

**ALCOHOL AS AN ADDITIVE TO INCREASE CO₂ AND
CRUDE OIL MISCIBILITY**

By

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DISSERTATION

**Submitted to Petroleum Engineering Programme in Partial Fulfillment of the
Requirements for the Degree Bachelor of Engineering (Hons)**

(Petroleum Engineering)

Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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**A project dissertation submitted to the
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Universiti Teknologi PETRONAS
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(Petroleum Engineering)**

Approved,



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May 2011

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

Alcohol as a solvent can reduce minimum miscibility pressure (MMP) of CO₂ flooding for enhanced oil recovery (EOR). CO₂ is not feasible for high temperature and waxy reservoir. The objective of this study is to solve the problem by using alcohol in order to reduce minimum miscibility pressure between CO₂ and crude oil. In this research, the author used benzyl alcohol, branched alcohol and normal alcohol. Although alcohol is often used as a co-surfactant and only a small amount is needed, but alcohol can be used as the main IFT reducing agent if it can be produced cheaply. Alcohol enhances the solvating power and polarity of carbon dioxide in crude oil. In this project, an attempt had been done by using four types of alcohol which are phenol, 2-methyl-2-butanol, 2-methyl-1-butanol and 2-butanol. The alcohols were tested on Dulang crude oil at 60 °C in order to see the effect of branching, cyclic and straight chain alcohol on solubility of CO₂ into crude oil. Vanishing interfacial tension method is used to obtain MMP. All alcohols had been tested and the results showed that branched alcohol is a very good MMP reduction agent compared to benzyl and normal alcohol. The branched alcohol reduced MMP up to 23%. Optimum concentration is being tested for branched alcohols. The optimum concentration was 50% pore volume for pressure at 1500 psi. Branched alcohol is efficient in lowering the MMP and should be considered in EOR.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Multicontact miscible displacement process is becoming increasingly popular in enhance oil recovery method. In a miscible flooding operation, a solvent is injected into the reservoir to form a single phase solution with the oil in place so that the oil can be removed as a more highly mobile phase from the reservoir ^[1]. Carbon dioxide is a multiple contact miscible solvent which forms a single phase only after a period of time when the first carbon dioxide extracts the light hydrocarbon containing from 2 to 6 carbon atom from the crude oil. The single phase solution is able to dissolve other heavier hydrocarbon C₆+ and progressively enters the solution to form a desired new single phase solution which is then carried forward through the reservoir. As the flooding front advances through the reservoir, the composition of the displaced fluid gradually changes from crude oil to pure carbon dioxide. Multiple contact miscibility is a function of the reservoir pressure and minimum pressure required to achieve multiple contact miscibility is called minimum miscibility pressure (MMP). Estimate minimum miscibility pressure (MMP) CO₂ for Malaysia crude is in the range of 2300 to 4380 psig ^[22]. Alcohol is semi polar, where it has polar and non polar part ^[16]. Oil and CO₂ are essentially non polar and will mix with the non-polar part of alcohol molecules. The OH of the alcohol molecule does not bond much with oil and CO₂. The OH dissolves in CO₂ and oil will form specific solvent–solute interactions. When alcohol injected with carbon dioxide it lowered the MMP of CO₂ with crude oil. This is because when oil is added to alcohol, it will enhance the solvating power and polarity of

CO₂ caused by the formation of special interaction between solute and co-solvent molecule ^[11].

1.2 Problem Statement

1.2.1 The current CO₂ miscible injection problem

CO₂ lacks polarity and the capacity to form specific solvent-solute interactions in order to be miscible. Therefore, there is a great incentive to improve its polarity, and it has been found that the addition of a small amount of suitable co-solvent can greatly enhance its solvent power by using alcohol ^[16].

1.2.2 Problem Identification

In order to identify the high MMP between CO₂ and crude oil, MMP is measured by using IFT 700 equipment. For MMP which have greater pressure than 2000 psi, it is considered as high. The experiment is designed to observe the difference between cyclic, branched and straight alcohol effect to MMP. Two branched alcohols were used because the author wanted to test the effect on MMP when the polarity is varied. The highest polar alcohol is expected to give the lowest MMP. When alcohol injected along with carbon dioxide, alcohol lowers the MMP between CO₂ and crude oil composition in reservoir ^[11].

1.2.3 Significance of Project

This project is significant to improve the current miscible CO₂ injection by lowering the minimum miscibility pressure. The experimental results can be used for further study in choosing more effective alcohol.

1.3 Objectives

- **To determine the best alcohol in reducing MMP using vanishing interfacial method**

Alcohol will lower the IFT between CO₂ and crude oil. The decrease in IFT will give lower MMP reading. In the experiment, the author used straight, benzyl and branched alcohols.

- **To find the optimum concentration of alcohol in order to reduce the MMP**

Different concentrations of alcohol will give different IFT readings. In the experiment, the author compared the MMP with different concentration

- **To check alcohol concentration with relation to crude oil viscosity**

Alcohol will cause the reduction in viscosity of the crude oil because alcohol has lower viscosity.

1.4 Scope of Study

Throughout this project, the scope of study includes:

phenol, 2methyl2butanol, 2methyl1butanol and 2butanol are measured for MMP, IFT at different concentration and viscosity.

1.4.1 The Relevancy of Project

Malaysia field is currently in period of tertiary recovery where injecting CO₂ is an option as a method of EOR. Miscible CO₂ injection is suitable for Malaysian reservoir but it could not be achieved. This research could provide a way for MMP to be achieved in lower pressure by using alcohol as an additive ^[22].

1.4.2 Feasibility of the Project within the Scope and Time frame

The project is done by using four different types of alcohol which are 2-butanol, 2-methyl-2-butanol, 2-methyl-1-butanol and phenol. All objectives had been achieved within the time frame that was given. More alcohols could be used if the time frame is wider.

CHAPTER 2

LITERATURE REVIEW / THEORY

2.1 Type of surfactants

Generally, there are four types of surfactant based on its molecules active site. The types are:

- Anionic
- Non-ionic
- Cationic
- Zwitterionic

2.1.1 Non-ionic surfactants

The characteristic of non-ionic surfactant is the surface active portion allows no apparent ionic charge. The hydrophilic group is non-dissociable such as alcohol, phenol ether, ester or amide.

2.2 CO₂ miscible flooding

The solubility of CO₂ in oil is a function of oil properties, pressure and temperature. Some light oils thermodynamic miscibility can be achieved at pressure of 2000 to 3000 psi. This is around 700 to 1400 psi less pressure in the case of high pressure gas injection. Miscibility pressure can never be reached with viscous oil. CO₂ dissolves in the oil has a direct effect on the

properties of the mixture and the viscosity reduction will give benefits.

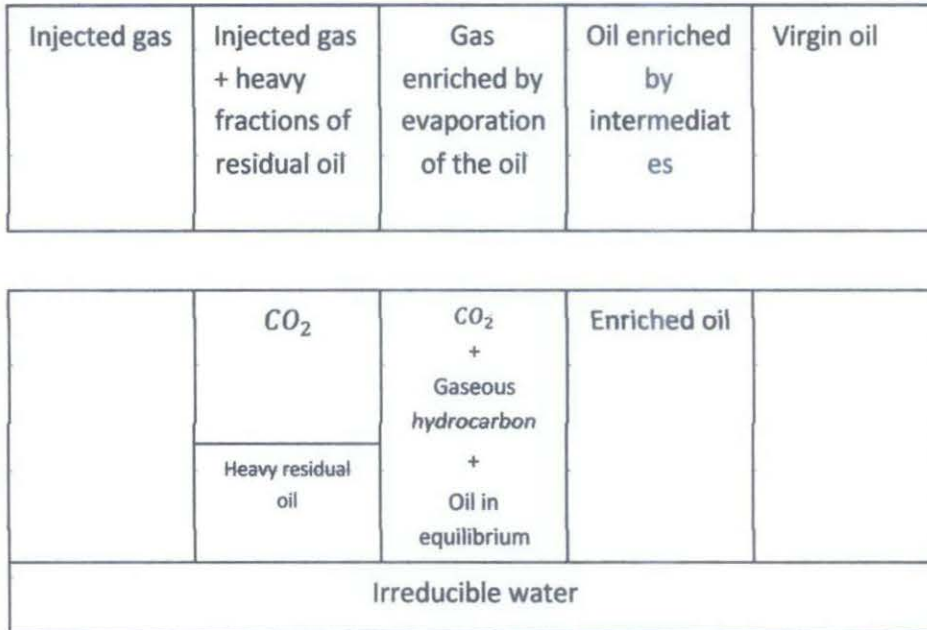


Figure 1: CO₂ miscible diagram [8]

a) Formation of the miscible bank

During displacement of the CO₂ within the porous medium there is a large contact area between gas and oil. A rapid mass transfer between the oil and the CO₂ takes place.

The frontal part of the mixing zone becomes progressively richer in light hydrocarbon fractions. If the oil contains a significant quantity of methane, it may be extracted from the oil and travel just ahead of the CO₂ front. The formation of the methane bank between the oil and the CO₂ saturated zone is observed when the injection pressure is lower than the miscibility pressure of methane.

In the mixing zone, the intermediate and CO₂ made the oil significantly lighter. The oil becomes progressively heavier behind the CO₂ front and has lower mobility due to the loss of its entire light component.

2.2.1 Use of surfactant to reduce CO₂ mobility in oil displacement

At reservoir conditions, carbon dioxide exists in critical state as a very dense fluid where the viscosity is about 1/8 of crude oil viscosity. Generally, this unfavourable viscosity and mobility produce inefficient oil displacement. This study shows that surfactant reduces CO₂ mobility and should improve oil displacement by using CO₂. Presumably by reducing flow through the most permeable zone, it increases the areal and vertical sweep efficiencies.

Based on study, using all three classes of surfactant (anionic, cationic and non-ionic) are very stable under conditions encountered during CO₂ flood in lime stones formation. Surfactant generates foams or emulsions with CO₂ at reservoir conditions (1000 to 3000 psi and 135 F) will reduce CO₂ flow through sandstone and carbonate core.^[12]

Preferably about 1% to about 4% by weight, of polar alcohol or polar glycol to carbon dioxide increases the viscosity of the carbon dioxide mixture. The mixture is injected at supercritical pressure and temperature (31 C and 72.9 atmospheres).^[15]

Foam potentially presents more efficient method of reducing CO₂ mobility. The inherent advantage of foam over water for mobility improvement is that foam is 85% to 95% gas, which means that a relatively small amount of water can be used to decrease CO₂ mobility.

Foam should be used in CO₂ flooding. However, it is not known whether the beneficial properties of foam would exist at the very high flooding pressures used in this experimental program. At these high densities, CO₂ is considered to be a dense fluid resembling of fluid more than gas. Thus the term “emulsion” is more descriptive of the true state of the mixture rather than “foam”. Alcohol can creates foam when reacts with CO₂.

2.2.2 CO₂ under effect of high pressure and temperature

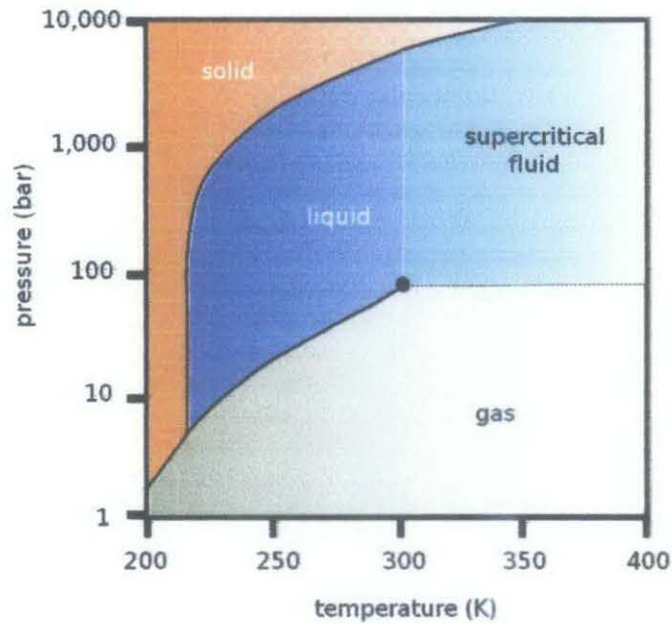


Figure 2: Phase diagram of CO₂ under effect of pressure and temperature ^[20]

Figure 2 shows the phase diagram of the CO₂, where CO₂ state under high pressure at temperature of 333 K.

2.2.3 Factor influencing Minimum Miscibility Pressure

Miscibility is strongly related to reservoir temperature and oil composition, particularly C₅₊ molecular weight. It also indicates that CO₂ miscibility is related to the volatile and intermediate fraction of the oil. ^[8]

Six characteristics including the intensive properties of temperature and pressure are use to define the condition of the system. The reservoir oil described in terms of three characteristics which are volatile oil fraction, intermediate oil fraction and stock tank oil API gravity. The solvent are characterized by their CO₂ content.

In order to test the idea of the volatile and intermediate fractions of the oil to MMP, a series of slim tube recovery is plot as a function of the methane/intermediate ratio. There is significant effect on the volatile and intermediate fraction to MMP.

It is also will be affected by the presence of impurities such as nitrogen or methane, as it increases the MMP to level beyond those attainable by reservoir pressure. For example, ten mole percentage of methane in CO₂ increased the MMP of West Texas oil from 1200 psi to 1800 psi. The same amount of nitrogen increased the MMP of the same oil to 3300 psi ^[11].

2.3 Alcohol as surfactant

The basic physic behind the surfactant flooding EOR process is to increase the fluid flow, viscous force or decreasing the capillary force holding the oil in place required before oil can be pushed through the pore throat and send on to a production well. For successful surfactant flood, the interfacial tension between the crude oil and the aqueous phase needs to be reduced to ultra low values (target 0.0001 mN/m). Beside the requirement to achieve a low in-situ IFT, another factor that determines the technical and economical success of surfactant flood is to minimize the injected surfactant ^[1].

a) Branched alcohol propoxylated sulfates

Branched alcohol propoxylated sulfates have emerge as an effective type of surfactant for the removal of oil. Propoxylated sulfate surfactant is use to create middle phase micro emulsions versus crude oil, presumably achieve low interfacial tension. Branched chain alkyl group shows that it has lower IFT than those with straight chain alkyl group ^[1].

ALFOTERRA is the name for branched alcohol propoxylated sulfate which are characterized by mn (m= 1-5, n =3, 5, 8), where n indicates the

average number of propoxy group in the molecule while m is the size of the branched alkyl chain.

Figure 3 and Table 1 show that the Branched alcohol propoxylated of Alforterra 38 and 23 as surfactant to reduce IFT ^[1].

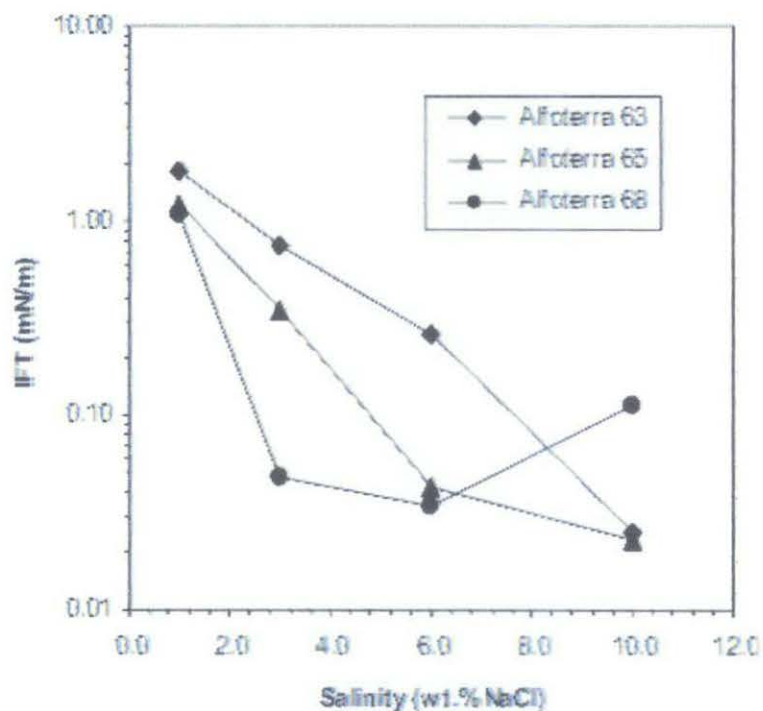


Figure 3: IFT result of Alforterra 63, 65 and 68 at low concentration (0.2 wt. %) in various salinity (Oil phase: n-octane, room temperature) ^[1]

Table 1: Result of IFT of Alfoterra surfactant

Table 1. IFT Results of Alfoterra[®] Surfactants at 0.2 wt.% (Oil Phase: n-Octane)

Surfactant	IPA (wt.%)	NaCl (wt.%)	IFT (mN/m)
Alfoterra [®] 23	0	6.0	0.009
Alfoterra [®] 23	0.1	6.0	0.006
Alfoterra [®] 28	0	3.0	0.040
Alfoterra [®] 28	0.1	3.0	0.019
Alfoterra [®] 33	0.1	3.0	0.006
Alfoterra [®] 33	0	6.0	0.111
Alfoterra [®] 38	0	3.0	0.081
Alfoterra [®] 38	0.1	3.0	0.121
Alfoterra [®] 38	0.1	6.0	0.249
Alfoterra [®] 45	0	6.0	0.012
Alfoterra [®] 45	0.1	6.0	0.011
Alfoterra [®] 48	0.1	3.0	0.014

IPA: iso-propanol.

Table 2. IFT Results of Alfoterra[®] Surfactants at 0.1 wt.% (Oil Phase: n-Octane)

Surfactant	IPA (wt.%)	NaCl (wt.%)	IFT (mN/m)
Alfoterra [®] 23	0	6.0	0.016
Alfoterra [®] 23	0.05	6.0	0.011
Alfoterra [®] 28	0	3.0	0.050
Alfoterra [®] 28	0.05	3.0	0.024
Alfoterra [®] 33	0.05	3.0	0.011
Alfoterra [®] 33	0	6.0	ND
Alfoterra [®] 38	0	3.0	ND
Alfoterra [®] 38	0.05	3.0	ND
Alfoterra [®] 38	0.05	6.0	ND
Alfoterra [®] 45	0	6.0	0.018
Alfoterra [®] 45	0.05	6.0	0.034
Alfoterra [®] 48	0.05	3.0	0.048

IPA: iso-propanol. ND: Not determined.

Figure 4 shows one example of ALFOTERRA structure. It produces cheaply from Alcohol dimeration process (Guerdet reaction)^{[14][15]}. Extensive research on surfactant has established a clear relationship between surfactant structure and fluid properties and performance related to EOR. For example, the optimum salinity decreases with increasing hydrophobe length due to the water phobic effect. Hydrophobe is the carbon molecule in branched alcohol. Weakly hydrophobic functional group such as propylene oxide (PO) is characterized as having interface affinity and increases the breadth of the ultra low IFT region^[1]. The addition of hydrophobic group lowers the optimum salinity and adds calcium tolerance, changes the degree of propoxylation to consider the surfactant to given crude oil, temperature and salinity.

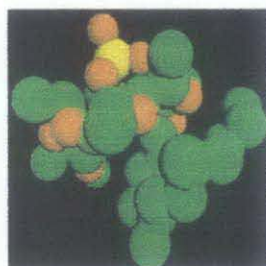


Figure 4: Branched alcohol propoxy C₁₆₋₁₇-7PO Sulfate structure^[1]

b) Straight alcohol

Several combinations of alcohols are the subject of laboratory studies, principally at Pennsylvania State University. The disadvantages of isopropyl alcohol are expensive and absorb water very rapidly thus reducing the efficiency. Around 13% of the displacement pore volume is required to ensure almost total recovery of the oil. [8]

Other studies show that part of the isopropyl alcohol can be replaced, at the leading and trailing edges of the slug by methyl alcohol. The methyl alcohol rapidly absorbs water, leaving the isopropyl alcohol at the centre of the slug practically water free and thus retaining its oil displacement efficiency. A slug consists of three equal parts, each being 4% of the displaceable pore volume, with the central part of isopropyl alcohol and the outer parts of methyl alcohol, has the same efficiency as a 13% slug of pure isopropyl alcohol. Methyl alcohol is much cheaper than isopropyl alcohol. This combination is closer to being a commercial proposition.

Finally, if normal butyl alcohol is used in front of the methyl alcohol behind the isopropyl alcohol, the total slug volume is reduced up to 10% pore volume. However, the cost of butyl alcohol is prohibitive.

Even though this type of miscible displacement has not yet found commercial application due to the high cost of the various alcohols studied, the advantages of the method are evident, and the discovery of economically attractive process should still be regarded as possible. [8]

Branched alcohol and normal alcohol can effectively reduce the interfacial tension between water and oil in order to achieve miscibility pressure.

The alcohols used in the experiment were 2-Methyl-2-Butanol, 2-Methyl-1-Butanol, 2-Butanol and Phenol. 2-Methyl-2-Butanol and 2-Methyl-1-Butanol are branched alcohol. Branched alcohol reduced more IFT than straight chain alcohol. The branched alcohol is an isomer to check the

different of polarity effect to the IFT. 2- Butanol is chosen in order to test the effectiveness of straight alcohol toward IFT while Phenol is chosen in order to check the effect of the aromatic cyclic on IFT.

2.3.1 Alcohol dimerization process (Guerbet reaction)

This process is used to create large alcohol structure for the production of the corresponding alkoxy sulfate surfactant. In alcohol industry, Guerbet (dimer) alcohols are considered the “gold” standard for large, branched alcohol. These Guerbet alcohols tend to be more expensive than other alcohols when produce in high purity for various industrial applications. The high cost is mainly due to drive the reaction, to complete and/or stripping off of the unreacted monomer alcohol and to produce high purity. However, inexpensive Guerbet alcohols (GA) can be prepared by aiming for less than quantitative conversion during the alcohol dimerization process. The resultant blend of 85-95% GA and 5-15% monomer alcohol are subsequently used in the alkoxylation process to add propylene oxide and/or ethylene oxide, followed by sulfation. By using this new Guerbet process, this surfactant can be manufactured at low cost when make as sulfates compared to sulfonates. For example, a C32 GA can be produced from C16 alcohol. The C32 GA and other sulfate surfactants can be stabilized at high temperature with alkali. ^[13]

2.3.2 Production of pyrolytic oil to produce phenol for enhanced oil recovery

Enhanced oil recovery is an oil recovery process by the injection of materials not normally present in the reservoir. Chemical flooding of oil reservoir is one of the most successful processes to enhance oil recovery from depleted reservoirs at low pressures. However, chemical flooding is not widely applied due to the high cost of chemicals. Malaysia as the world's largest producer of palm oil generates a significant solid wastes annually.

More than 7 million tons of empty fruit bunches, 6.0 million tons of fibre and 2.4 million ton of palm shell are estimated to be generated annually. [20]

Pyrolysis may be described as the thermal degradation of materials in the complete absence of inadequate presence of oxygen. Three products are usually obtained from pyrolysis process which are gas, liquid and char. Both the product yield and chemical composition of pyrolysis oil can be varied according to the pyrolysis methods and process conditions. [20]

Pyrolysis is being considered to be an emerging, new and potential technology to produce value added products, fuels and chemicals from oil palm waste. Chemicals have been produced from biomass in the past, are being produced at present, and will be produced in the future due the demand for the organic chemicals has increased on a worldwide basis. For example, isolation of chemicals at the industrial scale has been performed to recover commodity compounds such as methanol, acetone, acetic acid and mixture of phenols. [20]

2.4 Experiment method

2.4.1 Interfacial tension

Capillary forces cause large quantities of oil to be left behind after water flooding of an oil reservoir. Capillary pressure force arises from the interfacial tension (IFT) between the oil and water phases that resist externally applied viscous forces and causes the injected water to bypass the resident oil. The predominant mechanism to recover residual oil is lowering the IFT by the addition of suitable chemical (surfactant). Lower interfacial tension recovers additional oil by reducing the capillary force. This trapping of the resident oil can be expressed as a competition between viscous forces, which mobilize the oil and capillary forces that trap the oil [7]. IFT needs to be reduced to values in the range of 0.01 to 0.0001 dyne.cm to get increase oil recovery

2.4.2 Pendant drop method

In the pendant drop method, few drops of live crudes oil are being introduced through a metal capillary tube into the gas filled optical cell and images of pendant drop are capture and analyze using an image analysis technique to obtain the gas/oil IFT. The commercial image analysis software named drop shape analysis (DSA) was used for determining the IFT for CO₂/alcohol/synthetic oil ^[4].

The experimental system used in this work can measured the tension of liquid/gas and liquid/liquid phases up to 6000 psia [41.37 MPa] and a temperature range of 70 to 300 F [21 to 149 C] . The IFT minimum reading is 0.5 dyne/cm [0.5 mN/m].

Several liquid drops are used for each tension measurement, and then the average value and the standard deviation are reported.

The IFT between gas and liquid at high pressure is commonly measured by using pendant drop apparatus. The shape of liquid droplet at static conditions, controlled by the balance of gravity and surface forces, is determined and related to the gas-liquid IFT ^[18].The basic formula to calculate the IFT with pendant drop method is displayed in Equation (1).

$$\sigma = \frac{gde}{f}(p_l - p_v) \quad (1)$$

σ = interfacial tension, mN/m

g = gravity acceleration, m/s²

f = Drop shape factor, ratio of d_s/d_e dimensionless

d_e = equatorial diameter,m

d_s = diameter of the drop at the height d_e above the bottom of drop,m

p_l = liquid phase density, kg/m³

p_v = vapour phase density, kg/m³

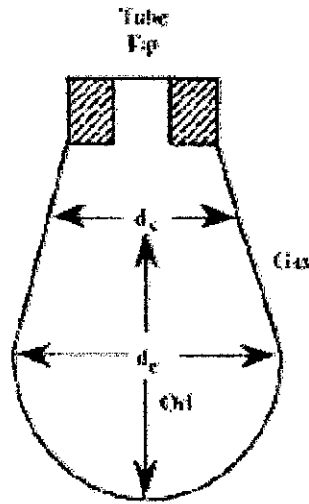


Figure 5: IFT measurement by using pendant drop method

2.4.3 Viscometer

A viscometer is an instrument to measure the viscosity of a fluid. For liquids with viscosities which vary with flow conditions, an instrument called a rheometer is used.

2.4.4 Vanishing interfacial method

Vanishing interfacial (VIT) is a new method used in order to obtain MMP. MMP from VIT is obtained from IFT data at different pressure. In a typical experiment, a high pressure cell is initially filled with gas and oil, with oil occupying approximately 10% of the cell volume. Drops of oil were introduced into the top of the cell. Images of the shapes of the pendant drop and oil and gas density data are then used to calculate the IFT on the basis of the drop shape. In other experiment, capillary rise measurements were used to determine IFTs. Similar observations were made at a sequence of increasing pressure obtained by introducing more gas into the cell. A plot of IFT versus pressure is then extrapolated to zero IFT, and the resulting pressure is taken to be estimate of the MMP. A second version of the experiment procedures which the overall composition in the cell was held constant as the pressure increased. The method is referred to as constant composition VIT experiment. ^[4]

VIT method is only accurate for static MMP not for dynamic MMP but researches have been done showing that VIT method is accurate compared to other MMP method such as slim tube test in measuring the dynamic MMP. The VIT method is also fast and cheap compared to slim tube test. [4]

2.5 Empirically derived correlation for estimating MMP

Empirically derived correlation is used to estimate MMP, MMP has been correlated with temperature, oil C5+ molecular weight, volatile oil fraction, intermediate oil fraction and composition of the CO₂ stream. The effects of temperature and oil C5+ molecular weight on pure CO₂ MMP have been well documented [8]. CO₂ sources are rarely pure and solution gas usually presents in reservoir oils. In the correlation it takes into account the presence of volatile component and intermediate component in the reservoir oil. The correlation also capable to estimate MMP for contaminated CO₂ stream [3]. Below is the step for MMP correlation:

Calculation MMP from correlation

The correlation takes into account for impurities in the CO₂. Correlations were applied to pure CO₂ streams as well as streams with impurities [3]. For pure CO₂, the MMP, P_{co2} is given by

$$P_{co2} = 8.78 \times 10^{-4} * Tr^{1.06} * M(c5+)^{1.78} * \frac{Xvol^{0.136}}{Xint} \quad (5)$$

Tr = reservoir temperature, R

M = molecular weight for the crude oil

X_{vol}/X_{int} = fraction of volatile to intermediate.

The molecular weight was 189.85 and the fraction that the author used is 2 in order to calculate the correlation MMP between CO₂ and crude oil.

Next the author calculated the impure CO₂ injection MMP using equation 6 and 7.

$$T_{cm} = \sum w_i T_{ci} - 459.7 \quad (6)$$

w_i = the molecular weight

T_{ci} = the critical temperature

$$F_{imp} = \frac{87.8}{T_{cm}} * 1.935 * \frac{87.8}{T_{cm}} \quad (7)$$

T_{cm} =, cumulative critical temperature, F

The correction factor for the impure CO₂ can be measured from equation 8.

$$P_{impure} = P_{CO_2} * F_{imp} \quad (8)$$

Then calculate the pressure impure with the MMP (pure CO₂) multiplied with the correction factor.

2.6 Effect of Injection Pressures on CO₂ Flood Oil Recovery

In order to reduce the residual oil, carbon dioxide injection must be above the thermodynamic MMP. At lower pressure condition, the pressure is not high enough to allow sufficient CO₂ to dissolve into the oil or vaporize sufficient oil into the CO₂ so that the two phases become miscible.

The effects of CO₂ are to swell the oil and to reduce its viscosity. Swelling causes some of the residual oil to become recoverable. Miscibility development between CO₂ and oil is a function of both temperature and pressure, but for an isothermal reservoir, the only concern is pressure. Oil can dissolve more CO₂ as the pressure escalates and more oil component can

be vaporized by the CO₂. At some pressures, when the CO₂ and oil are in contact, it will become miscible. [9]

When the contact between oil and CO₂ occurs with little or no reservoir mixing, the pressure at which miscibility happened is defined as the thermodynamic MMP. The purpose of miscible injection is to reduce the residual oil saturation by lowering the IFT between oil and the displacing fluid. As shown in Figure 6, the displacement efficiency of CO₂ is plotted against the reservoir pressure. At pressures above MMP (higher than 1300 psig), the displacement efficiency exceeds 90% and it is considered miscible. However, at pressures below MMP, the displacement efficiency decreases as the pressure reduced. [9]

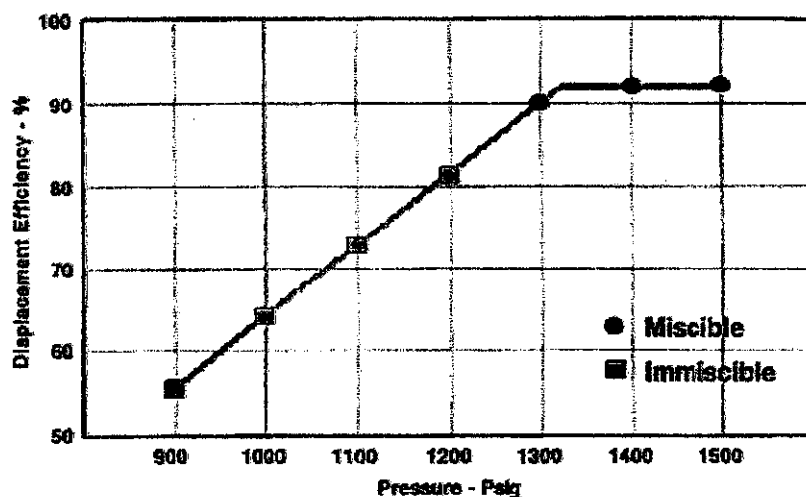


Figure 6: Slim tube miscibility test.

Based on this study it is known that by achieving miscibility pressure in CO₂ injection can enhanced the recovery from the reservoir.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology:

- a) Sample of 2-methyl-2-butanol, 2-methyl-1-butanol, phenol and 2-butanol with different concentration were prepared.
- b) Density was measured by using density meter and it was measured in order to calculate IFT.
- c) Minimum miscibility pressure (MMP) of CO₂ and Dulang crude oil had been calculated by using correlation and vanishing interfacial method.
- d) Minimum miscibility pressure with alcohol additive had been determined by using vanishing interfacial method (crude oil, branched alcohol/alcohol and CO₂).
- e) Different alcohol concentration ranging from 10% to 100% had been used for 2-methyl-2-butanol and 2-methyl-1butanol to get the optimum concentration to reduce MMP.
- f) Different alcohol concentration ranging from 10% to 100% had been used for every alcohol in order to measure the oil viscosity.

3.2 Project work Flow

The project activities flow is shown in Figure 7.

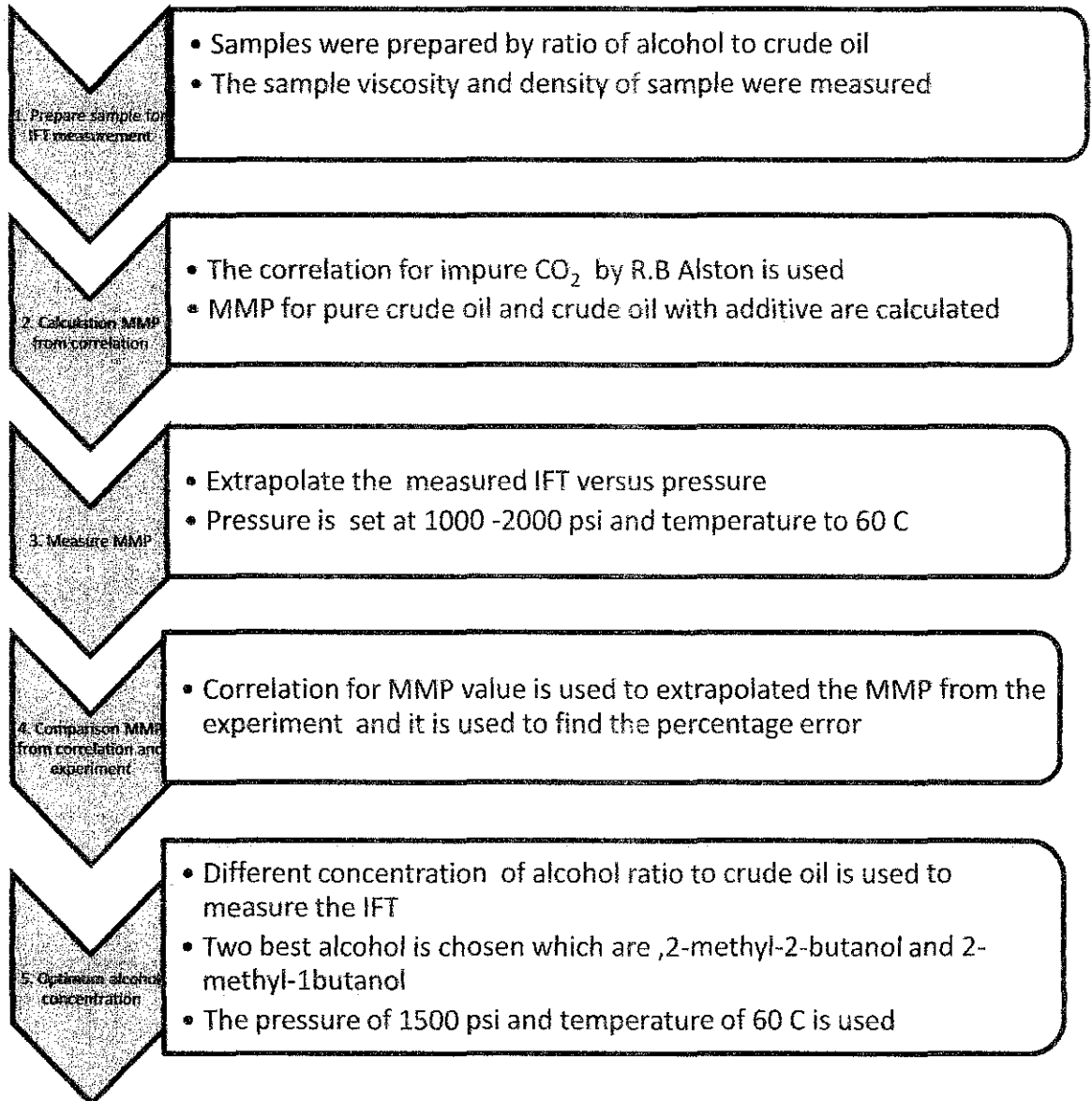


Figure 7: Project work flow

3.3 Density measurement

The density of liquid used in this study is measured by using Anton Paar DMA.

Procedure:

1. Set up the experiment
2. List the solutions to be measured
3. Set the temperature to 60°C
4. Calibrate the density to 0.09 g/cm³ on the screen of the equipment
Note: 0.09 g/cm³ is density of air
5. Inject the chemical inside the measurement equipment
6. Click run
7. Wait until equipment reach the design temperature
8. Then check readings
9. Clean the equipment using solvent and ethanol
10. Use next chemical (Repeat step5)

Density is important in order to use in IFT calculation. The solution densities need to be measured for every pressure and temperature in the experiment.

3.4 CO₂-Crude-alcohols MMP Measurement

Interfacial Tension measurement between crude oil and CO₂ in this study was conducted experimentally by using IFT-700. This experiment setup consists of Smart Software interface, camera, positive displacement pump, and high pressure chamber and accumulator. The pendant drop method is used in this experiment because the density of crude oil is lower than the density of CO₂ during all experiment condition.

Figure 8 shows the IFT flow diagram. After obtained the IFT result from IFT-700 equipment, all of the IFT is plotted on graph. The MMP is

obtained using VIT method by extrapolating the line plotted on the graph to zero IFT. The following below are the procedures for the VIT:

1. Plot the IFT versus pressure data.
2. Make a straight line that represents the distribution of the data of the graph
3. Extrapolate the line of the data until intersect IFT is equal to zero.
4. The pressure that intersects the line is the MMP.

The flowchart diagram below for IFT measurement

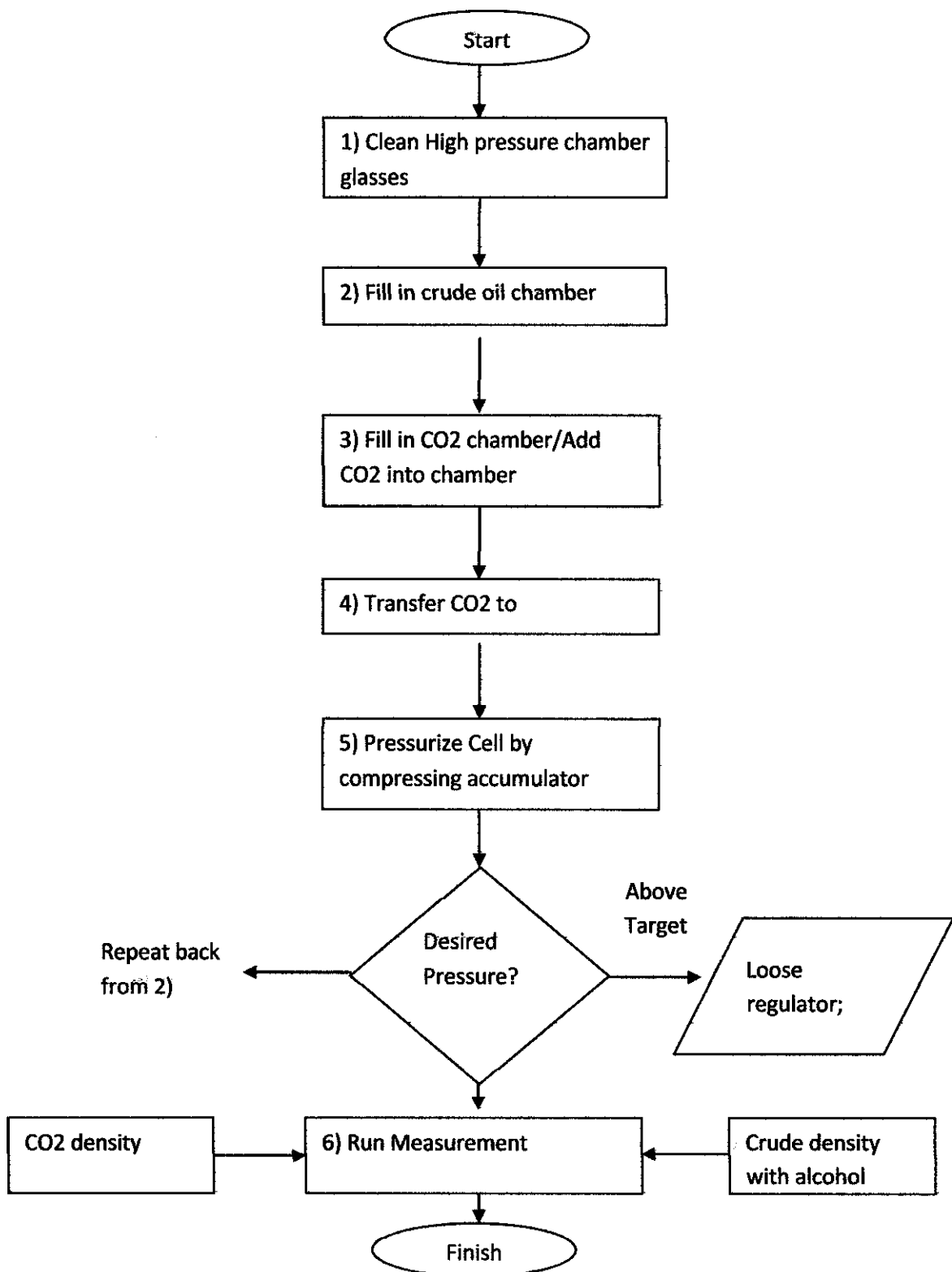


Figure 8: Flow diagram of IFT measurement

3.5 Crude oil- alcohol viscosity measurement procedure using a direct indicating viscometer

Viscose oil makes MMP unattainable. Crude oil viscosity had been measured when added with alcohol at different concentration ratio. Below is the apparatus used and procedure to measure viscosity.

Apparatus

- 1. Direct indicating viscometer**
- 2. Stop watch**
- 3. Suitable Container**
- 4. Thermometer with range of 0 C to 105 C (32 F to 220 F)**

Procedure:

- a) Prepare fluid inside the container or beaker**
- b) Heat the container to desirable temperature (60° C)**
- c) Choose the correct measurement apparatus**
- d) Set the speed of rotation to 30 rpm or 60 rpm**
- e) Wait for 20 minutes before taking the readings**

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Minimum miscibility pressure results

Minimum miscibility pressure experiments were done for

1. CO₂ and crude oil with no surfactant
2. CO₂ and crude oil with phenol
3. CO₂ and crude oil with 2butanol
4. CO₂ and crude oil with 2methyl2butanol
5. CO₂ and crude oil with 2methyl1butanol

IFT measurements were done at 1000, 1500, 1820 and 2000 psi and at constant temperature of 140 F.

- a) MMP result between CO₂ and crude oil with no surfactant

Table 2: Pressure, angle and IFT table (CO₂ and crude)

Pressure(psi)	Angle	IFT(mN/m)
1000	111.11	11.82
1500	102.67	5.5
1820	99.42	1.38

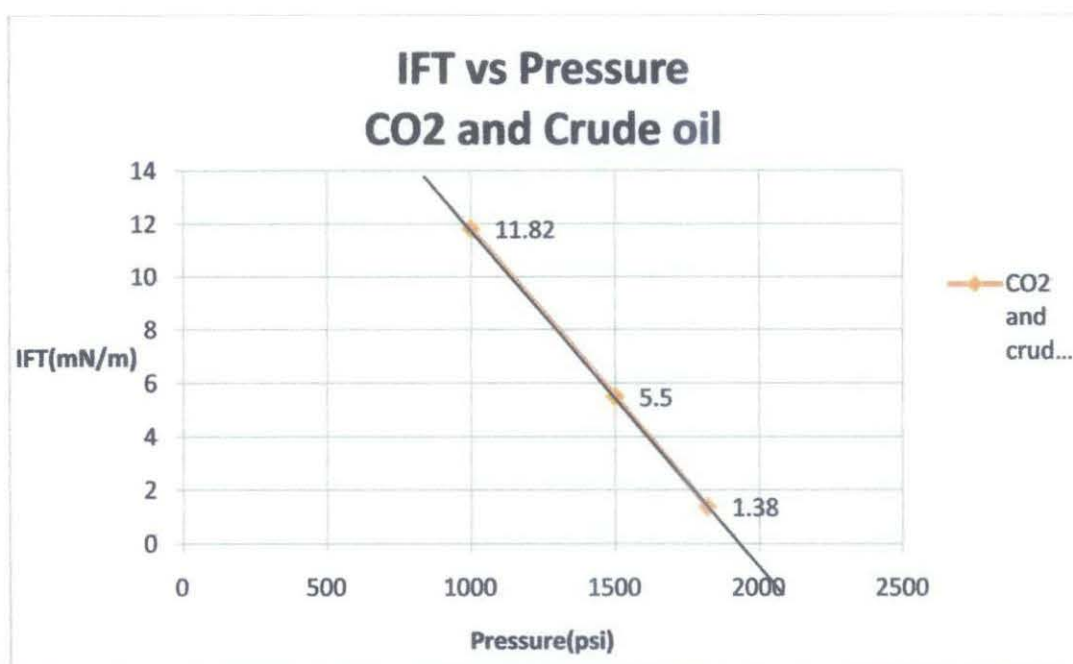


Figure 9: IFT versus pressure graph for crude oil and CO2

IFT measurement results were linear with the pressure. The trend can be seen on Figure 9. From the graph, the MMP was 2000 psi by extrapolated it to zero IFT. CO₂ and crude oil MMP that were measured was used as the base case. Using correlation the MMP was 2064 psi. The percentage error was 8% with relative to the IFT result.

- b) MMP result between CO₂ and crude oil with 2-Methyl-1-Butanol

Table 3: Pressure, angle and IFT table (2-Methyl-1-Butanol)

Pressure(psi)	Angle	IFT
1000	101.5	6.46
1500	110.96	0.88

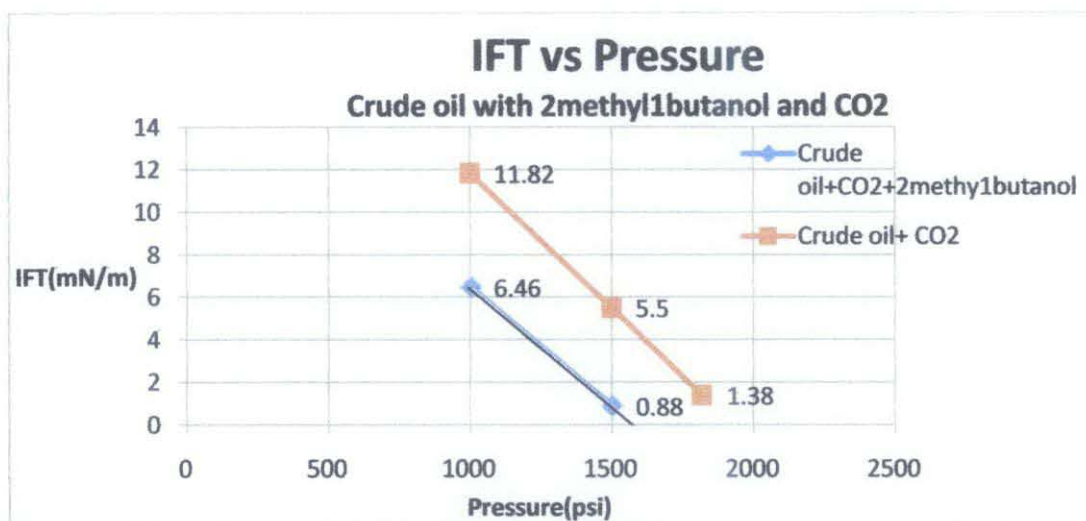


Figure 10: IFT versus pressure graph for crude oil with 2-Methyl-1-Butanol and CO₂

Based on the Figure 10 above, 2-Methyl-1-Butanol reduced the IFT measurement higher than 2-Butanol. From the graph it shows that 2-Methyl-1-Butanol reduced the IFT and it also proven that branched alcohol reduced the IFT more than straight alcohol. From the above graph, the MMP was 1550 psi. The MMP based from the correlation was 1146 psi and the percentage error compared to experiment data was 26%.

- c) MMP result between CO₂ and crude oil with 2-Methyl-2-Butanol

Table 4: Pressure, angle and IFT table (crude oil and 2-Methyl-2Butanol)

Pressure(psi)	Angle	IFT
1000	102.97	6.91
1500	95.59	1.3

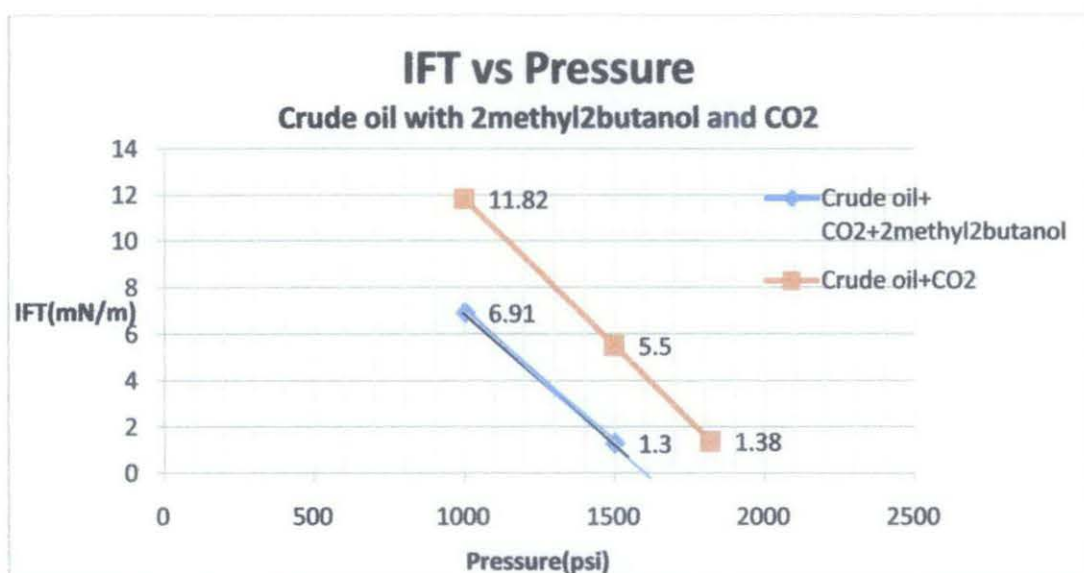


Figure 11: IFT versus pressure graph for crude oil with 2-Methyl-2-Butanol and CO₂

The IFT measurements were compared with the base case. Based from the Figure 11 above, 2-Methyl-2-Butanol reduced the IFT measurement higher than 2-Butanol but lower than 2-Methyl-1-Butanol. From the above graph, the MMP was 1600 psi. The MMP from the correlation data was 1387 psi and the percentage error was 13% compared to experiment data.

2-butanol and phenol MMP estimation are attached at APPENDIX H and APPENDIX I. Table below shows all the results obtained.

Table 5: summarize all the result of the IFT and MMP measurement

	Crude oil	Crude oil and Phenol	Crude oil and 2-Methyl-1-Butanol	Crude oil and 2-Butanol	Crude oil and 2-Methyl-2-Butanol
1000 Psi	11.82	8.63	6.46	2.84	6.91
1500psi	5.5	4.5	0.88	2.6	1.3
1820 psi	1.38	1.96	-	0.98	-
2000 psi	-	0.06	-	-	-
MMP (Psi)	2000	2000	1550	1820	1600
correlation	2064	1255	1146	1111.76	1387

4.2 Optimum alcohol concentration results

The results obtained from the MMP shows that 2-Methyl-1-butanol and 2-Methyl-2-Butanol are the most effective in reducing the MMP.

Figure 12 shows the IFT at different concentration for 2-methyl-1-butanol. The IFT was compared at pressure of 1000 psi and constant temperature of 140 F. The lowest IFT reading is 10% alcohol concentration.

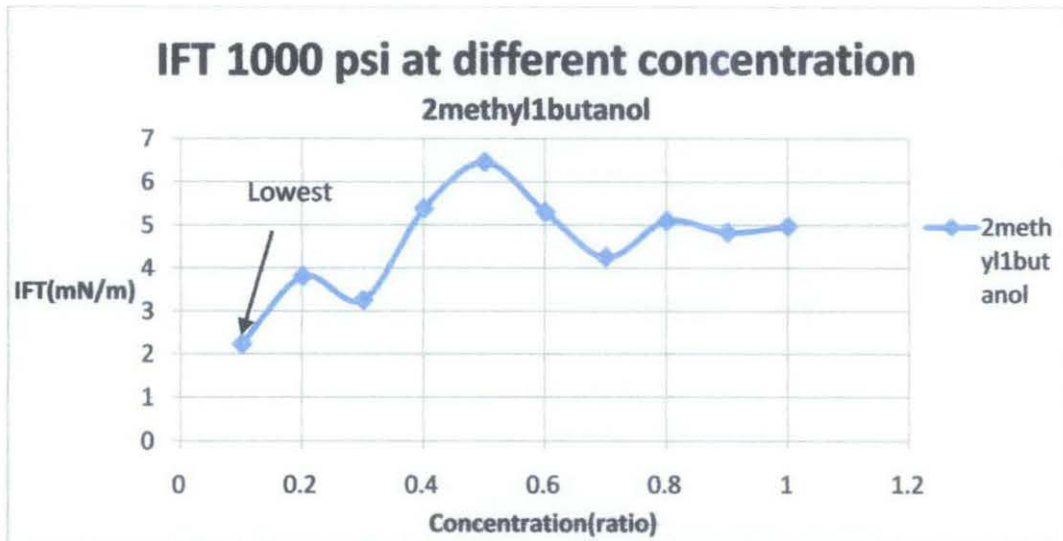


Figure 12: IFT vs. concentration for 2-Methyl-1-butanol

Figure 13 shows the IFT measurement for 2-Methyl-2-butanol at different concentration. The IFT was measured at pressure 1000 psi and constant temperature of 140 F. The lowest IFT reading was 10% alcohol concentration.

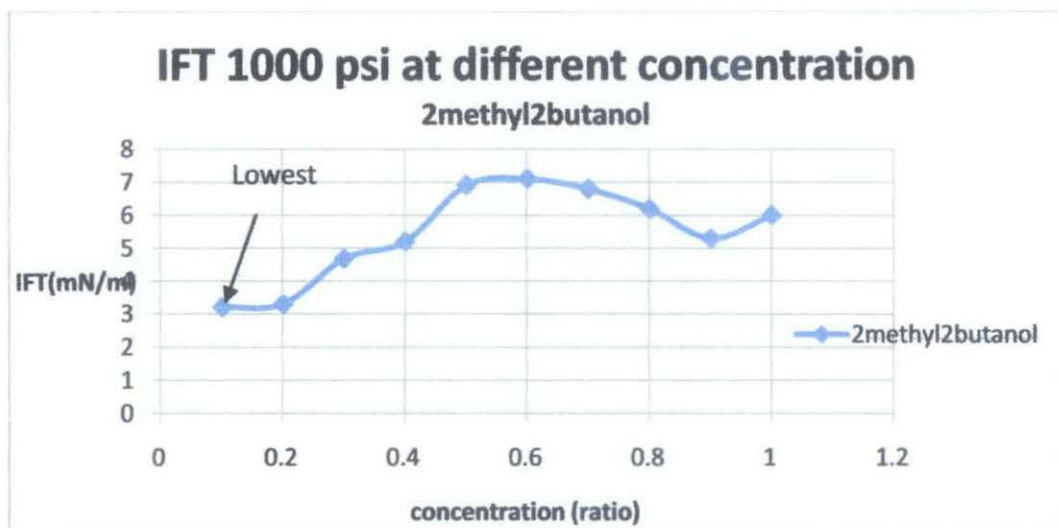


Figure 13: IFT vs. concentration for 2-Methyl-1-butanol

Figure 14 shows the IFT measurement for 2-Methyl-2-butanol at different concentration. The IFT was measured at pressure 1500 psi and constant temperature of 140 F. The lowest IFT reading was 50% alcohol concentration.

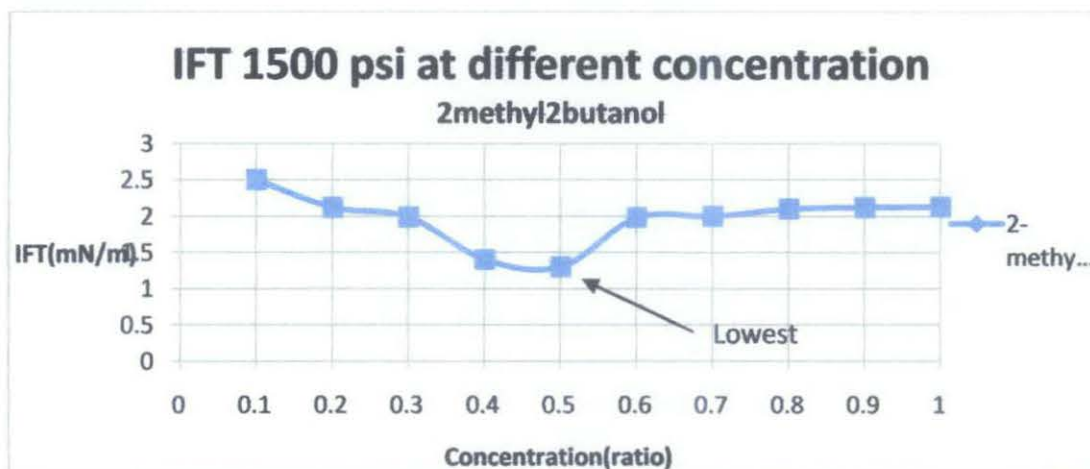


Figure 14: IFT vs. concentration for 2-Methyl-2-butanol

Figure 15 shows the IFT measurement for 2-Methyl-1-butanol at different concentration. The IFT was measured at pressure 1500 psi and constant temperature of 140 F. The lowest IFT reading was 50% alcohol concentration.

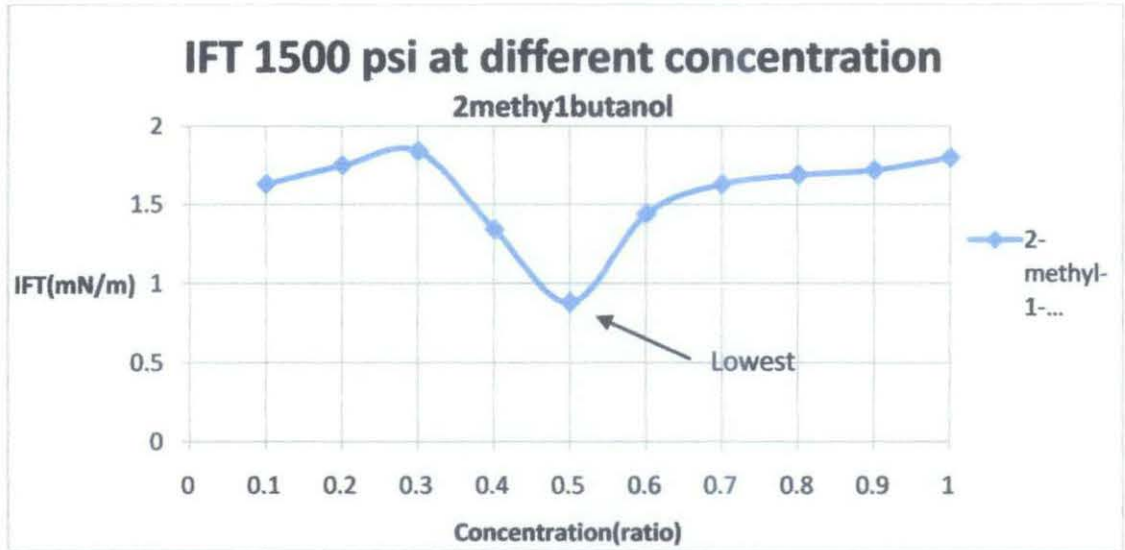


Figure 15: IFT vs. concentration for 2-Methyl-1-butanol

Pressure obtained from Figure 12 and 15 were plotted for IFT versus pressure graph. The graph can be seen on Figure 18. Different concentration gave the results in different MMP. The lowest MMP obtained was at the optimum concentration.

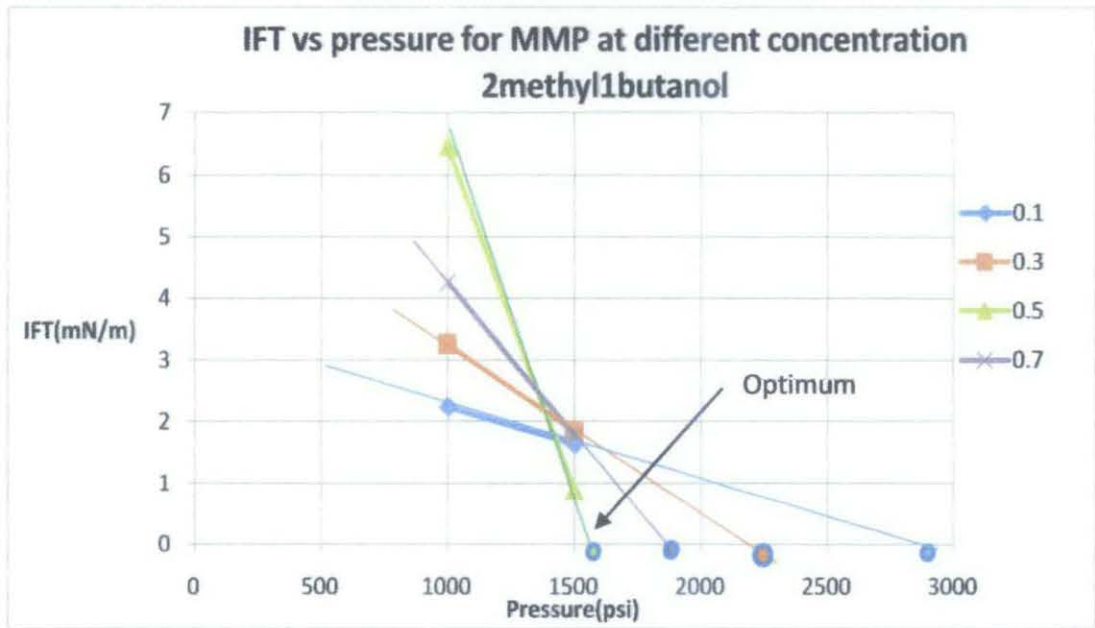


Figure 16: MMP at different 2-Methyl-1-butanol concentration

Pressure obtained from Figure 13 and 14 were plotted for IFT versus pressure graph. The graph can be seen on Figure 19.

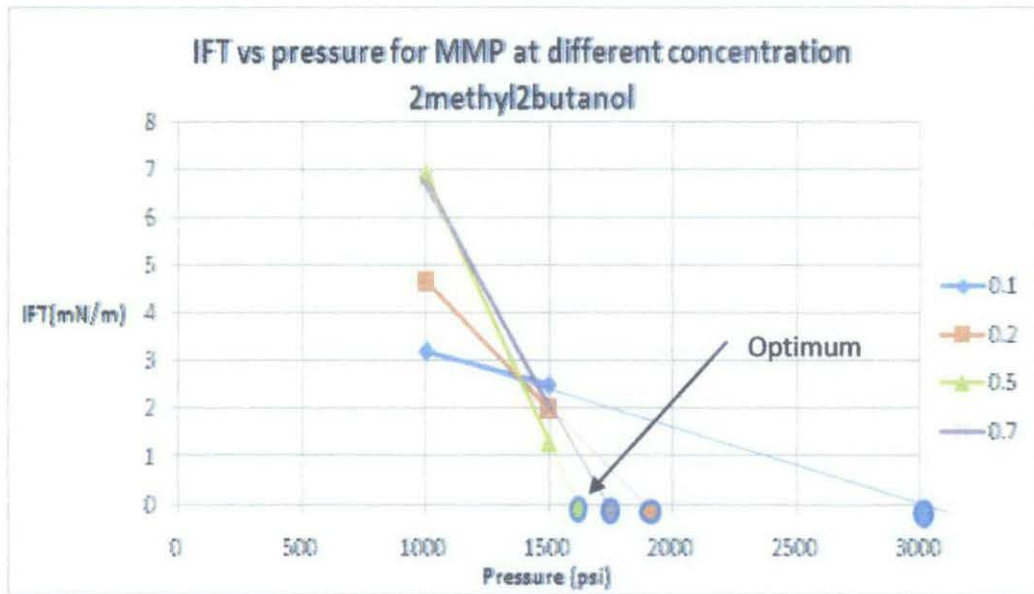


Figure 17: MMP at different 2-Methyl-2-butanol concentration

4.3 Viscosity and density measurement

Viscosity was being measured because viscose oil made MMP unattainable.

The viscosity was measured when it is added with alcohol.

Summarized viscosity and density measurement are shown in Table 10

Table 6: Density and viscosity result for alcohol and crude oil

Sample	crude oil and 2butanol	crude oil and 2methyl2butanol	crude oil and phenol	crude oil and 2methyl1butanol	crude oil
Viscosity(cp) (0.5:1)	3.33	2.22	4.01	2.23	-
Viscosity (cp) (1:1)	1.09	1.01	2.98	1.21	4.33
Density (g/cc) (0.5:1)	0.787	0.766	1.011	0.791	-
Density (g/cc) (1:1)	0.7756	0.7817	1.112	0.789	0.802

4.4 Correlation MMP result

MMP from correlation was calculated. The results from correlation were used for comparing with experiment results.

Table 7: Summary of MMP correlation result

Fluid	MMP(psi)
Crude oil+ CO ₂	2064
Crude oil+ CO ₂ +phenol	1255
Crude oil+ CO ₂ +2butanol	1111
Crude oil+ CO ₂ +2methyl2butanol	1387
Crude oil+ CO ₂ +2methyl1butanol	1146

4.5 Discussion

4.5.1 MMP and Interfacial tension discussion

Interfacial tension is similar to surface tension. However, the main forces involved in interfacial tension were adhesive forces (tension) between the liquid phase of one substance and either a solid, liquid or gas phase of another substance. The interaction occurred at the surfaces of the substances involved at their interfaces. The experiment was done between gas (CO₂) and liquid (crude oil and alcohol). The lower IFT between the CO₂, the better MMP of crude oil.

The IFT were measured at concentration ratio of 0.5. It is done to observe the effect of lower volume of alcohol to MMP of CO₂. Benzyl alcohol was tested at 1000 to 2000 psi. Based on the results, phenol will increase the IFT at higher pressure. The IFT increased because CO₂ already enter the supercritical state.

For 2-Methyl-1-butanol, it will give lower IFT at high pressure. 2-Methyl-1-butanol shows high potential in reducing the MMP. The MMP reduction is 23% lower from crude oil and CO₂ MMP. 2-Methyl-1-butanol

shows high IFT reduction due to the high polarity. The polarity would enhance the CO₂ capacity to form interaction with the crude oil.

The results for 2-Butanol are promising but compared with branched alcohol, the MMP is higher. From the results, low IFT at lower pressure than 1000 psi was compared with the other alcohol. From the literature review^[2], 2-Butanol does not have higher polarity compare to branched alcohol. The MMP was only reduced 9% for 2-Butanol.

For 2-Methyl-2-butanol, the result from IFT shows a very promising MMP reduction agent. The reduction in MMP was 20% less than crude oil and CO₂ MMP. 2-Methyl-2-butanol also has high polarity based on the literature review. The polarity enhanced the CO₂ solubility to merge together with crude oil.

The reduction of MMP was depending on the polarity of the alcohol. The higher the polarity, the better it is for CO₂ to form specific solvent–solute interactions.

For 2-Methyl-2-butanol and 2-Methyl-1-butanol, the IFT was only done at two different pressures or points. When CO₂ added with alcohol, fog will occur inside the IFT-700 cell. The fog will block the camera view and made the reading inconsistent. The reason fog occurred was due to the increase in crude oil stain that is not properly clean when inside the tubing or cell. Fog was also occurred when crude oil is drop into the cell.

4.5.2 *Optimum alcohol concentration discussion*

The existent of optimal alcohol concentration can produced ultra low interfacial tension and solubilise maximum amount of oil and brine. The optimal alcohol concentration also depends on brine salinity. Even salinity is 0% , the optimum alcohol concentration still exists.^[23]

By comparing the IFT at 1000 psi and 1500 psi with different concentration, the optimum alcohol concentration for 2-Methyl-1-butanol and 2-Methyl-2-butanol can be obtained.

Based on Figure 16 and 17, at 1000 psi 2-methyl-1-butanol and 2-methyl-2-butanol the 0.1 concentration ratio gave the lowest IFT compared to other concentration. The result for 2-Methyl-2-butanol and 2-Methyl-1-butanol at 1500 psi showed that optimum IFT was at 50% concentrations.

The concentration of the alcohol also could lead to a different MMP between CO₂ and crude oil. Figure 21 and 22 showed that 50% concentrations obtained the lowest MMP reading, the highest MMP was at the lowest concentration. The optimum concentration ratio for 2-Methyl-2-Butanol and 2-Methyl-1-Butanol was 50% alcohol.

MMP estimated using only two points because a fog is formed at higher pressure and due to time constraint.

4.5.3 *Viscosity discussion*

Based on the results in Table 10, alcohol reduced the viscosity of the crude with increasing concentration.

The reduction of viscosity is good for displacement efficiency so that the displacement is stable between CO₂ and crude oil. The viscosity is lowest for 2-Methyl-2-butanol at concentration ratio of 1.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The MMP results and consequence of alcohols concentration to the MMP had been analysed. Below are the summarized conclusions for my project:

1. Experiments were done for branched, cyclic and straight alcohol. All alcohols except phenol reduced the MMP. Higher polarities of alcohol give the lowest MMP because it enhanced more the solubility power of the CO₂. The results showed that the best alcohol to reduce MMP was branched alcohols. The reduction of MMP was 20 to 23%.
2. Optimum concentration of branched alcohol at 50% concentration. The MMP and IFT result was lowest at 50% alcohol concentrations. This result will only apply at 0% salinity of brine.
3. From the viscosity measurements, crude oil viscosity will reduce with increasing in alcohols concentrations. The highest viscosity drop was for branch alcohols and the result was similar to MMP result where branched alcohol reduces MMP the most.

5.2 Recommendations

There are some improvements need to be done in order to obtain the desired and excellent results. From the experiment, it showed that there was foam produced when CO₂ interacted with alcohol. Foam is a good tool for enhanced oil recovery in order to reduce the mobility of CO₂. In the future, the author suggests that the foam factor will be taken into consideration. The author recommends using high pressure for the IFT experiment. This will give better estimate of the minimum miscibility pressure of CO₂ with crude oil. The author also recommends for further research in making branched alcohol from cheap source in order to make the project more feasible. The calculation for MMP could be done using software rather than using correlation because it would be more accurate.

REFERENCES

- [1]. Y. Wu, SPE, P. Shuler, SPE, M. Blanco, Y. Tang and W. A. G. Goddard (2000) : "Study of branched alcohol propoxylate sulphate surfactant for improve EOR" SPE paper 95404, 2005
- [2]. Carl Gatlin, R. L. Slobod (1980) "The Alcohol slug process for increasing Oil recovery" SPE paper T.P 8106, 1960
- [3]. R.B. Alston, SPE, G.P. Kokolis, SPE, C.F. James, SPE (1989). "CO₂ Minimum Miscibility pressure: A correlation for impure CO₂ streams and live oil systems" SPE paper 11959
- [4]. Dayanand Saini, SPE, Dandina N. Rao, SPE (2001) "Experimental Determination of Minimum Miscibility Pressure (MMP) by Gas/Oil IFT Measurement for a Gas Injection EOR Project" SPE paper SPE 132389
- [5]. Kristian Jessen, Franklin M. Orr Jr (2003). "On Interfacial Tension Measurement To Estimate Minimum Miscibility Pressures" SPE Reservoir Evaluation and Engineering" SPE paper 110725
- [6]. Noridah Kechut, SPE, Zahidah Md. Zain, SPE, Noraini Ahmad, Petronas Research & Scientific Service sdn bhd, DM Anwar Raja DM Ibrahim, SPE, PETRONAS Carigali sdn bhd "New Experimental Approaches in Minimum Miscibility Pressure (MMP) Determination (2007)" SPE paper 5728

[7]. Subhash C. Ayirala, SPE, Daryl S. Sequeira, Dandina N. Rao, SPE (2001) "Solubility, Miscibility and Their Relation to Interfacial Tension for Application in Reservoir Gas-Oil Systems" SPE paper 91918

[8]. M.Latil (1980), "Enhanced oil recovery"(1st ed.), Institute Francais Du Petrole Publication, Vol.5,pp. 113-223

[9]. Donaldson, E.C, Chilingarian (1989), "Enhanced oil recovery", Elsevier Science Publisher B. V., Vol.8,pp. 200

[10]. Don W. Green, G. Paul Willhite (1998),"Enhanced oil recovery", Henry L. Doherty Memorial Fund of AIME, Society of Petroleum Engineers, Vol 6.,pp. 198

[11]. Nizar F. Djabbarah, Richardson, Tex (1973) "Miscible Oil Recovery Process Using CO₂ And Alcohol" Patent storm 4899817

[12]. George G. Bernard, SPE, Union oil, L.W. Holm, SPE, Union oil, Craig P. Harver, Union oil (1960) "Use of Surfactant to Reduce CO₂ Mobility in Oil Displacement"

[13]. Stephanie Adkins, Pathma J. Liyanage, Gayani W.P. Pinnawala Arachchilage, Thilini Mudiyansele, Upali Weerasooriya (2004) "A New Process for Manufacturing and Stabilizing High Performance EOR Surfactant at Low Cost for High-Temperature, High Salinity Oil Reservoir" SPE paper 129923, Paper presented at 2008 SPE symposium in USA, 8-9 November 2004

[14]. D.B.Levitt, SPE,A.C.Jackson, SPE,C.Heinson, SPE, and L.N.Britton, U. of Texas at Austin; T. Malik and V. Dwarakanath, SPE, Intera Inc; and G.A. Pope, SPE, U. of Texas at Austin (2003)

“Identification and Evaluation of High Performance EOR surfactant”
SPE paper 100089

[15]. Steven, Jr.et al. “ Recovering Hydrocarbons with a Mixture of Carbon Dioxide and Alcohol” Patent storm 480095

[16]. Qunsheng Li, Zeting Zhang, Chongli Zhong, Yancheng Liu, Qingrong Zhou (2001) ”Solubility of solid solutes in supercritical carbon dioxide with and without cosolvent” Science Direct Fluid phase equilibria 207(2003)183-192

[17]. Zahidah Md. Zain, Nor idah Kechut, Ganesan Nadeson, Petronas research & Scientific service sdn bhd, Noraini Ahmad, Oil business, petronas, Dr.DM anwar raja, Technology management unit, Petronas Carigali sdn bhd (2003) “Evaluation of CO₂ gas injection for Major oil production fields in Malaysia-Experimental Approach case study: Dulang Field” SPE 72106

[18]. Vinci technologies IFT 700 for inter face tension determination operating manual

[19]. John D. Offerman, Orono, MN (US); Delman R. Hogen, Spring Lake Park, MN (US); Jeffrey W. Lighthart, Minnetonka, MN (US); Hugh Mc Tavish, Birchwood, MN (US)”Ethanol Production From Biological Waste” United States Patent US2008/0026442

[20]. Goh Meng Seng¹, Mariyamni Awang^{1*}, LimXin Yi², Farid Nasir Ani², “Production of Pyrolytic Oil for Enhanced Oil Recovery” ¹Faculty of Chemical and Natural Resources Engineering,

[21]. Azman ikhsa:" The CO₂ flooding prospect and challenge on malay oil field" UTM respiratory paper B1-12

[22]. Hui H.L (1995):" Penganggaran dan penentuan MMP CO₂" UTM respiratory paper B1-11

[23]. W.E Hsieh and D.O Shah (1960)"Effect of chain length of oil and alcohol as well as surfactant to alcohol ratio on the solubilisation, phase behaviour and interfacial tension of oil, brine, surfactant alcohol system" SPE 6594

APPENDIX

APPENDIX A

Dulang crude oil composition

Component	Sep Gas (MOL%)	Sep oil (MOL%)	Wellstream (MOL%)
CO2	49.93	0.196	20.743
N2	0.13	0.094	0.109
C1	34.8	1.168	15.062
C2	5.88	0.984	3.007
C3	4.71	1.301	2.71
IC4	1.72	0.548	1.032
nC4	1.41	0.463	0.854
icC5	0.71	0.208	0.415
nC5	0.5	0.13	0.283
C6	0.21	4.823	2.917
C7	0	4.827	2.833
C8	0	2.189	1.285
C9	0	4.209	2.47
C10	0	4.016	2.357
C11+	0	74.844	43.923
Total	100	100	100

APPENDIX B

Gantt chart

Semester	Semester 1					Semester 2						
	6	7	8	9	10	11	1	2	3	4	5	
Arbitrarily fixed												
Selection of FYP topic		█										
Research on the topic		█										
Preliminary report												
Study on correlation and VII method to get MDP												
Study on structural reliability with Nord method and CEC												
Study on how to use gradient drop method												
Study on how to use viscoelastic												
Preparing material												
Progress report												
Interim Report												
Oral presentation												
Experiment on AF												
Experiment on Vibration												
Progress report												
Interim Report												
Final Oral presentation												

APPENDIX C

Concentration and IFT for 2 methyl 2 butanol at 1000 psi

Concentration	IFT(mN/m)
0.1	3.2
0.2	3.3
0.3	4.68
0.4	5.2
0.5	6.91
0.6	7.1
0.7	6.8
0.8	6.2
0.9	5.3
1	6.01

APPENDIX D

Concentration and IFT for 2 methyl 2 butanol at 1500 psi

Concentration	IFT(mN/m)
0.1	2.5
0.2	2.12
0.3	1.99
0.4	1.4
0.5	1.3
0.6	1.98
0.7	2
0.8	2.1
0.9	2.12
1	2.13

APPENDIX E

Concentration and IFT for 2 methyl 1 butanol at 1000 psi

Concentration	IFT(mN/m)
0.1	2.23
0.2	3.81
0.3	3.26
0.4	5.38
0.5	6.46
0.6	5.3
0.7	4.26
0.8	5.1
0.9	4.83
1	4.97

APPENDIX F

Concentration and IFT for 2 methyl 1 butanol at 1500 psi

Concentration	IFT(mN/m)
0.1	1.63
0.2	1.75
0.3	1.84
0.4	1.34
0.5	0.88
0.6	1.44
0.7	1.77
0.8	1.69
0.9	1.72
1	1.8

APPENDIX G

IFT Measurement Apparatus

The main component of IFT-700 in this experimental set-up is a see-through windowed high-pressure cell. The maximum operating pressure and temperature of this pressure cell are equal to 10,000 psig and 200°C, respectively. Pendant drop is chosen due to higher density value of crude oil compared to CO₂ at the respected condition and also due to the many sample used in this project. The equilibrium pressure inside the pressure cell is measured by using a digital pressure gauge.

A microscope camera is used to capture the digital images of the pendant oil drop inside the pressure cell at different times. The high pressure cell is positioned horizontally between the light source and the microscope camera



Figure 18: IFT 700 equipment

APPENDIX H

MMP result between CO₂ and crude oil with 2-Butanol

Table 6: Pressure, angle and IFT table (crude oil and 2-Butanol)

Pressure(psi)	Angle	IFT
1000	98.58	2.84
1500	99.12	2.6
1820	99.89	0.98

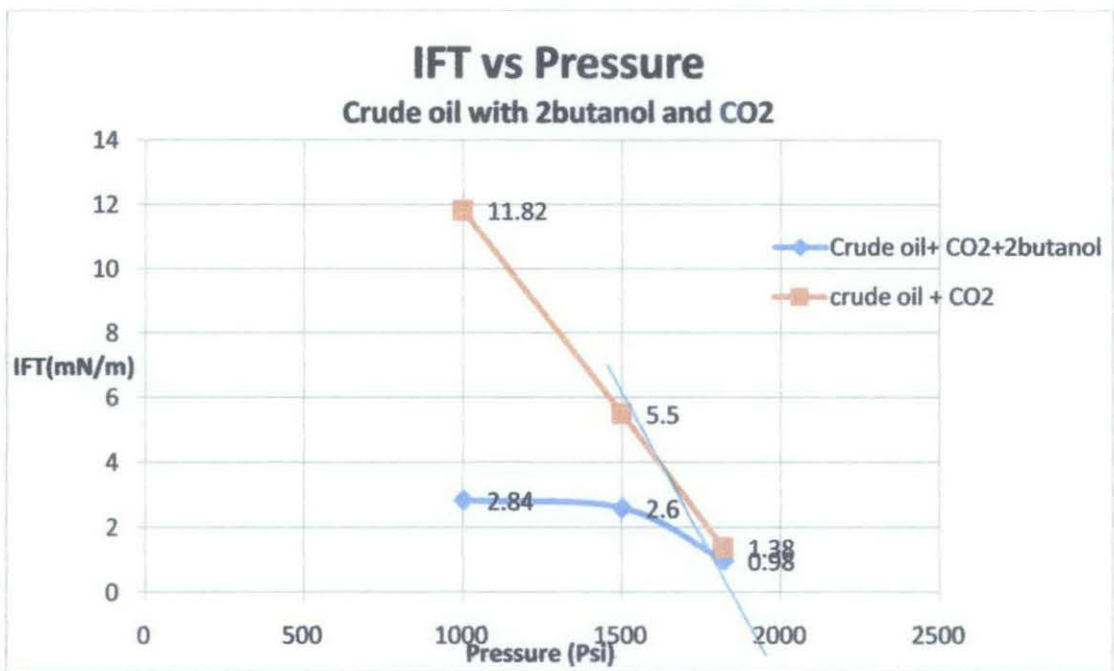


Figure 19: IFT versus pressure graph for crude oil with 2-Butanol and CO₂

The IFT measurement is compared with the base case. Based on the Figure 11 above, 2-Butanol reduced the IFT measurement until 1820 psi.

From this graph also the MMP is 1850 psi. From the correlation, the MMP is 1111.76 psi and the percent error is 38% compared to experiment data.

APPENDIX I

MMP result between CO₂ and crude oil with phenol

Table 5: Pressure, angle and IFT table (crude and phenol)

Pressure(psi)	Angle	IFT
1000	106.17	8.63
1500	101.24	4.5
1820	101.91	1.96
2000	103.81	0.06

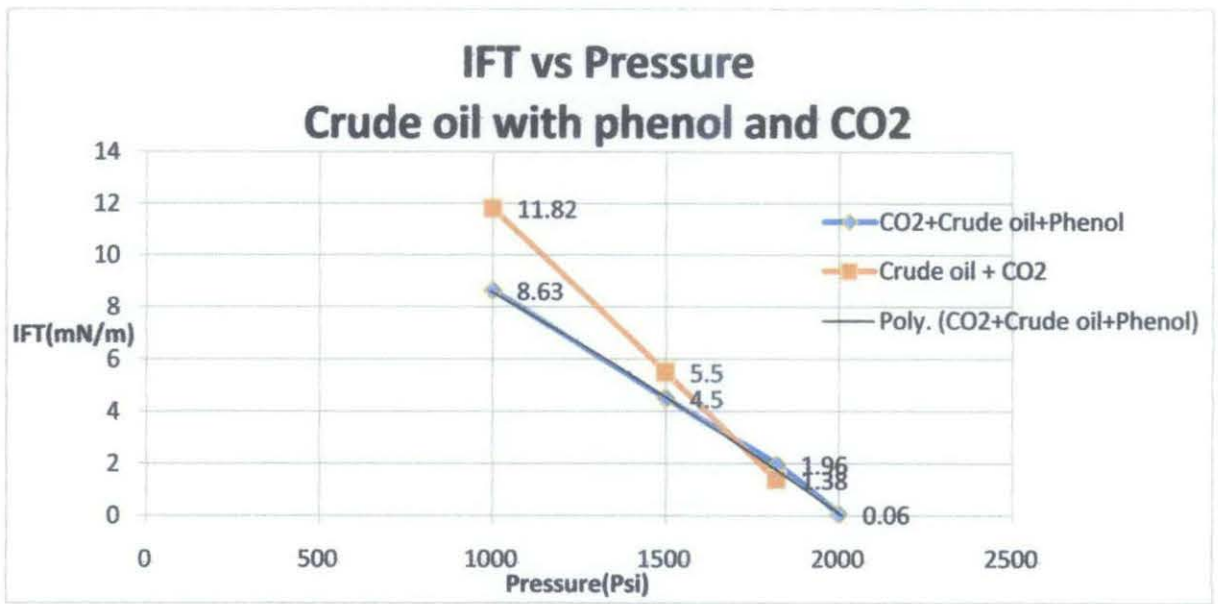


Figure 20: IFT versus pressure graph for crude oil with Phenol and CO₂

The IFT measurements were compared with CO₂ and crude oil. Based on the Figure 10 above, phenol reduced the IFT measurement until 1500 psi. Above 1820 psi the IFT reading is higher.

From this graph, the MMP is 2000 psi. The correlate MMP for impure CO₂ injection using phenol is 1255 psi. By comparing the result with the IFT, it shows that there is 37% error.