

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Oil Recovery

Recovery of oil from a reservoir is generally divided into three phases, i.e. primary, secondary and tertiary recovery chronologically in order. Primary recovery refers to the recovery of oil from reservoirs by its own energy sources, such as depletion drive, rock and liquid expansion drive, aquifer drive, gas cap drive and gravity drainage. Secondary recovery is generally interpreted as some ways to improve the recovery of oil through energies from outside of the reservoir which often comes by ways of pressure maintenance through the injection of water or gas. Since water injection is commonly used at this stage, the term recovery has become nearly synonymous with waterflooding. Tertiary recovery would then come after secondary recovery to further improve the recovery of oil and is usually used to describe processes, such as chemical injection, gas drives or thermal injection. Although the tertiary recovery is often considered as the tertiary phase in the production of a reservoir in the chronological order, it is not always so it can be implemented after the primary production or even as the only recovery method. The tertiary recovery is known as enhanced oil recovery (EOR) (Bon, 2009).

2.2 Enhanced Oil Recovery (Tertiary Production Phase)

EOR processes are important as technologies that could help meet the growing demand for oil in the world. It is applied when roughly 65% of the original oil in place (OOIP) remains in the reservoir after primary and secondary recoveries (Ezekwe, 2010). EOR can be divided into two major types, thermal and non-thermal recoveries as shown in Fig. 2.1.

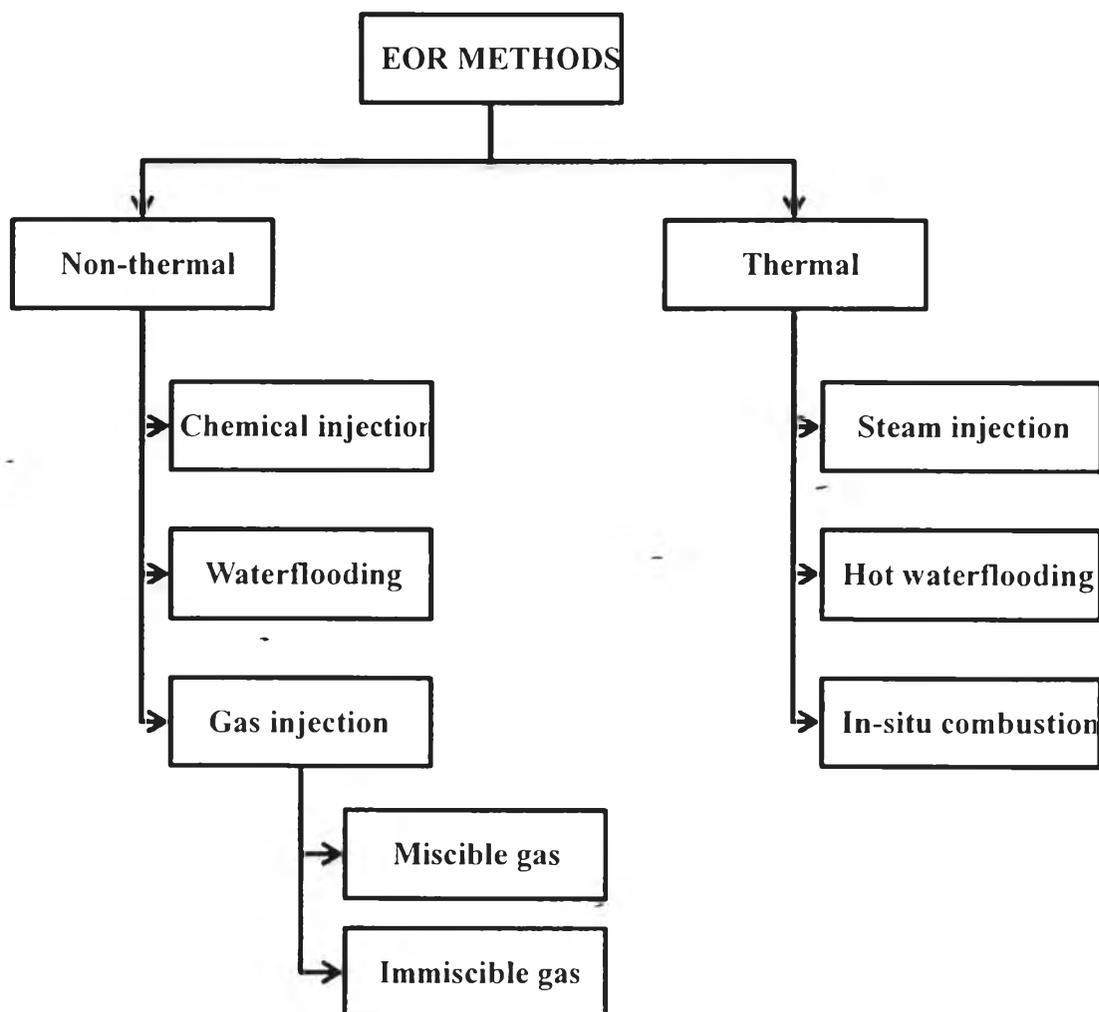


Figure 2.1 EOR Methods (Al-Anazi, 2007).

2.2.1 Thermal EOR Processes

Thermal recovery refers to oil recovery processes in which heat plays the principle role. The most widely used thermal techniques are in-situ combustion and continuous injection of hot fluids.

2.2.1.1 *Steam Injection*

Injection of steam decreases the viscosity of the reservoir fluid which is normally used in heavy oil fields. Three main methods of steam injection include cyclic steam stimulation (CSS), steam drive (SD) and steam assisted gravity drainage (SAGD). A cyclic steam stimulation (CSS) is to inject steam into a well for several weeks, to shut the well in as long as necessary to allow the steam to heat the

oil in the areas around the well, and to put the well back on production to recover the heated oil. A steam drive (SD) is to inject steam continuously at the injectors with the aim of driving oil towards producers. A steam assisted gravity drainage (SAGD) is to inject steam into the top horizontal well, while the horizontal well below it functions as the producer. The steam creates an expanding steam chamber around the injector as more steam is injected. The viscosity of oil is reduced which causes the oil mobility to increase to drain under gravity towards the production well (Ezekwe, 2010).

2.2.1.2 Hot Waterflooding

This process is the same as waterflooding, which hot water is injected to decrease the viscosity of the reservoir fluid. This process is widely used in heavy oil fields.

2.2.1.3 In-situ Combustion

Injection of compressed air into heavy oil reservoirs under conditions such that the oxygen in the injected air reacts with a small fraction of the crude oil at high temperatures to create a combustion front (Ezekwe, 2010). In some cases water can be injected to create steam at the reservoir and combined its positive effect with the fire to reduce the oil viscosity, which is called wet combustion.

2.2.2 Non-thermal EOR Processes

2.2.2.1 Chemical Injection

Chemical flooding is another technique to increase the mobility of oil in order to enhance oil recovery. This technique is based on adding additives or chemicals to the displacing fluid or to the residual oil to control the viscosity and interfacial tension (Al-Anazi, 2007). Chemical processes include (1) polymer/surfactant flooding which is injecting a slug of micellar solution (consisting of water, surfactant, electrolytes, etc.) into the reservoir. The micellar slug is followed with a mobility buffer slug made up of polymer and water for mobility control. (2) Alkali/surfactant/polymer (ASP) flooding is more widely used than micellar polymer flooding and the main functions of the alkaline component are to promote emulsification of the crude oil, reduce interfacial tension, reduce adsorption of the surfactants and regulate phase behavior of the mixture. (3) Polymer flooding which is considered as a waterflooding process is an addition of polymers to

improve mobility control and volumetric sweep efficiency. (4) Microbial enhanced oil recovery (MEOR) uses microbial activities in the reservoir by altering wettability of the rock, reducing interfacial tension and oil viscosity, and generation of gases, such as carbon dioxide, production of surfactants, etc (Ezekwe, 2010).

Mechanism of chemical injection is involved with emulsion formation in the system. Fig. 2.2 (a) is the separation of oil and water phase and interfacial tension (γ) between the two phases is high. An addition of emulsifier (water soluble surfactants) into the system reduces the interfacial tension between the oil and water (γ_{ow}). In a surfactant flooding, the interfacial tension is reduced to an ultralow level, so that the oil trapped in a cap rock reservoir can easily mobilize into the oil-in-water (o/w) emulsion phase. Alkaline is generally used to optimize and reduce the interfacial tension. Increase of the alkaline concentration increases the oil solubilizing in the o/w emulsion phase causing the emulsion phase to swell at the expense of oil phase and γ_{ow} is also further reduced (Fig 2.2(b). Fig. 2.2(c) shows middle three phase region (miscible phase region), where more oil and water are solubilized, more reduction of γ_{ow} and the interfacial tension (γ_{ow}) is displaced by the new interfacial tension between water and middle phase (γ_{wm}) and the interfacial tension between oil and middle phase (γ_{om}). The interfacial tension in the middle phase region becomes very low or ultralow which the ultralow interfacial tension is required for enhanced oil recovery. The optimized condition is obtained by scanning the alkaline concentration. Fig. 2.2(d) shows oil and water swollen in the surfactant phase with no excess oil and water remaining. Thus, surfactant flooding solubilizes and mobilizes oil into the emulsion phase.

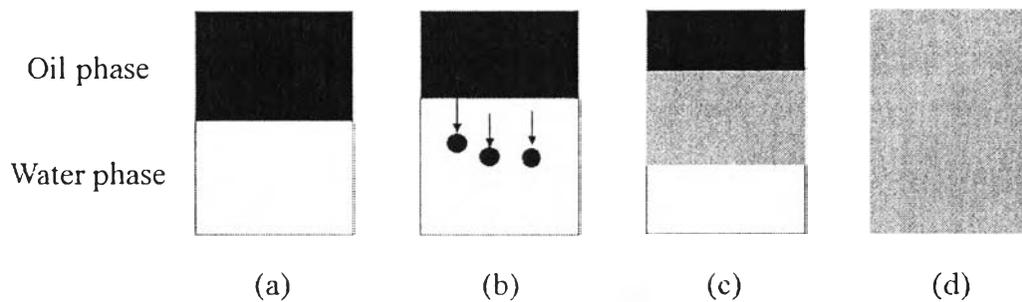


Figure 2.2 Emulsion formation between oil and water, (a) phase separation, (b) addition of emulsifier, (c) middle phase microemulsion (Winsor type III), and (d) microemulsion in single phase (Winsor type IV).

2.2.2.2 Waterflooding

The water is injected through injection wells to push crude oil toward producing wells. The production can be increased after a decline in pressure from the water drive or pressure maintenance. Water is pumped into the productive layer at injection pressure through bore holes in a volume equal to (or greater than) the volume of oil extracted, so the formation energy in the deposit is kept at the optimum level. The original lifetime of the well is prolonged, which greatly reduces the amount of drilling operations and consequently reduces the cost of the oil (Al-Anazi and Al-Jarba 2009).

2.2.2.3 Gas Injection

Gas injection uses gases, such as natural gas, nitrogen, or carbon dioxide that expands in the reservoir to push additional oil to a production wellbore, or other gases that dissolve in the oil to lower its viscosity and improve its flow rate. The gas injection accounts for nearly 50 percent of EOR production. The gas injection processes could be immiscible gas injection and miscible gas injection. Whether a miscible or immiscible injection to be implemented, it is dictated by the injection pressure and the minimum miscibility pressure (MMP) of the gas with the oil (Al-Anazi and Al-Jarba 2009). For the immiscible gas injection, there exists an interface between the two fluids and thus, there also exists a capillary pressure caused by the interfacial tension between the oil and gas. The benefits of the flood

are primarily due to reservoir pressure maintenance and displacement of the fluid. Since the two fluids are immiscible, higher residual oil saturations can be expected than with a miscible injection. Hence the immiscible injection achieves lower oil recoveries than the miscible injection.

2.3 Miscible Gas Injection

Miscibility is defined as a physical condition between two or more fluids that permits them to mix in all proportions without the existence of an interface. The injection is considered miscible when there is no phase boundary between the displacing fluid and the displaced fluid. Miscible injection is recognized as an effective enhanced oil-recovery method. Light hydrocarbon gas mixtures, carbon dioxide, nitrogen and flue gas mixtures are the common driving fluids (Zou *et al.*, 1993). The key parameter required for evaluating and designing a miscible injection is the MMP. The two main categories of miscible injection mechanisms include (1) first contact miscibility (FCM) and (2) multiple contact miscibility (MCM).

2.3.1. First-contact Miscibility (FCM)

The solvent (can be liquid or gas mixture) and oil are miscible upon first contact in all proportions under injection pressure and temperature. To achieve the first contact miscibility (FCM), the injection pressure should be higher than minimum miscibility pressure. As a simple illustration of FCM, pure CO₂ will achieve FCM with reservoir fluid in the shaded region in Fig. 2.3 (Ezekwe, 2010).

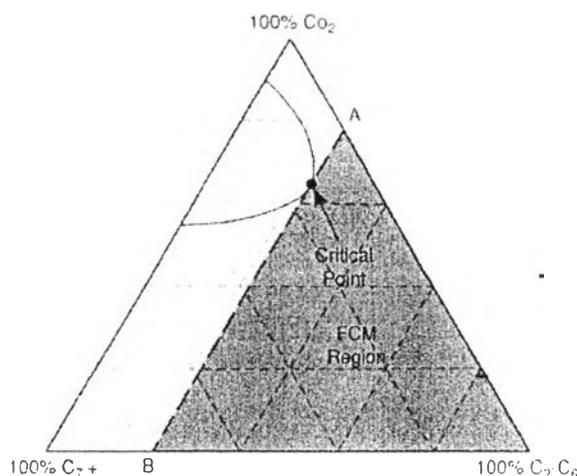


Figure 2.3 Pseudoternary diagram for CO₂-hydrocarbon system (Ezekwe, 2010).

2.3.2. Multiple-contact Miscibility (MCM)

Miscibility between the reservoir oil and the injected gas is generated through in-situ mass transfer of components, after multiple contacts between the two fluids. There are mainly two types of MCM processes, (1) condensing gas drive and (2) vaporizing gas drive.

2.3.2.1 *Condensing Gas Drive*

The injected hydrocarbon generally contains large amounts of intermediate molecular weight. In this approach, reservoir oil near the injection well is enriched in composition by contact with the injected gas since the hydrocarbon components from the injected gas are condensed to form miscible bank with some of the oil components (Ezekwe, 2010). The mechanism of attaining MCM by condensing gas drive is illustrated with a pseudoternary diagram shown in Fig. 2.4 which the composition of gas and reservoir fluid is shown at the point G and O, respectively. At the first contact, the composition of mixture in liquid phase is appear at point L₁. The phase of mixture is changed with time, after gas contact with liquid L₁, it will created a new composition of mixture fluid in liquid phase at L₂. The phenomena will continue until the tie line from gas to liquid (L_i) is not pass the two phase regions that means the mixture achieved the miscibility.

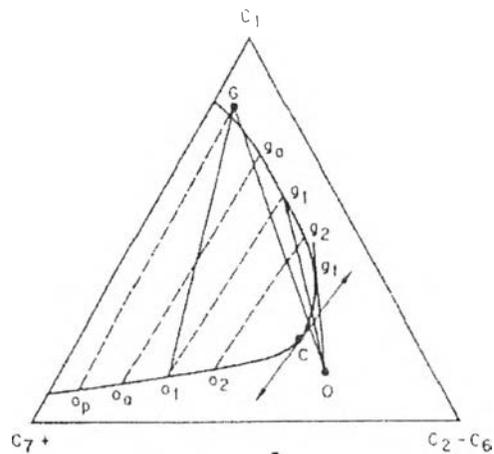


Figure 2.5 MCM by vaporizing gas mechanism (Jütner, 1997).

The miscibility of the hydrocarbon system could be explained by a binary phase diagram. Yu *et al.*, (2006) reported the binary phase diagram of the CO_2 - C_5 system and the CO_2 - C_7 system in Fig. 2.6. The critical curve, which is plotted between critical pressure and critical temperature, shows that the critical condition of the system above the critical line is the miscible condition and could be the MCM below the critical line. However, the mechanism of the condensing gas drive or vaporizing gas drive could not be identified.

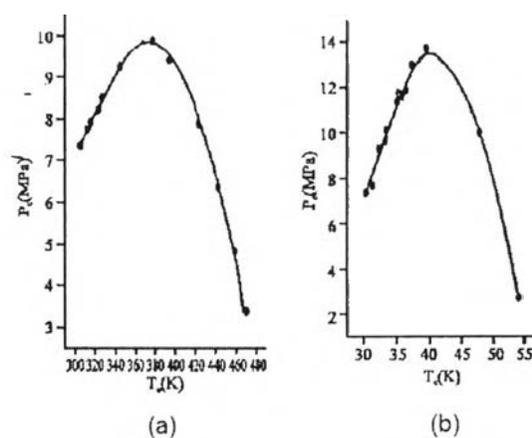


Figure 2.6 Binary phase diagram (a) CO_2 - C_5 and (b) CO_2 - C_7 systems (Yu *et al.*, 2006).

The miscible gas injection can be achieved by injecting different types of gases or gas mixtures including nitrogen, flue gas, light hydrocarbons (HC) and carbon dioxide. Gas mixtures of nitrogen and flue gas are sometimes selected because they are relatively cheap and abundantly available and they can achieve miscibility at higher MMP than HC and carbon dioxide; however, the condition may limit the application due to corrosivity of flue gas. Miscible gas injection of HC is undesirable due to its high economic value. In most cases, carbon dioxide gas is a very effective agent for miscible gas injection.

2.4 Carbon Dioxide Gas Injection

CO₂ injection is considered as the most promising EOR technique for recovering light to medium oils in the near future. The CO₂ injection also plays a very important role in reducing the greenhouse gas emissions by sequestering the emitted CO₂ into depleted oil reservoirs (Li *et al.*, 2012). The advantage of using CO₂ in EOR is that the pressure required for achieving dynamic miscibility is lower than the pressure required for dynamic miscibility using other gases, such as natural gas, flue gas or nitrogen. Typically, injected gas compositions are ranged from 97% to 99% purity and the impurities can be constituted of N₂, CH₄, H₂, etc. At this production stage, the major mobile oil has already been produced and the significant volume of remainder oil cannot be produced without EOR.

2.5 Minimum Miscibility Pressure of CO₂

Minimum miscibility pressure (MMP) at which the crude oil and CO₂ becomes miscible is a key factor. In general, CO₂ is immiscible at first contact with reservoir oils, but may achieve dynamic miscibility through multiple contacts. An inaccurate prediction of MMP may have significant consequences. For example, if the injection pressure is lower than MMP, the displacement is still two-phase implying immiscibility. Therefore, the local displacement efficiency will be below the desired level and, the process becomes ineffective leading to a high risk of lower

recovery. CO₂-oil MMP depends on the purity of CO₂, oil composition, and reservoir temperature (Eissa *et al.*, 2007, Li *et al.*, 2012).

The impurities that can impact on the CO₂-oil MMP are N₂, O₂, C₁, hydrocarbon components (C₂-C₄), and H₂S. Whereas C₁ and N₂ have a higher negative impact on the MMP, O₂ provides less negative impact than N₂ (Yang *et al.*, 2007), and H₂S and hydrocarbon components (C₂-C₄) have a positive impact on the MMP (Eissa *et al.*, 2007).

For oil composition, increase of heavy component fraction in the oil will increase the oil MMP as illustrated by Li *et al.* (2012).

Increase of reservoir temperature can affect MMP either increases MMP more or less linear with temperature (Elsharkawy *et al.*, 1996).

2.6 Experiment for CO₂-MMP Measurement

Several methods can be used to measure MMP for an oil-solvent system. Traditionally, slim-tube studies are conducted for the purpose. The rising bubble apparatus (RBA) approach was developed in the early 1980s. Other methods are swelling factor experiment and vanishing interfacial tension experiment. (Elsharkawy *et al.*, 1996, Dong *et al.*, 2001, Rudyk *et al.*, 2009, Cao *et al.*, 2013, Tsau, 2010, and Siagian and Grigg, 1998)

2.6.1 Slim-tube Apparatus (Elsharkawy *et al.*, 1996)

The slim-tube displacement test is often referred to as the “Industry standard” for determining MMPs. It determines the oil recovery as a function of injection pressure, and miscibility and breakthrough time of the injection gas is observed. Furthermore, the change in produced gas and oil properties can be monitored by placing gas chromatograph (GC) at the outlet. The recoveries determined are unrealistically high due to the idealize properties of the slim-tube (ultra-high permeability, no water in pore volume). From measurements of several oil recoveries at a variety of pressures, the MMP can be determined. This is a key motive for the slim-tube test (Bon, 2009). The setup of equipment of slim-tube apparatus is temperature controlled by air bath as shown in Fig. 2.7. Packing materials (sand, glass bead) are filled in the coiled slim-tube. The end of slim-tube is

connected to back pressure regulator and connected to the separator or gas chromatography (Elsharkawy *et al.*, 1996).

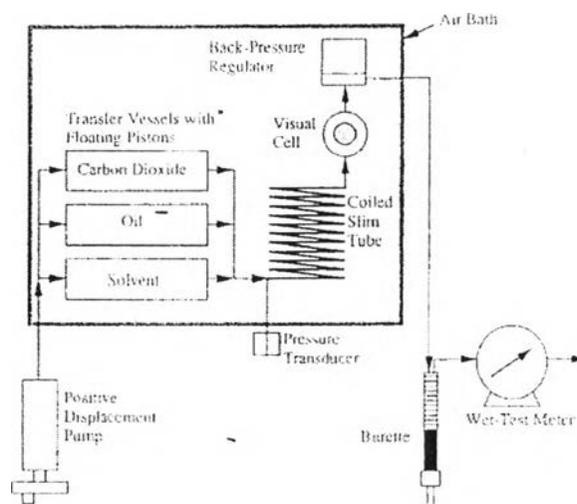


Figure 2.7 Schematic diagram of slim-tube apparatus (Elsharkawy *et al.*, 1996).

Solvent (solvent can be gas, liquid or mixture) is injected at different pressure (mostly use 5 different pressures) into the slim-tube that is saturated with oil sample at reservoir temperature. The data of oil recovery are collected after injecting solvent 1.0 or 1.2 pore volume, PV (PV is calculated from porosity of packing material). The oil component that come out from slim-tube is separated and measured for its amount to calculate the oil recovery. The injection rate of solvent is varied by pore volume of the slim-tube. The experiment could take 12 to 24 hours in one injection pressure.

The result of slim-tube tests is the oil recovery data at each injection pressure. The MMP is defined from the graph that plots oil recovery against injection pressure. The MMP is the point at which a breakover occurs in the curve plotting the oil recovery against the injection pressure shown in Fig. 2.8. MMP is the intersection point of the two straight-line sections. The uncertainty could come from an accuracy of fitting data to obtain the interception (MMP), especially the immiscible region of the curve (Dong *et al.*, 2001).

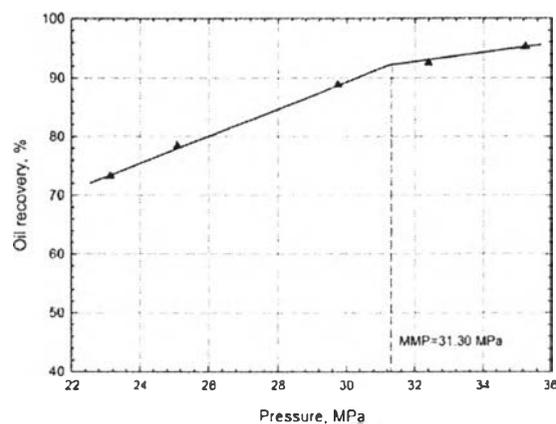


Figure 2.8 Result from slim-tube apparatus with heavy crude oil (Li *et al.*, 2012)

2.6.2 Rising Bubble Apparatus (RBA)

A schematic of RBA is illustrated in Fig. 2.9. RBA has gained acceptance in the petroleum industry as an alternative method for measuring MMP because it is quicker than the slim-tube method. The essential parts of RBA consist of a high pressure visual cell equipped with a camera to record observations during the experiment. Inside the visual cell, there is a flat glass tube into which the reservoir fluid is charged before the experiment is initiated. The glass tube is made flat so that bubbles rising in the oil can be seen more clearly.

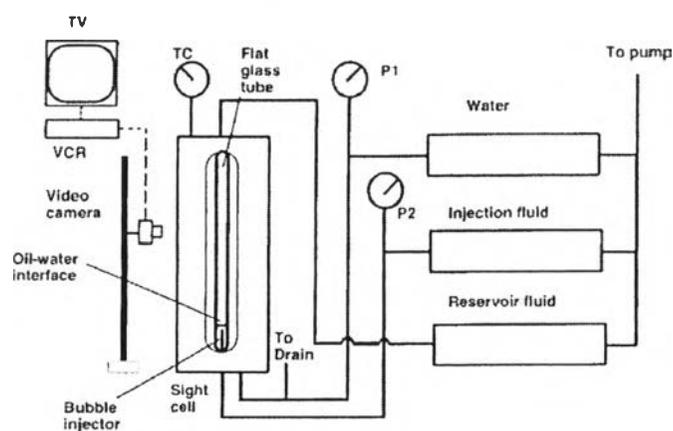


Figure 2.9 Schematic diagram of a rising-bubble apparatus (Dong *et al.*, 2001).

RBA is started by filling distilled water into a flat glass tube and pressurized at the pressure above the bubblepoint of the reservoir fluid being investigated and then injecting the reservoir oil into the glass tube from the top to displace the water at a slow rate until the oil–water interface is slightly above the injector. Next, a CO₂ bubble is launched into the water just beneath the oil–water interface. Its shape and motion are recorded. Rising bubble experiments are repeated over a range of pressures. The MMP is defined as the pressure at which the bubble and the oil show a multiple-contact miscibility (Dong *et al.*, 2001). As shown in Fig. 2.10, RBA is demonstrated with Weyburn reservoir fluid and CO₂ pressures ranging from 7.3 to 15.4 MPa. The bubble shape is varied with pressure, where 7.3 MPa retained its initial near-spherical shape indicating this pressure is far below MMP and 11.2 MPa shows the shape of bubble transforming to be a bullet-shape which indicates close to proximity of MMP. At 12.0 MPa, the shape of bubble has become a short tail indicating the pressure above MMP and at 14 MPa, tail-shaped like indicates the pressure far above MMP. MMP point is observed where the pressure transfers from the bullet-shaped to the tail-shaped bubble. The CO₂ MMP for the Weyburn reservoir fluid is estimated at 11.7 MPa.

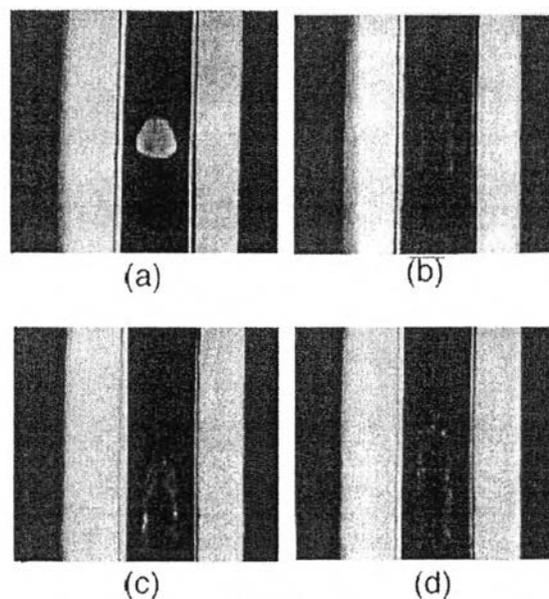


Figure 2.10 Photograph of rising bubbles (a) at 7.3, (b) at 11.2, (c) at 12.0 and (d) at 14.0 MPa (Dong *et al.*, 2001).

2.6.3 Supercritical Reactor Experiment (Rudyk *et al.*, 2009)

Since the cost for MMP measurement of CO₂-oil system by the slim-tube method is high, Rudyk *et al.* (2009) proposed supercritical (Spe-ed SFE) reactor for high pressure and oil saturated core sample (Fig. 2.11).

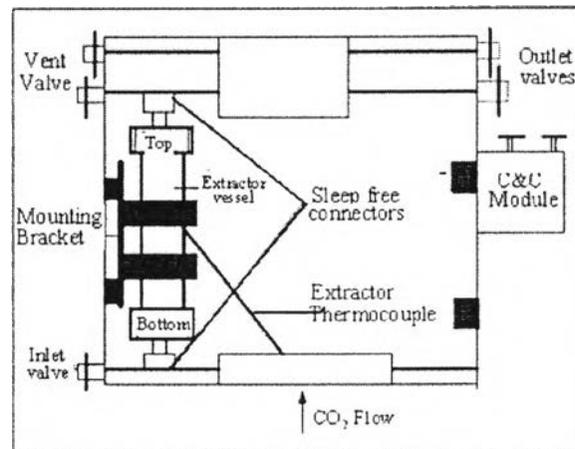


Figure 2.11 Schematic diagram of supercritical reactor (Rudyk *et al.*, 2009).

A core sample which has been dried to remove moisture, cleaned, weighed and saturated with oil is extracted in the Spe-ed SFE reactor at a reservoir temperature. Carbon dioxide is then injected into the reactor using the gas pump until it reaches desired pressure. The collection tubes are weighed before and after oil collection to determine the weight of extracted oil. The experiment is repeated at different pressures. The graph obtained (Fig. 2.12) is similar to the plot of the slim-tube experiment. The oil recovery grows gradually at first and then sharply to the breakover point for MMP determination. Above the breakover point, the volume of extracted oil does not increase with the pressure.

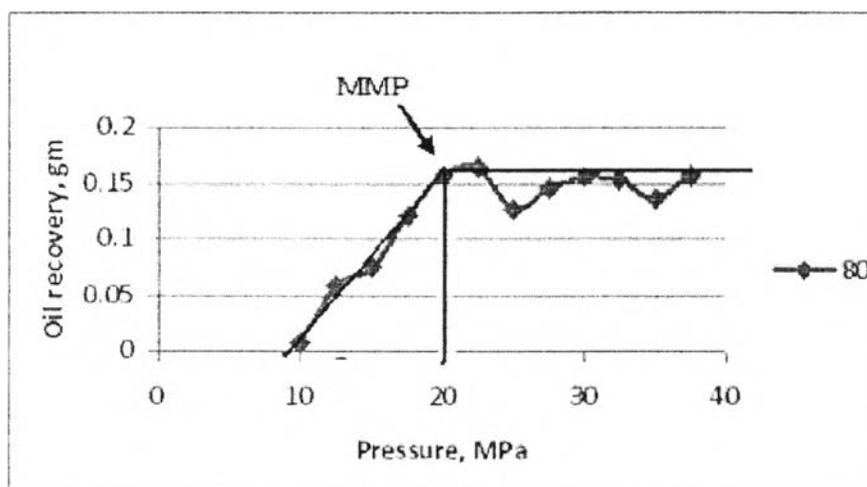


Figure 2.12 Graph for the determination of MMP with medium crude oil (Rudyk *et al.*, 2009).

2.6.4 Interfacial Tension Experiment (Cao *et al.*, 2013)

Initially, two fluids are immiscible, separated by an interface possessing a certain interfacial tension governed by the thermodynamic conditions (pressure, temperature and composition) of the system. For the two fluids to approach miscibility, their interfacial tensions must approach zero or ultralow interfacial tension. This means that the thermodynamic state of the system must change, in either pressure, temperature or composition to impose on the system under consideration (Rao, 1997). A vanishing interfacial tension (VIT) technique which is based on the miscibility concept that the interfacial tension (IFT) between a crude oil and CO₂ becomes zero at the miscibility is determined (Cao *et al.*, 2013). In the experiment, the equilibrium IFTs between the crude oil and CO₂ are measured at different equilibrium pressures and the actual reservoir temperature (Nobakht *et al.*, 2008).

The VIT experiment set-up is illustrated in Fig. 2.13. The pressure cell is first filled with CO₂ at a pre-specified pressure and a constant temperature. The crude oil is introduced from the crude oil sample cylinder to the pressure cell to form a pendant oil drop at the tip of the syringe needle. Once a well-shaped pendant oil drop is formed, the sequential digital images of the dynamic pendant oil drop are

acquired and automatically stored in the computer as tagged image file format files. Axisymmetric drop shape analysis (ADSA) is the technique that used for measuring IFT between crude oil and CO₂. Then the ADSA program can determine the dynamic and equilibrium IFTs of the pendant oil drop. The IFT measurement is repeated for at least three different pendant oil drops.

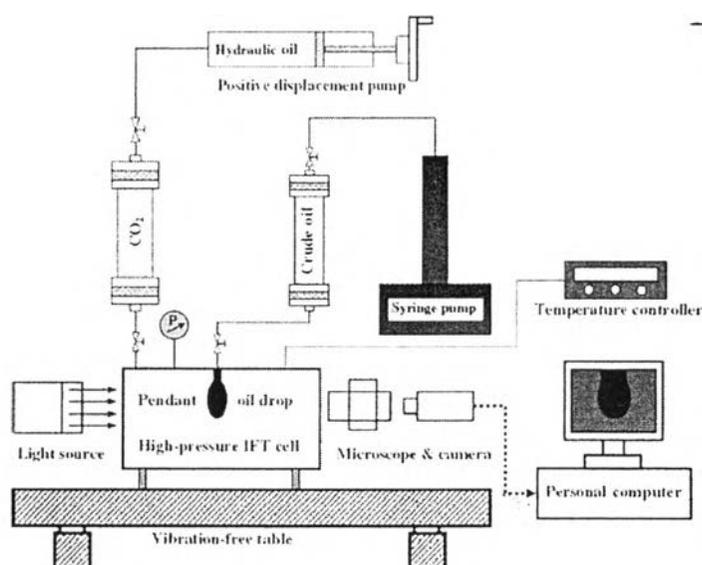


Figure 2.13 Experimental diagram for measure interfacial tension (Cao *et al.*, 2013).

ADSA gives the information of equilibrium IFT at each pressure. The MMP is determined by linearly extrapolating the measured equilibrium IFT versus equilibrium pressure (Fig. 2.14). MMP is determined by extrapolation of the first slope to the point which equilibrium interfacial tension equal to zero (i.e., 10.6 MPa with light crude oil).

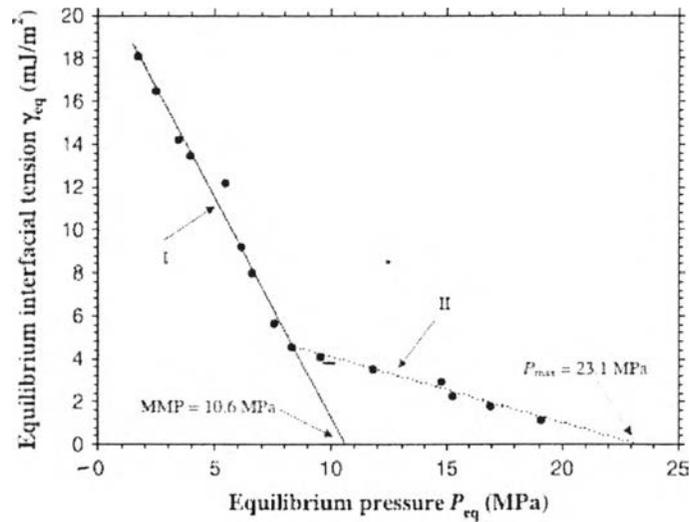


Figure 2.14 MMP measure from interfacial tension method with light crude oil (Cao *et al.*, 2013).

2.6.5 Measurement of MMP by Swelling/Extraction

Swelling/extraction tests are performed to examine oil recovery mechanisms in the near-miscible region and to provide data to tune a phase behavior mode (Tsau, 2010). The swelling tests are conducted to determine the relationship between saturation pressure, swelling factor and CO₂ volume injected, while the extraction tests are carried out to examine the extraction of liquid hydrocarbon into a CO₂-rich phase and the effect of pressure on the extraction. The swelling factor (SF) of oil is the ratio of liquid volume at the test pressure divided by the liquid volume at atmospheric pressure and at a reservoir temperature. SF is determined by measuring the change of the interface level as a result of CO₂ dissolution in the oil or as a result of hydrocarbon extracted into the CO₂ rich vapor phase. Swelling factor is equal to 1 at initial conditions. As a result of CO₂ dissolution into the liquid phase, the liquid phase swells and the swelling factor is greater than 1. As pressure increased, hydrocarbon components of the crude oil are removed from the liquid phase, the liquid phase shrink and SF is reduced.

The experiment setup is illustrated in Fig. 2.15. The key component of this setup is the high pressure view cell with high pressure gauge glass window allowing visual observations of fluids under experimental conditions. At the first

step, a predetermined volume of crude oil is carefully injected into the view cell to avoid liquid droplets on the wall of the view cell. The cell pressure is increased in discrete steps by CO₂ injection from the top of the view cell. CO₂ injection is stopped when a desired pressure is achieved and the height of the liquid sample in the view cell, the pump condition (temperature, pressure & final volume of CO₂) are recorded manually.

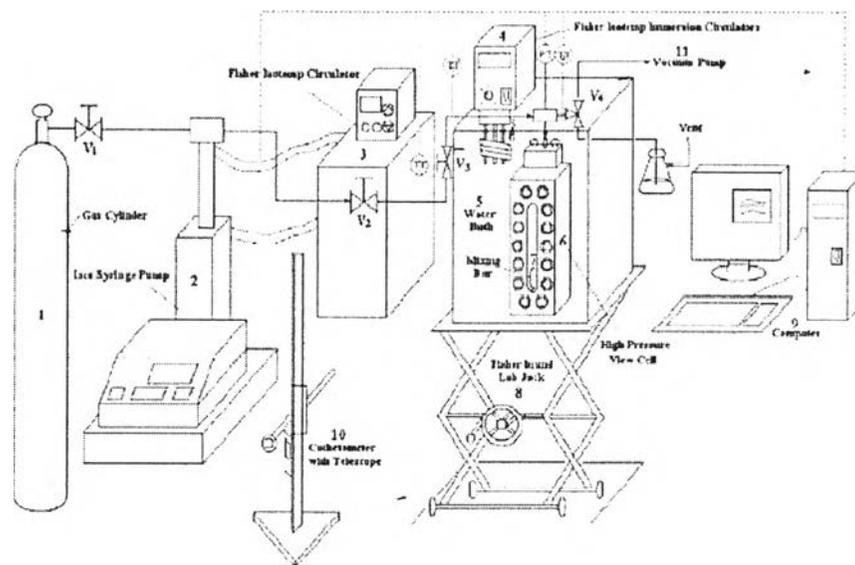


Figure 2.15 Swelling/extraction experimental setup (Tsau, 2010).

Fig. 2.16 illustrates the observations of Ogallah oil/CO₂ phase behavior in the view cell. The volume of oil in the liquid phase increases with the increasing pressure (P_1) as CO₂ dissolves in and swells the oil. As the pressure (P_2) further increases, CO₂ density increases. Since the ability of CO₂ to extract hydrocarbon components from crude oil is enhanced as its density increases with the pressure, CO₂ starts extracting hydrocarbons from the crude oil. The volume of oil in the liquid phase is reduced at pressure above P_1 as the rate of extraction becomes greater than the rate of swelling.

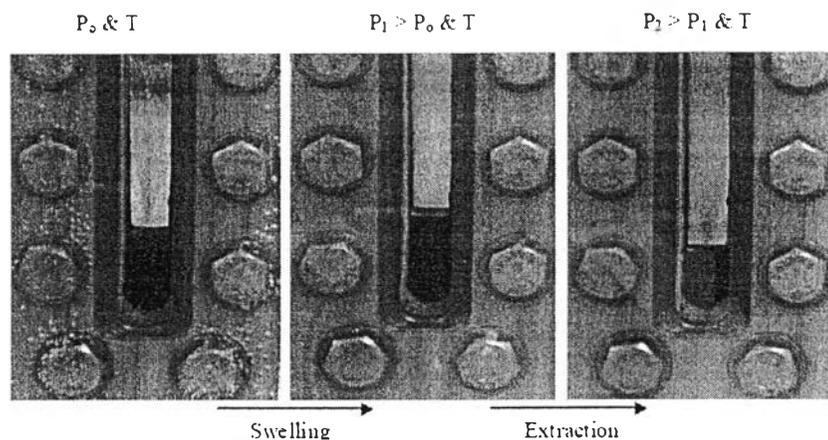


Figure 2.16 Change of initial oil (medium oil) volume with pressure (Tsau, 2010).

Fig. 2.17 shows the swelling/extraction curve for this experiment. The swelling factor of oil is the ratio of liquid volume at the test pressure divided by the liquid volume at atmospheric pressure and at reservoir temperature. From the curves, the rate of slope change is found in two distinct stages in each of the two extraction curves. Drawing lines through the major extraction and secondary stages, the pressure at the intersection of these two lines is MMP. The results are confirmed by the slim tube test and similar study for light oil system done by Abedini and Torabi (2013) as shown in Fig. 2.18. They also reported that the increase of temperature will increase the MMP of the system due to the decrease of CO₂ solubility in the oil.

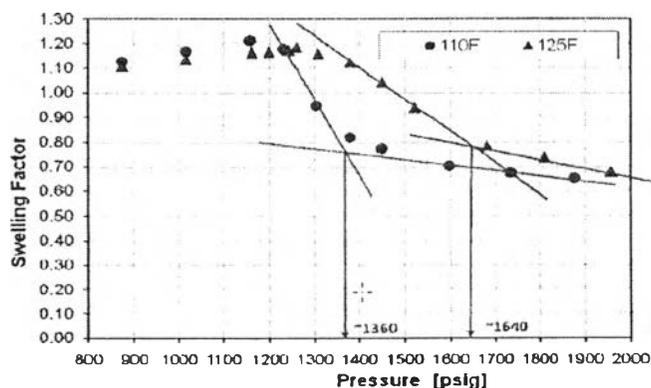


Figure 2.17 Relation between swelling factor/CO₂ injection pressure in CO₂ with medium crude oil (Tsau, 2010).

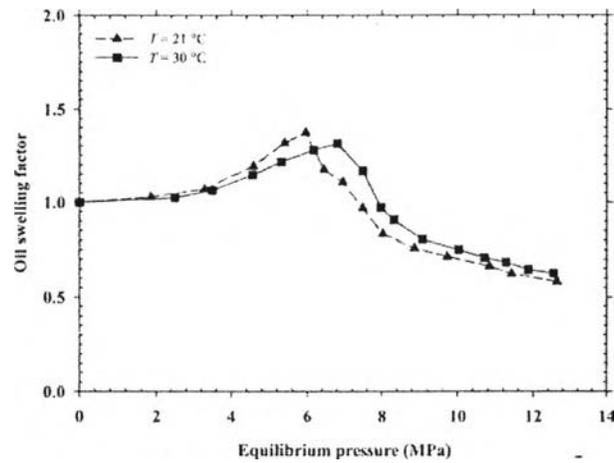


Figure 2.18 Swelling factor of crude oil and CO₂ system (Abedini and Torabi, 2013).

2.6.6 Measuring MMP by Extraction Test (Siagian and Grigg, 1998)

Sincere the slim-tube test takes two weeks for one MMP. The extraction test takes just 2 days. During CO₂ injection processes, CO₂ is able to dissolve in the oil, vaporizing and/or extracting hydrocarbons from the crude oil depending on the pressure and temperature. The vaporization process takes place at a temperature where the fluid at the displacement front is a CO₂-rich gas, and the extraction process will prevail at a temperature where the fluid at the moving front is a CO₂-rich liquid (Al-Marzouqi *et al.*, 2007). CO₂ extraction capacity is found to be strong function of pressure and temperature. The extraction capacity is increases with pressure and decrease with temperature. This phenomenon can be used to determine CO₂-oil MMP. However, Siagian and Grigg (1998) report that this result cannot be used to determine a definite value of CO₂-oil MMP, the critical pressure ranges can be used as a CO₂-oil MMP estimation.

Siagian and Grigg (1998) described the experiment of crude oil extraction by high pressure CO₂ that is illustrated in Fig. 2.19. CO₂ tank is connected to the accumulator before injecting into the extractor which is a high pressure vessel and filled inside with oil. The top of extractor is connected to a recycling pump and a condenser for separating produced gas for recycling and oil produced. The experiment is started by filling the oil in the extractor at reservoir temperature. CO₂

in the accumulator is heated to the reservoir temperature, and injected into the extractor to increase pressure to the desired value. After the pressure reaching the desired level, CO₂ flow is stopped and the system is allowed for 4 hours to equilibrate. The upper phase fluid is taken out by recycling pump and separated at atmospheric pressure. During separating the product, recycle CO₂ will maintain the system pressure. This experiment will record mass and volume of CO₂ injected, mass and volume of produced gas and produced liquid by wet test meter. For one oil and one temperature, it is required six pressures to determine one MMP value.

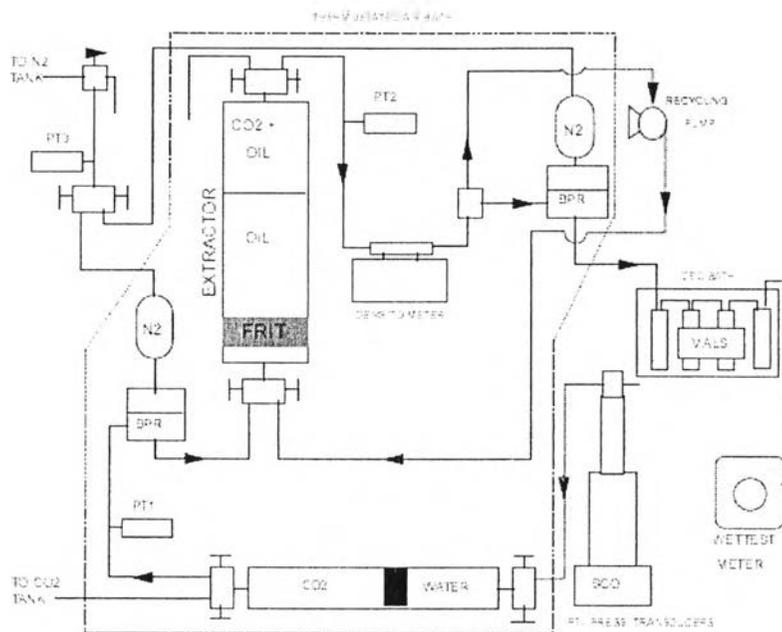


Figure 2.19 Schematic diagram of extraction apparatus (Siagian and Grigg, 1998).

CO₂ extraction capacity (gram oil produced / gram CO₂ injected) is the parameter used to evaluate the performance of CO₂-oil extraction. The extraction capacity at different pressure are plotted and shown in Fig. 2.20, where the MMP is the intersection point in the graph.

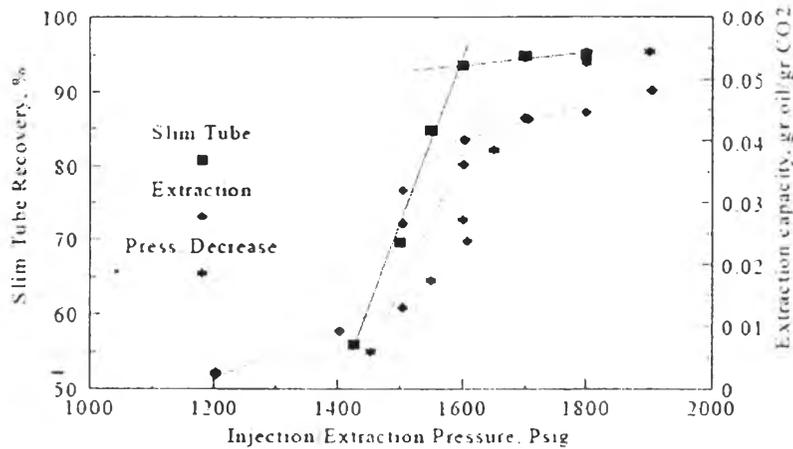


Figure 2.20 The result from extraction test with crude oil API 40 (Siagian and Grigg, 1998).

2.7 CO₂-Oil MMP Correlation

Existing experimental methods to determine the CO₂-oil MMP can be time-consuming and expensive, while theoretical models require an accurate characterization of the fluid systems by using an equation of state. In addition, empirical correlations have their own limitations for each specific scenario, though they are extremely useful for fast prescreening reservoir candidates for potential CO₂ injection. Therefore, it is of fundamental and practical importance to develop reliable and accurate correlations for determining the MMP for a given crude oil–CO₂ system (Li *et al.*, 2012). There are many common CO₂-oil MMP correlations, such as Alston correlation, Emera and Sama correlation, Li *et al.* correlation etc.

2.7.1 Alston Correlation

The Alston CO₂-oil MMP correlation considers the effect of reservoir temperature, C₅₊ molecular weight, and mole fraction ratio of volatile components (CH₄ and N₂) to intermediate components (CO₂, H₂S, and C₂–C₄).

$$MMP = 6.0536 \times 10^{-6} (1.8T_R + 32)^{1.06} (MW_{C5+})^{1.78} \left(\frac{X_{VOL}}{X_{INT}}\right)^{0.136} \quad (2.1)$$

Where X_{VOL} is mole fraction of volatile components including N₂ and CH₄, and X_{INT} is mole fraction of intermediate components including CO₂, H₂S, and

C_2 - C_4 and T_R was the reservoir temperature. If bubble point pressure (P_b) < 0.345 MPa, the following alternative Alston correlation, obtained by removing the volatile to intermediate ratio term.

$$MMP = 6.0536 \times 10^{-6} (1.8T_R + 32)^{1.06} (MW_{C_{5+}})^{1.78} \quad (2.2)$$

2.6.7.2 Emera and Sama Correlation

Emera and Sarma modified Alston correlation as follows:

$$MMP = 5.0093 \times 10^{-5} (1.8T_R + 32)^{1.164} (MW_{C_{5+}})^{1.2785} \left(\frac{X_{VOL}}{X_{INT}}\right)^{0.1073} \quad (2.3)$$

If $P_b < 0.345$ MPa, the alternative Emera and Sarma correlation, obtained by removing the volatile to intermediate ratio term.

$$MMP = 5.0093 \times 10^{-5} (1.8T_R + 32)^{1.164} (MW_{C_{5+}})^{1.2785} \quad (2.4)$$

2.7.3. Li *et al.* Correlation

Li *et al.* modified Alston correlation by replacing C_{5+} with C_{7+} , the correlation parameter are reservoir temperature, molecular weight of C_{7+} fraction, and mole fraction ratio of volatile components (N_2 and CH_4) to intermediate components (CO_2 , H_2S , and C_2 - C_6).

$$MMP = 7.3099 \times 10^{-5} [\ln(1.8T_R + 32)]^{5.33647} [\ln(MW_{C_{7+}})]^{2.08836} \left(1 + \frac{X_{VOL}}{X_{INT}}\right)^{2.01658 \times 10^{-1}} \quad (2.10)$$

X_{INT} is mole fraction of the intermediate component (CO_2 , H_2S , and C_2 - C_6) and X_{VOL} is fraction of volatile components (N_2 and CH_4)

2.8 Pressure Decay Technique

Pressure decay technique is used to measure the solubility and diffusion coefficient of oil-gas system. Zhang *et al.* (2000) measured gas diffusivity in heavy oil in a high pressure view cell by using the pressure decay technique. The gas is introduced into the cell until the pressure reached the desired test pressure. As time passes, the gas diffuses into the oil and pressure tends to drop. The diffusivity is determined from the recorded pressure. The solubility is calculated from the real gas equation.

Normally, a pressure decay technique is used to study the solubility and diffusion coefficient of CO₂-oil system, but there are still differences of pressure decay between below and above MMP point. MMP measured by the pressure decay technique was done in a Parr reactor. The main objective of this work was to study the possibility to use the pressure decay technique to determine MMP of CO₂-oil system and study the effect of molecular weight of oil and the effect of temperature on the MMP of CO₂-oil. For the effect of oil molecular weight, the CO₂-oil and CO₂-hydrocarbon (n-pentane (C₅) and n-heptane (C₇)) system were studied. A pressure range was limited by the pressure of CO₂ in the tank up to 950 psi. For the effect of temperature, two different temperature were 30 °C and 40 °C. The crude oil with API 62.1 was supplied by PTT Exploration and Production Public Company Limited (PTTEP). The MMP of n-decane (C₁₀) at 20 °C was measured and compared with the result reported by Yong-Chen *et al.* (2011).