CERTIFICATION OF APPROVAL

INVESTIGATION OF THE EFFECTS OF WAX CONTENT ON MINIMUM MISCIBILITY PRESSURE OF CARBON DIOXIDE IN WAXY OIL

By

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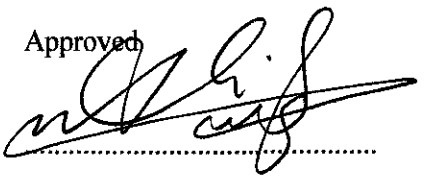
Approved



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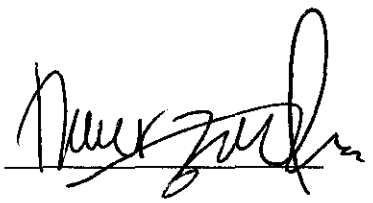
TRONOH, PERAK
September 2011

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.



MAERZAD MOHAMED NAZMI

Abstract

The reservoir engineer's objective is to produce from oil and gas reservoirs with the highest economical recovery factor. For this reason, Enhanced Oil Recovery (EOR) methods were developed. EOR methods can increase field recovery factor and prolong field life, thus improving its economic value (E.Manrique and J.Wright, 2005). One of EOR methods that is becoming favourable is miscible displacement. For this method, there are a range of gasses suitable for miscible displacement (e.g. Propane and Methane), however, Carbon Dioxide (CO2) is most commonly used due to availability and less expensive than Liquefied Petroleum Gas (LPG). CO2 can also reduce the oil's viscosity.

In miscible displacement, one of the most important parameters that need to be investigated is minimum miscibility pressure (MMP). This is the pressure where the crude oil and CO2 gas will become miscible. MMP can be affected by wax content, however to an unknown degree. Waxy oil constitutes that the oil has paraffin content in it. After weighing the options, experimental work was chosen to determine MMP of oil samples and the effects of wax content on CO2 MMP; and a technique called the Vanishing Interfacial Tension (VIT) will be employed. The basic principal of this technique is that when MMP is achieved, the IFT between CO2 and oil will become zero. Several oil samples with varying wax content have been experimented to obtain the pressure at which the IFT approaches zero, also known as MMP.

5 samples were concocted for the experiment. However, the experiment failed to obtain one of the sample's MMP due to technical difficulties. MMP for the following samples were obtained; 3446 psi, 3706 psi, 3391 psi and 3332 psi for 5%, 15%, 20% and 25% wax content respectively. As noted from 5% and 15%, the MMP increases, however from 15% to 25%, it suddenly decreases. The theory is that there may be insufficient points to extrapolate because of equipment safety limitations. From the experiments, it is concluded that with increasing wax content, the MMP will also increase.

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Chapter1: Introduction/Background Studies

1.1: Introduction and Background

In the pursuit for the precious black gold, many methods for squeezing oil out of the reservoir have been developed. Tertiary or Enhanced Oil Recovery (EOR) is one of the methods developed for the above purpose. Tarek Ahmad[1] (2001) describes EOR methods as the additional recovery that is not obtained from both primary and secondary recovery methods. EOR can increase field recovery factor and prolong field life, thus improving its economic value (E.Manrique and J.Wright, 2005). This is because, EOR are designed to recover residual oil, those economically unrecoverable by primary and secondary method (Tarek Ahmad, 2001).

Miscible displacement is fast becoming favourable, especially using Carbon Dioxide (CO2) due to several reasons:-

1. Viscosity, density and compressibility are positively impacted.
2. Miscibility can be achieved at normal reservoir pressures.
3. Displacement efficiency is high compared immiscible displacement.
4. Aids recovery by solution gas drive.
5. Useful over a wider range of crude oil than hydrocarbon injection methods.
6. MMP can be achieved again even if it is lost.

CO2 is mostly selected over a wide range of gasses available (methane, propane, nitrogen) due to its availability and price. For CO2 to become miscible in oil, one key parameter needs to be known; minimum miscibility pressure. Minimum miscibility pressure is the pressure where two naturally immiscible fluids will achieve miscibility. There are many factors which affect MMP; however this research aims to find out the effects of wax content exclusively, on MMP in waxy oil.

Any oil which has wax content will fall into waxy oil regardless of the type of the reservoir fluid the oil falls into. Paraffin, a heavy hydrocarbon component, constitutes the wax content. Becker[5] (1997) stated that, during production, the lighter and volatile

components will first try to move out of the reservoir initially, leaving behind the heavier components which include wax. This will lead to the reservoir having a sharp drop of pressure, which decreases the natural drive force and the heavier components of the oil left will be hard to move, in other words, decreasing mobility. This oil will eventually be stuck in the reservoir and known as residual oil. As stated before, EOR methods are designed to recover residual oil stuck in the reservoir and miscible gas displacement could prove to be a solution to this problem.

Over the past years, research has proven miscible gas displacement to be very rewarding. Holm[8] (1987) did a field test on Mead Strawn in 1964 to find out the effects of CO2 miscible displacement on recovery factor. From the field test, it was found out that by using miscible displacement, oil recovery increased by 35%. This research paved the way for other miscible displacement researches as it showed very promising results. It is therefore essential to pursue a better understanding of the effects of wax content on MMP of CO2.

1.2: Problem Statement

According to Becker[5] (1997), primary recovery usually produces lighter hydrocarbons and the heavier components will be left behind. The heavier components may include waxy oil. Waxy oil has a much higher viscosity. Also considering the effect of reduced reservoir pressure, waxy oils, though very valuable, will be very hard to produce. All of this makes EOR using CO2 miscible displacement a perfect solution. In Malaysia alone, there are several fields which have wax content in its oil [Kelechukwu and Abu Azam[13], 2008].

Martin and Taber[18] (1992) concluded that CO2 can make the oil swell and reduce its viscosity. It is also proven in field studies conducted by them that ultimate recovery of CO2 miscible injection is always higher than hydrocarbon miscible injection. They also acknowledged that further research is needed in the CO2 miscible displacement area. However, for this method to work the reservoir pressure must be higher than CO2 MMP, otherwise CO2 will not be soluble in the oil. Certain reservoirs cannot withstand the high pressure required for dissolving CO2 in oil. Therefore, it is crucial to determine the MMP for CO2 before commencing a CO2 miscible displacement project.

Holm[8] (1987) concluded that MMP is mostly affected by temperature and the heavier fraction of the oil composition. At high temperature, it was found that MMP will be higher. The latter will have the most effect on MMP. However, it is yet unknown how wax content would affect MMP. Therefore, it is crucial that values of MMP for different percentage of wax content is obtained and further investigated to gain understanding of the trend of CO2 MMP with regards to wax content.

1.3: Objectives and Scope of Study

The objectives of this study are:

- To assess the most suitable method to ascertain CO2 MMP.
- To determine MMP of CO2 for oil samples with different wax content percentage.
- To study the effects of wax content on CO2 MMP.

The scopes of studies are as follows:

CO2 MMP Determination

This project focuses on determining the CO2 MMP for samples with different wax content. Regardless of condition, a CO2 miscible displacement project should not be hastily done without knowing the MMP first. From literatures available, MMP can be determined using calculation, correlation, simulation or experimental.

For this project, experimental work is chosen. In experimental work, there are 3 common ways to determine the MMP which is Vanishing Interfacial Tension (VIT), Rising Bubble Analysis (RBA) and Slim Tube Test. Due to the interest of time and availability of equipment, VIT will be the method of choice for this project.

VIT is basically placing a drop of fluid at the end of a needle, suspended in CO2 gas. The drop will be monitored through a camera which is connected to a computer. The computer will then calculate the Interfacial Tension (IFT) between the droplet and the gas. The basic idea is that when miscibility is achieved, the IFT will become zero. So, IFT will be observed while the pressure is increased and the pressure where IFT becomes zero or near-zero is noted as the MMP.

CO2 MMP – Wax Content Relationship Determination

Part of the objective is to analyse the effect of wax content on CO2 MMP. Oil sample with different wax content will be prepared and the MMP for each sample will then be determined. From the results obtained, it will be plotted and analysed. From there, the relationship between CO2 MMP and wax content can be determined.

Chapter 2: Literature Review

2.1 Carbon Dioxide Miscible Displacement

For CO2 miscible displacement, CO2 will be injected into the reservoir at a condition where CO2 will become miscible (S.C. Ayirala and D.N. Rao[2], 2006). Gas is considered miscible in the fluid or solvent if both gas and fluid can assume a single phase. The basic of this phenomenon is, mass will be transferred between the gas and the solvent. According to Lee *et al.*[15] (1988), the mass transfer mechanism involved is vaporizing gas drive. CO2 is a lean gas which will strip the liquid which is rich in intermediate and heavy hydrocarbons until the gas has similar composition or density with the solvent and become miscible. Due to the above stated property of CO2, CO2 is a very useful gas in terms of miscible injection for miscible displacement for crude oil with high intermediate hydrocarbon components than other gasses. He also stated that unlike methane injection, CO2 miscibility is multiple contact miscibility (MCM), which means that the mass transfer between the gas and the oil occurs with repeated contact and it would not achieve miscibility at first contact with the oil.

2.2 Minimum Miscibility Pressure

One of the drawbacks of miscible displacement is that the gas can only become miscible with the fluid after it exceeds a certain pressure. This pressure is defined as MMP. Miscible displacement is not suitable for reservoirs which have a fracture pressure lower than MMP. For this reason, miscible displacement method is only suitable for reservoirs deeper than 2500ft (F. David Martin and J.J. Taber[18], 1992).

2.3 Calculation Methods of Obtaining MMP

Mogensen *et al.*[19] (2009) conducted an investigation on different methods of obtaining MMP. They conducted a study on key tie line calculation method. The most basic calculation method for key tie line method uses the ternary diagram with multi-contact

miscible displacement. He summarized that there are 3 types of key tie line which were developed by Johns and Orr (1997), Wang and Orr (1997) and Jensen et al. (1998) and the difference between these calculation methods are respectively:

a) Tie line extending through initial oil composition
b) Tie line extending through initial injected gas composition
c) Series of cross over tie lines

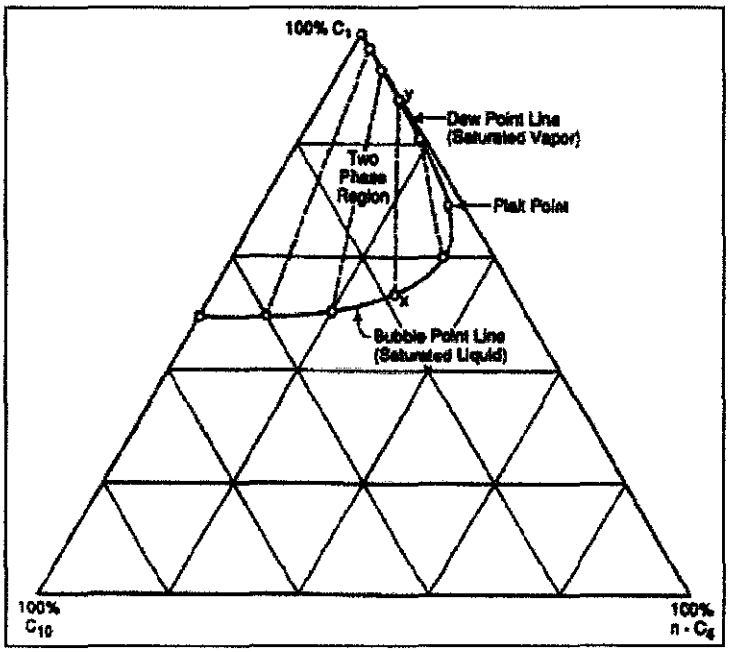

Figure 1: An example of a ternary diagram from Holm and Josendal[10]

2.4 Simulation Methods of Obtaining MMP

Mogensen et al.[19] (2009) also considered simulation methods, which are multiple mixing models. Simulation is either done through single cell or multiple cell simulation. In this method for CO2, finite volume of reservoir oil and CO2 are repeatedly contacted and changes in volume for oil and gas, density and composition of equilibrated oil and gas are measured. Both forward and reverse contact experiments are done. Forward contact experiment is done by changing the oil to a new oil sample after each repetition however the gas from the previous repetition is used again in the next repetition. Reverse contact experiment is done contrary to the forward contact experiment, whereby the gas remains the same while the oil is the same oil from the previous trial. The figure below

demonstrates how the experiments are done (Fig. 2 &3). This will simulate the vaporising and condensing mechanism.

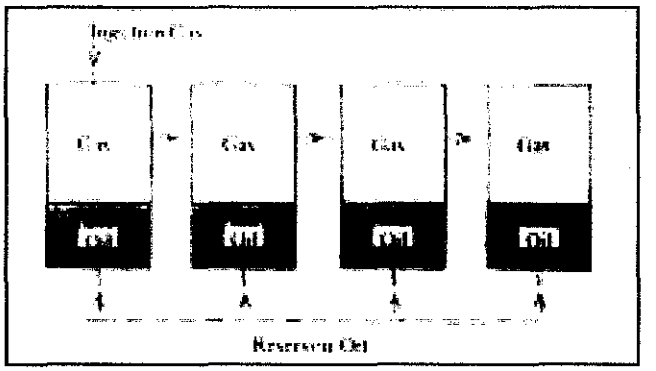

Figure 2: Forward Contact Experiment Setup

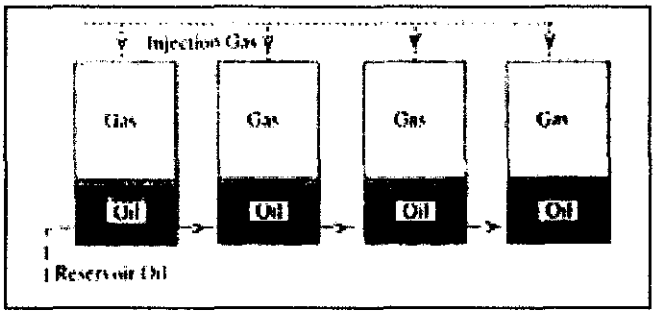

Figure 3: Reverse Contact Experiment Setup

However, Mogensen *et al.*[19] noted that the above method has a huge vice; they simulated both conditions separately. Ahmadi and Johns (2008) proposed a modification to the method which is claimed to be more robust. The first cell will be filled with equal amount of CO2 and oil. After the gas and oil has reached equilibrium, the gas will be brought to another cell containing a fresh sample of oil and the oil will be brought to another cell containing a fresh sample of gas. The tie lines will be developed and the minimum tie length is calculated. The pressure will be adjusted and the entire process is repeated until the key tie line in any cell is zero. This is the downside of this process as it is an iterative process.

2.5 Correlation Methods of Obtaining MMP

Mogensen *et al.*[19] also conducted a study on empirical calculation method or simply correlation method. Published correlations that are accepted by the industry are (with year of publication and their considerations):-

a) Cronquist Correlation (1978) uses molecular weight of C_{5+}
b) Yellig and Metcalfe Correlation (1980) which varies the MMP only to temperature
c) Holm and Josendal Correlation (1982) which is similar to Yellig and Metcalfe Correlation but they considered molecular weight of C_{5+}
d) Glaso Correlation (1985) utilises molecular weight of the plus fraction
e) Yuan *et al.* Correlation (2004) which uses the same basis as Glaso but incorporates intermediate $C_5 - C_6$

2.6 Experimental Methods of Obtaining MMP

There are 3 widely used methods for determining MMP experimentally. They are:-

2.6.1 Slim Tube Test

This method is the accepted method in determining MMP in the oil and gas industry. Its apparatus is designed so that it closely mimics the reservoir condition. According to Elsharkawy *et al.*[7] (1992), there is no standard design, condition or operating procedure for slim tube test. The apparatus need only to comprise of items described in Figure 4 below. Basically, the coiled slim tube is packed with uniform sized grain to represent the tightly connected pore spaces and oil will fill the coiled tubing initially. Then, CO2 will be injected to displace the oil mimicking CO2 displacement in the reservoir. Ultimate oil recovery will be plotted versus operating pressure and the pressure corresponding to 100% recovery is taken as the MMP. Eventually, MMP is determined as the pressure at the break over of the recovery curves. Ayirala and Rao[2] (2006) gave examples of miscibility criteria defined in their work which are 80% at gas breakthrough and in a range of 90% to 95% of ultimate recovery.

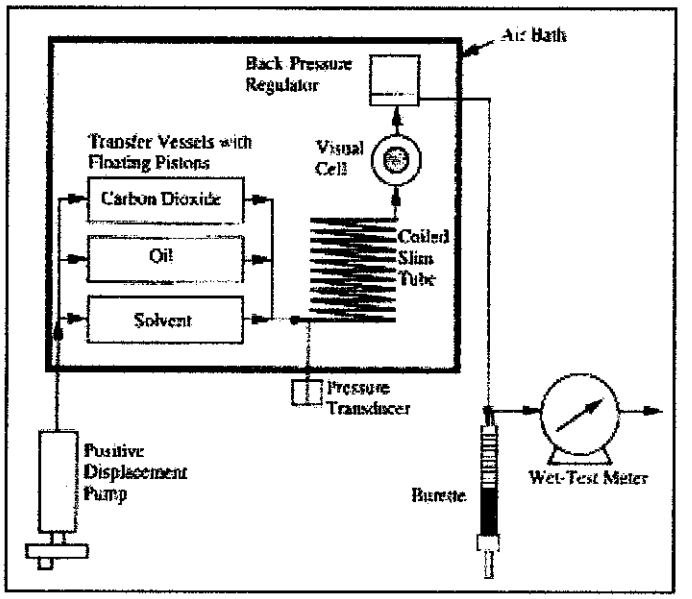

Figure 4: Essential Apparatus Schematics of Slim Tube Test from Elsharkawy *et al.*[7]

According to Ayirala and Rao[2], and Holm and Josendal[9], it was found that a slim tube test could take up to a few weeks and therefore this technique is very time consuming. The time limit for project is less than 10 weeks thus this method is considered unfeasible. Although this method is regarded as the most effective and accurate method, it is still unable to simulate the actual reservoir condition which includes effects like viscous fingering, dispersion and most importantly, heterogeneity (Ayirala and Rao[2], 2006). Recently, micro slim tube test has emerged and the only difference is that it utilises a much smaller tube to better represent the tight connected pore spaces.

2.6.2 Rising Bubble Analysis

Apart from the slim tube test, Elsharkawy *et al.*[7] (1992) also did a study on rising bubble analysis (RBA) method. It was developed in the 1980s. In this method, the shape of a bubble of gas rising in oil is observed. As MMP is reached, the bubble shape will gradually change shape from spherical until it becomes skirted ellipsoidal cap. Figure 5 below demonstrates the bubble shape as the pressure is increased to MMP.

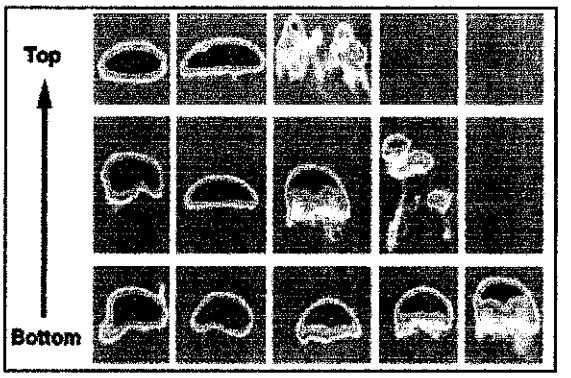

Figure 5: Bubble shape change as pressure is increased from left to right until finally, at the far right, MMP is achieved. (Zhou and Orr$_{28}$, 1998)

Zhou and Orr$_{28}$ (1988) conducted a study to specifically address rising bubble analysis. They confirmed that the change in bubble shape in mainly caused by the change in IFT between the oil and gas. Researchers have concluded that relatively, the cost of RBA is less than slim tube test. The test is considered as qualitative because the result requires observation of the change in shape and appearance of the bubble. It takes at most 2 hours to run this test. Figure 6 describes the apparatus used in this method. Note that its main feature is the glass tube for viewing the bubble shape.

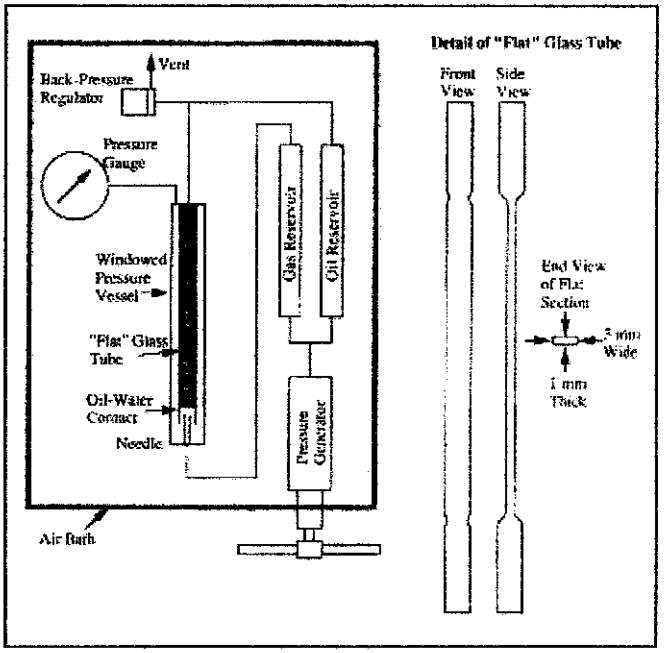

Figure 6: Rising Bubble Analysis apparatus and setup from Elsharkawy *et al.*$_7$

2.6.3 Vanishing Interfacial Tension

Jessen and Orr[12] (2008) stated that this technique has been proposed by a few researchers, notable ones include Ayirala, Rao et al[2,3,4]. Ayirala and Rao[2] (2006) explained the basic theory behind the method is that when miscibility is achieved, the interfacial tension between the oil and gas will become zero. This technique utilises measuring IFT at increased pressure at reservoir temperature (assuming reservoir temperature remains relatively constant throughout the reservoir). The experiment can be done by either employing capillary rise analysis or pendant drop analysis. In 2006, Ayirala and Rao conducted a capillary rise experiment to determine the MMP. Figure 7 below describes the results obtained from their experiment. From their graph, the value of MMP taken at IFT=0 is equivalent to 1775 psi.

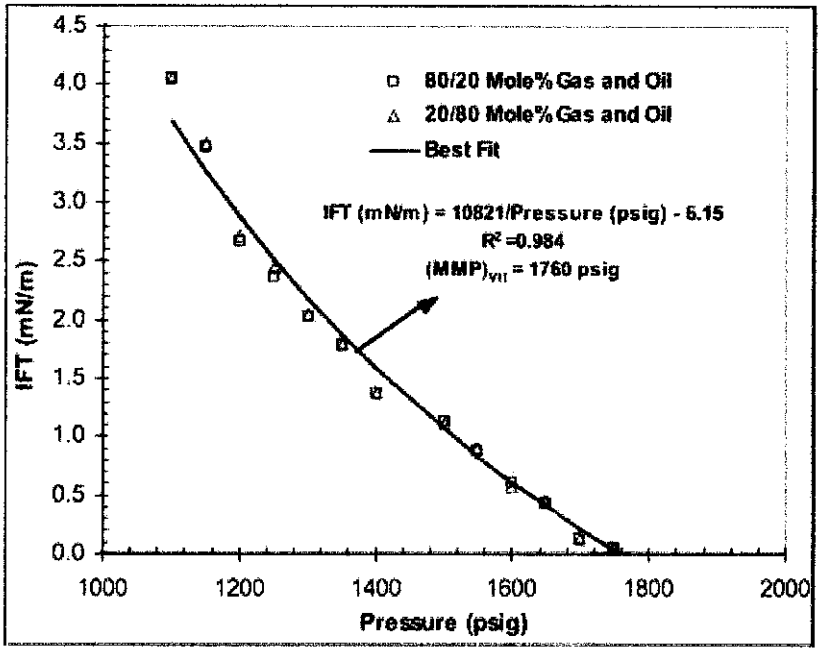

Figure 7: Example for vanishing interfacial tension test done by Ayirala and Rao[2] in 2006

2.7 Surface and Interfacial Tension

When two immiscible fluids are in contact, the fluids are separated by a well-defined interface, which are only a few molecular diameters in thickness. In the middle of liquid phase, a fluid molecule will be pulled at every direction whereas at the interface of the two fluids, there is an imbalance between the forces. This would create a barrier between

the fluids from becoming miscible (denoted by the dark blue line in Figure 8). High values of the surface tension means the molecules tend to interact strongly. Lower values mean the molecules do not interact as strongly and will easily become homogeneous. Interfacial tension is described as a measurement of energy on the barrier separating the two phases. IFT can be measured using the pendant drop method. They have the dimensions of force per unit length (Newtons/meter or Dynes/cm).

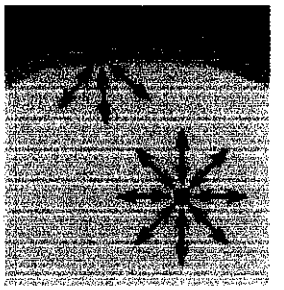

Figure 8: Diagram of the forces on two molecules of a fluid (blue) interfacing with another fluid (black) (Snacks, 2010)

Using the pendant drop method (Figure 9), the geometry of a drop is analysed optically. A drop is generated from the end of a capillary needle in a bulk fluid at reservoir conditions (Pressure and Temperature). With a calibrated and accurate video lens system, the complete shape of the drop is captured and analysed with software. Then, the Laplace equations of the analysis are solved numerically over its complete shape to get the IFT.

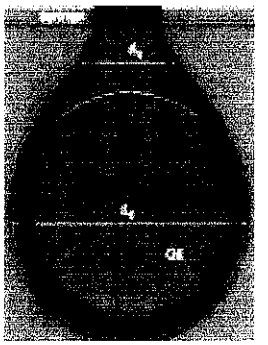

Figure 9: Droplet of oil suspended in gas

2.8 Waxy Oil

According to Mansoori[15],

> Any oil regardless of classification which has paraffin and naphthenic wax content is considered as waxy oil. Due to the composition, wax will precipitate out of the oil if the cloud point temperature is reached. Cloud point temperature is the temperature at which paraffin wax or other solid substance begins to separate from a solution of oil. The name is given due to a cloudy appearance of the oil at this temperature.

Klaus and Mieczysław[12] (1994) gave definition for paraffin and naphthenes. Paraffin are acyclic alkanes includes both normal and isoparaffins. Acyclic alkane means that normal paraffin is a straight chain saturated hydrocarbon chain where every carbon atom is fully attached with hydrogen atoms without any double bond. Its basic molecular formula is C_nH_{2n-2}. According to Lee *et al.*[15], paraffin ranges from C_{18} to C_{36}. Figure 10 shows an example of alkane molecule. Naphthenes are cycloalkanes with most of them have paraffinic side chains attached to them. Its basic molecular formula is C_nH_{2n}. Naphthene ranges from C_{30} to C_{60}. Figure 11 shows an example of a cycloalkane molecule taken from Klaus and Mieczysław[12] (1994).

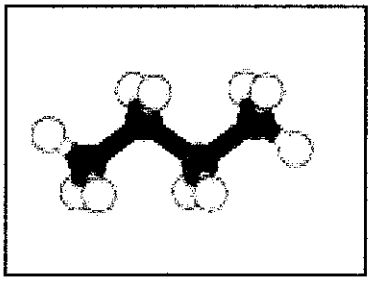

Figure 10: A ball and stick figure of C4H10

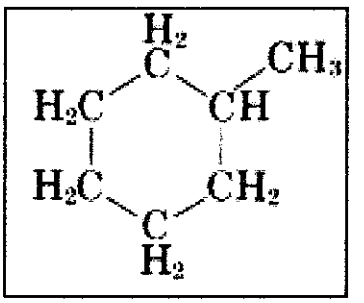

Figure 11: An example of a cycloalkane with a side chain

Chapter 3: Methodology

3.1 Methods Selection

Experimental work has been chosen to determine CO2 MMP for waxy oil, specifically utilising Vanishing Interfacial Technique (VIT). There are many techniques available to obtain CO2 MMP experimentally. Discussed in this project are using VIT, Rising Bubble Analysis (RBA) and slim tube test or micro slim tube test. These were thoroughly discussed in the literature review.

RBA method is a relatively fast way to obtain MMP. This is a qualitative type experiments. Bubble obtained from the apparatus will be compared with the charted bubble. This technique applies mass transfer principals to determine MMP. As explained in the literature review, IFT works much like a barrier. Lower IFT will permit more mass transfer between the two immiscible fluids. As mass transfer occurs more rapidly, the shape of the bubble will be less spherical. When the bubble no longer has a clear boundary separating between the two fluids, MMP is considered reached. Zhou and Orr (1998) conducted a study to compare RBA to that of Falling Drop Analysis (FDA). The difference between the two is that instead of releasing a bubble into the capillary tube, a drop is released instead. FDA method would also have a similar chart that would also require user observation to determine MMP. Currently, a rising bubble apparatus is not available in UTP

Slim tube test or micro slim tube test employs a tube which is packed with uniformly sized grains. Slim tube test is the accepted method for obtaining MMP in the industry since it closely mimics reservoir conditions compared to other methods. Currently, this machine is available in UTP, however the machine is still undergoing assembly.

VIT uses a very direct approach; when two immiscible fluids become miscible, IFT between the two fluids will become zero or approaching zero. Using VIT, IFT from different pressure points are obtained and plotted. The points will then be extrapolated to IFT=0. The pressure at the pressure axis intercept is noted as the MMP. VIT obtains fast and acceptable results.

In 1999, Kechut *et al.*[20] ran an experiment to determine an MMP using a technique similar to VIT. It employs a prototype machine called Vapour Liquid Equilibrium-Interfacial Tension (VLE-IT). Figure 12 below shows the setup used by Kechut. Although in UTP, a VLE-IT apparatus is not available, IFT 700 has every function VLE-IT has except for the high temperature density meter. Density in IFT 700 has to be obtained and input separately.

IFT 700 is an interfacial tension meter. The device will measure interfacial tension between two fluids according to the selected configuration of either perndant drop or rising bubble. IFT 700 can run measurement up to 10,000 psi and 200 °C. Figure 13 explains the setup. IFT 700 is readily available in UTP.

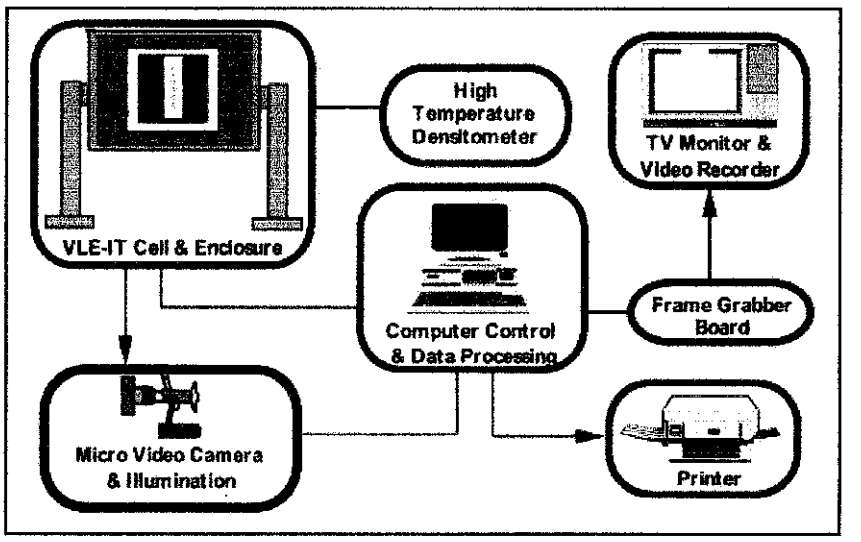

Figure 12: VLE-IT Major Components (Kechut *et al.*[20], *1999)*

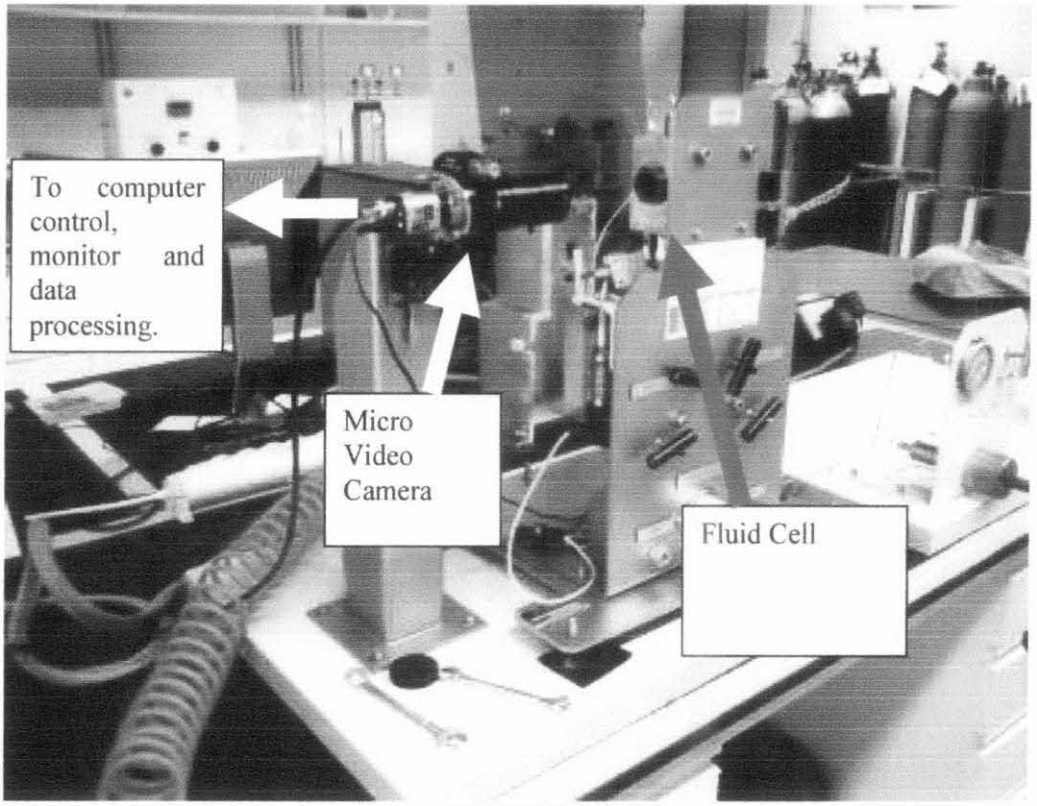

Figure 13: IFT 700 Setup

3.2 Waxy Oil Sample

Mineral Oil Mixture Preparation

As UTP does not have a cooling bath needed to properly determine crude oil sample's wax content, the experiment is done by using a synthetic oil sample. White mineral oil, also known as paraffin oil (CAS 8012-95-1) is utilised to control wax as the only manipulated variable. The following procedure describes steps taken to synthesize synthetic waxy oil sample:

1. Paraffin weight for 5%, 10%, 15%, 20% and 25% wax content was calculated using equation 1 below. The volume of light oil that was used is 50ml which weighs 42.381g at 25°C. The weights needed to concoct the samples are tabulated in table 1 below.

$$weight_{pure\ paraffin} = wax\ content\% \times weight_{light\ mineral\ oil}$$

Equation 1: Paraffin Weight Calculation

Table 1: Weight of Paraffin Used to Synthesize Synthetic Oil Sample

Wax content Percentage	Weight of Paraffin Needed (g)
5%	2.12
10%	4.24
15%	6.36
20%	8.48
25%	10.60

2. The paraffin block is heated and filtered to remove any impurities.
3. The filtered paraffin is heated again and mixed with 50ml of white mineral oil.

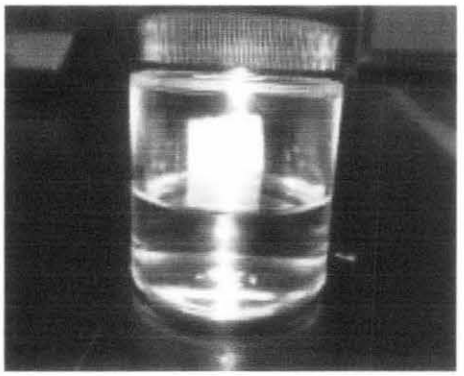

Figure 14: White Mineral Oil

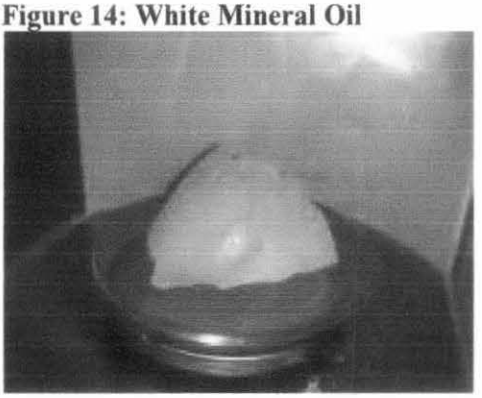

Figure 15: Pure Paraffin

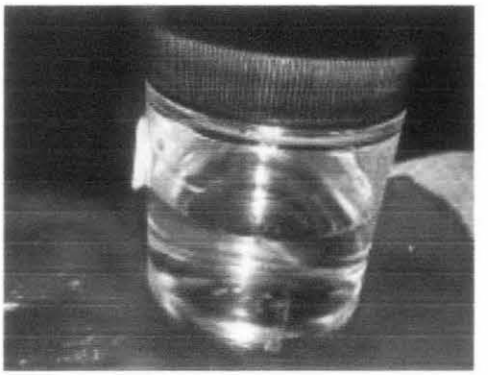

Figure 16: Waxy Mineral Oil at 80 °C

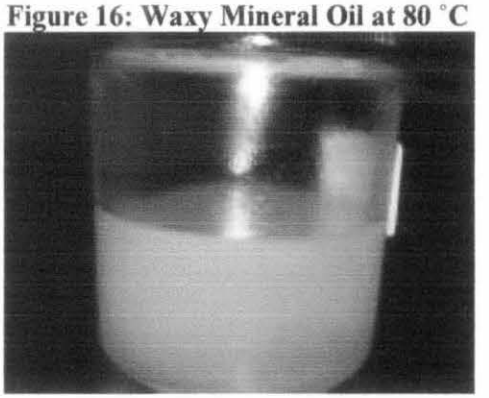

Figure 17: Waxy Mineral Oil at Room Temperature

3.3 IFT Measurement

Determining MMP

IFT will be the observed parameter in this experiment. IFT at pressure points from 1000 psi to 2800 psi are obtained. The experiment is supposed to continue until no drop of oil can be formed on the needle, however, due to equipment limitation; the maximum pressure allowable to obtain IFT is 2800 psi.

There already exists a new machine in UTP specifically used to determine MMP which is micro-slim tube machine. However, as of now, the machine is still undergoing assembly. Perhaps, in the future if another scholar were to pursue a similar topic, micro slim tube should be his choice of MMP determination device. Below are the procedures used to measure waxy oil-CO2 IFT:-

i. Determining the density

To measure IFT with IFT 700 requires the density of the fluids at pressure and temperature used in the investigation because fluid density is one of the variables used to calculate IFT. Density of CO2 is obtained from Peace Software by Berndt Wischnewski[6]. CO2 densities from this site are calculated from the real gas equation. CO2 densities obtained from this site are tabulated in Table 2 below. Density of waxy oil will change greatly with temperature however; it experiences small density changes with regard to pressure. Assuming negligible changes in density over pressure changes and negligible temperature change across the reservoir, the density of oil sample will only be measured at the reservoir temperature only. Below is the procedure describing how to obtain density using Anton Paar DMA 4500 M.

1. U-tube inside Anton Paar DMA 4500 M Density Meter (Density Meter) was flushed using toluene, a solvent repeatedly to ensure the tube is free of fluid.
2. The oil sample and device was heated to reservoir temperature at 80 °C.
3. 5ml of oil sample was injected into the device using a syringe.

4. Measurement was run.
5. The oil sample was withdrawn using a syringe
6. Repeat step 1 for all samples.
7. Clean off tube and pump with a large amount of toluene and dry off using ethanol until no bubbles or fluids can be observed.

8. Table 2: CO2 Density at 80 °C obtained from peace software.

Pressure (psi)	Density (g/cm³)
1000	0.13158
1500	0.235656
2000	0.377142
2200	0.432455
2400	0.478596
2500	0.501667
2600	0.524737
2800	0.570879

Figure 18: Anton Paar 4500 M

ii. Determining the IFT and MMP

For this experiment, pendant drop analysis is used. Although at very low IFT, the measurement would be quite inaccurate as a drop might not be able to be formed, it can be compensated as in UTP, there is no equipment suitable to run a capillary rise technique, which has better accuracy at very low IFT [Ayirala and Rao$_2$, 2006]. Below are the procedures to obtain IFT measurement and consequently, MMP using a machine readily available called IFT 700.

1. There are two inlet holes available. Waxy oil sample was injected into inlet A and CO2 gas through inlet B. Inlet A and B are shown in Figure 20 below.
2. After the fluids have entered their respective fluid tank, the valve was closed.
3. The valve for CO2 gas to flow from the fluid tank into the fluid cell chamber was opened. CO2 will fill the pressure chamber.
4. The temperature limit was set slightly above the temperature of interest, i.e. reservoir temperature so that the chamber would heat up and able to maintain reservoir temperature. The heating switch was turned on.
5. After the temperature has reached the desired temperature, the pressure was set to 1000psi.
6. A droplet of oil was released using the valve.
7. The machine was calibrated and IFT was measured.
8. Steps 5-7 was repeated for pressure increments of 200 psi until 2800 psi.

From the plot, obtain the point of the curve where IFT becomes zero. Using IFT 700 which is an IFT measuring device, it is impossible to obtain a zero IFT reading because, as explained earlier, IFT is a measure of strength the barrier between the two fluids has. If IFT is zero, there will be no barrier to separate the two fluids from mixing with each other. Figure 19 shows a picture of IFT 700. Figure 20 is a simplified IFT 700 schematic diagram.

The procedures for this experiment are made with reference to Wan Malinda's[27] (2010) work.

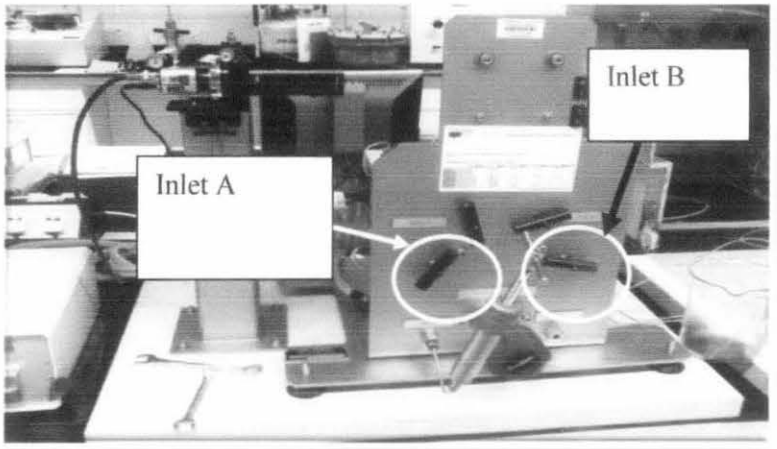

Figure 19: IFT 700, a machine to measure IFT

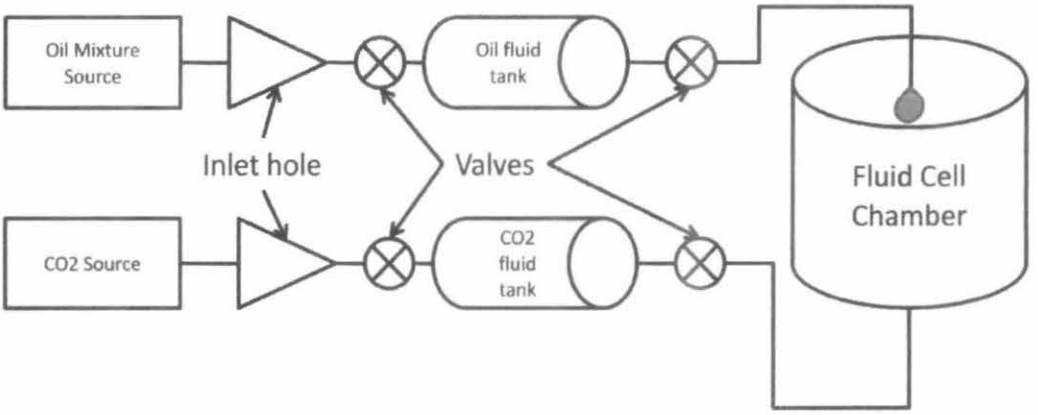

Figure 20: Simplified schematic diagram of IFT 700

3.4 Key Milestone

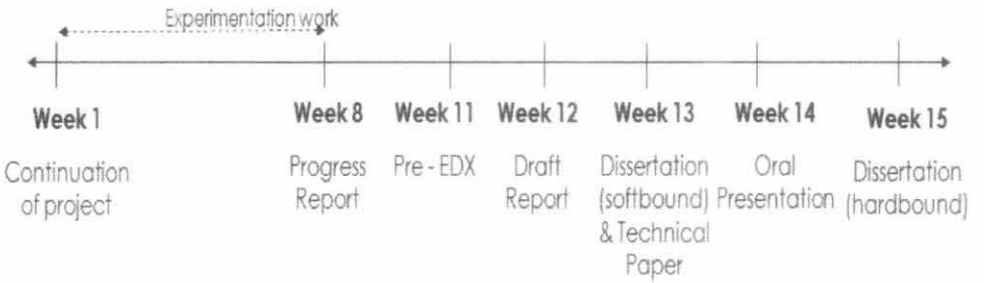

Figure 21: FYPII Key Milestone

The project was completed by week 11 with results prior to Pre-EDX poster submission.

3.3 Gantt chart

Table 3: Gantt chart showing project progress

FINAL YEAR SEMESTER (May 2011)		2nd														
No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1.	Collect chemicals and book apparatus involved								Mid-semester break								
2.	Preparation of samples																
3.	Determine MMP of Different Sample																
4.	Submission of Progress report																
5.	Analysis on MMP Values																
6.	Pre-EDX																
7.	Submission of Draft report																
8.	Submission of Dissertation																
9.	Submission of Technical Paper																
10.	Oral Presentation																
11.	Submission of Project Dissertation (Hard bound)																

Chapter 4: Results and Discussions

4.1Density Measurement

Using Anton Paar DMA 4500 M, waxy mineral oil density for all the samples were obtained at 80 °C. The results are tabulated in table 3.

Table 4: Waxy Oil Sample Density at 80 °C Obtained From Anton Paar DMA 4500M.

Weight Percentage (%)	Density at 80 °C (g/cm³)
5	0.8066
10	0.8051
15	0.8038
20	0.8022
25	0.8006

A major problem faced when using Anton Paar DMA 4500 M is the safety issue. The chemical solvent for waxy oil is toluene. Toluene is a very dangerous chemical which requires stringent handling of the chemical. Toluene is hazardous to health and is known to corrode certain materials.

4.2 IFT Measurements

4.2.1 5% Wax Content Oil Sample

Table 5: Pressure and IFT for 5% Wax Content

Pressure, psig	IFT, mN/m
1000	11.28
1500	6.98
2000	4.28
2200	3.94
2400	3.12
2500	2.87
2600	2.71
2800	2.09

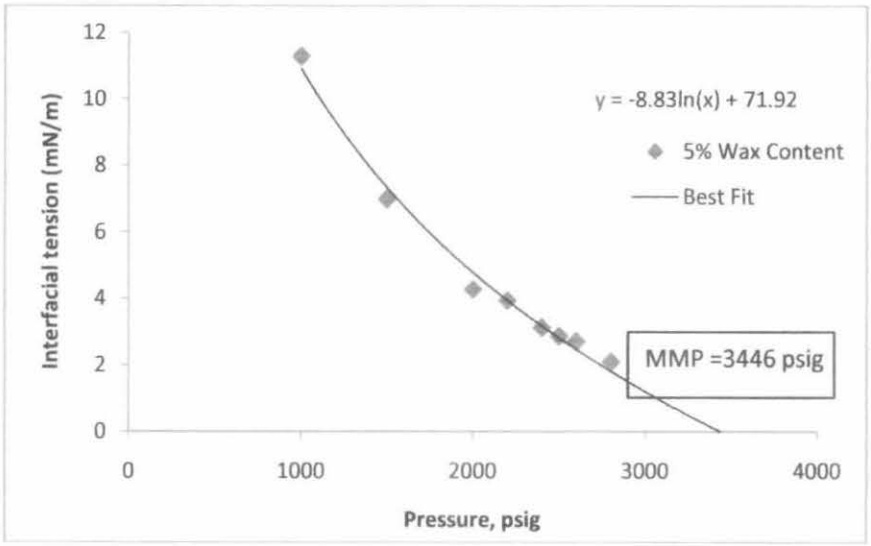

Figure 22: Determining MMP by Extrapolating IFT vs Pressure Plot for 5% Wax Content Waxy Oil Sample

Figure 22 shows how MMP is obtained by plotting IFT versus pressure and extrapolating it to zero. Using Excel, a best fit line was obtained. Using the equation provided by Excel, the pressure when IFT becomes zero is calculated and taken as MMP. In this example, MMP is taken to be 3446 psig.

4.2.2 10% Wax Content

Table 6: Pressure and IFT for 10% Wax Content

Pressure, psig	IFT, mN/m
1000	11.31
1300	9.54
1500	6.97

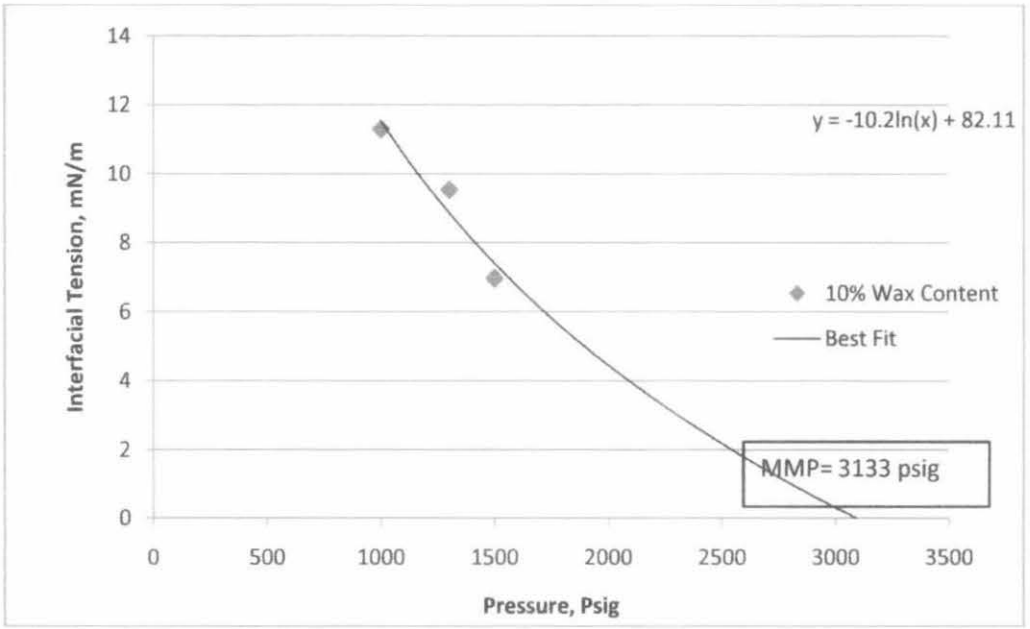

Figure 23: Determining MMP by Extrapolating IFT vs Pressure Plot for 10% Wax Content Waxy Oil Sample

For 10% wax content, only 3 pressure points were managed to be produced. During 10% wax content run, there was insufficient CO2 to run the experiment, so IFT only for pressure up to 1500 psig were managed to be obtained. To keep with the schedule, the 10% wax content sample experiment was pushed behind. Due to limited time available and machine malfunction, a rerun for 10% wax content was never done. The MMP obtained is very inaccurate because IFT is not linearly dependant on pressure and 1500 psig is too far from the MMP. MMP for 10% wax content is therefore dismissed.

4.2.3 15% Wax Content

Table 7: Pressure and IFT for 15% Wax Content

Pressure, psig	IFT, mN/m
2000	5.4
2200	4.7
2400	4.16
2800	2.34

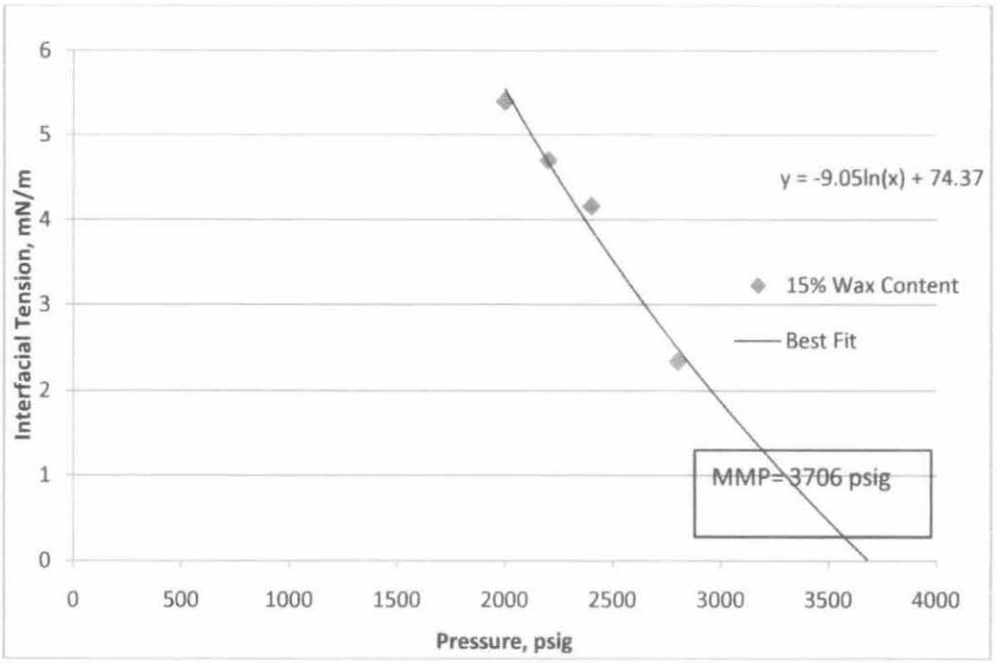

Figure 24: Determining MMP by Extrapolating IFT vs Pressure Plot for 15% Wax Content Waxy Oil Sample

For 15% wax content, only 4 points were obtained due to time constraint on laboratory working time. In the same day, a class was using the lab. By time estimation, only 4 points can be obtained, so pressures 2000 psig, 2200 psig, 2400 psig and 2800 psig were chosen. For 15%, MMP is taken to be 3706 psig.

4.2.4 20% Wax Content

Table 8: Pressure and IFT for 20% Wax Content

Pressure, psig	IFT, mN/m
1000	11.89
1500	7.73
2000	5.02
2200	3.99
2400	3.32
2500	2.85
2600	2.74

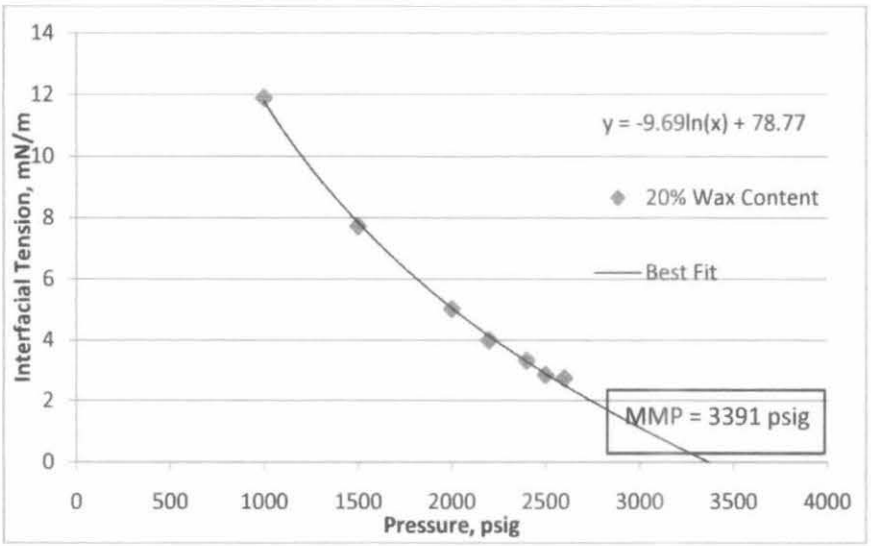

Figure 25: Determining MMP by Extrapolating IFT vs Pressure Plot for 20% Wax Content Waxy Oil Sample

Figure 25 shows how MMP is obtained by plotting IFT versus pressure and extrapolating it to zero. Using Excel, a best fit line was obtained. Using the equation provided by Excel, the pressure when IFT becomes zero is calculated and taken as MMP. In this example, MMP is taken to be 3391 psig.

4.2.5 25% Wax Content

Table 9: Pressure and IFT for 25% Wax Content

Pressure	IFT
1000	11.34
1300	9.62
1500	7.94
2000	4.9
2200	4.01
2400	3.11
2500	2.66
2600	2.04
2800	1.89

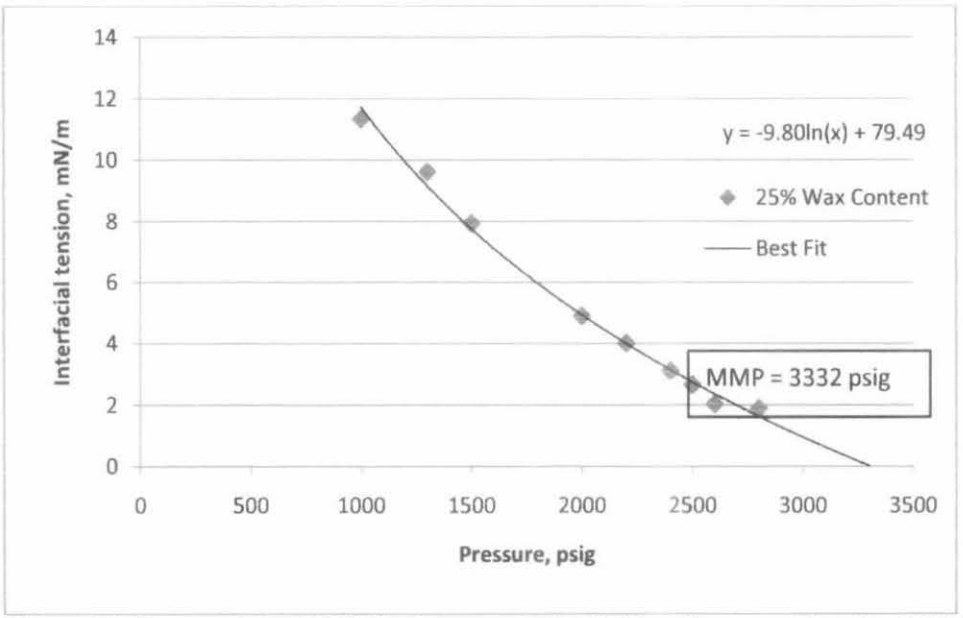

Figure 26: Determining MMP by Extrapolating IFT vs Pressure Plot for 25% Wax Content Waxy Oil Sample

Figure 26 shows how MMP is obtained by plotting IFT versus pressure and extrapolating it to zero. Using Excel, a best fit line was obtained. Using the equation provided by Excel, the pressure when IFT becomes zero is calculated and taken as MMP. In this example, MMP is taken to be 3332 psig.

4.2.6 Problems Encountered

The set of experiment needs to be proceeded until it comes to the pressure where a stable oil droplet cannot be produced anymore. The machine can withstand pressure up to 10,000 psi however; the tubing that connects the tubing into inlet B cannot sustain high pressure for temperatures exceeding 80 °C. Due to safety reasons, the pressure limit was set to 2800 psi only. This highly affected the accuracy of the experiments results.

For 10% wax content oil sample, the laboratory faced a shortage of CO2. With the CO2 remaining in the tank, only 3 runs were successfully done. To keep in track with the plan, the 10% sample was pushed back to be rerun after all the other samples are run. Unfortunately, the last o-ring ruptured; therefore, the 10% wax content sample didn't get to be run. The o-ring is responsible to keep the pressure cell sealed. The next batch replacement will arrive in the next 3 months which is beyond the time limit for the project.

The laboratory facility is owned by the Petroleum Engineering Department which means that the laboratory is shared with the other students. During the day the 15% wax content oil sample was supposed to be run, there was a class involving students from another batch. Due to this, the time allocated to run experiments for 15% oil sample was cut by half. Only 4 points managed to be run. With these circumstances, the points which could produce the lowest IFT readings were chosen; which were 2000 psig, 2200 psig, 2400 psig and 2800 psig.

4.2.7 Discussion and Interpretation of Experiment Results

Tabulated in Table 10 below is the MMP obtained from the experiment and these are plotted in Figure 27 with the exclusion of 10% wax content sample.

Table 10: Table of % Wax Content and Respective Minimum Miscibility Pressure

Sample (% Wax Content)	MMP (psig)
5	3133
15	3706
20	3391
25	3332

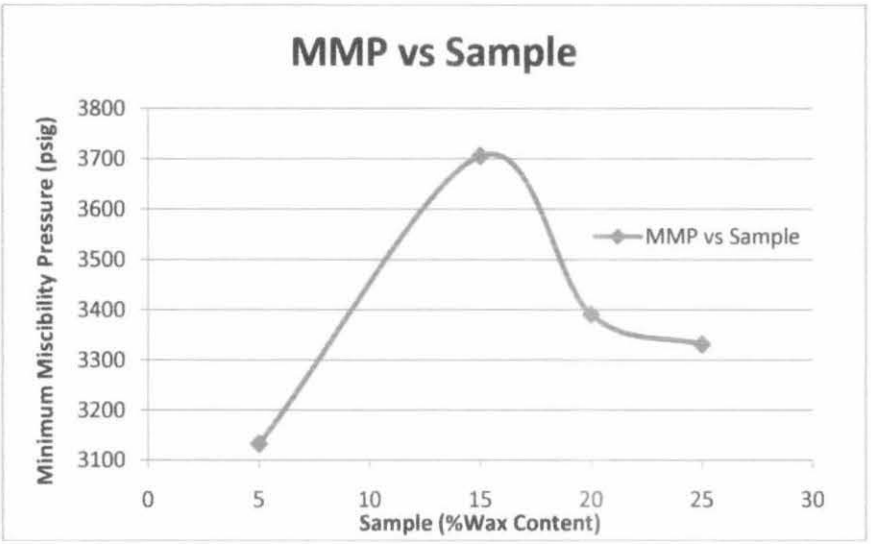

Figure 27: Graph of MMP vs % Wax Content

From the graph, we can see that from 5% to 15% there is an increment. However, for 20% and 25%, the MMP suddenly dropped. This phenomenon could be due to the pressure limit imposed, we may not be getting correct extrapolation on MMP. This is because when IFT is plotted against pressure, according to Ayirala and Rao's experiment, it will produce an exponential graph (Figure 7). Due to insufficient data points available, MMP estimated will drop.

Chapter 5: Conclusion and Recommendation

5.1 Conclusion

The entire objective for this project has been achieved. A suitable method to determine CO2-waxy oil MMP has been determined, which is using an experimental approach by employing Vanishing Interfacial Technique. VIT technique provides fast and reliable results while being a very easy technique to apply here due to the facilities available. The effect of wax content on CO2 MMP in waxy oil has also been determined. From the experiments conducted and by analysing MMP obtained from 5% wax content oil sample and 15% wax content oil sample, the conclusion is that with increasing wax content, CO2-waxy oil minimum miscibility pressure will also increase. A research done by Holm and Josendal[9] in 1980 has supported this conclusion because they concluded that an increment of C_6 - C_{30} components would linearly increase the MMP.

This is beneficial for fields or wells that plan to use CO2 miscible displacement for the long run. During production, the lighter components will be produced first; leaving behind heavier components which include wax. This would mean, as more oil is produced, the wax content will also increase. With the success of this project, engineers now know that after some time the reservoir pressure needs to be increased to stay above the increasing MMP.

5.2 Recommendation

The results would have a better quality had the tubing have better specifications. If the tubing was sturdier, IFT for pressure above 3000 psig can be obtained and with it, better results for the higher wax content oil samples can be obtained.

It is also recommended that the o-ring supply for the IFT 700 machine be made abundant. CO2 can easily hasten the rupturing process of the o-ring. During this experiment, a typical lifespan of an o-ring would be around 6-7 sample runs which is quite minimal.

It is also suggested that a purchase for a better densitometer be made. Anton Paar DMA 4500 M can only measure density with regards to temperature change only. However, there are other densitometers which could measure density at high temperature and pressure. Even though density changes with regards to pressure are often very small and negligible, it still would contribute toward inaccuracy in experiment's results.

In the future, if there are other researchers attempting to research similar topics, it is suggested that the new micro slim tube machine that will soon be available for use be utilised. Since it is the accepted standard in obtaining MMP, it would be better to use micro slim tube test.

References

1. Ahmad, T. 2001 *Reservoir Engineering Handbook,* Boston, Gulf Professional Publishing.

2. Ayirala, S.C. and Rao, D.N. (2006). *"Comparative Evaluation of a New MMP Technique", SPE 99606, SPE/DOE Symposium on Improved Oil Recovery*

3. Ayirala, S.C., Sequeira, D.S. and Rao, D.N. (2004). *"Solubility, Miscibility and Their Relation to Interfacial Tension for Application in Reservoir Gas-Oil Systems", SPE 91918, SPE International Petroleum Conference*

4. Ayirala, SC., Rao, D.N. and Casteel, J. (2003). *"New Comparison of Minimum Miscibility Pressures Determined From Gas-Oil Interfacial Tension Measurements with Equation of State Calculations", SPE 84187, SPE Annual Technical Conference*

5. Becker, J.R. *"Crude Oil Waxes, Emulsions and Asphaltenes"*, PennWell Publishing Company, Tulsa Oklahoma (1997): 103-124

6. Wischnewski B., Peace Software, http://www.peacesoftware.de/einigewerte/co2_e.html

7. Elsharkawy, A.M., Poettmann F.H. and Christiansen, R.L. (1992). *"Measuring Minimum Miscibility Pressure: Slim Tube or Rising Bubble Method?", SPE 24114, SPE/DOE Symposium on Enhanced Oil Recovery*

8. Holm L.W. *"Evolution of the Carbon Dioxide Flooding Processes"*, paper SPE 17134, Journal of Petroleum Technology (November 1987): 1337-1342.

9. Holm, L.W. and Josendal, V.A. *"Effect of Oil Composition on Miscible Type Displacement by Carbon Dioxide"*, paper SPE8814 presented at SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, 20-23 April (1980)

10. Holm, L.W. and Josendal, V.A. *"Mechanisms of Oil Displacement by Carbon Dioxide"*, paper SPE 4736 presented at SPE-AIME Symposium on Improved OilRecovery, Tulsa Oklahoma, 22-24 April (1974).

11. IFT 700 Manual Rev.1, VINCI Technology FRANCE (2007).

12. Jessen, K. and Orr Jr, F.M. *"On IFT Measurements to Estimate Minimum Miscibility Pressures"*, paper SPE 30786 presented at SPE Annual Technical Conference and Exhibition, Dallas, 22-25 October (1995).

13. Kelechukwu, E.M. and Md.Yassin, A.A. *"Potential Risk of Paraffin Wax-Related Problems in Malaysian Oil Fields"*, Jurnal Teknologi UTM, December 2010.

14. Klaus A. and Mieczyslaw B. 1994 *Composition and Analysis of Heavy Petroleum Fractions,* New York, Marcell Dekker

15. Lee, S.T., Lo, H. and Dharmawardhana B.T. (1988). *"Analysis of Mass Transfer Mechanisms Occuring in Rich Gas Displacements", SPE 18062, SPE Annual Technical Conference and Exhibition*

16. Luo, K. and Chen, G. (2001). *"Application of the Gas-Oil Interfacial Tension to Determine Minimum Miscibility Pressure" PETSOC 2001-135, Canadian International Petroleum Conference*

17. Mansoori, G.A. University of Illinois at Chicago (UIC). *"Paraffin / Wax and Waxy Crude Oil"*, <http://tigger.uic.edu/~mansoori/Wax.and.Waxy.Crude_html/>

18. Martin, F.D. and Taber, J.J. "*Carbon Dioxide Flooding*", paper SPE 23564, Journal of Petroleum Technology (April 1992): 396-400

19. Mogensen, K., Hood, P., Lindeloff, N., Frank, S. and Noman, R. *"Minimum Miscibility Pressure Investigations for a Gas Injection EOR Project in Al Shaheen Field, Offshore Qatar"*, paper SPE 124109 presented at Annual

Technical Conference and Exhibition, New Orleans, Louisiana, USA, 4-7 October (2009).

20. Nor Idah, K., Zahidah M.Z., Noraini A. and DM Anwar Raja. (1999). *"New Experimental Approaches in Minimum Miscibility Pressure (MMP) Determination", SPE 57286, SPE Asia Pacific IOR Conference .*

21. Perry J., Charles F., Michael S. And Steven W. 2002, *"Practical Aspects of CO2 Flooding"*, **(22),** Texas, Society of Petroleum Engineers

22. Samsudin, Y., Darman, N., Hussain, D. and Hamdan, M.K. *"Enhanced Oil Recovery in Malaysia: Making It a Reality (Part II)"*, paper SPE 95931 presented at SPE International Improved Oil Recovery Conference in Asia Pacific, Kuala Lumpur, Malaysia, 5-6 December (2005).

23. Stalkup Jr, F.I. 1983. *"Status of Miscible Displacement"*, paper SPE 9992 presented at SPE International Petroleum Exhibition and Technical Symposium, Beijing, China, 18-26 March (1982).

24. Stanley H. 2004, *Surface and Interfacial Tension,* **(119),** New York, Marcell Dekker

25. Teletzke, G.F., Patel, P.D. and Chen, A.I., *"Methodology for Miscible Gas Injection EOR Screening"*, paper SPE presented at SPE International Oil Recovery Conference in Asia Pacific, Kuala Lumpur, Malaysia, 5-6 December (2005)

26. Velasquez, D., Rey, O. and Manrique, E *"An Overview of Carbon Dioxide Sequestration in Depleted Oil and Gas Reservoirs in Florida, USGS Petroleum Province 50"*, paper ENE 067 presented at Fourth International Latin American and Caribbean Conference for Engineering and Technology (LACCEI) 21-23 June 2006, Mayagüez, Puerto Rico.

27. Wan Malinda M. 2010 *Determination of Minimum Miscibility Pressure of Carbon Dioxide in Waxy Oil,* Universiti Teknologi Petronas, Perak, Malaysia.

28. Zhou, D and Orr, Jr.F.M. *"Analysis of Rising Bubble Experiments to Determine Minimum Miscibility Pressure"*, paper SPE 30786 presented at SPE Annual Technical Conference and Exhibition, Dallas, 22-25 October (1995). SPE Journal (March 1998): 19-25.

Abbreviations

CO2	Carbon Dioxide
EOR	Enhanced Oil Recovery
FDA	Falling Drop Analysis
IFT	Interfacial Tension
LPG	Liquefied Petroleum Gas
MCM	Multiple Contact Miscibility
MMP	Minimum Miscibility Pressure
RBA	Rising Bubble Analysis or Rising Bubble Apparatus
UTP	Universiti Teknologi Petronas
VIT	Vanishing Interfacial Tension