CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Enhanced Oil Recovery (EOR) (Tertiary recovery)

The term enhanced oil recovery (EOR) refers to the recovery of oil by any method beyond the primary stage of oil production. It is defined as the production of crude oil from reservoirs through processes taken to increase the primary reservoir drive. These processes may include pressure maintenance, injection of displacing fluids, and other methods, such as thermal techniques. Therefore, by definition, EOR techniques include all methods that are used to increase oil produced (oil recovery) as much as possible. Two major types of techniques are thermal and non-thermal recoveries.

2.1.1 Thermal Process

Thermal recovery refers to processes in which heat is applied to decrease viscosity of oil. It can be categorized into stream injection, in situ combustion and hot waterflooding.

2.1.1.1 Steam Injection

Steam is injected into a reservoir to reduce the oil viscosity and improve the displacement efficiency which results in an improvement of mobilization efficiency of crude oil and thus, causes the oil to flow easily through the porous media to the wellbore. This process may include steam soak that is sometimes called steam stimulation or "huff and puff". In this process, steam is injected down a producing well at a high injection rate, after which the well is shut in and soak it. The injected steam heats up the area around the well bore and increases recovery of the oil (Al-Anazi and Duraya, 2007).

2.1.1.2 In Situ Combustion

In-situ combustion is a thermal process in which thermal energy produced at high temperature is generated in the reservoir by combustion. Recovery mechanisms include viscosity reduction from heating, vaporization of fluids, and thermal cracking.

2.1.1.3 Hot Waterflooding

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

2.1.2 Non-thermal Process

2.1.2.1 Water Flooding

The water is injected through the injection wells to push or maintain the reservoir pressure to increase the oil production. Water is pumped into the productive layer at injection pressure into the bore holes in a volume equal to (or greater than) the volume of oil extracted. Water flooding process is cheaper than other process because water is not high value.

2.1.2.2 Chemical Injection

Chemical flood is another technique to increase the mobility of oil. This technique is based on adding additives or chemicals to the displacing fluid or to the residual oil to reduce oil viscosity, reduce interfacial tension and to increase the oil flow rate. Chemical processes include micellar polymer flooding, caustic flooding, polymer flooding, and alkaline flooding.

2.1.2.3 Gas Injection

In a gas injection technique, gas is injected to increase production rate. Gas used in this technique can be nitrogen, methane, carbon dioxide and enriched hydrocarbon (C_2-C_6). Nitrogen and flue gas is sometimes selected, because it is cheap in comparison with other injection gases; but they can achieve miscibility at higher MMP than HC and carbon dioxide. However the condition may limit the application due to the flue gas corrosiveness in a process and for miscible gas injection of HC, it is high economic value. In most cases carbon dioxide gas is a very effective agent for miscible gas injection of oil.

The injected gas could form miscibility or immiscibility with oil in contact. In the miscible gas injection, the gas is injected at or above MMP which causes the gas to miscible in oil. In the immiscible gas injection, the gas is injected below MMP which causes the gas to be immiscible in oil.

2.2 Carbon Dioxide Injection

CO_2 injection technique can be divided into two categories, i.e. immiscible and miscible methods. In the immiscible method, CO_2 pressure applied is lower than MMP of the system and there is an interface between CO_2 gas and oil. In the miscible method, CO_2 pressure applied is above MMP and CO_2 forms a single phase with the oil. The miscibility can be achieved in place through mass transfer of components as a result of repeating contacts between oil and injected gas. At the pressure equal to or above MMP, CO_2 and oil form a single liquid phase that easily flows to the production well. Typically, purity of CO_2 used is at least 95 %. The impurities in CO_2 could be nitrogen, H_2S, and hydrocarbons component.

The main mechanisms to oil displacement by CO_2 injection are related to the phase behavior of CO_2–crude oil mixtures and also involved in reduction in the viscosity of the original crude oil, high solubility of CO_2 in crude oil, reduction of oil density, vaporization of intermediate components of the oil, reduction of CO_2–oil interfacial tension, and improvement of reservoir permeability, and eventually increase oil recovery (Ravagnani *et al.*, 2009).

2.3 Minimum Miscibility Pressure of CO_2

The minimum pressure at which the injected gas (CO_2 or hydrocarbon gas) can achieve dynamic miscibility with the reservoir oil is always needed to know. If the MMP is too low, the miscible displacement process becomes ineffective, it leads to a high risk of process failure. Thus, accurate estimation of MMP is economics concerned. Several methods can be used to measure MMP for an oil–solvent system. Traditionally, a slim tube test is conducted for that purpose. The rising bubble apparatus (RBA) approach was developed in the early 1980s and is gaining acceptance as an efficient method to measure MMP. MMP of the system depends on the purity of CO_2, oil composition, and reservoir temperature (Eissa and Shokir, 2007).

2.3.1 Oil Composition

Molecular weight of C_{7+} (MW_{C7+}) has an effect on MMP. If crude oil has high MW_{C7+}, it means that MMP is high and CO_2 will be difficult to diffuse in crude oil. In contrast, the crude oil has low MW_{C7+}, which means MMP is low, CO_2 can easily to diffuse in the crude, and light hydrocarbon is extracted from crude oil.

2.3.2 Reservoir Temperature

For crude oil, MMP increases with temperature increased (Yang et al., 2007). It can be explained by solubility of CO_2 in crude oil. If reservoir temperature is high, solubility of CO_2 will be low. Thus, it requires higher pressure for CO_2 to diffuse in the oil and thus, MMP will increase (Al-Anezi et al., 2008).

2.3.3 Purity of Carbon Dioxide

Carbon dioxide used in EOR process is not 100 percent purity. There are impurities, such as nitrogen, methane, oxygen, hydrogen sulfide, and hydrocarbon components (Table 2.1). Yang et al. (2007) reported that nitrogen, methane, and oxygen increase the MMP. Eissa et al. (2007) reported H_2S and hydrocarbon components (C_2–C_4) decrease the MMP.

Table 2.1 Specification of CO_2 quality suitable for EOR (Vandenhengel, 1993)

Component	Composition
CO_2	95 % min.
$N_2+CH_4+H_2$	4 % max
H_2S	20 ppm min.
SO_2	300 ppm min.
NO_x	100 ppm max.
O_2	100 ppm max.
CO	3 kPa max.

2.4 Miscible Gas Injection

Two fluids are considered miscible when they can be mixed together in all proportions and resulting mixtures remain a single phase, so there is no interface and consequently no interfacial tension (IFT) between the fluids (Ahmed and Meehan, 2012). Miscible injection is recognized as an effective enhanced oil-recovery method. Two different processes are proposed for miscibility achievement, (1) first contact miscibility (FCM) and (2) multiple contact miscibility (MCM) (Belhaj and Abukhalifeh, 2013).

2.4.1 First Contact Miscibility (FCM)

The solvent (liquid or gas mixture) and oil are miscible upon first contact in all proportions under injection pressure and temperature. A simple illustration can be easily understood shown in a pseudoternary phase diagram of CO_2-hydrocarbon system in Figure 2.1 The envelope is a two phase of fluid mixture where their compositions can be determined by a tie line, which is the line drawn between a composition of gas and reservoir fluid. In case of a tie line passing the phase envelope, it will be immiscible. However, it will be miscible, if a tie line shifts close to a critical point. To achieve the first contact miscibility (FCM), the injection pressure should be higher than MMP. As a simple illustration of FCM, pure CO_2 will achieve FCM with reservoir fluid in the dark region (above line AB) in Figure 2.1.
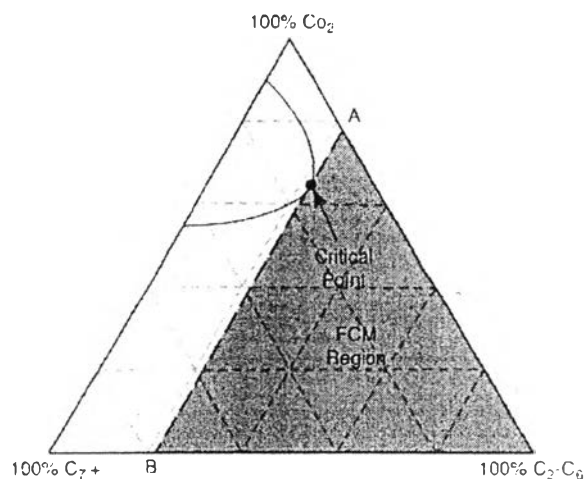

Figure 2.1 Pseudoternary diagram of CO_2-hydrocarbon system (Ezekwe, 2010).

2.4.2 Multiple Contact Miscibility (MCM)

Multiple-contact miscible (MCM) displacement is a process in which the injected fluid and the reservoir oil are not miscible in the first contact but miscibility could be developed after multiple contacts (dynamic miscibility). These processes are categorized into (1) vaporizing lean gas drive and (2) condensing rich gas drive (Ahmed and Meehan, 2012).

2.4.2.1 Vaporizing Lean Gas Drive

The injected gas is a relatively lean gas, for example, it contains mostly methane and other low molecular weight hydrocarbons or sometimes nitrogen. In this approach, the light components of oil are vaporized during the contacts and form a miscible bank with injected gas (Ezekwe, 2010). The mechanism of attaining MCM by vaporizing gas drive is illustrated with a pseudoternary diagram shown in Figure 2.2, which the compositions of gas and reservoir fluid are shown at the point 100% C_1 and O, respectively. At the first contact, the composition of mixture in vapor phase appears at point V_1. Phase of mixture is changed with time, after gas V_1 contact with reservoir fluid at point O, it will create a new composition of mixture fluid in vapor phase at V_2, this phenomena will continue until the tie line from gas (V_1) to liquid is not pass the two phase region, the mixture will be miscible.

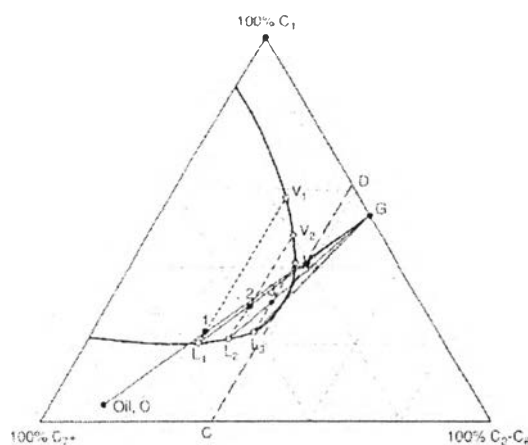**Figure 2.2** MCM by vaporizing gas mechanism (Ezekwe, 2010).

2.4.2.2 Condensing Gas Drive

The injected gas contains large amounts of intermediate molecular weight hydrocarbons. In this approach, reservoir oil near the injection well is enriched in composition by contact with the injected gas since hydrocarbon components from 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 Figure 2.3, 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 appears at point L_1. The phase of mixture is changed with time, after gas contact with liquid L_1, it will created a new composition of mixture fluid in liquid phase at L_2, this phenomena will continue until the tie line from gas to liquid (L_i) is not passed the two phase region, that mean the mixture will be miscible.

Figure 2.3 MCM by condensing gas mechanism (Ezekwe, 2010).

2.5 Experiment for CO_2-MMP

A slim tube test is accepted as a standard method for measuring MMP with high measurement accuracy and repeatability. In the early 1980s, the rising bubble apparatus approach was first developed by Christiansen and Haines (1987) and accepted as an alternative inexpensive method for the measured MMP. In recent

years, a vanishing interfacial tension technique, which is based on the interfacial tension theory, was developed to determine MMP of CO_2 flooding with simple and feasible characteristics. Although the methods give high measurement precision, these experimental approaches are usually difficult, time-consuming to achieve, and high operation cost. It is necessary to develop an inexpensive and quick method for CO_2-oil MMP estimation (Chen et al., 2014).

2.5.1 Slim-tube Apparatus

The slim-tube displacement test is often referred to as the "Industry standard" for determining MMPs. A solvent (gas, liquid or mixture) is injected at different pressure into the slim-tube that is saturated with oil sample at reservoir temperature. The setup Figure 2.4 is in the air bath to keep at the reservoir temperature. Packing materials (sand, glass bead) are filled in the coiled slim-tube. At the end of slim-tube, it is connected to back pressure regulator and connect to the separator or gas chromatography (Elsharkawy *et al.*, 1996). The change in produced gas and oil properties can be monitored by placing gas chromatograph (GC) at the outlet. The amount of oil separated from the slim-tube is measured and calculated for the oil recovery. The oil recovery is determined as a function of injection pressure. The MMP can be determined from a plot of oil recovery against the injection pressure, where it is the point at which a breakover occurs as the curve shown in Figure 2.5 the intersection point of the two straight-line sections. The uncertainty could come from how one draws the immiscible part of the curve (with a very limited number of test data) which intercepts the miscible part of the curve, to obtain the MMP value (Dong *et al.*, 2001).
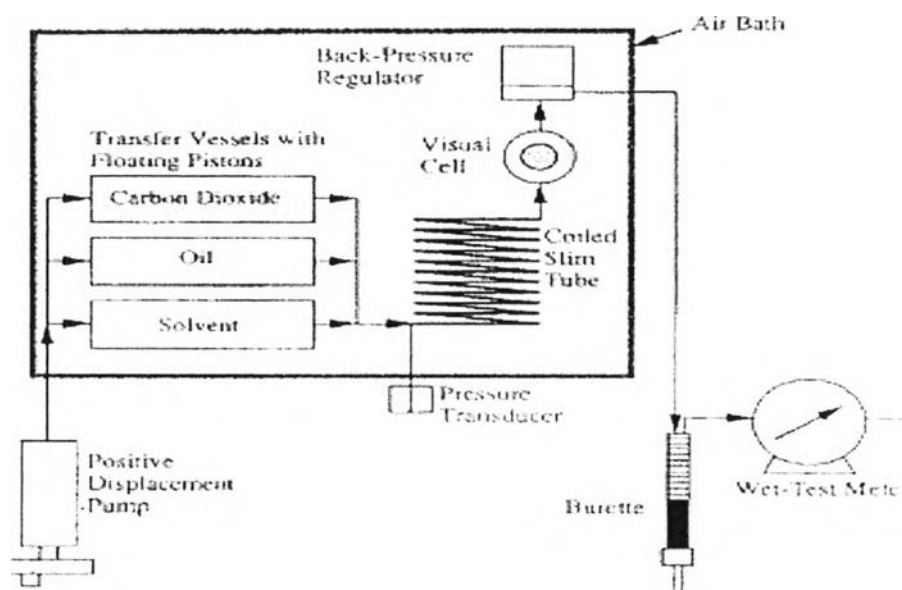
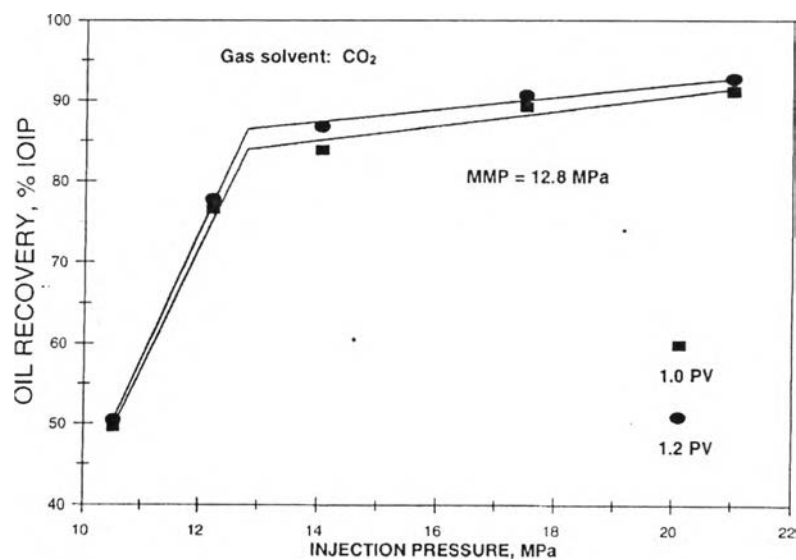**Figure 2.4** Schematic of a slim-tube apparatus (Elsharkawy *et al.*, 1996).

Figure 2.5 Result from slim-tube apparatus (Dong *et al.*, 2001).

2.5.2 Rising-bubble Apparatus

The rising-bubble apparatus (RBA) is developed in the early 1980s (Elsharkawy, 1996). A flowsheet for the RBA appears in Figure 2.6. RBA has gain acceptance in the petroleum industry as an alternative method for measuring MMP

because it is quicker than the slim-tube method. RBA is recording of the shape of bubbles for estimate the MMP. (Elsharkawy *et al.*, 1996).
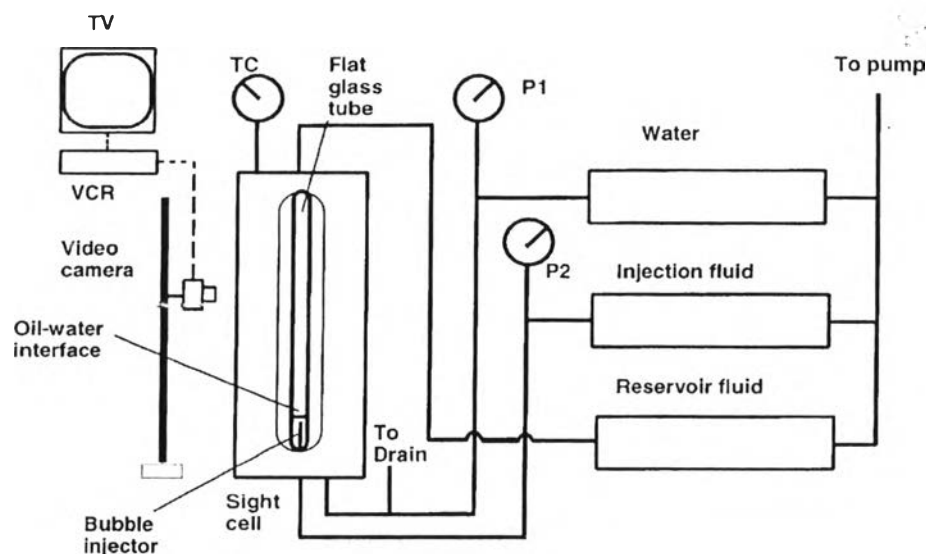
Figure 2.6 Schematic diagram of a rising-bubble apparatus (Dong *et al.*, 2001).

Distilled water is contained in the sight gauge and flat glass tube. The reservoir oil is injected into the glass. A CO_2 bubble is injected into the water just under the oil–water interface. As the bubble rises through the oil–water interface and then the reservoir oil, its shape and motion are recorded. The MMP is defined as the pressure at which the bubble and the oil show a multiple-contact miscibility (Dong *et al.*, 2001). The result of rising bubble experiments for the Weyburn reservoir fluid with CO_2 at pressures ranging from 7.3 to 15.4 MPa. The bubble shape at each pressure is shown in Figure 2.7. The bubble shape at 7.3 MPa retained their initial near-spherical shape that mean this pressure is below from MMP. When increasing pressure to 11.2 MPa, the shape of bubble transform to be a bullet-shape this pressure is closed to MMP. At 12.0 MPa and above, the shape of bubble has become a short tail that means this point is above MMP. MMP point is referred to the pressure transfer from the bullet-shaped bubble to the tail-shaped bubble (c to d). Conclude the CO_2 MMP for the Weyburn reservoir fluid is estimate about 11.7 MPa.
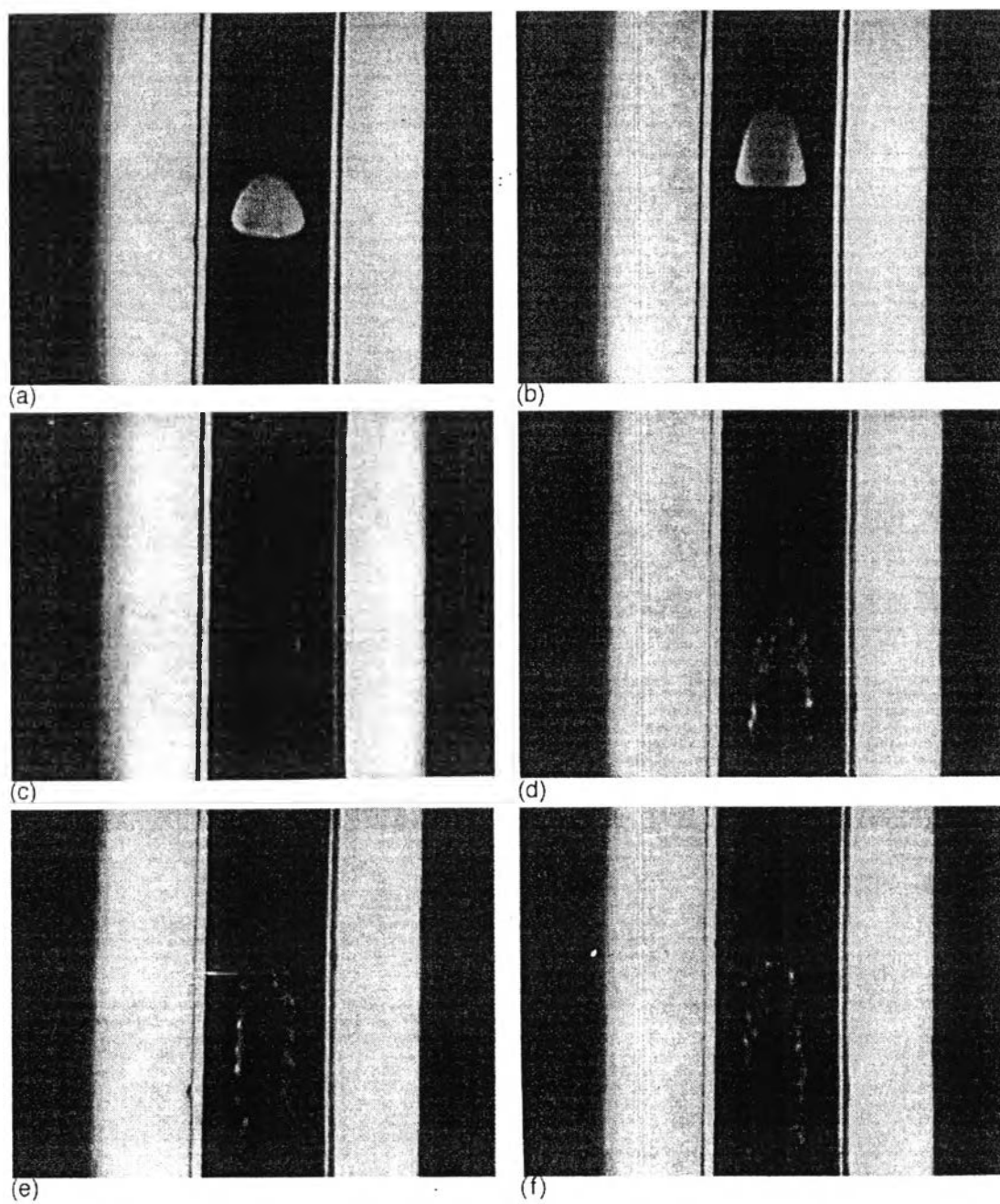
Figure 2.7 Photograph of rising bubbles (a) at 7.3, (b) at 11.2, (c) at 12.0, (d) at 14.0 MPa, (e) at 12.9, and (f) 14.0 MPa (Dong *et al.*, 2001).
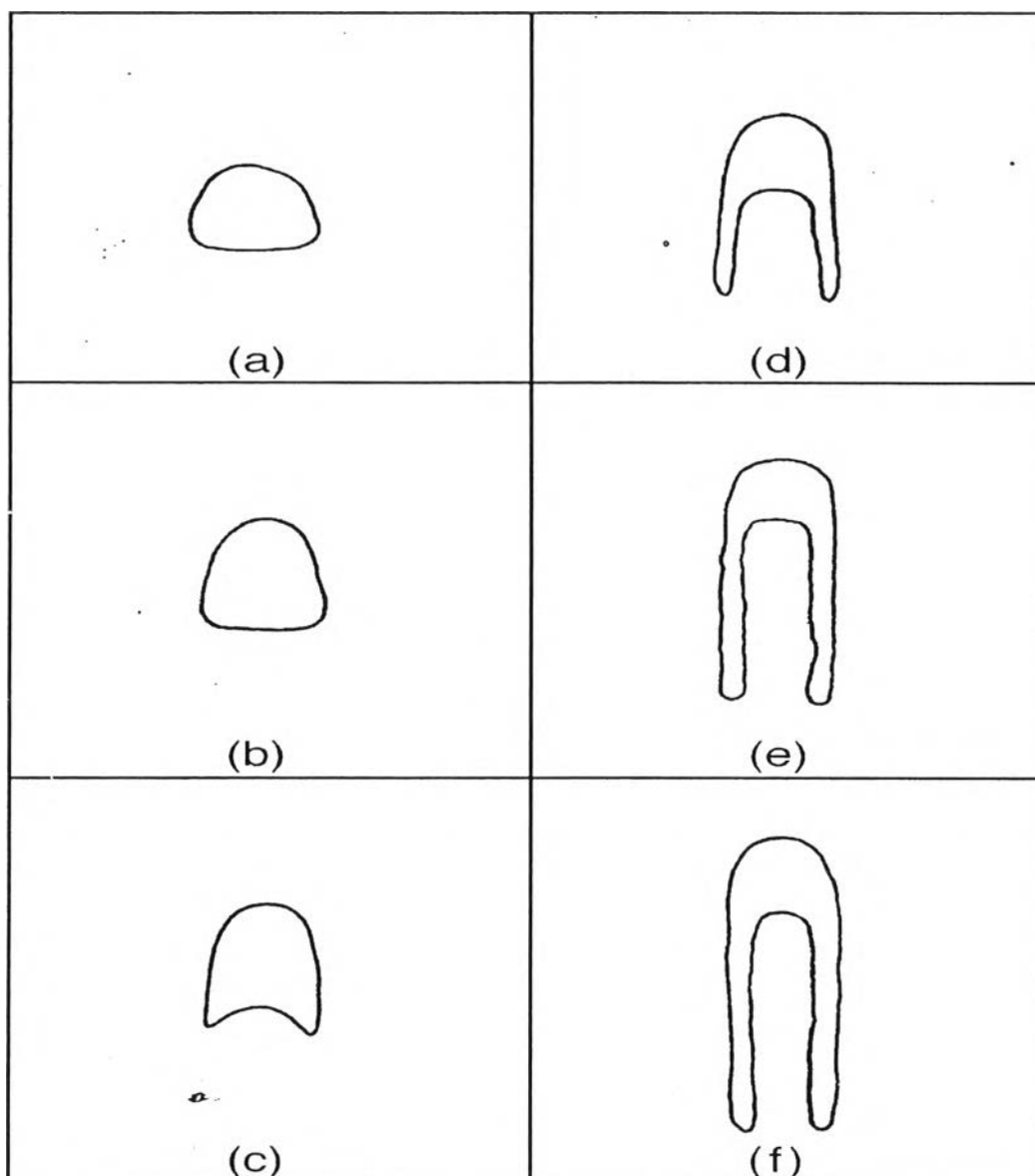
Figure 2.8 Shape of rising bubbles traced from photographs in Figure 8 (a) at 7.3 MPa, (b) at 8.8 MPa, (c) at 11.2 MPa, (d) at 12.0 MPa, (e) at 12.9 MPa, and (f) at 14.0 MPa (Dong *et al.*, 2001).

2.5.3 Interfacial Tension Experiment

Miscibility is the absence of an interface between the injected gas and the crude oil at reservoir conditions, that the interfacial tension between two immiscible fluids must become zero at miscibility. However, it is impossible to measure interfacial tension when it becomes zero (Rao and Lee, 2003). The MMP is

taken to be the pressure at which the IFT plotted against pressure and extrapolates to zero IFT (Orr and Jessen, 2007). Vanish interfacial tension (VIT) experiment set-up is shown in Figure 2.9. The pressure cell is first fill with CO_2 at a pre-specified pressure and a constant temperature. After the pressure and temperature in the pressure cell have stable values, the crude oil is introduced from the crude oil sample cylinder to the pressure cell to form a pendant oil drop. A well-shaped pendant oil drop is formed. The sequential digital images of the dynamic pendant oil drop are received. Axisymmetric drop shape analysis (ADSA) is the technique that used for measuring IFT between crude oil and CO_2.
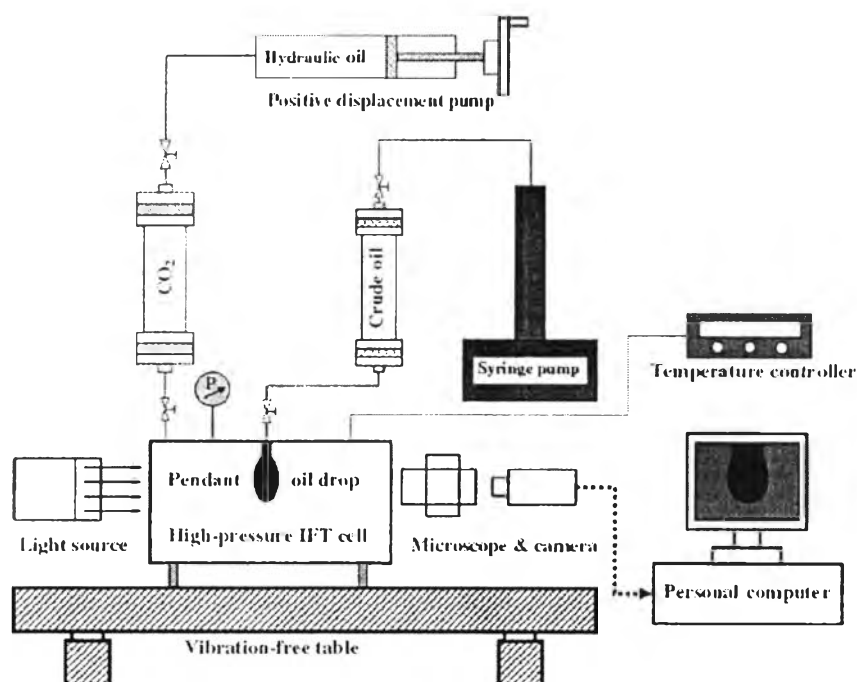
Figure 2.9 Schematic diagram of the experimental set-up used for measuring the equilibrium interfacial tension (IFT) (Cao and Gu, 2013).

ADSA gives the information of equilibrium IFT at each pressure. Therefore, the MMP is determined by linearly extrapolating the measured equilibrium IFT versus equilibrium pressure. Figure 2.10 shows the gas–oil interfacial tensions measured at varying pressure levels in the cell for all the three C_2 + enrichment levels of 9.3, 20.7, 21.4, and 29.4 %. Linear lines are fit to each set of

data and extrapolated to zero gas–oil interfacial tension to determine the minimum miscibility pressures. Which interfacial tension equals zero is the MMP. The MMP determines from the VIT technique closely matches that from slim-tube process.
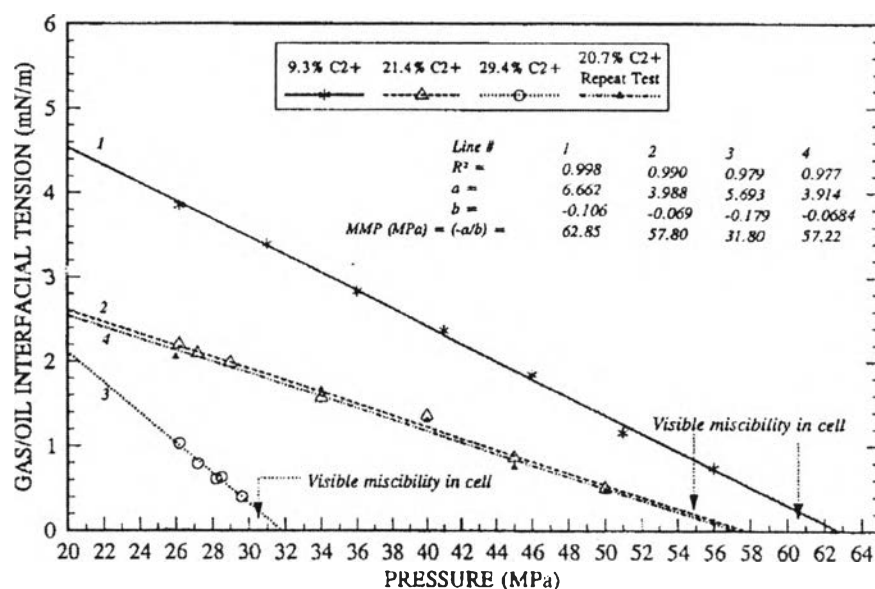
Figure 2.10 Effect of pressure on interfacial tension of Terra Nova live oil in three solvents at 96 °C (Rao and Lee, 2003).

2.5.4 Supercritical Reactor Experiment

The slim-tube studies are used for measuring MMP, but not widely available for universities due to high cost. To study MMP of CO_2-oil, other method uses supercritical reactor (Spe-ed SFE), high pressure and oil saturated core sample. The supercritical extractors are also accurate and effective to measure oil recovery (Rudyk *et al.*, 2009). Setup of this experiment is shown in Figure 2.11 using oil saturated chalk samples. The core sample is cleaned, dried, weight measured and then saturated by soaking in the oil flask for one day, after that the core sample is weight measured again. The equipment and the core sample are transferred into the oven at reservoir temperature. Carbon dioxide is injected into the reactor by the gas pump until pressure reaching at a setting value. The collection tubes are weighed before and after oil collection to determine the weight of extracted oil.
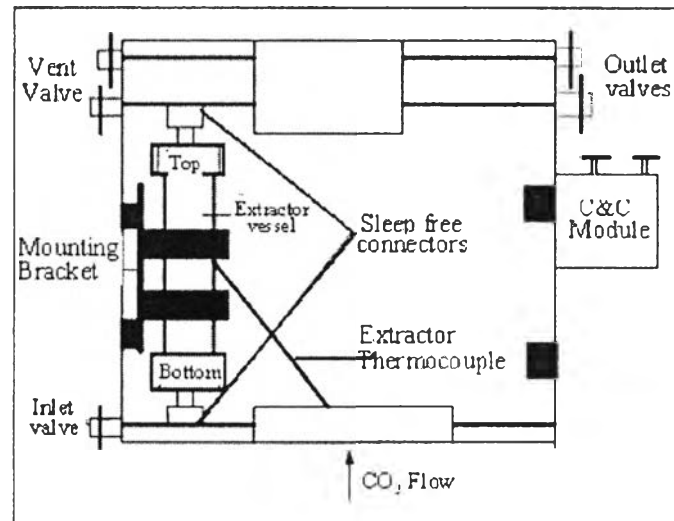
Figure 2.11 Schematic diagram of supercritical reactor Spe-ed SFE (Rudyk *et al.*, 2009).

Figure 2.12 shows the results of varying pressure in a range from 10 to 40 MPa. In the first oil recovery, it is increased with increasing process pressure until grows to the breakover point. After treating oil recovery, it is increased from 1.4624 g to 1.822 cm^3. And percentage of oil recovery is 29 %.
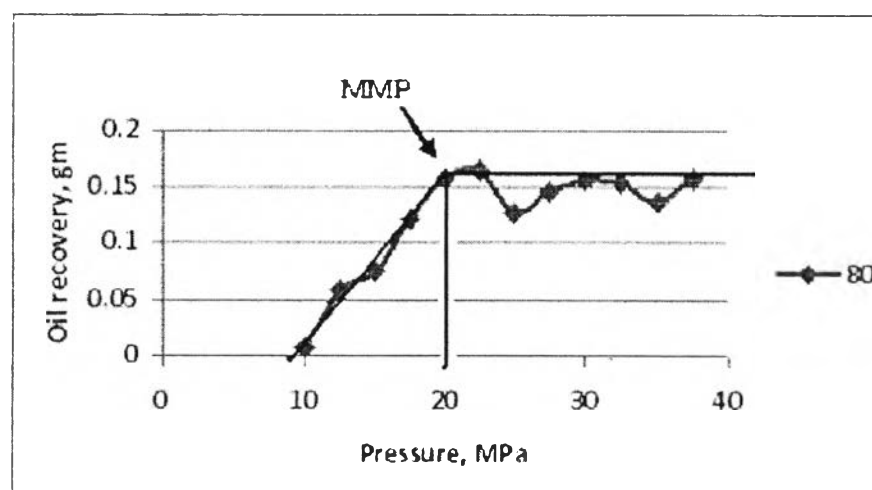

Figure 2.12 The graph for the determination of MMP (Rudyk *et al.*, 2009).

2.5.5 CO₂ Solubility and Oil Swelling Factor Experiment

The solubility of CO_2 in the crude oil and the oil swelling process as a result of experiment are the main mechanisms in the CO_2-EOR techniques. Oil swelling and other mechanisms, such as oil viscosity reduction and oil interfacial tension reduction depend on the solubility of CO_2 in oil. The experimental methods can determine these parameters more accurate than VLE equations of state and other correlations (Abedini and Torabi, 2013).
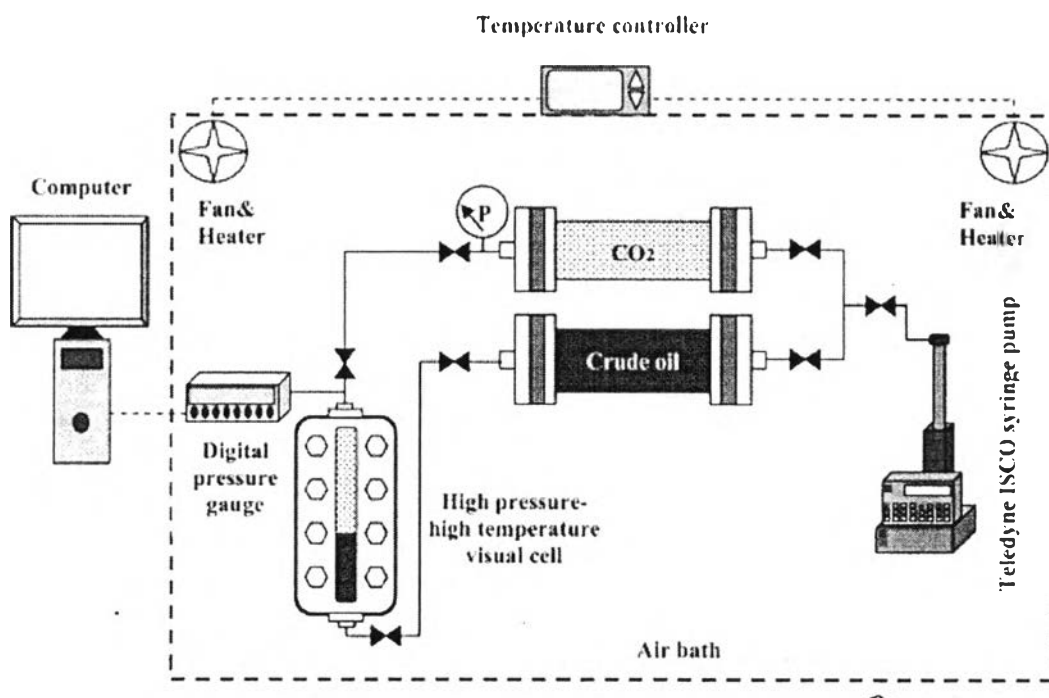

Figure 2.13 Schematic diagram of the experimental setup used for CO2 solubility and oil swelling factor measurements (Abedini and Torabi, 2013).

The visual cell is pressurized by CO_2 to initial pressure (P_i), the pressure of the cell is allowed to stabilize while CO_2 is dissolved into the oil sample. Lastly, initial and final CO_2 volume in visual cell, $V_{CO2,i}$ and $V_{CO2,f}$, respectively, are determined by taking photos and utilizing image analysis technique. The mass balance analysis is shown in Equation 2.1, the amount of dissolved CO_2 and the CO_2 solubility in the crude oil sample (χ_{CO2}) is determine.

$$m_{CO2,dissolved} = m_{CO2,I} - m_{CO2,f}$$

$$= (P_i V_{CO2,i} MW_{CO2} \div Z_i RT) - (P_i V_{CO2,f} MW_{CO2} \div Z_f RT)$$

$$= \frac{MW_{CO2}}{RT} [(P_i V_{CO2,i} \div Z_i) - (P_f V_{CO2,f} \div Z_f)] \qquad \text{Eq. 2.1}$$

Furthermore, the oil swelling factor (SF) due to the dissolution of CO_2 at the specific operating condition is calculated by the ratio of the initial volume to final volume of the oil of the experiment is presented in Equation 2.2,

$$SF = V_{o,i}/V_{o,f} \qquad \text{Eq. 2.2}$$

Figure 2.14 shows solubility of CO_2 in oil samples increase with equilibrium pressure in system. The concentration of dissolved CO_2 is proportional to the pressure of the CO_2. Since the pressure is high, the numbers of CO_2 contact with the surface of oil sample is increased. Thus, more CO_2 is dissolved in the crude oil with increases equilibrium pressure. Figure 2.15 shows oil swelling factor. The volume of the crude oil increases by increasing the equilibrium pressure due to the higher solubility of CO_2 in the crude oil. The pressure increases, the density of CO_2 increases and the CO_2 phase changes from gas to liquid. Since liquid phase CO_2 has a higher ability to extract lighter hydrocarbon components, CO_2 starts to vaporize or extract hydrocarbons from the crude oil. As a result, the volume of the crude oil is reduced. Oil swelling factor is increased. After this point, oil swelling factor is decreased because CO_2 diffuses in the crude oil. This phenomenon shows the crude oil swelled. Thus, volume of oil in final point is higher than initial volume. Following Equation 2.2, oil swelling factor will be decrease.
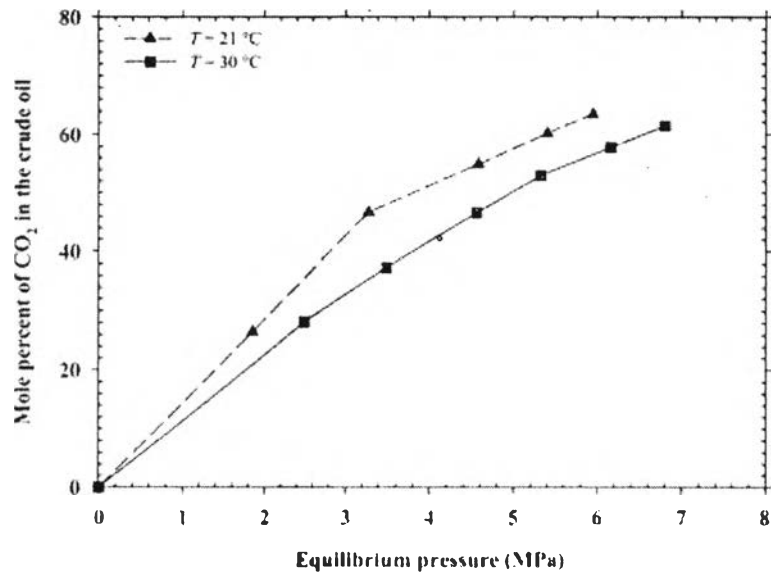
Figure 2.14 Solubility of CO_2 in the light crude oil sample at temperatures T = 21 and 30 °C (Abedini and Torabi, 2013).
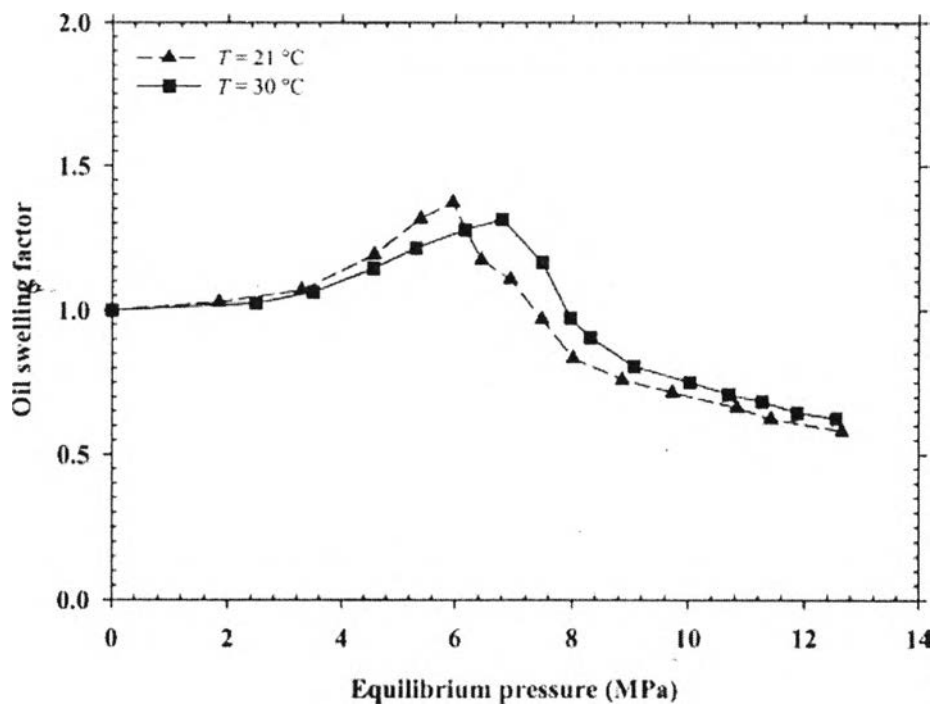

Figure 2.15 Oil swelling factor of crude oil–CO2 system at temperatures T = 21 and 30 °C (Abedini and Torabi, 2013).

2.5.6 Effect of Impure Oxygen in CO_2 on MMP

O_2 is one of contaminants in CO_2 injection. The effect of oxygen content in injected CO_2 gas on the MMP is important to design cost-effective CO_2 enhanced oil recovery process. Yang et al. (2007) used a slim-tube apparatus to measure MMP of the crude oil and used a multiple-mixing-cell model to model a continuous gas injection process in the slim-tube experiment by assuming constant temperature and pressure in each cell, no physical dispersion, no capillary force in each cell, and perfect mix in each cell. The multiple-mixing-cell model is then converted to pure thermodynamic P/T flash calculation. A block-algebra simultaneous flash algorithm was used with the Peng-Robinson (PR) cubic equation of state (EOS).

The results showed that MMP of oils were increased with the O_2 concentration in the CO_2. The multiple-mixing-cell model was accurate to predict the MMP values, which was found to capture the effects of compositions of gas injection and temperature in process. The effect of temperature, The MMP is increased with temperature increased (Solubility of CO_2 in crude oil). The extent of the MMP is increased due to O_2 contamination. Calculations also indicate that the effect of N_2 impurity on the MMP is larger than the effect of O_2 impurity.

2.5.7 Impurity (N_2 and Hydrocarbon) in CO_2 injection

Purity of carbon dioxide gas injection is not 100 %. There are some impurities such as nitrogen gas, enriched hydrocarbon, hydrogen sulfide, oxygen. In this work, concerned about the effect of impurity (N_2 and Hydrocarbon) concentration in CO_2 gas injection on MMP and oil recovery factor. Belhaj *et al.* (2013) uses simulation with Peng-Robinson equation of state and WINPROP software to estimate MMP. The MCM option of the simulator can assess MMP or the FCM condition for oil sample, and make up gas compositions at a specific temperature.

The MMP of CO_2 miscible flooding which contaminates with N_2 and other hydrocarbon gas in oil sample could increase with N_2 and/or CH_4 concentration in the CO_2 stream (Figure 2.16). The other simulation results are shown, the MMP of rich gas/CO_2 is increased with rich gas concentration increased. The MMP of N_2/CH_4 is increased with N_2 and CH_4 concentration increased. N_2 has more effect on MMP

than CH_4. And The MMP of N_2/C_2H_6 is decreased with C_2H_6 concentration increased. The conclusion N_2 and CH_4 are difficult to miscible in the crude oil. It is required high pressure for miscible in the crude oil. Thus, MMP will be high. And C_2H_6 is easy to miscible in crude oil. It is required low pressure for miscible in the crude oil. Thus, MMP will be low.
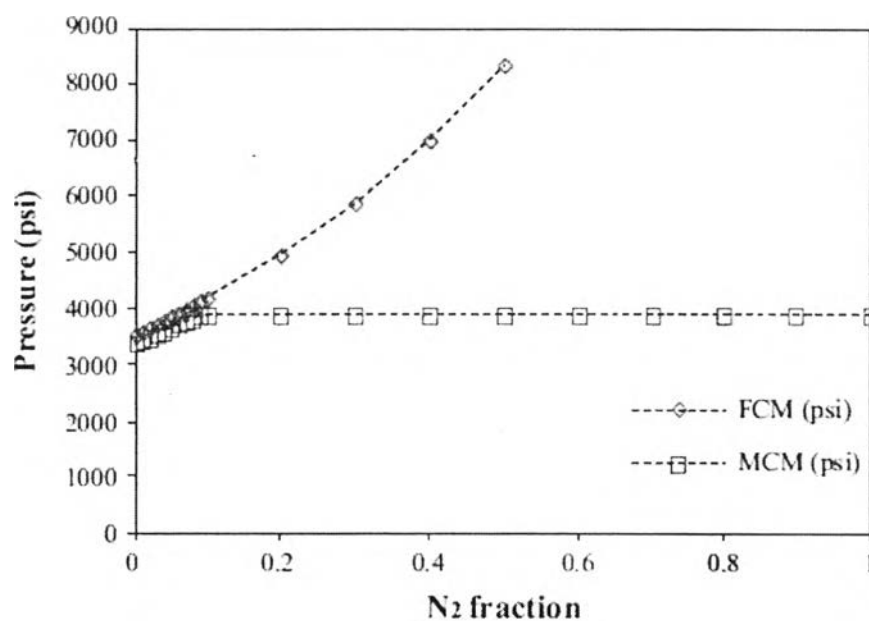

Figure 2.16 Minimum miscibility pressures for Oil and CO_2/N_2 (Belhaj et al., 2013).

2.5.8 Modified Pressure Decay Technique to Measure MMP

CO_2 is commonly used in gas injection of EOR. CO_2 injection can store the emitted CO_2 into oil reservoirs. An advantage of using CO_2 in EOR is that the pressure required for achieving dynamic miscibility within the reservoir is lower than the pressure required for dynamic miscibility with other gases (nitrogen and flue gas) Typically, injected gas compositions are at least 95 % CO_2 purity and the impurities can be constituted of N_2, CH_4, H_2, etc. A key parameter for CO_2 miscible injection is MMP. In general, CO_2 is not miscible at first contact with reservoir oils, but achieved in dynamic miscibility with multiple contacts (Li *et al.*, 2012). There are many methods to determine MMP, such as rising bubble apparatus, slim-tube

apparatus, and interfacial tension. But previous work, used a pressure decay technique to determine MMP using a Parr reactor and the MMP point was the ultimate point of the total pressure drop curve as shown in Figure 2.17. Petroleum samples are represented by liquid hydrocarbons and PTTEP crude oil. The MMP point was studied as a function of pressure, molecular weight and temperature. At high reservoir temperature, the solubility of CO_2 in the crude oil was decrease which required higher pressure for CO_2 miscibility. For crude oil with high molecular weight, it was difficult for CO_2 to solubilize. Thus, it requires high pressure to measure MMP.
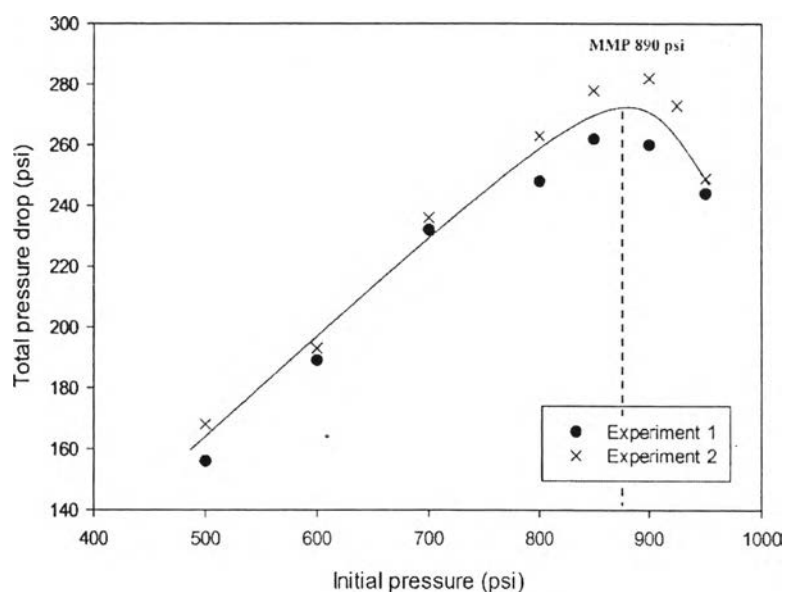

Figure. 2.17 Pressure drop curve of crude oil at 30 °C.

2.6 Correlation for CO_2-MMP

The existing experimental methods 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 for potential CO_2 injection. Therefore, it is of fundamental and

practical importance to develop reliable and accurate correlations for determining the MMP for a given crude oil−CO_2 system (Li *et al.*, 2012).

2.6.1 Alston Correlation

Alston *et al.* (2012) required reservoir fluid composition, molecular weight and reservoir temperature for prediction. This correlation is regarded to be more reliable than other effects which use one of the above parameters. It can predict the effect of contaminants in the injection gas (Dong et al., 2001).

$$(CO_2\ MMP)_{LO} = 6.05 \times 10^{-6}(1.8T_R+32)^{1.06} \times (MW_{C5+})^{1.78}(X_{vol}/X_{int})^{0.136} \qquad \text{Eq. 2.3}$$

where $(CO_2\ MMP)_{LO}$ = CO_2 minimum miscibility pressure for live oil (MPa),

T_R = reservoir temperature (°C),

MW_{C5+} = molecular weight of the C_{5+} fraction (g/g mol),

X_{Vol} = volatile oil fraction consisting of C_1 and N_2 (mol %),

X_{Int} = intermediate oil fraction consisting of C_2, C_3, C_4, CO_2, and H_2S (mol %).

For the impure gas in CO_2, a correction factor to predict the MMP is calculated from the critical temperature of the gas stream. The pseudo-critical temperature of the solvent stream is calculated by using the weight-fraction mixing rule as follows,

$$T_{cm} = [\textstyle\sum_{i=1}^{N} w_i T_{ci}] \qquad \text{Eq. 2.4}$$

where T_{cm} is the weight average critical temperature of the solvent stream (°C), w is the weight fraction of component i, and Tc,i is the critical temperature of component i (°C)

The correction factor for impure CO streams (F_{imp}) is calculated,

$$F_{imp} = (87.8/(1.8T_{cm}+32))^{(1.935*87.8/(1.8T_{cm}+32))} \qquad \text{Eq. 2.5}$$

The impure CO_2 MMP is calculated as,

$$(CO_2MMP)_{imp\text{-}LO} = (CO_2\ MMP)_{LO} \times Fimp \qquad Eq.2.6$$

2.6.2 Cronquist Correlation

Cronquist (2012) studies CO2–oil MMP with reservoir temperature, C5+ molecular weight, and mole fraction of the main volatile component, that is, CH4, and is expressed as follows,

$$MMP = 0.11027(1.8T_R+32)^{0.744206+0.0011038MW_{C5+}+0.0015279C_1} \qquad Eq.2.7$$

where T_R is reservoir temperature in °C, MW_{C5+} is C_{5+} molecular weight, and C_1 is mole fraction of CH_4 in the reservoir oil.

2.6.3 Lee Correlation (Li *et al.*, 2012)

$$MMP = 7.3924 \times 10^{2.772-[1519/(492+1.87T_R)]} \qquad Eq.2.8$$

where T_R is the reservoir temperature.

2.6.4 Yellig–Metcalfe Correlation (Li *et al.*, 2012)

$$MMP = 12.6472+0.01553(1.8T_R+32)+1.24192\times10^{-4}(1.8T_R+32)^2-(716.9427/(1.8T_R+32)) \qquad Eq.2.9$$

where T_R is reservoir temperature.

2.6.5 Glaso Correlation

Glaso (2012) proposed a CO2–oil MMP correlation that considered the effect of reservoir temperature, C_{7+} fraction molecular weight, and mole fraction of the intermediates (C_2–C_6) if the mole fraction of the intermediates is less than 18

%. If the mole fraction of the intermediates $x_{INT} > 18$ %, the Glaso correlation is expressed as follows,

$$MMP =$$
$$5.5848 - 2.3470 \times 10^{-2} MW_{C7+} + 1.1721 \times$$
$$10^{-11} MW_{C7+}{}^{3.73} e^{786.8 MW_{C7+}{}^{-1.058}} (1.8T_R + 32) \qquad \text{Eq.2.10}$$

If $X_{INT} < 18$ %, the Glaso correlation is expressed as follows,

$$MMP =$$
$$20.3251 - 2.3470 \times 10^{-2} MW_{C7+} + 1.1721 \times$$
$$10^{-11} MW_{C7+}{}^{3.73} e^{786.8 MW_{C7+}{}^{-1.058}} (1.8T_R + 32) - 8.3564 \times 10^{-1} X_{INT} \qquad \text{Eq.2.11}$$
X_{INT} is mole fraction of the intermidates component (C_2-C_6).

2.6.6 Emera and Sama Correlation

Emera and Sama (2012) modified Alston correlation as follows,

$$MMP = 5.0093 \times 10^{-5} (1.8T_R + 32)^{1.164} (MW_{C5+})^{1.2785} \left(\frac{X_{VOL}}{X_{INTi}}\right)^{0.1073} \qquad \text{Eq.2.12}$$

If $P_b < 0.345$ MPa, the following alternative equation obtained by removing the volatile to intermediate ratio term.

$$MMP = 5.0093 \times 10^{-5} (1.8T_R + 32)^{1.164} (MW_{C5+})^{1.2785} \qquad \text{Eq. 2.13}$$

Equation is an alternative of Emera and Sama correlation. If $P_b < 0.345$ MPa.

2.6.7 Yuan *et al.* Correlation

Yuan *et al.* (2012) developed a CO_2-oil MMP correlation by using an analytical theory from an equation of state. The correlation, taking into account the

reservoir temperature, C_{7+} molecular weight, and mole fraction of the intermediates (C_2–C_6), is given by

$$MMP =$$

$$a_1 + a_2 MW_{C7+} - a_3 X_{INT} + \left(a_4 + a_5 MW_{C7+} + a_6 \frac{X_{INT}}{MW_{C7+}^2}\right)(1.8T_R + 32) +$$

$$\left(a_7 + a_8 MW_{C7+} - a_9 MW_{C7+}^2 - a_{10} MW_{C7+}\right)(1.8T_R + 32)^2$$

<div align="right">Eq. 2.14</div>

Where values of the empirical coefficients a_1–a_{10} are $a_1 = -9.8912$, $a_2 = 4.5588 \times 10^{-2}$, $a_3 = -3.1012 \times 10^{-1}$, $a_4 = 1.4748 \times 10^{-2}$, $a_5 = 8.0441 \times 10^{-4}$, $a_6 = 5.6303 \times 10^{1}$, $a_7 = -8.4516 \times 10^{-4}$, $a_8 = 8.8825 \times 10^{-6}$, $a_9 = -2.7684 \times 10^{-8}$, and $a_{10} = -6.3830 \times 10^{-6}$, respectively.

2.6.8 Shokir Correlation

Shokir (2012) proposed a CO2–oil MMP correlation based on the alternating conditional expectation algorithm. The Shokir correlation, which is a function of reservoir temperature, C_{5+} molecular weight, mole fraction of the volatiles, and mole fraction of intermediates (CO_2, H_2S, and C_2–C_4), is expressed as follows,

$$MMP = -0.068616z^3 + 0.31733z^2 + 4.9804z + 13.432 \qquad \text{Eq. 2.15}$$

for pure CO2–oil system,

$$z == \sum_{i=1}^{4} zi \qquad \text{Eq. 2.16}$$

and

$$z_i = A3_i y_i^3 + A2_i y_i^2 + A1_i y_i + A0_i \qquad \text{Eq. 2.17}$$

where y_i denotes the input variable ($y1 = T_R$, $y2 = x_{vol}$, $y3 = x_{int}'$, and $y_4 = MW_{C5+}$), $A3_i$, $A2_i$, $A1_i$, and $A0_i$ represent the polynomial coefficients for y_i. The values of coefficients in the Shokir correlation are provided as follows:

For $y_1 = T_R$, $A3_1 = 2.3660 \times 10^{-6}$, $A2_1 = -5.5996 \times 10^{-4}$, $A1_1 = 7.5340 \times 10^{-2}$, and $A0_1 = -2.9182$.

For $y_2 = x_{vol}$, $A3_2 = -1.3721 \times 10^{-5}$, $A2_2 = 1.3644 \times 10^{-3}$, $A1_2 = -7.9169 \times 10^{-3}$, and $A0_2 = -3.1227 \times 10^{-1}$.

For $y_3 = x_{int}'$, $A3_3 = 3.5551 \times 10^{-5}$, $A2_3 = -2.7853 \times 10^{-3}$, $A1_3 = 4.2165 \times 10^{-2}$, and $A0_3 = -4.9485 \times 10^{-2}$.

For $y_4 = MW_{C5+}$, $A3_4 = -3.1604 \times 10^{-6}$, $A2_4 = 1.9860 \times 10^{-3}$, $A1_4 = -3.9750 \times 10^{-1}$, and $A0_4 = 2.5430 \times 10^{1}$.

2.6.9 Li *et al.* Correlation

Li *et al.* (2013) applied this equation from Alston correlation which they replacing C_{5+} with C_{7+}, the parameters 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).

$$MMP = 7.3099 \times 10^{-5}[\ln(1.8T_R + 32)]^{5.33647} [\ln(MW_{C7+})]^{2.08836} \left(1 + \frac{x_{VOL}}{x_{INT}}\right)^{2.01658 \times 10^{-1}}$$

Eq. 2.18

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).