### FUNDAMENTAL OF MINIMUM MISCIBILITY PRESSURE DETERMINATION METHODS

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@ Hak Cipta dilindungi undang-undang Dilarang memperbanyak karya tulis ini dalam bentuk dan dengan cara apapun tanpa ijin tertulis dari penerbit.

## PREFACE

The book of "Fundamentals of Minimum Miscibility Pressure Determination Methods" provides a practical reference source for knowledge regarding minimum miscibility pressure (MMP) methods. This book contains some methods to determine minimum miscibility pressure based on literature review that may be used for the better understanding to industries, researchers, students, and many more. In other hand, the book results valuable information for lesson-learn, planning, execution, and monitoring the  $CO_2$  projects in the near future.

Chapter I serves as an introduction to the subject. Chapter II is more specialized describing some of the methods to determining minimum miscibility pressure. Chapter III describes about advantages and disadvantages of the methods.

Suggestions of many readers were evaluated in preparing this book. Any further comment and suggestion for improvement of the book will be gratefully appreciated. Please feel free to contact us directly.

#### Pekanbaru, August 2020

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# Chapter I INTRODUCTIONS

Enhanced oil recovery (EOR) is an important method to increase oil production in mature fields [Alvarado and Manrique, 2010]. This method has been proved to enhance the recovery or prolong the life of an oil field. Several oil fields have been implemented EOR methods such as Daqing Oil Field in China [Corlay et al., 1992], Sacroc Unit in Texas [Gill, 1982], Duri Field in Indonesia [Pearce and Megginson, 1991], and Bate Raman in Turkey [Sahin et al., 2007]. Regardless of its successful implementation, the EOR method is still considerably expensive due to the high initial capital investment cost. Also, long-time preparation process that is required from laboratory studies to field implementation contributes to the high cost [Sutadiwiria and Azwar, 2011].

 $CO_2$  injection is one of the promising EOR and it has been proved to increase oil recovery during the last decade [Espie, 2005], especially in the low-permeability and tight/shale reservoirs [Jia et al., 2019]. This method has at least two advantages. It does not only increase the oil recovery from mature fields but also contribute to gas emission reduction by storing the  $CO_2$  in the reservoir depth [Gorecki et al., 2012; Saini and Jimenez, 2014].

of the main challenges in the CO<sub>2</sub>-EOR One implementation is its requirement of having high reservoir pressure in order to maximize the oil recovery from the injection [Holm and Josendal, 1974]. At high reservoir pressure condition, the  $CO_2$  and crude oil are miscible easily. In this case, the  $CO_2$ requires a minimum threshold pressure to be miscible with crude oil. This lowest pressure to achieve the miscibility between the injected CO<sub>2</sub> and the oil within the reservoir is called the minimum miscibility pressure [Mungan, 1981]. In this book, the minimum miscibility pressure is often abbreviated as MMP. Accurate determination of the MMP for a given oil-gas system is an important parameter for screening and selecting reservoirs for the injection system design of CO<sub>2</sub> miscible flooding projects in the oil field. For the highest oil recovery, a candidate reservoir capable of withstanding an average reservoir must be pressure greater than the CO<sub>2</sub> MMP. Also, knowledge of the accurate determination of CO<sub>2</sub> MMP is important for simulation of reservoir performance as a result of CO<sub>2</sub> injection [Shokir, 2007].

Despite the tremendous success of miscible  $CO_2$  in increasing oil recovery of tight reservoirs, the  $CO_2-C_3H_8$ mixture is found to be substantially more effective than  $CO_2$ alone in terms of oil viscosity reduction and swelling (Luo *et al.*, 2012). Zheng *et al.* (2016) have reported that  $C_3H_8$  is able to diffuse into heavy oil better than  $CO_2$  when both gases meet the same conditions. Choubineh *et al.* (2019) revealed that increasing  $C_3H_8$  concentration leads to a significant decrease in  $CO_2$  MMP oil systems.

Numerous methods have been published for predicting the MMP including slim tube tests as performed by Yellig and Metcalfe [1980] and Holm and Josendal [1982]; correlations as conducted by Johnson and Pollin [1981], Sebastian et al. [1985], Glaso [1985], Orr and Silva [1987], and Johnson and Orr Jr [1996]; tests using rising bubble apparatus (RBA) as conducted by Christiansen and Kim [1987], El-Sharkawy et al. [1996], Hagen and Kossack [1986], and Zhou and Orr [1998]; simulation work as performed by Ahmed [2000], Stalkup and Yuan [2005], and Dzulkarnain et al. [2011]; vanishing interfacial tension tests (VIT) as conducted by Rao [1997], Ayirala and Rao [2006], Nobakth et al. [2008], and Jessen and Orr Jr [2008]; swelling tests as conducted by Tsau et al. [2010] and Abdurrahman et al. [2015]; visual observation as conducted by Hagen and Kossack

[1986], Wang [1986], and Abdurrahman et al. [2015]. However, it has long been recognized that each method has its own advantages and disadvantages in estimating the MMP. For example, slim tube experiment is time consuming, requires a lot of samples, and no standardized specification and procedure as noted by Jarrel et al. [2002] and Johns et al. [2000]. Simulation method must have very good quality of input data while over tuning the parameters may affect the final results as mentioned by Lee and Reitzel [1982] and Firoozabadi and Khalid [1986]. The correlation method must also be used with caution as the correlations may not reflect all the necessary process parameters needed in a typical CO<sub>2</sub> flooding as noted by Menouar [2013]. Rising bubble apparatus testing and visual observation have also disadvantages as their results are very subjective and very rough as mentioned by Thomas et al. [1994], Farzad and Amani [2012] and Abdurrahman et al. [2015]. Furthermore, the MMP through swelling tests cannot be determined when there is a lack of extraction stage in the experiment as shown by Tsau et al. [2010]. As a result, the method may have to be further examined to obtain satisfying results. Nevertheless, the majority of these methods are generally acceptable in the oil industry for predicting the MMP while at the same time many investigators are still questioning these methods including Thomas et al.

[1994], El-Sharkawy et al. [1996], Johns et al. [2000], Ayirala and Rao [2006], Johnson and Orr Jr [1996], Rao [1997], Luo and Chen [2001], and Zhang et al. [2019].



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### Chapter 2 OVERVIEW OF THE MINIMUM MISCIBILITY PRESSURE DETERMINATION METHODS

#### 2.1 Minimum Miscibility Pressure

The efficiency of oil displacement by  $CO_2$  gas strongly depends on the pressure. The lowest pressure at which the  $CO_2$ gas can develop miscibility with the reservoir crude oil at the reservoir temperature is defined as the minimum miscibility pressure [Mungan, 1981]. For the purpose of simplicity, the minimum miscibility pressure is often abbreviated as MMP throughout this book. There are five conventionally commonlyused experimental methods for the MMP determinations of various oil-gas systems, including the slim-tube test, coreflood test, rising-bubble apparatus (RBA), vanishing interfacial tension (VIT) technique, and pressure-volume-temperature (PVT) or swelling test [Zhang et al., 2019]. Slim tube displacement tests are widely used for determining the MMP for a given crude oil. There are several factors that affect the MMP including:

- reservoir temperature

- oil characteristics and properties such as the API gravity
- injected gas composition
- concentration of  $C_1$  and  $N_2$  in crude oil
- oil molecular weight
- concentration of intermediate components (C<sub>2</sub>-C<sub>5</sub>) in the oil phase.

There is a strong relationship between the reservoir temperature and the MMP. Obviously, a high reservoir temperature leads to the higher MMP. At higher temperature, the gas is getting difficult to dissolve into the crude oil. Also, the MMP increases when the molecular weight is high and the oil contains higher concentrations of  $C_1$  and  $N_2$ . Lighter gas and higher pressure is required to change from the gas state to critical state. In gas injection cases, the optimum oil recovery can be achieved if the gas state is in critical fluid and at the same time the density between gas and crude oil is close to each other. Low molecular weight gasoline range hydrocarbons are particularly effective to lead the decreases of the MMP. High oil molecular weight means more heavy component exists in the crude oil. The heaviest component tends to increase the MMP. On the other hand, the existence of more intermediate concentration in crude oil leads to the decreases of the MMP. The figures below show the effect of some parameters on the MMP. The effect of temperature is shown in Figure 2.1, effect of molecular weight is shown in Figure 2.2, and effect of injected gas composition is shown in Figure 2.3.



Figure 2.1 Effect of temperature on the MMP [Yellig and Metcalfe, 1980]



Figure 2.2 Effect of oil molecules on the MMP [Mungan, 1981]



Figure 2.3 Effect of injected gas composition on the MMP [Wilkinson et al., 2010]

#### 2.2 Previous Research

Based on previous studies, there are three different methods to predict MMP; (1) Experimental measurements, (2) Empirical correlations based on experimental results, and (3) Phase-behavior calculations based on an equation of state (EOS) and computer modeling.

#### **2.2.1 Experimental Measurements**

Numerous researchers have conducted MMP determination using experimental measurements methods including slim tube tests, coreflood tests, rising-bubble apparatus (RBA) tests, vanishing interfacial tension (VIT) tests, and pressure–volume–temperature (PVT) or swelling tests. A slim tube test has been widely used in the oil industry for determining the MMP. However, this method has still some disadvantages such as time consuming and requires a lot of samples. To obtain satisfying MMP value some investigators combined several methods and compare the results to each other. The methods that have been used for this purpose were rising bubble apparatus tests, interfacial tension tests, and swelling tests. Among the reasons why they used those methods were fewer requirements of oil samples and the ability to rapidly produce the MMP. Regardless the methods chosen by the previous researchers, the fastest ways to obtain the MMP are in fact the simulation and the correlation methods. However, the two methods require accurate oil and reservoir properties input data in order to obtain proper results.

#### 2.2.1.1 Slim Tube Test

The slim tube test is a well-known method for measuring the MMP. Despite having several disadvantages, this method is often considered as the industry standard by many investigators. They believe that there is no other effective alternative experimental method that can measure the gas-oil miscibility as correctly as the slim tube test [Ayirala and Rao, 2006; Zheng et al., 2019]. Using the slim tubes, the interaction of flow with phase behavior is accommodated. Moreover, condensing and vaporizing of mass transfer can be developed and it is called multi contact miscibility. The miscibility states are resolved indirectly from oil recovery in this method. Unfortunately, slim tubes used in the industry vary greatly in designs. The slim tube variety is in term of length, permeability, porosity, diameter, and type of packing. During the present study, more than 40 studies have been found in the literature that demonstrate the effect of different design on the MMP. Due to the different designs, some of the conclusions of the miscibility studies using slim tube have been found to be contradictory [El-Sharkawy et al., 1996]. Figure 2.4 shows the general schematic of commonly used slim tube arrangement. Table 2.1 shows a range of reported specifications of slim tube as usually used in the laboratory.



Figure 2. 4 Schematic of a slim tube apparatus [El-Sharkawy et al., 1996].

The typical experimental procedure is as follows. The slim tube apparatus is initially saturated with reservoir oil, and the gas is injected at different pressures, temperatures and injection rates to simulate the liquid–gas fluid flow in porous media. The volume of the produced fluid is collected as a function of the pressure and temperature. This enables detection of the displacement front at the exit end of the slim tube.

| Specification | Unit   | Literature        |
|---------------|--------|-------------------|
| Tube internal |        |                   |
| diameter      | Inch   | 0.12 - 0.63       |
| Tube Length   | Ft     | 5 - 120           |
| Packing       | Mesh   | Glass beads, sand |
| material      | number | 50 - 270          |
| Porosity      | %      | 32 - 45           |
| Permeability  | Darcy  | 2.5 - 250         |

Table 2.1 Range of specifications of slim tube found in the literature

The purpose of using a long slim tube is to diminish the effect of transition zone length. The small diameter tubing is justified to foil the viscous fingering. There are several opinions among the researchers about slim tube measurement. According to some of them, the packing material has no effect to the minimum miscibility. Others, however, mentioned that the oil recovery depends on dispersion level. Also, the range of porosity in the slim tube does not appear to be a critical factor. In contrary, the permeability influences the injection rate during the flooding. With high permeability, the pressure drop would be low while operating at a high frontal displacement rate [El-Sharkawy et al., 1996].

The oil recovery determined is high due to the idealized properties of slim tube such as high permeability and absence of water in the pore. Oil recovery should be measured in several times at a variety of pressure then the minimum miscibility can be determined. Figure 2.5 shows the recovery factor vs. pressure. This figure emphasize the MMP determined when the break over point occurred.



Figure 2.5 MMP determination from break over point

The slim tube experiment to measure the MMP was used in oil industry since 1950. This method represents a single chain of connected reservoir pores exhibiting realistic solvent displacement efficiency. However, this method is not the three dimensional sweep efficiencies characteristic like core flooding experiments of a real reservoir element. The displacement usually is terminated after injection achieved 1.2 pore volumes (PV) gases. The recovery at that point is referred to as the ultimate recovery. Various recovery levels, involves 80% at gas breakthrough, or 90-95% ultimate recovery has been suggested as the criteria for miscible displacement. However, the oil recovery depends on the slim tube design and operating conditions [Ahmed, 2007]. The most acceptable criteria MMP on the break over point of the ultimate oil recovery as shown in Figure 2.5.

#### 2.2.1.2 Rising Bubble Apparatus Test

Rising bubble apparatus (RBA) was first developed by Christiansen and Kim [1986] and then followed by Christiansen and Haines [1987]. In their experiments, the MMP was determined by monitoring the shape of the gas bubble as it rises through an oil column at the altered pressure level and certain temperature. The specification that apparatus involves a glass tube thick was 1 mm, width was 5 mm, and length was 28 cm. Figure 2.6 shows the schematic diagram of rising bubble apparatus (RBA) used in the laboratory.



Figure 2. 6 Schematic description of RBA [Adekunle and Hoffman, 2014].

Regarding to observation the gas bubble and its behavior, the gas bubble was captured and stored using video camera. The magnified view of the bubble is observed on the screen. The time for a bubble to travel through the column between 4 second for a spherical bubble and 10 seconds for spherical caps. The experiment should be repeated three times to record bubble images at the bottom, the middle, and the top of the column [Zhou and Orr Jr., 1998].

The MMP is indicated by the evolution of shape of the bubbles through the oil in rising bubble apparatus. In the vaporizing gas process, at immiscible condition or below the MMP, a gas bubble has a similar shape. However, at the MMP, the upper surface of bubble retains its bullet shape, moreover, the bubble which moves up in the column to the bottom of the bubble degrades and quickly disperses into the oil. At pressure above the MMP, the gas bubbles disperse immediately upon contact with the oil without any indication of interface [El-Sharkawy et al., 1996]. Figure 2.7 shows the bubble behavior in the vaporizing gas process during rising bubble apparatus.

The rising bubble apparatus also can be used for predicting the MMP in a condensing gas process. Around 5 to 10 bubbles of enriched gas are sequentially injected at each pressure. Below the MMP, the evolution of bubble shape is similar for each of sequentially injected bubbles. However, above the MMP, the evolution of bubble shape changes with each successive bubble injected into the column of oil [El-Sharkawy et al., 1996]. Figure 2.8 shows the bubble behavior for condensing gas process.



Figure 2. 7 Bubble behavior of vaporizing gas process [El-Sharkawy et al., 1996]





The rising bubble apparatus is qualitative method to predict the MMP. Visual observation is subjective method and its results somewhat arbitrary. However, rising bubble apparatus is cheaper due to its rapidity and consumes less oil compare to slim tube test. The MMP determined by using this method can be obtained in less than two hours. The disadvantages this method involves subjective interpretation, lack of quantitative evidence to satisfy the results and some arbitrariness with miscibility interpretation.

#### 2.2.2 Empirical Correlation Methods

Numerous correlation methods have been published in order to estimate the MMP since 1978. Researchers conducted experiments and it yielded correlation method such as proposed by Cronquist [1978], Yellig and Metcalfe [1980], Johnson and Pollin [1981], Glaso [1985], Alston et al. [1985], Sebastian et al. [1985], Orr and Jensen [1986], Orr and Silva [1987], Yuan et al. [2004], National Petroleum Council [1976], Shokir [2007]; Chen et al. [2013]; Zhang et al. [2015].

#### **Cronquist Correlation**

According to 58 data point from Cronquist experiments in 1978 [Cronquist, 1976]. He proposed the correlation method for estimating MMP. The MMP is affected by several parameters such as temperature, molecular weight of the oil pentanes-plus fraction, and mole percentage of impurity gas such as methane and nitrogen. The correlation has following:

 $MMP = 15.988 (T \, 460)^A \dots (1)$ 

With:

 $A = 0.744206 + 0.0011038 M_{C5+} + 0.0015279 y_{C1-N2} \dots (2)$ 

Where,

T = reservoir temperature,  $^{\circ}R$ 

 $Y_{C1-N2}$  = mole percentage of methane and nitrogen in injected gas.

#### Yellig and Metcalfe Correlation

Yellig and Metcalfe [1980] performed experiments and they proposed a correlation for predicting the MMP as a function of temperature. The correlation has the form of the following:

MMP = 1833.7217 + 2.2518055 (T - 460) +

 $0.0180067 (T - 460)^2 - \frac{103949.93}{T - 460} \dots (3)$ 

where,

T = reservoir temperature,  $^{\circ}$ R

Yellig and Metcalfe emphasized that if the bubble point pressure of the oil is greater than the MMP then the MMP is equal to the bubble point pressure.

#### Sebastian Correlation

Sebastian et al. (1985) proposed correlation method to predict the MMP. The correlation has following:

 $MMP_{imp} = [C]MMP \dots (4)$ 

Where the correction of parameter C is given by:

 $C = 1.0 - A [0.0213 - 0.000251 A - 2.35 (10^{-7}) A^{2}]....(5)$ With,

$$A = \frac{[T_{cm} - 87.89]}{1.8}$$
$$T_{cm} = \Sigma_{yi} (T_{ci} - 460)$$

Where,

MMP = The MMP of pure  $CO_2$ 

MMP  $_{imp}$  = The MMP of the contaminated CO<sub>2</sub>

 $y_i$  = mole fraction of component I in the injected gas

 $T_{ci}$  = critical temperature of component in the injected gas, °R

To give an improved match to their data, the authors adjusted  $T_c$ , of H<sub>2</sub>S between 212 °F and 125 °F.

#### Alston's Correlation

Alston, Kokolis, and James introduced correlation method for predicting the MMP since 1985 [Alston et al., 1985]. Alston et al. pointed out some of the data, such as the temperature, oil  $C_{5+}$  molecular weight, volatile oil fraction, intermediate oil fraction, and the composition of the CO<sub>2</sub> stream. The correlation has following:

$$MMP = 0.000878 (T - 460)^{1.06} (M_{C5+})^{1.78} \left[ \frac{X_{vol}}{X_{int}} \right]^{0.136} \dots (6)$$

where,

T = system temperature,  $^{\circ}R$ 

 $M_{C5+}$  = molecular weight of pentane and heavier fraction in the oil phase

 $X_{int}$  = mole fraction of intermediate oil components (C<sub>2</sub> - C<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>S)

 $X_{vol}$  = mole fraction of the volatile (C<sub>1</sub> and N<sub>2</sub>) oil components

Contamination of  $CO_2$  with volatile component such as  $C_1$ and  $N_2$  has been shown to have effect on increasing the MMP of  $CO_2$ . Vice versa, the addition of intermediate components to  $CO_2$ has shown to decrease the MMP. The authors tried to take account effect of the presence of contaminants in the injected  $CO_2$ . They pointed out of the pseudo critical temperature ( $T_{pc}$ ) of the injected gas and the pure  $CO_2$  MMP correlation as follows:

$$MMP_{imp} = MMP \left[\frac{87.8}{T_{pc}}\right]^{\frac{168.893}{T_{pc}-460}}....(7)$$

The pseudo critical temperature of the injected gas is following:  $T_{pc} = \Sigma \omega_i T_{ci} - 460$  ......(8)

where,

MMP = The MMP of pure  $CO_2$ 

MMP  $_{imp}$  = The MMP of the contaminated CO<sub>2</sub>

- $\omega_i$  = weight fraction of component I in the injected gas
- $T_{ci}$  = critical temperatures of component in the injected gas, in °R
- T = system temperature, in  $^{\circ}R$

The authors emphasized that the uniform critical temperature value of 585 °R for  $H_2S$  and  $C_2$  in the injected gas.

#### National Petroleum Council Method

The National Petroleum Council (NPC) proposed the correlation to estimate the MMP [Council NP, 1976]. The correlation uses two parameters namely the API gravity and the temperatures. The correlation is as follows:

| Oil Gravity, API | MMP, psi |
|------------------|----------|
| < 27             | 4,000    |
| 27 - 30          | 3,000    |
| >30              | 1,200    |

Table 2.2 Correlation API with MMP

| T (°F)    | Additional Pressure, psi |
|-----------|--------------------------|
| < 120     | 0                        |
| 120 - 150 | 200                      |
| 150 - 200 | 350                      |
| 200 - 250 | 500                      |
|           |                          |

Table 2.3 Reservoir temperature correction

#### Orr and Jensen

Orr and Jensen proposed the correlation method for predicting the MMP in 1986 [Orr and Jensen, 1986]. Their method emphasized for low reservoir temperature (T < 120 °F). The correlation has following:

$$EVP = 14.7 \exp\left[10.91 - \frac{2015}{255.372 + 0.5556 (T - 460)}\right] \quad \dots \dots \dots (9)$$

where,

EVP = extrapolated vapor pressure, psia

T = temperature,  $^{\circ}R$
#### Yuan's Correlation

Yuan et al. proposed the correlation for predicting the MMP in 2005 [Yuan et al., 2005]. They conducted 41 experiments through a slim tube test. Then, the conclusion from their experiment shown some of parameter affected to the MMP such as molecular weight of heptane's-plus fraction, temperature, mole percent of the intermediate components ( $C_2$ - $C_6$ ). The correlation has following:

$$MMP = a_1 + a_2 M_{C7+} + a_3 C_M + \left[a_4 + a_5 M_{C7+} \frac{a_6 C_M}{(M_{C7+})^2}\right] (T - 460) + (a_7 + a_8 M_{C7+} + a_9 (M_{C7+})^2 + a_{10} C_M (T - 460)^2 \dots (10)$$

with the coefficients as follows:

| $a_1 = -1463.4$ | $a_6 = 8166.1$               |
|-----------------|------------------------------|
| $a_2 = 6.612$   | $a_7 = -0.12258$             |
| $a_3 = -44.979$ | $a_8 = 0.0012283$            |
| $a_4 = 21.39$   | $a_9 = -4.052 (10^{-6})$     |
| $a_5 = 0.11667$ | $a_{10} = -9.2577 (10^{-4})$ |

#### 2.2.3 Simulation/EOS

Ahmed [2000] proposed a practical and simple procedure for determining the MMP. The methodology is created by applying the Peng and Robinson equation of state. However, predictions with the equation of state are compared with the measured MMP from a slim tube test. There is no guarantee to be sure either the MMP prediction using EOS properly or not [Stalkup and Yuan, 2005]. There are two methods for predicting the MMP using an EOS. First, slim tube simulations with a compositional simulator and second is analytically. The analytical way predicts a true thermodynamic MMP in the lack of dispersion of the oil and injected gas.

The following stages are used in the commercial simulator, WinProp/CMG [2014] to determine the MMP at a given temperature:

- Choose an initial pressure below the MMP;
- The solvent is formed by mixing the primary gas with a specified mole fraction of make-up gas;
- The solvent is added to oil at specified solvent in oil molar ratio increments and flash calculations are performed until two phase region is detected;
- Using the first point in the two phase region detected in step 3, the flashed liquid is mixed with the original solvent at the specified solvent to liquid ratio and the flash calculation is performed. This process simulates a condensing gas drive process;

- The procedure is repeated until the liquid composition is same as the vapor composition and the MMP is the pressure at which this occurs;
- If it is not true, then the pressure is increased to a new value and steps 3 to 5 are repeated;
- The procedure is the same for a vaporizing drive process except step 4, where the flashed vapor is mixed with the original oil in the specified gas oil mixing ratio and then flash calculation is performed.

The gas injection process usually involves a multiple contact calculation to point out the vaporization or extraction process. A pseudo ternary diagram is constructed from the calculations to assist the interpretation of the results. The multiple contact miscibility (MCM) option in WinProp can be used for predicting the MMP or first contact miscible pressure (FCM) at given temperature, pressure, oil composition, primary and make-up gas composition. The MMP can be determined for a given solvent composition by entering a range of pressure to be tested. The program reported the MMP, if found and the mechanisms by which miscibility is occurring, that is vaporizing or condensing drive mechanism.

#### 2.3. Current Research

Numerous approaches have been published for determining the MMP using slim tube and rising bubble apparatus. Those researchers involve are Holm and Josendal [1974], Christiansen and Haines [1987], Yellig and Metcalfe [1980], El-Sharkawy et al. [1996], Thomas et al. [1994]. However, other researchers have been introduced difference approaches for predicting the MMP, such as using the interfacial tension test, swelling test, and visual observation involves Rao [1997], Nobakth et al. [2008], Jessen and Orr Jr [2008], Ayirala and Rao [2006], Hawthorne et al. [2014], Tsau et al. [2010], Abdurrahman et al. [2015].

#### 2.3.1. Interfacial Tension Test

Rao [1997] proposed a new technique for estimating the MMP during the interfacial tension test. His method is namely vanishing interfacial tension (VIT). Figure 2.9 shows the experimental systems used by Rao. He pointed out that the miscibility is occurred when no interface separating the phases, or the value of interfacial tension between the two phases is zero. Figure 2.10 shows the MMP is obtained from the interfacial tension test. In recent year, some of researcher followed Rao method to predict the MMP. This method can be used to

determine the MMP properly and quickly. Numerous researchers performed VIT such as Rao [1997], Nobakth et al. [2008], Jessen and Orr Jr [2008], Ayirala and Rao [2006], and Hawthorne et al. [2014]. Figure 2.11 shows the experimental systems developed [Nobakth et al., 2008].

The interfacial tension measurements are performed with computer digitization of the image of the profiles of the sessile or pendant drops of crude oil covered in the surrounding of injection gas. By fitting these actual drop profiles with the iterative solution of the Laplace capillary equation, the value of interfacial tension is achieved at each pressure or enrichment level.



Figure 2. 9 Experimental systems [Rao, 1997].

The Laplace theory point out that an attractive force stands between all atoms and molecules carrying them as close together as the repulsion forces arising from overlapping electron shells will allow. Young and Laplace recognized that the attraction forces between molecules would build a pressure differences around a curved liquid-fluid interface. The derivation of pressure difference in terms liquid surface tension of following Eq. (11).

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right) \quad 1.....(11)$$

where,

 $\Delta P$  = the pressure difference across the interface

 $\gamma$  = interfacial tension

 $R_1$  and  $R_2$  = principal radius of curvature

The basis of balancing the pressure difference around an interface with the gravitational forces has been known, resulting in the well-known expressions of sessile (captive) and pendant (hanging) drops and bubbles. The method is known as the axisymmetric drop shape analysis (ADSA). It method depend on numerical integration of the Laplace capillary equation. The strategy employed in the ADSA method is to create an objective function which expresses the deviation of the physically monitored curve of the profile of the interface from a theoretical curve which meets the above equation. This aim function is to minimize numerically using the method of incremental loading in conjunction with the Newton-Raphson iteration technique. The input data required such as oil gravity, densities of liquid and fluid phases, and coordinate points that describe the observed profile of the interface.

The ADSA technique is different from other methods due to some reason. First, the objective function, which is the value the discrepancy between the calculated Laplacian curve and the evaluated curve, is the sum of the squares of the normal distances between the measured and the computed curve. Second, the drop shape can be measured through any appropriate reference frame. Third, no specific starting values are needed for the interfacial tension, radius of curvature at the apex, and the coordinates of the origin. Fourth, the analytically determined integrands diminish the loss of accuracy in the computation of the objective function and its first and second derivative. Fifth, the numerical process combines both the sessile and pendant drop method without the need for any table of shape factors.



Figure 2.10 Determination of MMP during interfacial tension test [Ayirala and Rao, 2007].



Figure 2.11 Experimental systems [Nobakth et al., 2008]

#### 2.3.2. Swelling Test

Hand and Pinczweski [1990] pointed out that swelling/extraction tests are simple single contact phase behavior experiments that offer a measurement of the amount of hydrocarbon that CO<sub>2</sub> can extract or vaporize from crude oil. However, Tsau et al. [2010] proposed for predicting the MMP through swelling test. This method has been proved by Abdurrahman et al. [2015]. In their experiments, the MMP through swelling test is close to the slim tube measurement. The discrepancies between both of method are in the range of 0.6% - 0.7% of Tsau et al. [2010] and 1.2% - 3.9% of Abdurrahman et al., 2015). Figure 2.12 shows the plots swelling test vs pressure to predict the MMP.



Figure 2.12 Estimation of MMP from swelling test [Tsau et al., 2010]

Tsau et al. [2010] proposed the MMP to be determined through swelling tests when the straight-line curve of the extraction-condensation stage and the extraction stage intersects each other. However, the MMP cannot be determined graphically from the plot when it lacks of the extraction stage (see Figure 2.13).



Figure 2.13 The MMP cannot be determined due to lack of extraction stage [Tsau et al., 2010]

#### 2.3.3. Visual Observation

Hagen and Kossack [1986] proposed to predict the MMP through the visual sapphire cell. The MMP is determined by observations of droplets of gas passing through the reservoir fluid. By making multiple contacts between the injected gas and reservoir fluid, the injected gas will dissolve into the reservoir fluid at the MMP. Wang [1986] proposed a method for predicting the MMP during CO<sub>2</sub> extraction process through the high pressure view cell. In his experiment, Wang [1986] divided three zones when the CO<sub>2</sub> interaction with the crude oil. First zone is namely  $CO_2$  condensation. In this condition the crude oil began to swell beyond this point signifying CO<sub>2</sub> condensation into the crude oil phase. Second zone is namely extraction-condensation zone. Abundant micro sized particles were evaporated from the oil, it was the coalesced, condensed, and fell back into the crude oil. This extraction condensation process became increasingly robust as the pressure was further increased. Meanwhile, the oil phase continued to swell and gradually altered its color from black to reddish brown. Third zone, the oil phase swelled to its highest volume. At this point, a light colored CO<sub>2</sub> rich phase emerged and grew rapidly with increased pressures. The growth of CO<sub>2</sub> rich liquid phase was accompanied by shrink of the oil rich phase and precipitations of asphalting flakes. The interface between the  $CO_2$  rich phase and CO<sub>2</sub> vapor disappeared and this pressure was defined as the MMP. Figure 2.14 shows the illustration miscibility process through visual cell.



Figure 2.14 Illustrating the miscibility process through visual observation [Wang, 1986]



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### Chapter 3 ADVANTAGES AND DISADVANTAGES OF THE MINIMUM MISCIBILITY PRESSURE DETERMINATION METHODS

# 3.1. Advantages and Disadvantages of Experimental Methods

Several experimental methods were conducted in order to estimate the MMP in this research. These methods involve slim tube test, interfacial tension test, and swelling test. Each method has several advantages and disadvantages during experiments. Advantages and disadvantages of each method will be described as below.

#### 3.1.1. Slim Tube Test

The slim tube test is regularly referred to as the industry standard for estimating the MMP. Unfortunately, this method has several weaknesses such as nonexistence of the standard design, nor standard operating procedure, nor a standard setting of criteria for determining the MMP. Slim tube length, diameter, type of packing, the permeability and porosity of the packing have varied greatly in the design used in industry. Slim tube experiments can even yield misleading results depending on the level of physical dispersion present [Johns et al., 2000]. The actual displacement of fluids in a reservoir is strongly influenced by several factors such as viscous fingering, gravity over ride, dispersion, reservoir heterogeneity and it's impossible to simulate all these mechanisms in a slim tube. Moreover, the slim tube test is consuming as much oil and gas during experiments, time consuming and hence it is expensive. For obtaining one MMP with a slim tube would probably take 6-8 weeks to complete. Among the criteria used in determining the MMP are as follows: MMP is the pressure at which the ultimate recovery approaches 100%, the break over pressure in the recovery curves is deemed as the MMP. If the break over is not sharp, MMP can be chosen when the oil recovery is 90% or 95% [El-Sharkawy et al., 1996]. Even though there are some of weakness in using this method, numerous researcher believed that until today this method is the most appropriate way to determine the MMP include Yellig and Metcalfe [1980], Holm and Josendal [1982], Wang [1986], Christiansen and Haines [1987], Rao [1997], Avirala and Rao [2006], and Abdurrahman et al. [2015]. Moreover, the slim tube test is also most widely favored by industry for miscibility evaluation. This principally appears to be due to the fact that the industry still believes there is no other

effective alternative experimental technique that can measure gas oil miscibility as accurately as slim tube.

The slim tube test has several advantages in determining the MMP. One of the main advantages of using the slim tube for miscibility determination is its ability to include the interaction of flow with phase behavior, thereby accommodating the condensing and vaporizing mode of mass transfer that enable the development of the so-called multi contact miscibility [Avirala and Rao, 2006]. Another advantages of slim tube test involving: first, using long tubing has been able to minimize the effect of transition zone length. Second, using small diameter tubing is justified to prevent viscous fingering. Third, sight cell is connected at the downstream of slim tube in which helpful for interpreting the interface between oil and CO<sub>2</sub>. The minimum miscibility occurred when no interface between both of oil and  $CO_2$ . That phenomenon can be observed during the slim tube experiment.

#### 3.1.2. Interfacial Tension Test

The MMP can also be predicted by an interfacial tension test. This test is also called the vanishing interfacial tension (VIT). The name of this method came after Rao [1997] and later Rao and Lee [2003]. This method has been demonstrated to reveal the relationship between interfacial tension and miscibility. It's also easy, cost effective and rapid (1-2 days) for determining of the MMP using less crude oil sample. Vanishing interfacial tension is the best available logical means to preclude all the incapability existing in the slim tube technique such as the inability to represent the effect of viscous fingering, heterogeneity, gravity over ride and dispersion on oil recoveries.

However, this technique has been criticized due to the perceived absence of compositional path specification, as well as for lack of the confirmation against standard gas oil systems. Another concern is that this technique may achieve as single contact technique and hereafter multi stages of contact displacement process may not cover [Ayirala and Rao, 2006].

#### 3.1.3. Swelling Test

Swelling tests are simple single contact phase behavior experiments that provide a measure of the amount of hydrocarbon that CO<sub>2</sub> can extract or vaporize from crude oil [Hand and Pinczweski, 1990]. Recently, this method has been developed for predicting the MMP. Tsau et al. [2010], Abedini et al. [2014], and Abdurrahman et al. [2015] as a few researchers introduced MMP during swelling test/extraction process. Less oil consuming and quickly are the main advantages of swelling test method. For one set experiment in order to predict the MMP only use 3-4 cc crude oil. Also, MMP data obtained from this test are quickly even after several hours.

However, limited experiments were performed using swelling test to predict the MMP. It still needs further study to get approval from the oil industry. Other disadvantages of this method is the MMP cannot be determined graphically when extract line is not happening during experiments. Tsau et al. [2010] and Abdurrahman et al. [2015] explained that condition in their experiments. Lack of secondary stage (extraction line) due to low concentration of extractable hydrocarbon is the main failure reason in estimating the MMP using this method and this is become a main weakness of this method.

#### 3.2. Advantages and Disadvantages of Simulation Method

Simulation method is quicker and less time consuming in determining the MMP. WinProp (Computer Modelling Group) is offering the simple procedure for determining the MMP. Lee and Reitzel [1982] and Firoozabadi and Khalid [1986], they compared the experimental results between slim tube test and Peng-Robinson-Equation of State (PR-EOS) calculation. They found that the EOS predictions were higher than the experimental slim tube test within 4%-8%. The weakness of EOS towards calculation of some specific properties, the reliability of data and the target of fluid properties study affect the values of different weight factors. However, if the input parameters of EOS were adjusted widely by assigning weight factors, it would lead to unrealistic results. That condition, we called over the tuning of EOS. Danesh [1998] pointed out in general, any leading EOS, which predicts the phase behavior data reasonably well without tuning. In some cases, the MMP from experiments reasonably matched the un-tuned EOS calculation [Ayirala and Rao, 2006].

### 3.3 Advantages and Disadvantages of Visual Observation Method

Visual observation is a rough method in order to predict the MMP and its requiring another method to clarify the result [Abdurrahman et al., 2015]. This method also subjective due to the method is conducted under visualization, even produced qualitative results and each person may give different interpretation. Farzad and Amani [2012] found in their experiments the MMP data from visual observation produce higher value than slim tube experiments but fall within a 200 psi difference. Absence of the porous medium, small injected gas volume relative to the oil volume and short contact time may cause the MMP results through visual observation to be higher than results from slim tube experiments. Wang [1986] purposed by visual observation to predict the MMP through view cell during the swelling test experiment. He pointed out the MMP occurred when the interface between the  $CO_2$ -rich phase and  $CO_2$  vapor disappeared. Despite roughness of this method, visual observation is worthy to clarify the miscibility occurred through the view cell. Using the view cell observe can see clearly when  $CO_2$  and crude oil become one phase. Therefore, this method is proper to support another method in determining the MMP.



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