm	3.80
Length, cm	7.52
Volume Bulk, cc	85.42
Volume Pore, cc	15.66
Volume Grain, cc	69.76
Grain Density, g/cc	2.55
Bulk Density, g/cc	2.09
Dry Weight, gm	178.12

Run 4 Core Name	K-2
Porosity (%)	18.37
Permeability (air,mD)	142.21
Permeability (infinite,mD)	139.11
Diameter, cm	3.80
Length, cm	7.52
Volume Bulk, cc	85.42
Volume Pore, cc	15.69
Volume Grain, cc	69.73
Grain Density, g/cc	2.55
Bulk Density, g/cc	2.09
Dry Weight, gm	178.12

Run 5 Core Name	K-3
Porosity (%)	18.35
Permeability (air,mD)	103.42
Permeability (infinite,mD)	82.12
Diameter, cm	7.34
Length, cm	83.72
Volume Bulk, cc	83.68
Volume Pore, cc	15.35
Volume Grain, cc	68.32
Grain Density, g/cc	2.55
Bulk Density, g/cc	2.08
Dry Weight, gm	174.36

Appendix 4: Saturation Volume

Run 1 (Dulang)	Original Water Saturation (PV)	15.367
	Oil-in-place (PV)	10.970
	Critical Water Saturation (PV)	4.397
Run 2 (Dulang De-Acidified)	Original Water Saturation (PV)	15.379
	Oil-in-place (PV)	11.150
	Critical Water Saturation (PV)	4.229
Run 3 (Waxy)	Original Water Saturation (PV)	15.656
	Oil-in-place (PV)	11.382
	Critical Water Saturation (PV)	4.274
Run 4 (Waxy De-Acidified)	Original Water Saturation (PV)	15.692
	Oil-in-place (PV)	11.251
	Critical Water Saturation (PV)	4.441
Run 5 (Dulang Added Acid)	Original Water Saturation (PV)	15.355
	Oil-in-place (PV)	11.078
	Critical Water Saturation (PV)	4.277

Appendix 5: Displacement Results

Run 1

Oil Saturate	Original Water Saturation (cc)	15.37
	Displaced Brine (cc)	16.00
	Corrected Brine (cc)	10.97
	Original-Oil-in-place (cc)	10.97
	Residual Water (cc)	4.40
	Oil Saturation, So (Ratio)	0.71
	Critical Water Saturation, Swc (Ratio)	0.29
Water Flooding	Displaced Oil (cc)	8.16
	Residual Oil (cc)	2.81
	Water Saturation (cc)	12.55
	Critical Oil Saturation, Sor (Ratio)	0.18
	Water Saturation, Sw (Ratio)	0.82
Alkaline Flooding	Oil in Place before Alkaline (cc)	2.81
	Additional Oil Displacement (cc)	1.19
	Residual Oil (cc)	1.62
	Critical Oil Saturation, Sor (Ratio)	0.11

Run 2

Oil Saturate	Original Water Saturation (cc)	15.38
	Displaced Brine (cc)	16.18
	Corrected Brine (cc)	11.15
	Original-Oil-in-place (cc)	11.15
	Residual Water (cc)	4.23
	Oil Saturation, So (Ratio)	0.73
	Critical Water Saturation, Swc (Ratio)	0.27
Water Flooding	Displaced Oil (cc)	8.31
	Residual Oil (cc)	2.84
	Water Saturation (cc)	12.54
	Critical Oil Saturation, Sor (Ratio)	0.18
	Water Saturation, Sw (Ratio)	0.82
Alkaline Flooding	Oil in Place before Alkaline (cc)	2.84
	Additional Oil Displacement (cc)	0.69
	Residual Oil (cc)	2.15
	Critical Oil Saturation, Sor (Ratio)	0.14

Run 3

Oil Saturate	Original Water Saturation (cc)	15.66
	Displaced Brine (cc)	16.41
	Corrected Brine (cc)	11.38
	Original-Oil-in-place (cc)	11.38
	Residual Water (cc)	4.27
	Oil Saturation, So (Ratio)	0.73
	Critical Water Saturation, Swc (Ratio)	0.27
Water Flooding	Displaced Oil (cc)	8.73
	Residual Oil (cc)	2.65
	Water Saturation (cc)	13.00
	Critical Oil Saturation, Sor (Ratio)	0.17
	Water Saturation, Sw (Ratio)	0.83
Alkaline Flooding	Oil in Place before Alkaline (cc)	2.65
	Additional Oil Displacement (cc)	0.80
	Residual Oil (cc)	1.86
	Critical Oil Saturation, Sor (Ratio)	0.12

Run 4

Oil Saturate	Original Water Saturation (cc)	15.69
	Displaced Brine (cc)	16.28
	Corrected Brine (cc)	11.25
	Original-Oil-in-place (cc)	11.25
	Residual Water (cc)	4.44
	Oil Saturation, So (Ratio)	0.72
	Critical Water Saturation, Swc (Ratio)	0.28
Water Flooding	Displaced Oil (cc)	8.85
	Residual Oil (cc)	2.40
	Water Saturation (cc)	13.29
	Critical Oil Saturation, Sor (Ratio)	0.15
	Water Saturation, Sw (Ratio)	0.85
Alkaline Flooding	Oil in Place before Alkaline (cc)	2.40
	Additional Oil Displacement (cc)	0.52
	Residual Oil (cc)	1.88
	Critical Oil Saturation, Sor (Ratio)	0.12

Run 5

Oil Saturate	Original Water Saturation (cc)	15.35
	Displaced Brine (cc)	16.11
	Corrected Brine (cc)	11.08
	Original-Oil-in-place (cc)	11.08
	Residual Water (cc)	4.28
	Oil Saturation, So (Ratio)	0.72
	Critical Water Saturation, Swc (Ratio)	0.28
Water Flooding	Displaced Oil (cc)	8.47
	Residual Oil (cc)	2.60
	Water Saturation (cc)	12.75
	Critical Oil Saturation, Sor (Ratio)	0.17
	Water Saturation, Sw (Ratio)	0.83
Alkaline Flooding	Oil in Place before Alkaline (cc)	2.60
	Additional Oil Displacement (cc)	1.72
	Residual Oil (cc)	0.89
	Critical Oil Saturation, Sor (Ratio)	0.06

***Corrected Brine represents the actual displaced brine from oil saturation processes; this is due to the reduction of the additional water which is previously occupying the outlet tubing, not the actual water being displaced.**

Appendix 6: End-Points Relative Permeability

Run 1: Dulang Crude
Water Flooding

Core Temperature	Inlet Pressure	Outlet Pressure	Delta Pressure		Overburden Pressure	End-Points Relative Permeability Water
Celcius	Psia	Psia	Psia	Atm	Psia	Ratio
70.62	1055.8485	1047.32	8.5285	0.5802	1796.8	0.2357
70.62	1017.2664	1006.3756	10.8908	0.7409	1780.3	0.1846
70.62	1016.6136	1008.9664	7.6472	0.5202	1777.12	0.2628
70.62	1025.0388	1019.51	5.5288	0.3761	1774.58	0.3635
70.62	1026.9768	1019.22	7.7568	0.5277	1773.31	0.2591
70.62	1030.2102	1020.21	10.0002	0.6803	1773.31	0.2010
70.62	1035.3918	1028.2	7.1918	0.4892	1772.68	0.2795
70.62	1037.9826	1022.32	15.6626	1.0655	1772.68	0.1283
70.62	1037.34	1022.32	15.02	1.0218	1772.68	0.1338
70.62	1042.5216	1033.2	9.3216	0.6341	1773.95	0.2156
70.62	1038.6354	1032.22	6.4154	0.4364	1774.58	0.3133
70.62	1018.5618	1011.32	7.2418	0.4926	1776.49	0.2775
70.94	1021.1526	1012.36	8.7926	0.5981	1777.76	0.2286
70.94	1012.7376	1004.4376	8.3	0.5646	1780.93	0.2422
70.94	1009.494	1000.26	9.234	0.6282	1782.84	0.2177
70.94	1010.1468	1001.32	8.8268	0.6005	1784.74	0.2277
70.94	1012.0848	1003.6348	8.45	0.5748	1786.64	0.2379
70.94	1012.7376	1005	7.7376	0.5264	1789.18	0.2598
70.94	1013.3802	1005	8.3802	0.5701	1792.36	0.2398
71.25	1014.6756	1011.5	3.1756	0.2160	1796.17	0.6329
71.25	1017.2664	1013	4.2664	0.2902	1798.07	0.4711
71.25	1017.909	1008.9	9.009	0.6129	1806.96	0.2231
71.25	1018.5618	1009	9.5618	0.6505	1809.5	0.2102
71.25	1018.5618	1009.3	9.2618	0.6301	1811.4	0.2170
71.25	1019.8572	1011.32	8.5372	0.5808	1813.94	0.2354
71.57	1021.1526	1010.5	10.6526	0.7247	1815.21	0.1887
71.25	1023.0906	1013.2	9.8906	0.6728	1820.29	0.2032
					Average Krw@Sor	0.2552

Run 1: Dulang Crude
Alkaline Flooding

Core Temperature	Inlet Pressure	Outlet Pressure	Delta Pressure		Overburden Pressure	End-Points Relative Permeability Water
Celcius	Psia	Psia	Psia	Atm	Psia	Ratio
70.62	1005.57	998.74	6.83	0.4646	1823.46	0.1763
70.62	997.32	989.22	8.1	0.5510	1821.56	0.1486
70.62	996.68	990.49	6.19	0.4211	1811.4	0.1945
70.62	1004.94	997.47	7.47	0.5082	1744.75	0.1612
70.62	1006.84	1000.01	6.83	0.4646	1732.69	0.1763
70.62	1010.01	1003.18	6.83	0.4646	1721.9	0.1763
70.62	1015.09	1008.26	6.83	0.4646	1716.18	0.1763
70.62	1017.63	1010.71	6.92	0.4707	1710.47	0.1740
70.62	1017	1008.21	8.79	0.5980	1705.39	0.1370
70.62	1022.08	1015.88	6.2	0.4218	1700.32	0.1942
70.62	1018.27	1011.44	6.83	0.4646	1694.6	0.1763
70.62	998.59	992.2	6.39	0.4347	1688.89	0.1884
70.94	1001.13	992.39	8.74	0.5946	1685.08	0.1378
70.94	992.88	983.67	9.21	0.6265	1684.45	0.1307
70.94	989.7	982.24	7.46	0.5075	1681.27	0.1614
70.94	990.34	980.87	9.47	0.6442	1680	0.1271
70.94	992.24	983.41	8.83	0.6007	1678.1	0.1363
70.94	992.88	983.45	9.43	0.6415	1678.1	0.1277
70.94	993.51	983.41	10.1	0.6871	1677.46	0.1192
71.25	994.78	985.31	9.47	0.6442	1676.83	0.1271
71.25	997.32	990.3	7.02	0.4776	1676.19	0.1715
71.25	997.95	989.22	8.73	0.5939	1676.19	0.1379
71.25	998.59	988.21	10.38	0.7061	1676.19	0.1160
71.25	998.59	988.49	10.1	0.6871	1676.19	0.1192
71.25	999.86	992.32	7.54	0.5129	1678.73	0.1597
71.57	1001.13	992.39	8.74	0.5946	1680	0.1378
71.25	1003.03	994.7	8.33	0.5667	1681.27	0.1445
					[redacted]	
					Average Krw@Sor	0.1531

Run 2: De-Acidified Dulang Crude
Water Flooding

Core Temperature	Inlet Pressure	Outlet Pressure	Delta Pressure		Overburden Pressure	End-Points Relative Permeability Water
Celcius	Psia	Psia	Psia	Atm	Psia	Ratio
70.62	1006.84	999.82	7.02	0.4776	1619.7	0.3003
70.62	1006.84	1000.09	6.75	0.4592	1636.84	0.3123
70.62	1006.84	1001.36	5.48	0.3728	1654.61	0.3847
70.62	1006.84	1000.32	6.52	0.4435	1673.65	0.3233
70.62	1006.21	999.32	6.89	0.4687	1686.35	0.3060
70.62	1001.13	995.21	5.92	0.4027	1700.95	0.3561
70.62	1005.57	999.21	6.36	0.4327	1716.82	0.3315
70.62	1008.11	1001.36	6.75	0.4592	1733.96	0.3123
70.62	1006.21	999.51	6.7	0.4558	1752.37	0.3146
70.62	1005.57	998.82	6.75	0.4592	1769.51	0.3123
70.62	1004.94	998.32	6.62	0.4503	1788.55	0.3184
70.62	1004.94	998.22	6.72	0.4571	1809.5	0.3137
70.94	1004.94	998.25	6.69	0.4551	1829.17	0.3151
70.94	1004.94	997.31	7.63	0.5190	1850.76	0.2763
70.94	932.57	925.87	6.7	0.4558	1873.61	0.3146
70.94	970.66	964.21	6.45	0.4388	1895.19	0.3268
70.94	1002.4	996.1	6.3	0.4286	1918.68	0.3346
70.94	1006.84	1000.09	6.75	0.4592	1942.16	0.3123
70.94	1006.21	999.51	6.7	0.4558	1967.56	0.3146
71.25	1006.21	1000.32	5.89	0.4007	1992.31	0.3579
71.25	938.28	932.21	6.07	0.4129	2018.34	0.3473
71.25	974.47	967.8	6.67	0.4537	2045.63	0.3161
71.25	1002.4	995.21	7.19	0.4891	2071.66	0.2932
71.25	1006.21	999.51	6.7	0.4558	2098.95	0.3146
71.25	1005.57	998.26	7.31	0.4973	2127.52	0.2884
71.57	1006.21	998.9	7.31	0.4973	2156.72	0.2884
71.25	1005.57	997.65	7.92	0.5388	2184.65	0.2662
					Average Krw@Sor	0.3167

Run 2: De-Acidified Dulang Crude
Alkaline Flooding

Core Temperature	Inlet Pressure	Outlet Pressure	Delta Pressure		Overburden Pressure	End-Points Relative Permeability Water
Celcius	Psia	Psia	Psia	Atm	Psia	Ratio
70.62	978.28	970	8.28	0.5633	1704.12	0.1525
70.62	978.28	970.62	7.66	0.5211	1706.03	0.1649
70.62	977.64	969.21	8.43	0.5735	1708.57	0.1498
70.62	978.28	969.82	8.46	0.5755	1709.84	0.1493
70.62	980.18	972.89	7.29	0.4959	1712.38	0.1732
70.62	981.45	972.91	8.54	0.5810	1714.28	0.1479
70.62	982.72	974.32	8.4	0.5714	1716.82	0.1503
70.62	982.72	974.21	8.51	0.5789	1718.72	0.1484
70.62	983.99	975.44	8.55	0.5816	1721.26	0.1477
70.62	982.72	974.36	8.36	0.5687	1724.44	0.1511
70.62	984.62	976.31	8.31	0.5653	1725.71	0.1520
70.62	986.53	979.21	7.32	0.4980	1728.25	0.1725
70.94	986.53	977.93	8.6	0.5850	1730.15	0.1468
70.94	986.53	978.02	8.51	0.5789	1732.69	0.1484
70.94	988.43	980.21	8.22	0.5592	1735.86	0.1536
70.94	989.07	981.26	7.81	0.5313	1737.13	0.1617
70.94	987.8	979.18	8.62	0.5864	1739.04	0.1465
70.94	988.43	979.84	8.59	0.5844	1741.58	0.1470
70.94	989.07	980.98	8.09	0.5503	1744.11	0.1561
71.25	989.7	981.09	8.61	0.5857	1746.02	0.1467
71.25	989.07	980.52	8.55	0.5816	1748.56	0.1477
71.25	990.34	982.23	8.11	0.5517	1750.46	0.1557
71.25	980.81	972.25	8.56	0.5823	1752.37	0.1475
71.25	981.45	973.12	8.33	0.5667	1754.27	0.1516
71.25	982.08	973.5	8.58	0.5837	1756.81	0.1472
71.57	977.64	969.04	8.6	0.5850	1758.71	0.1468
71.25	975.74	967.14	8.6	0.5850	1761.25	0.1468
					Average Krw@Sor	0.1522

Run 3: Waxy Crude
Water Flooding

Core Temperature	Inlet Pressure	Outlet Pressure	Delta Pressure		Overburden Pressure	End-Points Relative Permeability Water
Celcius	Psia	Psia	Psia	Atm	Psia	Ratio
70.62	1004.44	1002.5	1.94	0.1320	1694.6	0.5579
70.62	1004.44	1002.4	2.04	0.1388	1688.89	0.5306
70.62	1004.44	1002.9	1.54	0.1048	1685.08	0.7029
70.62	1004.44	1002.35	2.09	0.1422	1684.45	0.5179
70.62	1004.44	1002.36	2.08	0.1415	1681.27	0.5204
70.62	1004.44	1002.36	2.08	0.1415	1680	0.5204
70.62	1003.8	1001.7	2.1	0.1429	1678.1	0.5154
70.62	997.45	995.38	2.07	0.1408	1678.1	0.5229
70.62	1002.53	1000.43	2.1	0.1429	1006.34	0.5154
70.62	1004.44	1002.35	2.09	0.1422	1006.34	0.5179
70.62	1003.8	1001.74	2.06	0.1401	1006.34	0.5254
70.62	1002.53	1000.5	2.03	0.1381	1006.34	0.5332
70.94	1001.9	999.83	2.07	0.1408	1007.61	0.5229
70.94	1002.53	1000.47	2.06	0.1401	1003.8	0.5254
70.94	1001.9	999.81	2.09	0.1422	1003.8	0.5179
70.94	1001.9	999.82	2.08	0.1415	1004.44	0.5204
70.94	931.44	929.99	1.45	0.0986	1004.44	0.7465
70.94	968.89	966.82	2.07	0.1408	1005.07	0.5229
70.94	1001.26	999.19	2.07	0.1408	1005.07	0.5229
71.25	1004.44	1002.35	2.09	0.1422	1005.07	0.5179
71.25	1003.8	1001.75	2.05	0.1395	1005.07	0.5280
71.25	1003.8	1002.1	1.7	0.1156	1005.07	0.6367
71.25	937.15	935.07	2.08	0.1415	1005.07	0.5204
71.25	973.33	971.26	2.07	0.1408	1005.07	0.5229
71.25	1000.63	998.51	2.12	0.1442	1005.07	0.5106
71.57	1003.8	1001.73	2.07	0.1408	1005.71	0.5229
71.25	1002.53	1000.45	2.08	0.1415	1005.07	0.5204
					Average Krw@Sor	0.5422

Run 3: Waxy Crude
Alkaline Flooding

Core Temperature	Inlet Pressure	Outlet Pressure	Delta Pressure		Overburden Pressure	End-Points Relative Permeability Water
Celcius	Psia	Psia	Psia	Atm	Psia	Ratio
70.62	981.58	980.02	1.56	0.1061	1724.44	0.4156
70.62	982.22	980.73	1.49	0.1014	1725.71	0.4351
70.62	979.68	978.2	1.48	0.1007	1728.25	0.4381
70.62	981.58	980.1	1.48	0.1007	1730.15	0.4381
70.62	960.64	959.21	1.43	0.0973	1732.69	0.4534
70.62	970.16	968.21	1.95	0.1327	1735.86	0.3325
70.62	982.22	980.74	1.48	0.1007	1737.13	0.4381
70.62	983.49	981.78	1.71	0.1163	1739.04	0.3792
70.62	982.22	980.73	1.49	0.1014	1741.58	0.4351
70.62	982.22	980.71	1.51	0.1027	1744.11	0.4294
70.62	982.22	980.74	1.48	0.1007	1746.02	0.4381
70.62	984.76	983.25	1.51	0.1027	1748.56	0.4294
70.94	984.12	982.63	1.49	0.1014	1750.46	0.4351
70.94	980.31	978.81	1.5	0.1020	1752.37	0.4322
70.94	971.43	969.84	1.59	0.1082	1754.27	0.4078
70.94	951.75	950.42	1.33	0.0905	1756.81	0.4875
70.94	947.94	946.59	1.35	0.0918	1758.71	0.4803
70.94	941.59	940.1	1.49	0.1014	1761.25	0.4351
70.94	939.69	938.21	1.48	0.1007	1763.16	0.4381
71.25	935.88	934.37	1.51	0.1027	1765.7	0.4294
71.25	933.98	932.5	1.48	0.1007	1768.24	0.4381
71.25	932.71	931.22	1.49	0.1014	1769.51	0.4351
71.25	932.71	931.1	1.61	0.1095	1772.04	0.4027
71.25	933.34	931.85	1.49	0.1014	1773.95	0.4351
71.25	933.98	932.55	1.43	0.0973	1776.49	0.4534
71.57	935.25	933.76	1.49	0.1014	1778.39	0.4351
71.25	935.88	934.38	1.5	0.1020	1780.3	0.4322
					Average Krw@Sor	0.4311

Run 4: De-Acidified Waxy Crude
Water Flooding

Core Temperature	Inlet Pressure	Outlet Pressure	Delta Pressure		Overburden Pressure	End-Points Relative Permeability Water
Celcius	Psia	Psia	Psia	Atm	Psia	Ratio
70.62	1001.76	999.35	2.41	0.1639	1817.11	0.4893
70.62	1001.76	999.354	2.406	0.1637	1809.5	0.4901
70.62	1001.76	999.32	2.44	0.1660	1805.69	0.4833
70.62	1001.76	999.21	2.55	0.1735	1804.42	0.4624
70.62	1001.76	999.37	2.39	0.1626	1803.15	0.4934
70.62	1006.84	1004.43	2.41	0.1639	1801.88	0.4893
70.62	1006.84	1004.51	2.33	0.1585	1801.24	0.5061
70.62	1006.84	1004.45	2.39	0.1626	1801.24	0.4934
70.62	1008.11	1005.69	2.42	0.1646	1802.51	0.4873
70.62	1006.84	1004.49	2.35	0.1599	1802.51	0.5018
70.62	1006.84	1004.43	2.41	0.1639	1804.42	0.4893
70.62	1004.94	1002.55	2.39	0.1626	1804.42	0.4934
70.94	1006.84	1004.38	2.46	0.1673	1805.69	0.4793
70.94	1006.21	1003.82	2.39	0.1626	1808.23	0.4934
70.94	1006.21	1003.81	2.4	0.1633	1809.5	0.4913
70.94	1005.57	1003.2	2.37	0.1612	1811.4	0.4975
70.94	1005.57	1003.21	2.36	0.1605	1814.57	0.4997
70.94	1006.21	1003.84	2.37	0.1612	1816.48	0.4975
70.94	1005.57	1003.18	2.39	0.1626	1818.38	0.4934
71.25	1005.57	1003.17	2.4	0.1633	1820.29	0.4913
71.25	1005.57	1003.15	2.42	0.1646	1821.56	0.4873
71.25	1005.57	1003.13	2.44	0.1660	1822.83	0.4833
71.25	1005.57	1003.15	2.42	0.1646	1824.73	0.4873
71.25	1005.57	1003.19	2.38	0.1619	1826	0.4955
71.25	1005.57	1003.17	2.4	0.1633	1827.27	0.4913
71.57	1004.94	1002.56	2.38	0.1619	1829.17	0.4955
71.25	1005.57	1003.3	2.27	0.1544	1831.08	0.5195
					Average Krw@Sor	0.4919

Run 4: De-Acidified Waxy Crude
Alkaline Flooding

Core Temperature	Inlet Pressure	Outlet Pressure	Delta Pressure		Overburden Pressure	End-Points Relative Permeability Water
Celcius	Psia	Psia	Psia	Atm	Psia	Ratio
70.62	1004.3	1002.1	2.2	0.1497	1603.19	0.3211
70.62	1004.3	1002.21	2.09	0.1422	1601.92	0.3380
70.62	1004.3	1002.15	2.15	0.1463	1599.39	0.3285
70.62	1003.03	1000.84	2.19	0.1490	1596.85	0.3225
70.62	1004.3	1002.15	2.15	0.1463	1577.17	0.3285
70.62	1003.03	1000.81	2.22	0.1510	1586.06	0.3182
70.62	1003.03	1000.85	2.18	0.1483	1596.85	0.3240
70.62	1003.03	1000.81	2.22	0.1510	1601.29	0.3182
70.62	1003.03	1000.85	2.18	0.1483	1603.19	0.3240
70.62	1001.76	999.54	2.22	0.1510	1603.19	0.3182
70.62	997.95	995.73	2.22	0.1510	1601.92	0.3182
70.62	1001.13	998.91	2.22	0.1510	1684.45	0.3182
70.94	1001.76	999.56	2.2	0.1497	1685.72	0.3211
70.94	1001.76	999.32	2.44	0.1660	1686.35	0.2895
70.94	1002.4	1000.19	2.21	0.1503	1567.65	0.3196
70.94	1002.4	1000.42	1.98	0.1347	1584.15	0.3567
70.94	1001.76	999.68	2.08	0.1415	1600.66	0.3396
70.94	1001.76	999.54	2.22	0.1510	1619.7	0.3182
70.94	1002.4	1000.16	2.24	0.1524	1636.84	0.3153
71.25	1002.4	1000.19	2.21	0.1503	1654.61	0.3196
71.25	1002.4	1000.24	2.16	0.1469	1673.65	0.3270
71.25	997.95	995.78	2.17	0.1476	1678.1	0.3255
71.25	998.59	996.32	2.27	0.1544	1677.46	0.3112
71.25	999.86	997.65	2.21	0.1503	1676.83	0.3196
71.25	999.86	997.52	2.34	0.1592	1676.19	0.3019
71.57	999.86	997.15	2.71	0.1844	1676.19	0.2606
71.25	1001.76	999.56	2.2	0.1497	1676.19	0.3211
					Average Krw@Sor	0.3194

Run 5: Dulang Acid Added Crude
Water Flooding

Core Temperature	Inlet Pressure	Outlet Pressure	Delta Pressure		Overburden Pressure	End-Points Relative Permeability Water
Celcius	Psia	Psia	Psia	Atm	Psia	Ratio
70.62	1006.84	999.81	7.03	0.4782	1701.163	0.2841
70.62	1006.84	999.83	7.01	0.4769	1717.033	0.2850
70.62	1008.11	1001.04	7.07	0.4810	1734.173	0.2825
70.62	1006.84	999.85	6.99	0.4755	1752.583	0.2858
70.62	1006.84	999.81	7.03	0.4782	1769.723	0.2841
70.62	1004.94	997.91	7.03	0.4782	1788.763	0.2841
70.62	1006.84	999.84	7	0.4762	1809.713	0.2854
70.62	1006.21	999.19	7.02	0.4776	1829.383	0.2845
70.62	1006.21	999.13	7.08	0.4816	1850.973	0.2821
70.62	1005.57	998.53	7.04	0.4789	1873.823	0.2837
70.62	1005.57	998.5	7.07	0.4810	1895.403	0.2825
70.62	1006.21	999.23	6.98	0.4748	1918.893	0.2862
70.94	1005.57	998.55	7.02	0.4776	1942.373	0.2845
70.94	1005.57	997.91	7.66	0.5211	1935.393	0.2608
70.94	1005.57	998.32	7.25	0.4932	1857.313	0.2755
70.94	1005.57	998.56	7.01	0.4769	1766.543	0.2850
70.94	1005.57	998.59	6.98	0.4748	1686.563	0.2862
70.94	1005.57	998.51	7.06	0.4803	1613.563	0.2829
70.94	1005.57	998.54	7.03	0.4782	1552.623	0.2841
71.25	1004.94	997.92	7.02	0.4776	1557.073	0.2845
71.25	1005.57	998.14	7.43	0.5054	1567.863	0.2688
71.25	1004.94	998.32	6.62	0.4503	1577.383	0.3017
71.25	1004.94	998.23	6.71	0.4565	1586.273	0.2977
71.25	1001.76	995.36	6.4	0.4354	1597.063	0.3121
71.25	1004.3	997.27	7.03	0.4782	1601.503	0.2841
71.57	1004.94	999.32	5.62	0.3823	1603.403	0.3554
71.25	1004.3	997.27	7.03	0.4782	1850.76	0.2841
					Average Krw@Sor	0.2873

Run 5: Dulang Acid Added Crude
Alkaline Flooding

Core Temperature	Inlet Pressure	Outlet Pressure	Delta Pressure		Overburden Pressure	End-Points Relative Permeability Water
Celcius	Psia	Psia	Psia	Atm	Psia	Ratio
70.62	966.765	961.12	5.645	0.3840	1798.71	0.2120
70.62	966.765	961.14	5.625	0.3827	1801.24	0.2127
70.62	968.035	962.41	5.625	0.3827	1803.15	0.2127
70.62	967.94	962.31	5.63	0.3830	1805.05	0.2125
70.62	967.94	962.315	5.625	0.3827	1806.32	0.2127
70.62	967.94	962.295	5.645	0.3840	1884.645	0.2120
70.62	967.94	962.15	5.79	0.3939	1887.312	0.2067
70.62	968.035	962.41	5.625	0.3827	1888.6455	0.2127
70.62	968.035	962.38	5.655	0.3847	1891.302	0.2116
70.62	968.035	962.39	5.645	0.3840	1893.3075	0.2120
70.62	969.52	962.15	7.37	0.5014	1895.3025	0.1624
70.62	970.16	964.12	6.04	0.4109	1788.55	0.1981
70.94	970.16	964.555	5.605	0.3813	1791.09	0.2135
70.94	969.52	965.25	4.27	0.2905	1793.63	0.2802
70.94	1003.03	997.395	5.635	0.3833	1794.9	0.2123
70.94	1004.3	998.621	5.679	0.3863	1797.44	0.2107
70.94	1003.03	997.371	5.659	0.3850	1798.71	0.2114
70.94	1003.03	997.22	5.81	0.3952	1801.24	0.2059
70.94	1003.03	997.391	5.639	0.3836	1803.15	0.2122
71.25	1005.57	999.93	5.64	0.3837	1805.05	0.2122
71.25	1005.57	999.91	5.66	0.3850	1806.32	0.2114
71.25	1005.57	999.845	5.725	0.3895	1808.86	0.2090
71.25	1004.94	999.293	5.647	0.3841	1810.77	0.2119
71.25	1005.57	999.931	5.639	0.3836	1812.67	0.2122
71.25	1004.94	999.301	5.639	0.3836	1857.1	0.2122
71.57	1004.94	999.295	5.645	0.3840	1858.37	0.2120
71.25	1001.76	996.515	5.245	0.3568	1862.82	0.2281

Average Krw@Sor	0.2123

Appendix 7: Density of Synthetic Mixtures

Synthetic Mixture	Density (g/cc)	API
Crude + n-Heptanes (5%)	0.891	27.31
Crude + n-Heptanes (10%)	0.893	26.95
Crude + n-Heptanes (35%)	0.899	25.90
Crude + Alcohol (0.5%)	0.793	46.94
Crude + Alcohol (1%)	0.795	46.49
Crude + Alcohol (5%)	0.798	45.82
Crude + Oleic Acid (0.5%)	0.791	47.39
Crude + Oleic Acid (1%)	0.796	46.26
Crude + Oleic Acid (5%)	0.81	43.19

Appendix 8: IFT Measurements

Solution	Concentration (% wt)	IFT Reading Trial								Average
		1	2	3	4	5	6	7	8	
Alkaline + Crude Oil (Acidic)	2	2.11	2.21	2.25	2.23	2.34	2.35	2.25	2.21	2.244
Alkaline + Crude Oil (De-Acidified)	2	5.35	5.22	5.14	5.11	5.16	4.98	5.13	5.12	5.151
Alkaline + Crude Oil (Added n-Heptanes)	5	5.67	5.32	5.36	5.45	5.51	5.33	5.66	5.47	5.471
	10	6.96	7.02	7.06	7.11	7.12	6.93	7.04	7.13	7.046
	35	7.24	7.11	7.32	7.01	7.22	7.15	7.05	7.03	7.141
Alcohol + Alkaline + Crude Oil	0.5	1.32	1.45	1.55	1.52	1.34	1.41	1.57	1.45	1.451
	1	1.01	0.99	0.88	1.01	0.92	0.87	0.85	0.84	0.921
	5	0.11	0.12	0.16	0.14	0.13	0.15	0.14	0.16	0.139
Alkaline + Crude Oil (Oleic Acid Added)	1	4.85	4.89	4.87	4.81	4.82	4.99	4.92	4.99	4.893
	3	3.56	3.42	3.31	3.22	3.75	3.6	3.55	3.73	3.518
	5	0.29	0.3	0.24	0.22	0.24	0.25	0.21	0.2	0.244

Appendix 9: Sample Calculations

End-Points Relative Permeability

General Darcy Law Equation in SI units,

$$q = \frac{kA}{\mu}\frac{dP}{dX}$$

Q = Fluid flow rate (cm3/s)

K = Absolute permeability (Darcy)

A = Core area (cm2)

μ = Viscosity (Cp)

dP = Pressure Difference, Pinlet – Poutlet (Atm)

dX = Core length between inlet to outlet point (cm)

Incorporating relative permeability for water displacement in oil,

$$q_w = \frac{kk_{rw}A}{\mu_w}\frac{dP}{L}$$

Rearranging the whole equation in terms of relative permeability to water,

$$k_{rw} = \frac{q_w \mu_w L}{kAdP}$$

In the displacement experiments, once residual oil is established prior to water flooding or alkaline flooding, flow rate at the outlet is measured to ensure a near steady –state condition is achieved.

This is obtained once,

$$q_{injectedfluid@inlet} = q_{producedfluid@outlet}$$

This is vital in ensuring the equation for relative permeability derived from Darcy Law valid, as it requires a steady-state, isothermal, incompressible, laminar flow.

For example, calculation is performed to calculate the end-points water relative permeability, Krw' for Run 1 (Dulang Crude) for waterflooding

Results recorded:

Inlet Pressure (Psia) = 1055.85
Outlet Pressure (Psia) = 1047.32
Delta Pressure (Psia) = 8.53 In (Atm) = 0.5802
Absolute Permeability (D) = 0.079
Qinjectedwater (ml/s) = 0.017
Core Area (cm2) = 11.42
Core Length (cm) = 7.328
Viscosity of Water (cP) = 1.01
(Data taken from the first row from page 46)

$$K_{rw}{}' = \frac{q_w \mu_w L}{kAdP} = \frac{(0.017)(1.01)(7.328)}{(0.079)(11.42)(0.5802)} = 0.2357$$

To calculate mobility ratio knowing the end-points:

Krw' = 0.2357
Kro' = 1 (assume 1 as at residual water, only oil flow, thus relative permeability to oil is 1)
$\mu_w = 1.01$
$\mu_o = 4.26$
Thus,

$$M = \frac{krw/\mu_w}{kro/\mu_o} = \frac{0.2357/1.01}{1/4.26} = 0.9941$$

This procedure is applied to all the displacement runs to calculate the end-points relative permeability of either water or alkaline flooding.

Appendix 10: Summary of Chemical Reactions

Caustic Consumption Reactions [1]

Alkali – water reactions	$Ca^{2+} + 2OH^{-} \rightarrow Ca(OH)_2$ $Mg^{2+} + 2OH^{-} \rightarrow Mg(OH)_2$ $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$ $Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3$ $Ca^{2+} + H_2SiO_4^{2} \rightarrow CaH_3SiO_4$
Alkali – oil reactions	$HA_O \leftrightarrow HA_W$ $HA_W \leftrightarrow H_3O^{+} + A^{-}$ $Na^{+} + A^{-} \leftrightarrow NaA_W$ $NaA_W \leftrightarrow NaA_O$
Alkali – rock reactions	Ion exchange (a) $MH + Na^{+} \leftrightarrow MNa + H^{+}$ (b) $M_2Ca + 2Na^{+} \leftrightarrow 2MNa + Ca^{2+}$ Congruent dissolution: $SiO_2(s) + H_2O \leftrightarrow Si(OH)_4$ Incongruent dissolution $CaSO_4(s) + 2NaOH \leftrightarrow Ca(OH)_2(s) + Na_2SO_4$