Experimental Determination of Minimum Miscibility Pressure Between CO_2-CH_4 Mixtures and Crude Oil

by

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ABSTRACT

Impure gas flooding can be used as an effective method for enhancing oil recovery. The minimum miscibility pressure (MMP) is a key parameter in the design of impure gas injection. It is thus of great importance to accurately determine the MMP for the impure gas injection process. This study experimentally determines the MMP between CO_2-CH_4 mixtures and a crude oil; slim-tube experiments have been conducted to measure the MMPs between this light oil sample and CO_2-CH_4 mixtures with different CH_4 contents. At CH_4's molar fractions of 0 mol%, 5 mol%, 10 mol%, 20 mol% and 100 mol%, the corresponding MMPs are measured to be 17.74 MPa, 19.84 MPa, 22.79 MPa, 27.05 MPa and 58.64 MPa, respectively. The experimental results show that increasing the amount of CH_4 present in the mixture can increase the MMP between injection gas and crude oil. When CH_4's molar fractions are 5 mol%, 10 mol% and 20 mol%, Dong (1999) correlation yields absolute relative deviations (ARD%) of 0.00% and 2.98%, and 0.70%, respectively, for the MMP predictions; these errors are lower than those yielded by the other correlations (Kovarik, 1985; Sebastian *et al*., 1985; Alston *et al*., 1985; Emera and Sarma, 2006; Shokir, 2007). For the crude oil examined in this study, Dong (1999) correlation provides the most accurate prediction of CO_2-CH_4 (with CH_4 content up to 20 mol%) MMP among all the impure-CO_2 MMP correlations examined.

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CHAPTER 1 INTRODUCTION

1.1. Research Background

It is hard to maintain or improve oil production in mature oil fields. Thus, some techniques for enhancing oil recovery factor are needed. Thermal, chemical, and gas flooding methods are the three widely used methods for enhancing oil recovery (EOR) (Lake, 1989). Thermal methods include steam flooding, cyclic steam stimulation, steam-assisted gravity drainage, and in-situ combustion method. These methods can reduce oil viscosity and improve oil mobility by increasing reservoir temperature, leading to a higher oil recovery factor for heavy oil. Chemical methods include polymer flooding, surfactant flooding, alkaline flooding, and hybrids of these three chemical methods. Chemical EOR methods are generally expensive (Bahadori, 2018). Gas flooding is a widely used EOR method for light oil reservoirs. This research mainly focuses on miscible gas injection since it is regarded as one of the most efficient methods in increasing oil recovery (Firoozabadi and Aziz, 1986).

Miscible flooding can help decrease oil viscosity and interfacial tension between crude oil and injection gas, resulting in a higher sweep efficiency. Sometimes, CO_2 will be injected together with produced gas (mainly comprised of CH_4) into the reservoir to realize the miscibility, which in this case corresponds to the technique of impure CO_2 flooding. One key parameter in the gas injection design is the minimum miscibility pressure (MMP) (Stalkup, 1983). MMP refers to the pressure at which the injected gas will reach complete miscibility with reservoir oil, enabling a theoretical 100% oil recovery efficiency (Wang and Orr, 1997). When the gas injection pressure is lower than

the MMP, the gas injection becomes inefficient in enhancing oil recovery. Thus, accurate determination of MMP is of great significance for a gas injection project.

In order to reach miscibility with crude oil, the mixture of hydrocarbon (e.g., CH_4, C_2H_6, and C_3H_8) or nonhydrocarbon gas (e.g., CO_2, N_2, and H_2S) can be adopted as injection gas (Bahadori, 2018). Lean gas that is rich in CH_4 or N_2 generally requires a relatively high pressure to become miscible with crude oil (Firoozabadi and Aziz, 1986). CO_2 can be miscible with crude oil at a relatively lower pressure compared with other injection gases (such as N_2 or CH_4). Injection of CO_2 gas is being considered as a very promising EOR technique. Besides, the storage of injected CO_2 can mitigate global warming issue (Izgec *et al*., 2005; Denney, 2010). CO_2 injection has been successfully applied in a number of oil fields over the world.

1.2. Experimental, Theoretical, and Empirical Methods for Determining MMP

This subsection provides a general overview of the experimental, theoretical, and empirical methods for MMP determination.

1.2.1. Experimental Methods

Experimental methods include the slim-tube test method, rising bubble method, and vanishing interfacial tension (VIT) method.

Slim-tube Test Method. Slim-tube test is an industrially accepted method for MMP determination. The length of the slim-tube apparatus usually varies from 5 to 120 ft (Yellig and Metcalfe, 1980). The packing material for the slim-tube is 50-270 mesh glass bead or sand, which can simulate the porous media (Mihcakan, 1994). The outer diameter

of slim-tube ranges from 0.12 to 0.63 in (Izgec *et al*., 2005; Denney, 2010). In slim-tube experiments, oil is injected to the slim-tube at a constant temperature. After the slim-tube is saturated by oil, the gas is injected into the slim-tube at constant temperature and pressure. The final oil recovery corresponding to 1.2 pore-volume (PV) gas injection is recorded. The slim-tube experiment is repeated at several different pressures. Based on the measured data, a plot showing the final oil recovery factor at 1.2 PV gas injection versus pressure can be drawn. Normally two trend lines can be identified from the plot. MMP is determined at the intersection point of these two trend lines (Hudgins *et al*., 1990; Glaso, 1990; Danesh, 1998).

Slim-tube test is relatively time-consuming and expensive. In addition, the uncertainty in measuring MMP is relatively high due to the limited number of data points and the dispersion phenomenon involved in the porous-media flow (Orr *et al*., 1982; Walsh and Orr, 1990). But slim-tube test is still considered as the most reliable experimental method for estimating MMP in the oil industry because it can relatively well reproduce the dynamic interaction between oil and injection gas during the displacement process (Elsharkawy *et al*., 1996).

Rising Bubble Method. Christiansen and Haines (1987) first introduced the rising bubble test as a faster alternative for the slim-tube test. The rising bubble apparatus consists of eight-inch-long transparent glass column which is filled with oil. At given pressure and temperature, gas is injected to the bottom of the apparatus via a needle. The shape of the gas bubble rising in the oil column is then used to judge when miscibility develops between injection gas and crude oil. Compared with the slim-tube test, the rising bubble experiment is rapid and cheap. However, this method suffers from the drawbacks that: 1)

it does not well honor the actual displacement process during gas injection; 2) it cannot well predict the MMP whenever a condensing drive mechanism is involved in the displacement process (Zhou and Orr, 1998).

Vanishing Interfacial Tension Method. Rao (1997) first proposed the VIT experiment to determine MMP. In the VIT experiment, a crude oil drop is injected through a capillary tube into the cell filled with injection gas under a given temperature and pressure (Rao and Lee, 2002). One can obtain the interfacial tension (IFT) by analyzing the shape of the hanging oil drop in injection gas. The IFT measurement is repeated at different operating pressures; then MMP can be determined by extrapolating the plot of IFT versus pressure to zero (Rao and Lee, 2002).

Studies (Orr and Jessen, 2007; Saoyleh, 2016) have argued that VIT experiments cannot provide reliable MMP measurements for multi-component mixtures. Moreover, the MMPs estimated by VIT method could be inconsistent with those calculated by analytical methods for condensing/vaporizing floods. VIT method is thereby a less preferred method for MMP determination.

1.2.2. Theoretical Methods

In addition to the various experimental methods for MMP determination, theoretical methods relying on cubic equation of state (CEOS) computations have been also developed to predict MMP. There are two major theoretical methods that are widely applied in the industry: slim-tube compositional simulation method and multiple mixing cell (MMC) method.

Slim-tube Compositional Simulation Method. Slim-tube compositional simulation method is a numerical method to reproduce the slim-tube experiments by mimicking the porous-media flow that takes place in slim-tube experiments (Yelling and Metcalfe, 1980; Ahmadi and Johns, 2011). Similar to the slim-tube test method, MMP is determined as the intersection point of the two trend lines that are identified from the recovery-factor/pressure plot. A reliable estimation of MMP by this method requires an accurate characterization of the phase behavior of the crude oil and injection gas with CEOS, which can be a challenging task. In addition, slim-tube compositional simulation method is rather time-consuming (Johns *et al*., 1993).

Multiple Mixing Cell Methods. Mixing cell methods can predict the MMP based on the flash calculations for gas and oil equilibria. Many published MMC methods have been introduced in the literature (Hutchinson and Braun, 1961; Metcalfe *et al*., 1973; Jaubert *et al*., 1998; Zhao *et al*., 2006). The mixing of gas and oil in the MMC method is usually conducted in a series of imaginary PVT cells. A suite of flash computations at a given pressure is carried out in an attempt to cover all the possible mixing scenarios between gas and oil; such computations are repeated at different pressures in order to determine the pressure at which the miscibility can be achieved. In 2011, Ahmadi and Johns (2011) developed a robust and efficient version of the MMC algorithm to estimate MMP for multicomponent systems. Comparison between the calculated MMPs and measured ones proves that the MMC method developed by Ahmadi and Johns (2011) can well reproduce the gas-oil MMPs as long as the phase behavior of the gas/oil mixtures is properly characterized with CEOS models.

1.2.3. Empirical Correlations

Besides the experimental and theoretical methods, many empirical correlations for MMP determination have been developed based on the regression of experimental data. MMP correlations can be easily applied to estimate MMP values. In general, empirical MMP correlations consider the following variables: composition of the gas mixture, mole fractions of intermediate and volatile components in crude oil, the molecular weight of C_{7+} fraction in the oil sample, and reservoir temperature.

Several empirical correlations (Alston *et al*., 1985; Glaso, 1990; Kovarik, 1985; Dong, 1999; Yuan *et al*., 2005; Emera and Sarma, 2006; Shokir, 2007; Li *et al*., 2012) have been developed to predict the MMP between pure CO_2 and oil. In addition, some impure CO_2-oil correlations have been proposed by Alston *et al.* (1985), Sebastian *et al*. (1985), Kovarik (1985), Dong (1999), Yuan *et al*. (2005), and Shokir (2007). Note that although empirical correlations can only provide a rough estimation of gas-oil MMP, they are still quite useful for guiding slim-tube experiments and pre-screening reservoirs for gas injection treatments.

1.3. Problem Statement and Research Objectives

Impure CO_2-oil MMP correlations in the literature are not accurate enough. Thus, it is still challenging to obtain a reliable estimation of MMP for the impure CO_2 flooding based on the available impure-CO_2 MMP correlations, especially for injection gases containing a significant amount of CH_4. There are two major objectives to be achieved in this thesis research:

- To conduct slim-tube tests to measure MMP between CO_2-CH_4 mixtures with crude oil; and
- To compare the accuracy of the existing correlations in reproducing the measured MMP data.

1.4. Thesis Structure

This thesis contains four chapters:

- **Chapter 1** introduces research background, literature review, problem statement, research objectives, and thesis structure.
- **Chapter 2** presents the slim-tube tests conducted to measure the MMP between CO_2-CH_4 mixtures and a crude-oil sample.
- **Chapter 3** compares various empirical correlations for determining the MMP of CO_2-CH_4 mixtures with crude oil.
- **Chapter 4** summarizes the conclusions drawn from this study and the recommendations for future work.

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CHAPTER 2 SLIM-TUBE TESTS FOR DETERMINING MMP BETWEEN CO_2-CH_4 MIXTURES AND CRUDE OIL

2.1. Materials

In this study, slim-tube tests are conducted to measure the MMP between CO_2-CH_4 mixtures and a crude-oil sample. The compositions of the gas mixtures can be found in Table 2.1. Table 2.2 shows the composition of the crude oil sample used in the slim-tube tests; the composition of the oil sample is characterized by gas chromatography method. As seen from Table 2.2, the molecular weight of the C_{7+} fraction of this oil sample is measured to be 440.63 g/mol.

2.2. Equipment and Procedure

The schematic diagram of the slim-tube apparatus used in the experiments is shown in Figure 2.1. The key component in the slim-tube test apparatus is a stainless steel tube with an outer diameter of 6 mm and a length of 18 m. Quartz sands with a size of 160-200 mesh are packed in the slim-tube test to simulate the porous media where the multiple contacts take place between injected gas and reservoir oil. The total pore volume of the sand-packed tube is about 93.9 cm^3. For each displacement test, the sand-packed oil tube is first saturated with crude oil at given reservoir temperature (67˚C). At a given pressure, the gas is then injected into the oil-saturated tube at an injection rate of 9 cm^3/hr. The oil recovery factor is recorded during the displacement process. The test is terminated when 1.2 PV of gas has been injected. The displacement test is then repeated at a different pressure level. Note that it takes several months to finish all the slim-tube tests. At the end of slim-tube tests, we can then obtain a chart of oil recovery factor

measured at 1.20 PV gas injection versus pressure. Subsequently, the MMP can be determined by locating the inflection point at which the oil recovery factor exceeds 90%.

Table 2.1 Composition of the gas mixtures used in the slim-tube tests.

Gas mixtures	A	B	C	D	E
Mole fraction of CO_2, mol%	100.00	95.0	90.00	80.00	0.00
Mole fraction of CH_4, mol%	0.00	5.00	10.00	20.00	100.00
Total	100.00	100.00	100.00	100.00	100.00

Table 2.2 Composition of the crude oil sample used in the slim-tube tests.

Component	Mole fraction, mol%
N_2	0.16
CO_2	1.64
C_1	20.51
C_2	1.93
C_3	3.09
iC_4	1.95
nC_4	1.02
iC_5	2.07
nC_5	6.19
C_6	6.19
C_{7+}	55.25
Total	100.00
MW_{C5+}	404.69
MW_{C7+}	440.63

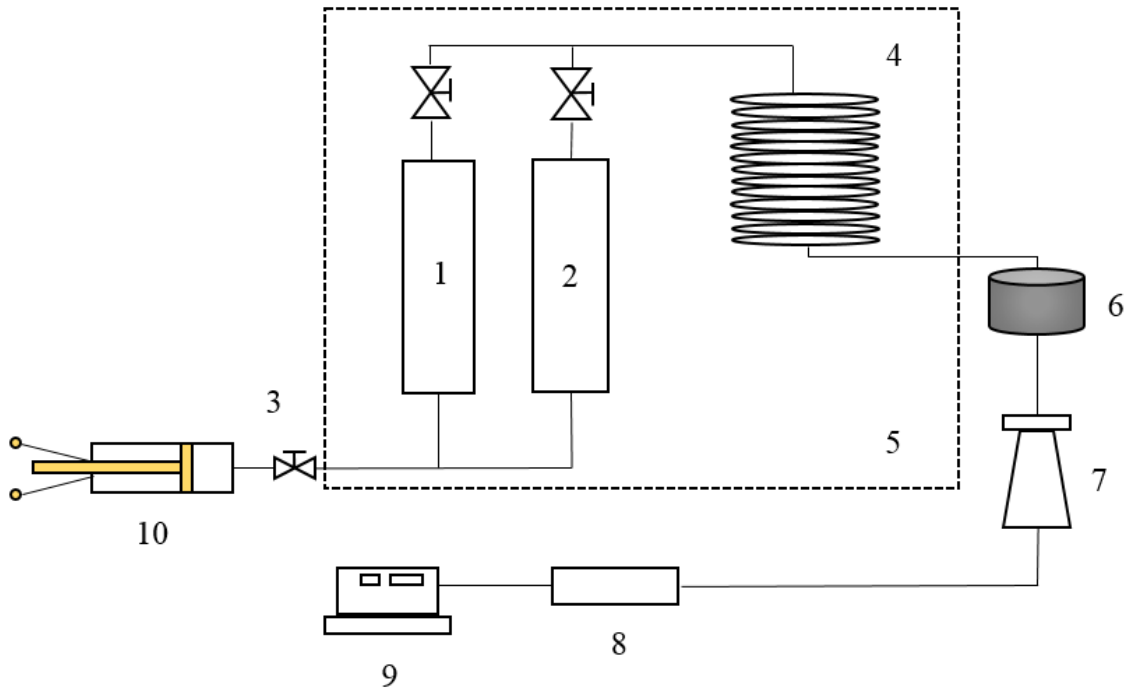


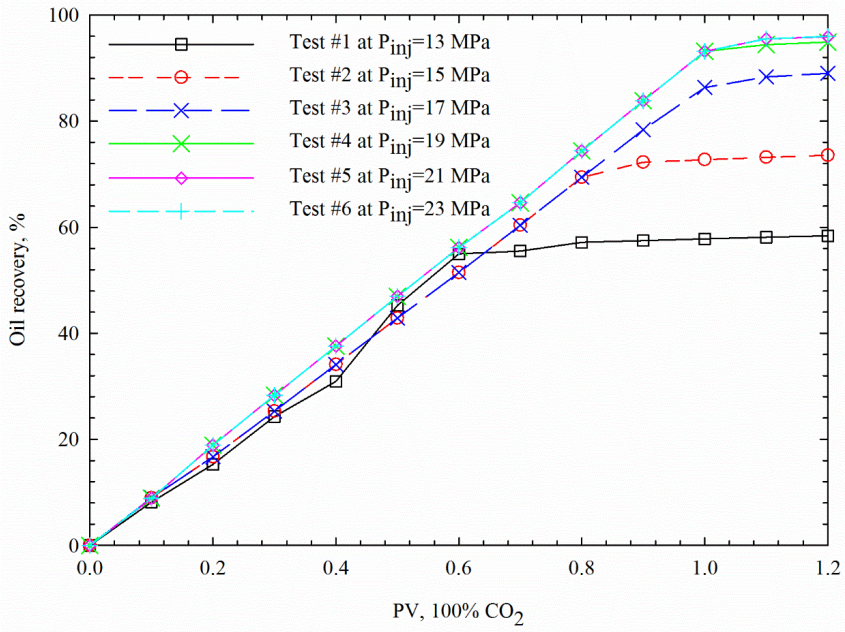
Figure 2.1 Schematic diagram of the slim-tube apparatus. (1. Injection gas. 2. Reservoir oil. 3. Valve 4. Slim-tube. 5. Constant temperature air bath. 6. Back-pressure regulator. 7. Separator. 8. Gas meter. 9. Gas chromatograph. 10. Injection pump.)

2.3. Measurement Results

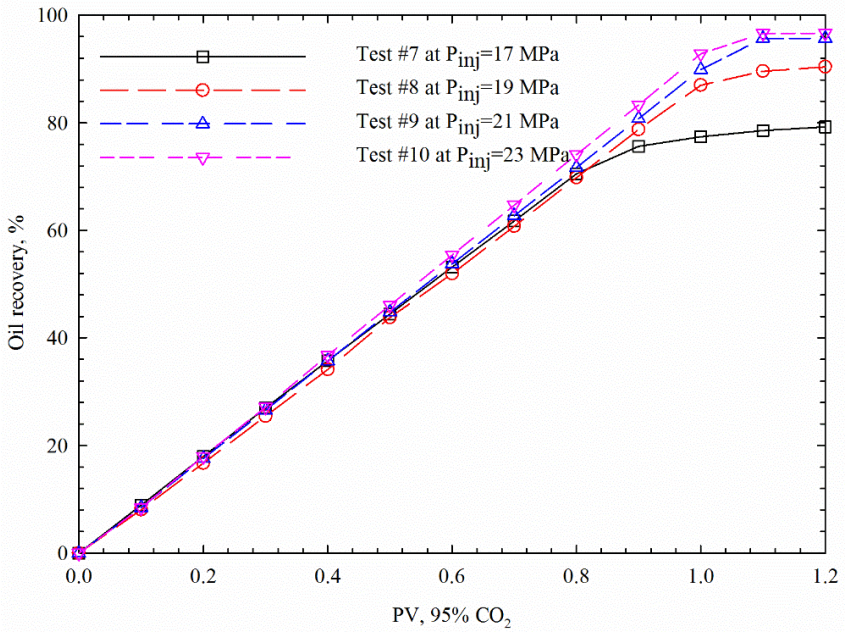
The slim-tube test results are presented in Figures 2.2 and 2.3. Figure 2.2 shows the detailed oil recovery curves plotted as a function of PV of gas mixture injected at different pressures and different levels of CO_2 enrichment. As for each test, the oil recovery at 1.2 PV injection is recorded as the final oil recovery factor. When the injection pressure is 13 MPa (as shown in Figure 2.2 (a)), the oil recovery first increases significantly with an increase in PV, and then shows a flattening trend as PV further increases. Based on the measured final oil recovery factor, we can plot a chart showing final oil recovery factor versus pressure. The MMP is determined at the intersection point

of two trending lines that can be identified from the plot. Figures 2.2b-e show the measurement results for the other four gas mixtures with different CH_4 fractions.

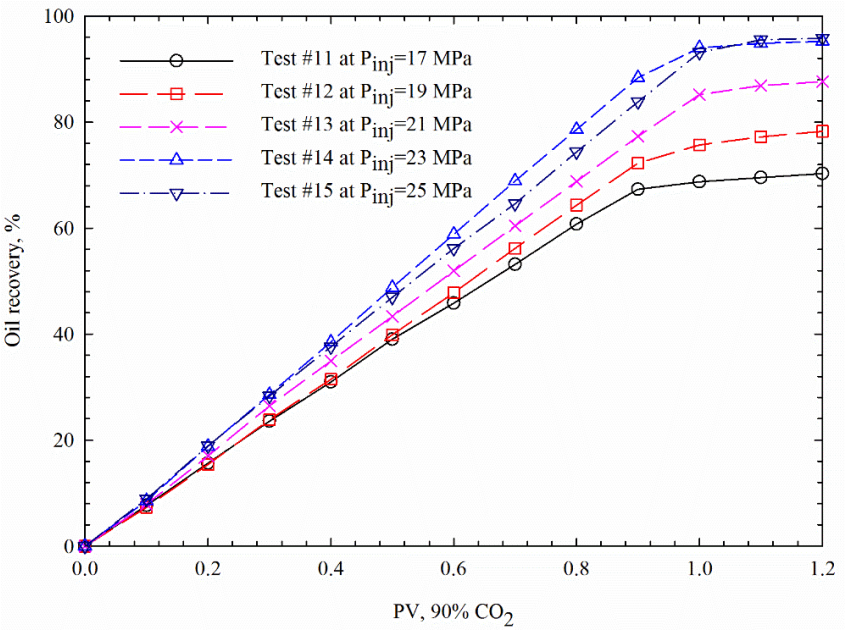
Figure 2.3 shows the oil recovery factors measured for CH_4-CO_2/oil mixtures at 1.2 PV of gas injected at various pressures. As illustrated in the subplots included in Figure 2.3, the MMP value is determined as the intersection point of two trending lines. By using such a method, the MMPs between the five gas mixtures (i.e., gas mixtures A-E) and crude oil are determined to be 17.74 MPa, 19.84 MPa, 22.79 MPa, 27.05 MPa and 58.64 MPa, respectively. An experimental error of around 5.0% accompanies these measured MMPs.



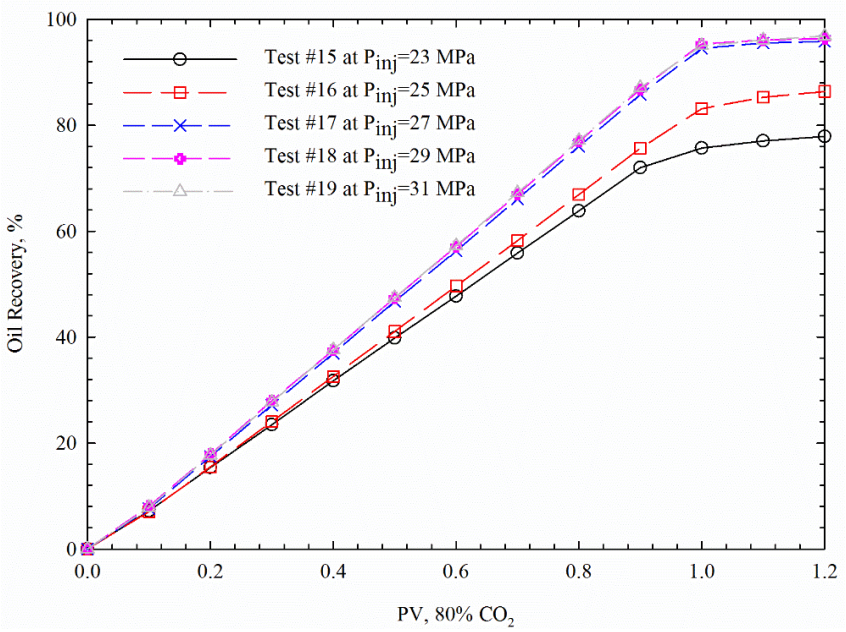
(a)


Test #7 at P_{inj}=17 MPa
Test #8 at P_{inj}=19 MPa
Test #9 at P_{inj}=21 MPa
Test #10 at P_{inj}=23 MPa
Oil recovery, %
PV, 95% CO_2

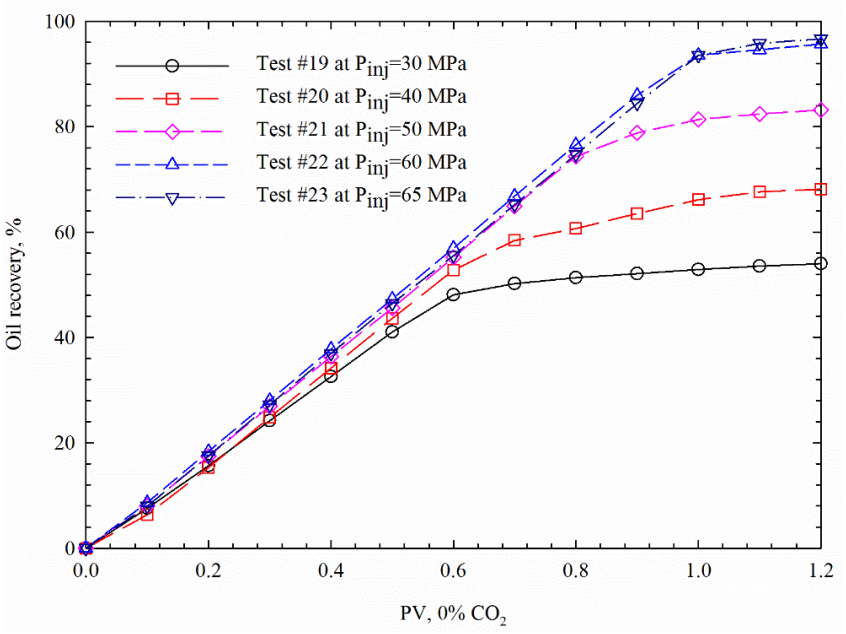
(b)


Test #11 at P_{inj}=17 MPa
Test #12 at P_{inj}=19 MPa
Test #13 at P_{inj}=21 MPa
Test #14 at P_{inj}=23 MPa
Test #15 at P_{inj}=25 MPa
Oil recovery, %
PV, 90% CO_2

(c)

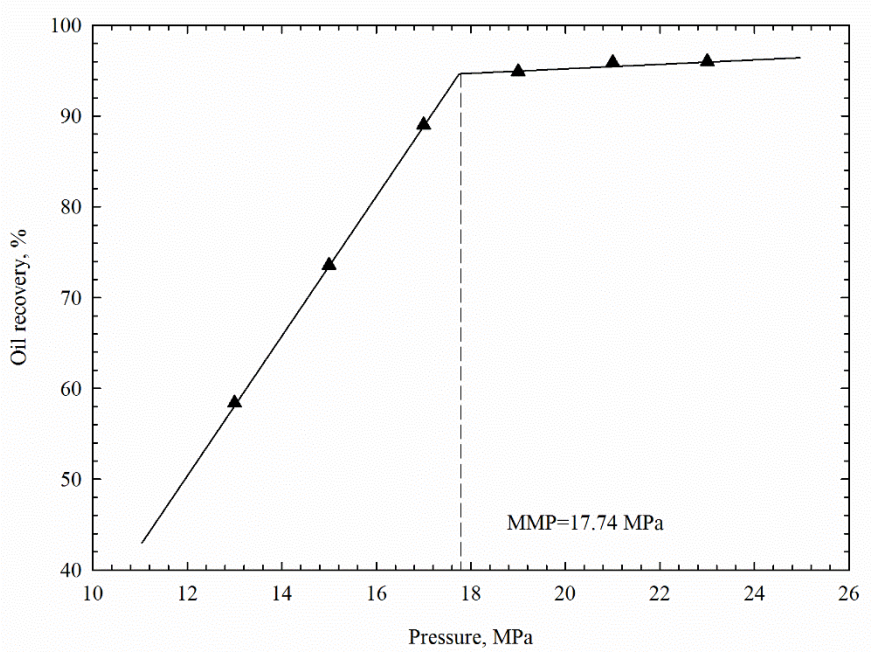


(d)

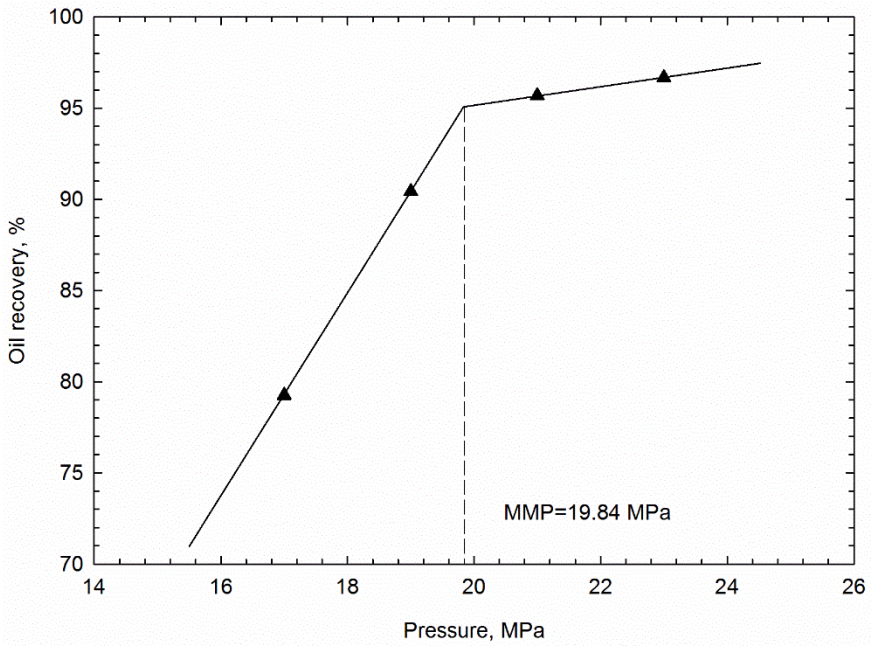


(e)

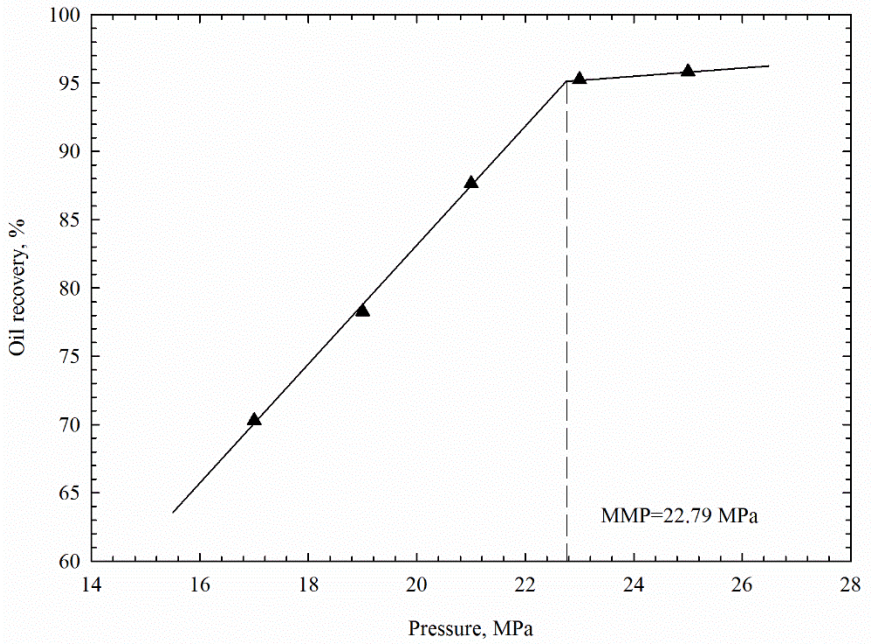
Figure 2.2 Oil recovery curves plotted as a function of PV of gas mixture injected at different pressures and different levels of CO_2 enrichment: (a) gas sample A (100 mol% CO_2+0 mol% CH_4); (b) gas sample B (95 mol% CO_2+5 mol% CH_4); (c) gas sample C (90 mol% CO_2+10 mol% CH_4); (d) gas sample D (80 mol% CO_2+20 mol% CH_4); (e) gas sample E (0 mol% CO_2+100 mol% CH_4).


Oil recovery, %
Pressure, MPa
MMP=17.74 MPa
100
90
80
70
60
50
40
10
12
14
16
18
20
22
24
26

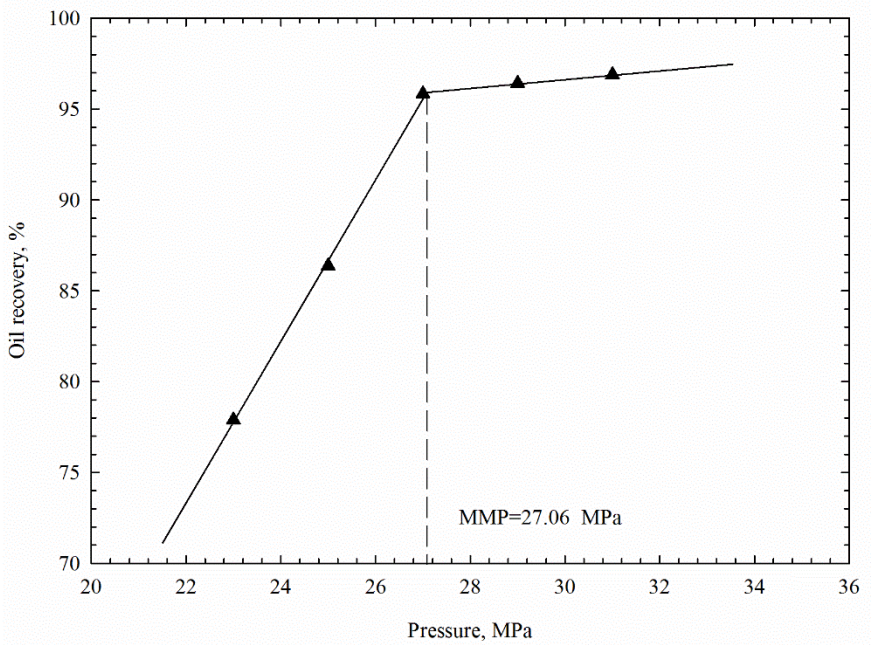
(a)


Oil recovery, %
Pressure, MPa
MMP=19.84 MPa
100
95
90
85
80
75
70
14
16
18
20
22
24
26

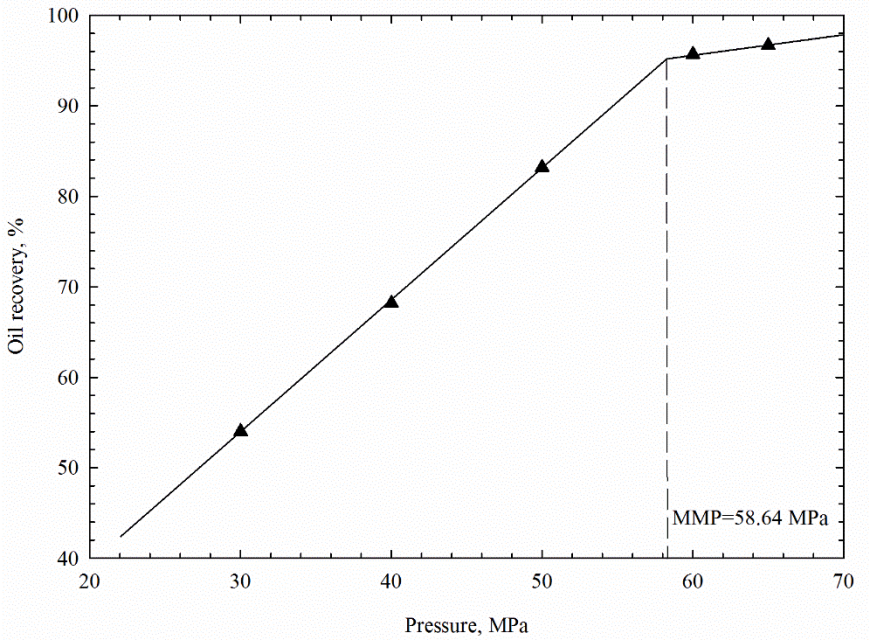
(b)


Oil recovery, %
Pressure, MPa
MMP=22.79 MPa
100
95
90
85
80
75
70
65
60
14
16
18
20
22
24
26
28

(c)


Oil recovery, %
Pressure, MPa
MMP=27.06 MPa
100
95
90
85
80
75
70
20
22
24
26
28
30
32
34
36

(d)



(e)

Figure 2.3 Oil recovery factors measured for CH_4/CO_2/oil mixtures at 1.2 PV of gas injected at various operating pressures: (a) gas sample A (100 mol% CO_2+0 mol% CH_4); (b) gas sample B (95 mol% CO_2+5 mol% CH_4); (c) gas sample C (90 mol% CO_2+10 mol% CH_4); (d) gas sample D (80 mol% CO_2+20 mol% CH_4); (e) gas sample E (0 mol% CO_2+100 mol% CH_4).

CHAPTER 3 PERFORMANCE COMPARISON OF EXISTING CORRELATIONS IN PREDICTING MMPS BETWEEN CO_2-CH_4 MIXTURES AND CRUDE OIL

3.1. Overview of Previously Developed MMP Correlations

CO_2 flooding is recognized as an effective and efficient method for enhancing oil recovery, especially for medium and light oil reservoirs (Teklu *et al*., 2012). From these reservoirs, a large amount of produced gas, which is mainly comprised of CH_4, can be produced together with oil production. Reinjection of the produced gas together with CO_2 can be possibly applied in oilfields for the purpose of enhancing oil recovery. A key design parameter in such gas injection process is minimum miscibility pressure (MMP) between the CO_2-CH_4 mixture and the *in-situ* oil. MMP refers to the pressure at which the injected gas will reach complete miscibility with reservoir oil (Jessen *et al*., 1998). MMP between the injection gas mixture and crude oil strongly depends on the composition of the injected gas mixture (Rutherford, 1962; Enick *et al*., 1998). Accurate determination of the MMP between crude oil and the injected CO_2-CH_4 mixture is thereby essential for providing a basic guideline for the design of impure CO_2 flooding in the oilfield applications.

Several experimental methods are widely used to determine the MMP of CO_2/oil mixtures. Two most commonly used methods are slim-tube test method (Elsharkawy *et al*., 1996) and rising bubble method (Christiansen and Haines, 1987; Jarrell *et al*., 2002). In the rising bubble test, a flat glass tube stands vertically in a visible high-pressure cell placed in a temperature-controlled bath. MMP is then measured by visually observing the change in the shape of gas bubbles rising in the glass tube at different pressures

(Christiansen and Haines, 1997; Jarrell *et al*., 2002); visual observations in the rising bubble test may be subject to subjective errors. The slim-tube test provides a more reliable means to determine the MMP of CO_2/oil mixtures (Elsharkawy *et al*., 1996). The test adopts a long slim-tube packed by sand beads to simulate the porous media. Before the test, the long slim-tube is first saturated with crude oil samples. Gas mixtures are then injected into the slim-tube to displace the oil at given temperature and pressure. A chart of oil recovery factor measured at 1.2 PV of gas injection versus pressure can be then obtained after the slim-tube test. The MMP is found by locating the inflection point of the two trend lines that can be identified from the oil recovery curves.

In addition to the experimental methods, several theoretical approaches were developed to predict the MMP of CO_2/oil mixtures. These theoretical approaches include the method of characteristics (MOC), slim-tube compositional simulation, and multiple mixing cell (MMC) methods (Wang and Orr, 1997; Jaubert *et al*., 1998; Ahmadi and Johns, 2011; Teklu *et al*., 2012). By examining the displacement path for the quaternary CO_2/methane/butane/decane mixtures, Monroe *et al*. (1990) firstly suggested the existence of a crossover tie line that corresponds to a third key tie line in the displacement path. Orr *et al.* (1993) and Johns *et al.* (1993) confirmed the existence of a crossover tie line; they also demonstrated that MMP can be determined as the pressure at which the length of crossover tie line becomes zero. Johns and Orr (1996) developed an improved MOC algorithm to calculate MMP for more complex mixtures. As stated by Yuan and Johns (2005), however, the possible convergence to the wrong set of key tie lines can be a potential drawback of the MOC method. The one-dimensional simulation of slim-tube displacement simulates the gas injection process in a slim-tube context. The experimental

data can be reliably matched by slim-tube simulation (Wang and Peck, 2000). However, these slim-tube simulations must be conducted with refined grids and repetitively conducted at different pressures, making this method more time-consuming compared with other theoretical approaches. Ahmadi and Johns (2011) developed a robust version of the MMC which is simple to use and has a good reliability in reproducing the measured MMP data.

Several empirical correlations were also developed to correlate the MMP with fluid properties at specific reservoir conditions (Alston *et al*., 1985; Kovarik, 1985; Sebastian *et al*., 1985; Eakin and Mitch, 1988; Dong, 1999; Yuan *et al*., 2005; Shokir, 2007; Emera and Sarma, 2006; Li *et al*., 2012). CO_2/oil MMP is generally considered to be a function of reservoir temperature, and the properties of injected gas and *in-situ* oil; experimental results show that the gas/oil MMP is highly related to the molecular weight of C_{5+} in oil (Rathmell *et al*., 1971; Holm and Josendal; 1974). Rathmell *et al*. (1971) suggested that a higher molar volume of volatile components in crude oil leads to an increased MMP, whereas a higher molar volume of intermediate components in crude oil leads to a decreased MMP. Metcalfe and Yarborough (1974) recommended that predicting the MMP of CO_2/oil mixtures should consider the presence of light and intermediate components in crude oil. By conducting slim-tube tests, Alston *et al*. (1985) reported that the oil recovery factor at gas breakthrough reduces by increasing the ratio of the volatile fractions to intermediate fractions in crude oil. They also suggested that the molecular weight of C_{5+} plays a more important role than oil gravity in predicting MMPs. Besides, the MMP between a gas mixture (such as impure CO_2) and oil can be affected by the existence of gases such as H_2S, N_2, CH_4, and C_2-C_4 in the injection gas. A previous study

indicated that the presence of C_1 and N_2 increases the impure CO_2 MMP, while the presence of H_2S decreases the impure CO_2 MMP (Lake, 1989). Most of these empirical correlations are generally obtained by the regression made on the slim-tube test data. These correlations are quick and easy to apply since they mainly require the inputs of the properties of the gas mixture, *in-situ* oil, and reservoir conditions. However, the application of these correlations is limited to specific fluids under specific reservoir conditions.

In this study, slim-tube tests are conducted to determine the MMP between oil samples and CO_2-CH_4 mixtures. We then conduct a comparative investigation of various empirical correlations in terms of their accuracy in predicting the MMP of CO_2-CH_4 mixtures with crude oil.

3.2. Empirical Correlations for Determining MMP

In the past decades, many empirical correlations have been developed for predicting pure-CO_2 or impure-CO_2 MMP. The pure CO_2-oil MMP correlation developed by Li *et al.* (2012) correlates MMP (in MPa) as a function of reservoir temperature, the molecular weight of C_{7+}, and mole fraction ratio of the volatile components to the intermediate components,

$$MMP_{pure} = 7.30991 \times 10^{-5}[Ln(1.8T_R + 32)]^{5.33647}\left[Ln\left(MW_{C_{7+}}\right)\right]^{2.08836}\left(1 + \frac{X_{vol}}{X_{int}}\right)^{0.201658} \quad (1)$$

where T_R represents the reservoir temperature in ˚C, MW_{C7+} is the molecular weight of C_{7+} fraction, X_{vol} is the mole fraction of volatile components including N_2 and CH_4, and X_{int} is the mole fraction of intermediate components including CO_2, H_2S, and C_2-C_6.

Below we summarize the representative ones that are frequently used by practicing engineers to predict impure CO_2 MMP (Sebastian *et al.*, 1985; Kovarik, 1985; Alston *et al.*, 1985; Dong, 1999; Emera and Sarma, 2006; Shokir, 2007). Kovarik (1985) developed the following impure-CO_2 MMP correlation which is a function of pure CO_2 MMP (MMP_{pure} in MPa) and the pseudocritical temperature of the gas mixture (T_C in ºC):

$$MMP_{impure} = MMP_{pure} + 0.2814[548 - (1.8T_C + 492)] \quad (2)$$

$$T_c = \sum_{i=1}^{n} x_i \times T_{Ci} \quad \text{or} \quad T_c = \sum_{i=1}^{n} w_i \times T_{Ci} \quad (3)$$

where x_i represents the mole fraction of the ith component in the gas mixture, w_i represents the weight fraction of the ith component in the gas mixture, and T_{ci} represents the critical temperature of the ith component in the gas mixture in ºC. Kovarik (1985) found that the mole-fraction-averaged pseudocritical temperature gives better MMP prediction than the weight-fraction-averaged pseudocritical temperature. It is noted that the pure-CO_2 MMP MMP_{pure} is measured by slim-tube tests or can be otherwise calculated with Li *et al.* (2012) correlation if the experimental pure-CO_2 MMP is not available.

Sebastian *et al.* (1985) used the mole-fraction-based mixing rule to determine the injected-gas pseudocritical temperature in developing impure CO_2-oil MMP correlation. The Sebastian *et al.* (1985) correlation is given below,

$$MMP_{impure} = MMP_{pure} \times [1.0 - 2.13 \times 10^{-2}(T_c - 304.2) + 2.51 \times 10^{-4}(T_c - 304.2)^2 - 2.35 \times 10^{-7}(T_c - 304.2)^3] \quad (4)$$

$$T_c = \sum_{i=1}^{n} x_i \times T_{Ci} \quad (5)$$

where T_C represents the mole-fraction-average pseudocritical temperature in K, and T_{Ci} is the critical temperature of the gas component i in K. The apparent critical temperature for H_2S they used is 325 K.

Alston *et al.* (1985) presented an impure CO_2-oil correlation that is also dependent on the pseudocritical temperature (in ^oC),

$$MMP_{impure} = MMP_{pure} \times \left(\frac{87.8}{1.8 \times T_C + 32}\right)^{\left(\frac{1.935 \times 87.8}{1.8 \times T_C}\right)} \quad (6)$$

$$T_c = \sum_{i=1}^{n} x_i \times T_{Ci} \quad (7)$$

Dong (1999) presented a correlation similar to that of Sebastian *et al.* (1985). Instead of using apparent critical temperature, he proposed a weighting factor for non-CO_2 components (H_2S, SO_2, O_2, N_2, and C_1) to capture the strength of these components in changing the apparent critical temperature of the injected impure CO_2 relative to pure CO_2 (Dong, 1999). The Dong (1999) correlation is given as,

$$MMP_{impure CO_2} = MMP_{pure CO_2} \times \left(\frac{T_c}{304.2}\right)^4 \quad (8)$$

$$T_c = \sum_{i=1}^{n} SF_i x_i T_{Ci} \quad (9)$$

where SF_i represents the strength of species i in changing the apparent critical temperature (in K) of the mixture relative to the critical temperature of pure CO_2. Values

of the empirical coefficients (SF_i) for H_2S is 0.7; for C_1, it is 2.5; for O_2, it is 5.0; for N_2, it is 7.5; for CO_2, it is 1.0; and for other non-CO_2 components, it is 1.0 (Dong, 1999).

Emera and Sarma (2006) proposed a genetic-algorithm-based correlation to predict the gas-oil MMP based on pseudocritical properties, including pseudocritical temperature (in ^oC) and pressure. The correlation is given as,

$$\frac{p_{r,impureCO_2}}{p_{r,pureCO_2}} = 3.046 + 5.786 \times \left(\frac{1.8T_C+32}{1.8T_{C,CO_2}+32}\right) - 23.0 \times \left(\frac{1.8T_C+32}{1.8T_{C,CO_2+32}}\right)^2 + 23.0 \times \left(\frac{1.8T_C+32}{1.8T_{C,CO_2+32}}\right)^3 - 5.7 \times \left(\frac{1.8T_C+32}{1.8T_{C,CO_2}+32}\right)^4 \quad (10)$$

where

$$p_{r,impure} = \frac{MMP_{impure}}{p_C} \quad (11)$$

$$p_{r,pure} = \frac{MMP_{pure}}{p_{C,CO_2}} \quad (12)$$

$$p_C = \sum_{i=1}^{n} w_i \, p_{Ci} \quad (13)$$

$$T_C = \sum_{i=1}^{n} MF_i w_i T_{ci} \quad (14)$$

where T_{C,CO_2} and p_{C,CO_2} are pure-CO_2 critical temperature and critical pressure, and values of MF_i are given in Table 3.1 (Emera and Sarma, 2006).

Table 3.1 Coefficient values in Equation (14) (Emera and Sarma, 2006)

Components	MF_i
SO_2	0.3
H_2S	0.59
CO_2	1.0
C_2	1.1
C_1	1.6
N_2	1.9
All other components	1.0

Shokir (2007) proposed a new correlation for estimating pure and impure CO_2-oil MMP, which is shown as follows,

$$MMP_{impure} = -0.068616 \times z^3 + 0.31733 \times z^2 + 4.9804 \times z + 13.432 \quad (15)$$

where

$$z = \sum_{n=1}^{8} z_n \quad (16)$$

$$z_n = A3_n {x_n}^3 + A2_n {x_n}^2 + A1_n x_n + A0_n \quad (17)$$

where x_n is the value of the nth input factor ($x_1=T_R$, $x_2=x_{vol}$, $x_3=x_{int}$, $x_4=MW_{C5+}$, $x_5=x_{C1}$, $x_6=x_{C2-C4}$, $x_7=x_{N2,}$ $x_8=x_{H2S}$), and the values of the coefficients *A3, A2, A1,* and *A0* are found in Table 3.2 (Shokir, 2007).

Table 3.2 Coefficient values in Equation (17) (Shokir, 2007)

n		*x*	*A3*	*A2*	*A1*	*A0*
1	Oil components	T_R	2.3660E−06	-5.5996E−04	7.5340E−02	-2.9182E+00
2		x_{vol}, %	-1.3721E−05	1.3644E−03	-7.9169E−03	-3.1227E−01
3		x_{int}, %	3.5551E−05	-2.7853E−03	4.2165E−02	-4.9485E−02
4		MW_{C5+}	-3.1604E−06	1.9860E−03	-3.9750E−01	2.5430E+01
5	Non-CO_2 components	x_{C1}, %	1.0753E−04	−2.4733E−03	7.0948E−02	-2.9651E−0
6		x_{C2-C4}, %	6.9446E−06	-7.9188E−05	-4.4917E−02	7.8383E−02
7		$x_{N2,}$, %	0	3.7206E−03	1.9785E−01	-2.5014E−02
8		x_{H2S}, %	3.9068E−06	−2.7719E−04	-8.9009E−03	1.2344E−01

3.3. Results and Discussion

3.3.1. Impact of CH_4 on the MMP of CO_2-CH_4-Oil Mixtures

Figure 3.1 presents the measured MMPs for oil samples displaced by CH_4/CO_2 mixtures at 67˚C. When CH_4's molar fractions are 0 mol%, 5 mol%, 10 mol%, 20 mol% and 100 mol%, the corresponding MMPs are measured to be 17.74 MPa, 19.84 MPa, 22.79 MPa, 27.05 MPa and 58.64 MPa, respectively. Figure 3.1 shows that the measured MMP increases with an increasing CH_4 fraction in the CO_2-CH_4 mixtures; this can be mainly attributed to the more volatile nature of CH_4 than CO_2. CH_4 has a lower critical temperature than CO_2, and thus an increase in the CH_4 content in the mixture will lead to a decrease in gas mixture's critical pseudotemperature.

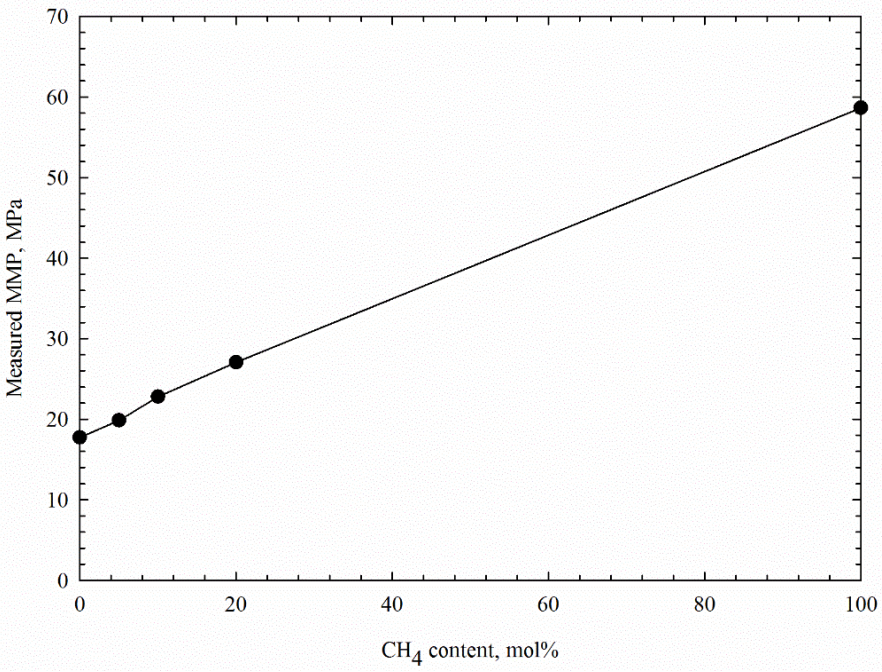


Figure 3.1 Measured MMPs between CO_2-CH_4 mixtures and crude oil versus CH_4 content in the CO_2-CH_4 mixtures at reservoir temperature of 67˚C.

3.3.2. Performance Comparison of Impure-CO_2 MMP Correlations

Table 3.3 compares the measured MMPs and predicted MMPs by different empirical impure CO_2-CH_4 correlations. Note that Shokir (2007) correlation gives very high MMP predictions due to the large MW_{C5+}, so the prediction results by Shokir (2007) correlation are excluded from Table 3.3. As can be seen in Table 3.3, Dong (1999) correlation provides the most accurate prediction of CH_4/CO_2 MMP among all the impure-CO_2 MMP correlations. When CH_4's molar fractions are 5 mol%, 10 mol% and 20 mol%, Dong's (1999) correlation yields absolute relative deviations (ARD%) of 0.00% and 2.98%, and 0.70%, respectively, for the MMP predictions,; these errors are lower than those yielded by the other correlations (Kovarik, 1985; Sebastian *et al*., 1985; Alston *et al*., 1985; Emera and Sarma, 2006; Shokir, 2007). When the CH_4 content is 100 mol%, only Kovarik (1985) correlation gives a proper MMP prediction; but the ARD is still quite large (i.e., 28.43%).

As seen above, Dong (1999) correlation can be used as a fast and efficient tool to predict the CO_2-CH_4 (with a CH_4 content up to 20 mol%) MMP for the oil sample used in this study, given that the experimental pure-CO_2 MMP is available and the CH_4 content is not two high. But it must be noted that each correlation has their own application ranges. It is always better to predict MMP based on the interpolation of the empirical correlations than the extrapolation of the empirical correlations. If an accurate EOS model can be built based on the measured PVT data, the MMC method developed by Ahmadi and Johns (2011) could be used to provide more reliable MMP predictions than empirical correlations.

Table 3.3 Comparison of measured MMPs and predicted MMPs by different empirical impure-CO_2 MMP correlations.

Gas mixture	Measured MMP (MPa)	Kovarik (1985) (MPa)	ARD, %	Sebastian *et al.* (1985) (MPa)	ARD, %	Alston *et al.* (1985) (MPa)	ARD, %	Dong (1999) (MPa)	ARD, %	Emera and Sarma (2006) (MPa)	ARD, %
Gas A (100 mol% CO_2+0 mol% CH_4)	17.74	17.74	0.00	17.74	0.00	17.74	0.00	17.74	0.00	17.74	0.00
Gas B (95 mol% CO_2+5 mol% CH_4)	19.84	20.65	4.08	20.03	0.96	19.38	2.32	19.84	0.00	18.82	5.14
Gas C (90 mol% CO_2+10 mol% CH_4)	22.79	23.53	3.25	22.61	0.79	21.66	4.96	22.11	2.98	20.83	8.60
Gas D (80 mol% CO_2+20 mol% CH_4)	27.06	29.28	8.20	28.67	5.95	29.72	9.83	27.25	0.70	26.78	1.03
Gas E (0 mol% CO_2+100 mol% CH_4)	58.64	75.31	28.43	124.24	111.87	N/A	N/A	106.8	82.13	N/A	N/A

3.4. Conclusions

Based on the results obtained in this chapter, the following conclusions can be drawn:

1) MMP between CO_2-CH_4 mixtures and crude oil shows an increasing trend with an increasing CH_4 content in the CO_2-CH_4 mixtures;
2) When CH_4's molar fractions are 5 mol%, 10 mol% and 20 mol%, Dong's correlation (1999) yields absolute relative deviations (ARD%) of 0.00% and 2.98%, and 0.70%, respectively; these errors are lower than those yielded by the other correlations (Kovarik, 1985; Sebastian *et al*., 1985; Alston, 1985; Emera and Sarma, 2006); and
3) As for the crude oil examined in this stucdy, Dong (1999) correlation provides the most accurate prediction of CO_2-CH_4 (with a CH_4 content up to 20 mol%) MMP

among all the impure-CO_2 MMP correlations (Kovarik, 1985; Sebastian *et al*., 1985; Alston, 1985; Dong, 1999; Emera and Sarma, 2006; Shokir, 2007) examined in this study.

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CHAPTER 4 CONCLUSIONS AND RECOMMENDATIONS

4.1. Conclusions

Minimum miscibility pressure is a key parameter in designing miscible flooding process. This parameter highly depends on the oil/gas properties and reservoir temperature. In this study, we experimentally determine the MMPs of CO_2-CH_4 mixtures with crude oil and compare them against the predicted ones by various correlations developed in the literature. This study experimentally determines the MMP between CO_2-CH_4 mixtures and crude oil; slim-tube experiments have been conducted to measure the MMPs between a light oil sample and CO_2-CH_4 mixtures with different CH_4 contents. When CH_4's molar fractions are 0 mol%, 5 mol%, 10 mol%, 20 mol% and 100 mol%, the corresponding MMPs are measured to be 17.74, 19.84, 22.79, 27.05 and 58.64 MPa, respectively. This result indicates that increasing the amount of CH_4 present in the mixture can increase the MMP between injection gas and crude oil. When CH_4 contents of the CO_2-CH_4 mixtures are 5 mol%, 10 mol% and 20 mol%, respectively, Dong (1999) correlation yields absolute relative deviations (ARD%) of 0.00% and 2.98%, and 0.70%, respectively, for the MMP predictions. The accuracy provided by Dong (1999) correlation is higher than those provided by the other correlations (Kovarik, 1985; Sebastian *et al*., 1985; Alston *et al*., 1985; Emera and Sarma, 2006; Shokir, 2007). For the crude oil examined in this study, Dong (1999) correlation provides the most accurate prediction of CO_2-CH_4 (with CH_4 content up to 20 mol%) MMP among all the impure-CO_2 MMP correlations examined in this study.

4.2. Recommendations

Due to the limited time and resources available, only five slim-tube tests have been conducted in this thesis work. Although the results obtained in this study show that Dong (1999) correlation provides the most accurate prediction of CO_2-CH_4 (with CH_4 content up to 20 mol%) MMP among all the impure-CO_2 MMP correlations, more slim-tube tests need to be conducted on other oil samples to further validate the accuracy of Dong (1999) correlation. In addition, most of the impure-CO_2 MMP correlations are only valid up to a limited range of impurity concentration in the CO_2-dominating mixtures; thus there might be a room for developing a more accurate impure-CO_2 MMP correlation that can perform well over a wide range of impurity concentration.

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