

Minimum Miscibility Pressure Calculation for CO₂ Injection Flooding Based on Oil PVT Properties

Ria Ayu Pramudita¹⁾ and *Won S. Ryoo²⁾

^{1), 2)} Dept. of Chemical Engineering, Hongik University, Seoul 121-791, Korea
²⁾ wsryoo@hongik.ac.kr

ABSTRACT

Enhanced oil recovery using supercritical CO₂ (CO₂-EOR) has been of great interest due to CO₂ effectiveness as an oil solvent under supercritical condition and potential application of CO₂ sequestration. For CO₂ injection process, pressure is an important parameter. The gas injection must be conducted below the fracture pressure of the reservoir formation and at the same time, the gas injection pressure must be above a certain pressure where miscibility can be achieved between the crude oil and the injected CO₂. This pressure is called Minimum Miscibility Pressure (MMP). MMP can be determined experimentally through slim-tube method, rising bubble analysis, or interfacial tension measurements. However, these experiments are time-consuming and have a low degree of reproducibility. Therefore, a computational method to estimate MMP based on the oil PVT properties was introduced. This method was a thermodynamic modeling of CO₂-crude oil phase behavior using Predictive Peng-Robinson (PPR78) equation of state, treating CO₂ and reservoir oil as two pseudocomponents. The MMP was predicted to be equal to the upper critical solution pressure (UCSP) of the mixture. The calculated MMP was compared with slim tube experiment results of published literature and showed the average error of 9.40%.

1. INTRODUCTION

CO₂-Enhanced Oil Recovery (CO₂-EOR) is one of the EOR methods of great interests. There are 151 CO₂-EOR projects reported worldwide in 2014 placing it in the top three of the list (Kootungal 2014). CO₂ effectiveness as an oil solvent under supercritical condition is well-known and CO₂-EOR is thought to have potential application of CO₂ sequestration. Including CO₂-EOR into a carbon capture, utilization, and storage (CCUS) framework is expected to build a strong foundation for a long term carbon policy.

Lake, *et al.* (2014) define solvent flooding as an EOR technique where the oil recovery function is mainly achieved by mass transfer. The injection of CO₂ into the oil

¹⁾ Graduate Student

²⁾ Professor

reservoir will encourage mass transfer between oil and CO₂, and a miscible zone of CO₂ and crude oil will be formed as illustrated in **Figure 1**. Continuous injection of CO₂ will drive this zone towards the production well. Additional production of oil will be achieved after CO₂ is separated from oil. After collecting CO₂ from oil, CO₂ is stored and re-injected into the well. Meanwhile, some of the CO₂ that does not flow towards the production well is permanently stored inside the reservoir. Added with CO₂ from the final injection before the well is closed, there is an appealing amount of CO₂ sequestered in the reservoir.

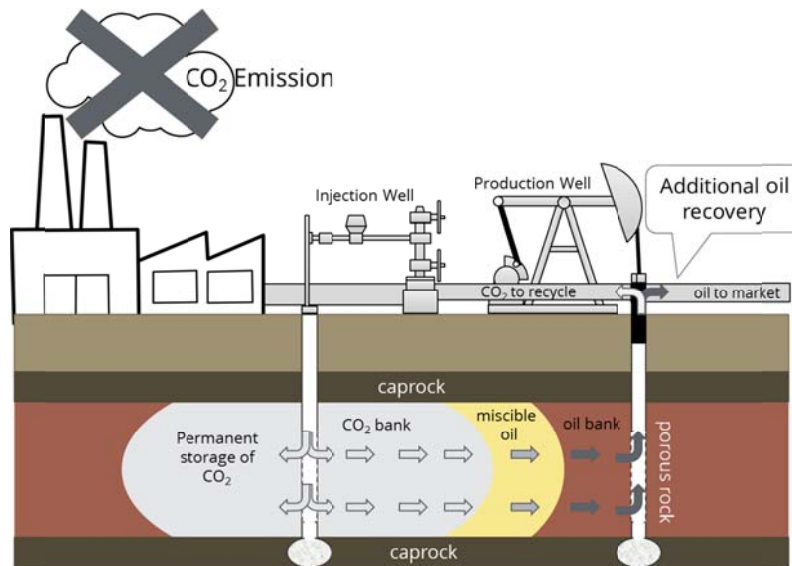


Figure 1 CO₂-EOR Mechanism

There are two mechanisms involved in the mixing of CO₂ and crude oil, which are (1) the dissolution of CO₂ into the crude oil (condensing mechanism), causing swelling, (2) the extraction of light hydrocarbons into the CO₂ phase (vaporizing mechanism), and (3) the combination of condensing and vaporizing mechanisms (**Pedersen and Christensen 2007**).

CO₂-crude oil is quite a complicated mixture because of its multicomponent nature. In order to understand the system, it can be simplified to a ternary mixture, with CO₂, heavy hydrocarbon, and light hydrocarbon component concentrations as its axes as seen in **Figure 2**. The diagram consists of a single-phase area where the components are miscible to each other and a two-phase area where the components are partially miscible and naturally separated into two phases.

The equilibrium line that is closer to the 100% CO₂ composition is the CO₂-rich line. It is also commonly called dew point line because the similarity of the hydrocarbon extraction into CO₂ phase to the vaporization phenomenon. On the other hand, the equilibrium line that is near to the hydrocarbon phase is the oil-rich line, which is also referred to as bubble point line. The point where CO₂-rich line and oil-rich line meets is called plait point, which is equivalent to the critical point found in thermodynamic phase behavior. If the composition of CO₂-crude oil mixture lies outside the two phase area, first-contact miscibility of the injection gas and the crude oil, independent of the mixing-ratio, will occur.

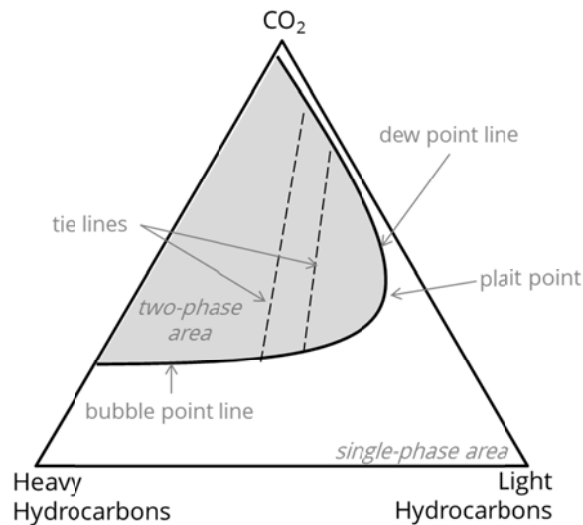


Figure 2 Ternary diagram of simplified mixture of CO₂, light hydrocarbon, and heavy hydrocarbon

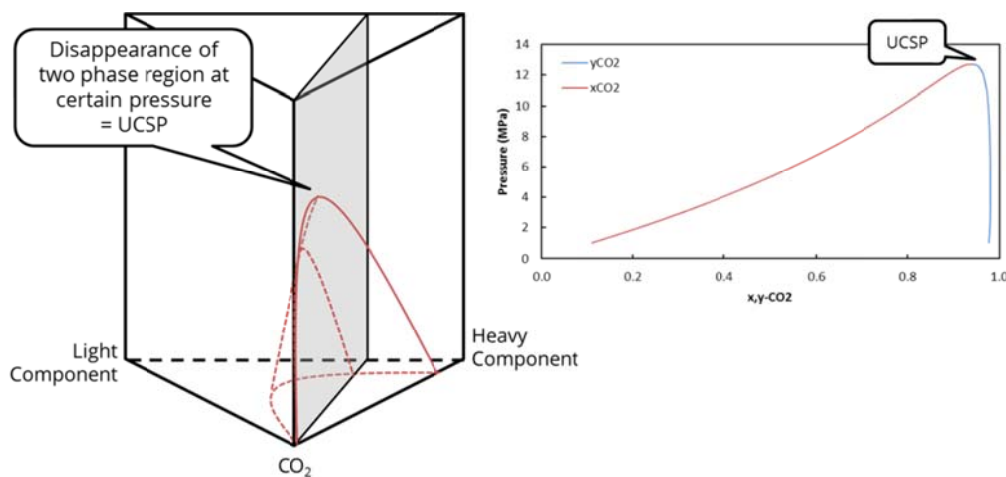


Figure 3 Effect of pressure to the miscibility development of CO₂-crude oil mixture

As the pressure increases, miscibility is more easily developed as the area of two-phase region decreases as depicted in **Figure 3**. At some pressure, the two-phase area will disappear and first-contact miscibility is ensured regardless of feed composition at fixed temperature. This pressure is called first-contact minimum miscibility pressure (FCMMP). Taking into account its thermodynamic properties, the pressure is also recognized as the upper critical solution pressure (UCSP). Besides FCMMP, there is a multi-contact MMP, at which miscibility is reached after multiple contacts of injection gas with the crude oil.

By definition, MMP is a thermodynamic term that relies only on the interaction of flow and phase behavior. It discounts the effect of dispersion in its determination. One advantage of this definition is that if there is any decrease in recovery while the operating pressure is at MMP or above, the cause should be dispersion or other physical processes that are able to be investigated separately (Lake, *et al.* 2014).

MMP is traditionally determined by experimental methods, such as slim-tube method, rising bubble method, and vanishing interfacial tension technique (Elsharkawy, *et al.* 1996, Rao and Lee 2002, Orr Jr. And Jensen 2007) Among the three, slim tube method is the most popular method to estimate the MMP (Elsharkawy, *et al.* 1996, Rahmatabadi 2011). The schematic diagram of slim-tube experiment apparatus are shown in Figure 4.

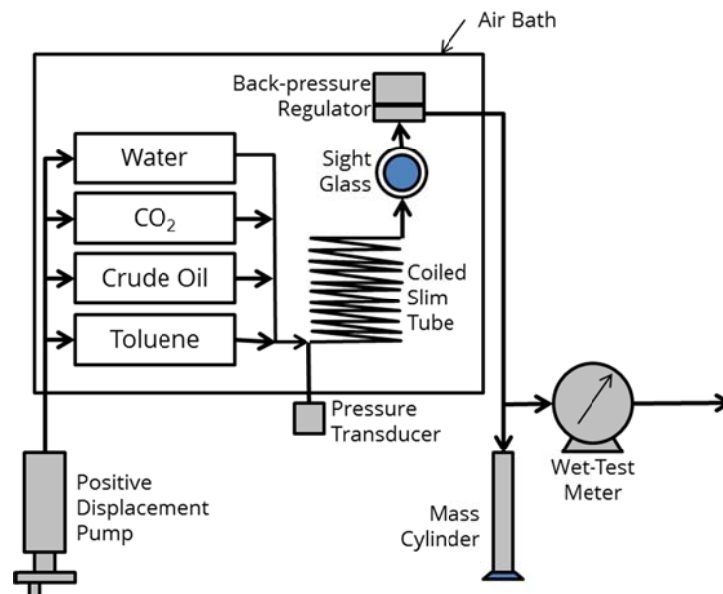


Figure 4 Schematic diagram of slim-tube experiment apparatus

A main part of the slim-tube apparatus is a metal tube with a large aspect ratio (length-to-diameter ratio) which is packed with particles such as sands or bead packs. The reason behind this is to suppress viscous fingering by decreasing the tube diameter and minimize the effect of longitudinal dispersion by increasing the tube length (Lake, *et al.*, 2014, Elsharkawy, *et al.* 1996).

The test procedure is first by saturating the tube with water to mimic the reservoir condition. Then, the slim tube is saturated with crude oil. Later, gas is injected to displace the oil at specific operating pressure with constant rate. To interpret the experiments, the oil recovery is plotted as a function of operating pressure (Lake, *et al.* 2014, Elsharkawy, *et al.* 1996). Oil will be collected in the mass cylinder and its amount divided by the original oil amount is called recovery factor. Recovery factor for several pressures are recorded and MMP is determined to be the pressure at which the oil recovery starts to be constant.

In order to give faster and cheaper alternatives, computational methods to estimate the FCMMP were developed. FCMMP was assumed to be equal to the upper critical solution pressure (UCSP) of the injection gas-crude oil mixture and determined through phase behavior modeling using the Predictive Peng-Robinson 1978 (PPR78) cubic equation of state. Using crude oil compositional data and reservoir temperature, the results of computational method were compared to those from experimental slim-tube test. Additionally, FCMMP was also calculated from previous literatures to investigate the robustness and the reproducibility of the methods.

2. THEORETICAL MODEL

The inputs of the calculation were the reservoir temperature and the compositional data of the injection gas and the crude oil. The compositional data of crude oil was limited to eleven compounds. Heavier compounds were lumped as heptane-plus (C7+) and its characteristics such as critical temperature (T_c), critical pressure (P_c), and acentric factor (ω) are calculated based on the normal boiling point (T_b) and liquid density (ρ).

Table 1 Estimation of heptane-plus physical properties by UNISIM

C7+in Sample	T _c (K)	P _c (bar)	ω
Oil A-Gas A	724.15	23.88	0.5248
Oil B-Gas B	736.45	20.86	0.5655
Oil C-Gas C	744.55	18.58	0.5991
Oil D-Gas D	688.65	21.41	0.5068
Oil E-Gas E	779.15	18.62	0.6166
Oil F-Gas F	766.75	17.43	0.6269
Oil G-Gas G	641.55	29.91	0.3742

The calculation was carried out by Honeywell® UNISIM Design as shown in **Table 1**. The critical temperature and pressure were calculated using Lee-Kesler correlation for compounds with liquid density larger than 1,067 kg/m³ or normal boiling point (NBP) larger than 800 K. when the NBP was less than 548.16 K and the liquid density was less than 850 kg/m³, the Bergman correlation was used, and the critical temperature and pressure of compounds that did not belong to either categories were calculated using Cavett calculation. Meanwhile, the acentric factor for hydrocarbons was calculated using Lee-Kesler correlation while other compounds' were calculated using Pitzer correlation (**Honeywell, 2013**).

The crude oil and injection gas composition for the calculation was obtained from the literatures (**Pedersen and Christensen 2007**) as shown in **Table 2** and **Table 3**, and some field data as shown in **Table 4**. Vapor-liquid equilibrium of crude oil-injection gas was determined through isothermal flash calculation.

Table 2 Molar fraction data and properties of crude oil and injection gas with slim-tube experimental results for the MMP estimation (1)

Component	Oil A	Gas A	Oil B	Gas B	Oil C	Gas C
N2	0.0047	0.0050	0.0092	0.0140	0.0018	0.0029
CO2	0.0049	0.0076	0.0036	0.0135	0.0044	0.0076
C1	0.4201	0.7204	0.4060	0.8217	0.4392	0.7305
C2	0.0605	0.1241	0.0522	0.0842	0.1071	0.1395
C3	0.0293	0.0860	0.0331	0.0453	0.0881	0.0817
iC4	0.0061	0.0119	0.0068	0.0049	0.0130	0.0077
nC4	0.0099	0.0255	0.0189	0.0095	0.0399	0.0189
iC5	0.0058	0.0058	0.0087	0.0018	0.0136	0.0029
nC5	0.0042	0.0065	0.0130	0.0019	0.0183	0.0033
C6	0.0092	0.0035	0.0192	0.0016	0.0255	0.0024
C7+	0.4453	0.0037	0.4293	0.0016	0.2491	0.0026
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
<i>C7+,M (g/mol)</i>	196.0		215.1		231.0	
<i>C7+,ρ (g/mL)</i>	0.883		0.869		0.855	
<i>T (°C)</i>	92		79		99	
<i>MMP (bar)</i>	390		470		360	

Table 3 Molar fraction data and properties of crude oil and injection gas with slim-tube experimental results for the MMP estimation (2)

Component	Oil D	Gas D	Oil E	Gas E	Oil F	Gas F
N2	0.0025	0.0000	0.0000	0.0248	0.0046	0.0000
CO2	0.0360	0.0000	0.0000	0.0000	0.0134	0.0000
C1	0.5683	1.0000	0.5039	0.8785	0.4901	1.0000
C2	0.0937	0.0000	0.0882	0.0750	0.0704	0.0000
C3	0.0548	0.0000	0.0591	0.0191	0.0493	0.0000
iC4	0.0146	0.0000	0.0089	0.0026	0.0095	0.0000
nC4	0.0261	0.0000	0.0328	0.0000	0.0252	0.0000
iC5	0.0120	0.0000	0.0094	0.0000	0.0116	0.0000
nC5	0.0139	0.0000	0.0129	0.0000	0.0152	0.0000
C6	0.0126	0.0000	0.0136	0.0000	0.0334	0.0000
C7+	0.1659	0.0000	0.2712	0.0000	0.2773	0.0000
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
<i>C7+,M (g/mol)</i>	183.3		249.6		250.2	
<i>C7+,ρ (g/mL)</i>	0.827		0.827		0.870	
<i>T (°C)</i>	171		107		151	
<i>MMP (bar)</i>	331		414		434	

Table 4 Molar fraction data and properties of crude oil and injection gas with slim-tube experimental results for the MMP estimation (3)

Component	Oil G	Gas G
N2	0.0039	0.0000
CO2	0.0006	1.0000
C1	0.1388	0.0000
C2	0.0175	0.0000
C3	0.0405	0.0000
iC4	0.0165	0.0000
nC4	0.0306	0.0000
iC5	0.0167	0.0000
nC5	0.0157	0.0000
C6	0.0270	0.0000
C7+	0.6922	0.0000
Total	1.0000	1.0000
C7+,M (g/mol)	135.9	
C7+,ρ (g/mL)	0.846	
T (°C)	70	
MMP (bar)	135.14	

In order to describe the crude oil-CO₂ phase behavior, Predictive Peng-Robinson 1978 cubic equation of state (PPR78 EOS), developed by Jaubert and coworkers (Vitu, *et al.* 2008, Privat, *et al.* 2008) was used. The expression of PR78 EOS for pure components is shown in Eq. (1).

$$P = \frac{RT}{v - b_i} - \frac{a_i(T)}{v(v + b_i) + b_i(v - b_i)} \quad (1)$$

$$R = 8.314472 \text{ J mol}^{-1}\text{K}^{-1} \quad (2)$$

$$b_i = 0.0777960739 \frac{RT_{c,i}}{P_{c,i}} \quad (3)$$

$$a_i = 0.457235529 \frac{R^2 T_{c,i}^2}{P_{c,i}} \left[1 + m_i \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right]^2 \quad (4)$$

$$\text{with } m_i = \begin{cases} 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 & \text{if } \omega_i \leq 0.491 \\ 0.379642 + 1.48503\omega_i - 0.164423\omega_i^2 & \text{if } \omega_i > 0.491 \end{cases}$$

where P is the system pressure, R is the ideal gas constant, T is the system temperature, and v is the molar volume. a_i and b_i are components' fitted parameters to match the critical properties, where a_i is dependent of temperature.

For the mixture of components, classical mixing rules with mixing parameters a and b are used.

$$a = \sum_{i=1}^N \sum_{j=1}^N z_i z_j \sqrt{a_i a_j} (1 - k_{ij}(T)) \quad (5)$$

$$b = \sum_{i=1}^N z_i b_i \quad (6)$$

There is a difference of PPR78 EOS from PR78 EOS in mixing rule, where binary interaction parameter, k_{ij} , is set to be dependent of the temperature (7).

$$k_{ij}(T) = \frac{-\frac{1}{2} \left[\sum_{k=1}^{N_g} \sum_{l=1}^{N_g} (\alpha_{ik} - \alpha_{jk}) (\alpha_{il} - \alpha_{jl}) A_{kl} \left(\frac{298.15}{T} \right)^{\left(\frac{B_{kl}}{A_{kl}} - 1 \right)} \right] - \left(\frac{\sqrt{a_i(T)}}{b_i} - \frac{\sqrt{a_j(T)}}{b_j} \right)^2}{2 \sqrt{\frac{a_i(T) a_j(T)}{b_i b_j}}} \quad (7)$$

where α_{ik} is the fraction of molecule i occupied by group k and calculated by dividing the occurrence of group k in molecule i by the total number of groups presents in molecule i (please notice the difference with alpha function in the EOS). A_{kl} and B_{kl} are constant parameters of the interactions of different groups, k and l (Vitu, *et al.* 2008; Privat, *et al.* 2008).

3. RESULTS AND DISCUSSION

First-contact minimum miscibility pressure (FCMMP) was estimated by calculating the bubble and dew point pressure of the mixture using Honeywell® UNISIM Design. UCSP method was proven to be able to estimate MMP values with 9.40% of average error to slim-tube experiment results as shown in Table 5. The method was likely to underestimate the MMP value, but at some samples such as sample E and F, the values were overestimated. This opens a possibility of other miscibility development under pressures lower than UCSP. UCSP is thought to be the miscibility that is developed right away after the first contact while there might be cases when miscibility is developed by multiple contacts of injection gas with crude oil, in lower pressures than UCSP.

The MMP of gas injection with CH_4 as main component were significantly higher than those of CO_2 , as seen in Figure 5. This might be caused by the molecular weight of CH_4 (16 g/mol) that is approximately one-third of the molecular weight of CO_2 (44 g/mol). While both of the molecules are non-polar and supposedly mix well with the large hydrocarbons in the crude oil, the larger molecular weight helped CO_2 to mix better with crude oil rather than CH_4 . On the other hand, CO_2 was very easily miscible with the crude oil, not only because of its relatively high critical pressure than CH_4 , but

also relatively smaller size of CO₂ (~0.34 nm) helped the molecule to penetrate bulk hydrocarbons, increasing the miscibility.

Table 5 MMP estimation results and comparison with experimental data

Sample	Injection Gas	T (°C)	MMP (MPa)		
			Experimental	Calculated	Error
Oil A-Gas A	Light HC (Mostly CH ₄)	92	39	37.66	-3.44%
Oil B-Gas B	Light HC (Mostly CH ₄)	79	47	43.47	-7.51%
Oil C-Gas C	Light HC (Mostly CH ₄)	99	36	33.46	-7.06%
Oil D-Gas D	Pure CH ₄	171	33.1	31.81	-3.90%
Oil E-Gas E	Light HC (Mostly CH ₄)	107	41.4	51.19	23.65%
Oil F-Gas F	Pure CH ₄	151	43.4	49.58	14.24%
Oil G-Gas G	Pure CO ₂	70	13.51	12.70	-6.00%

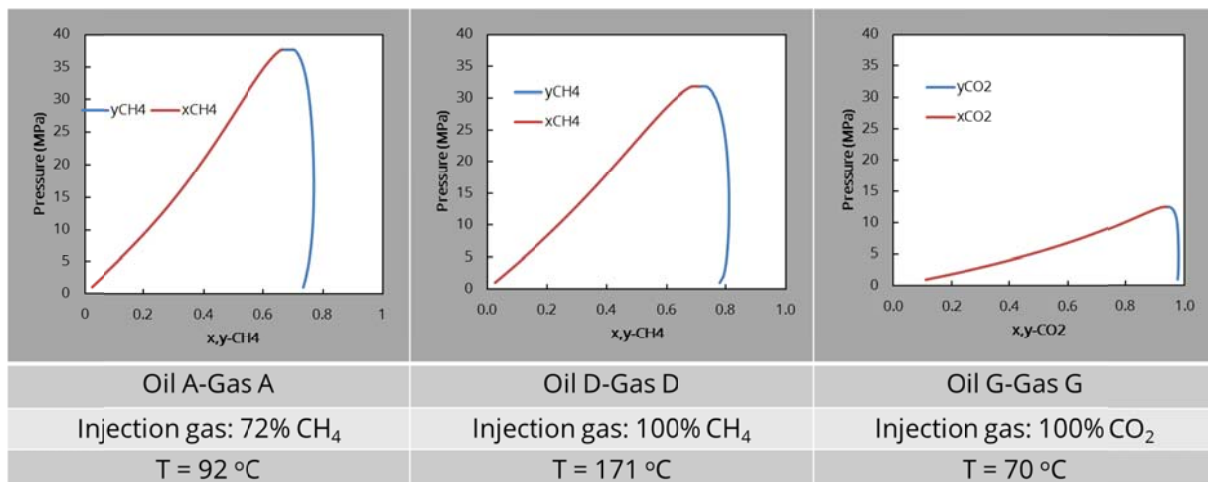


Figure 5 Comparison of the effect of injection gas to the estimated MMP

In order to investigate the effect of temperature change to the MMP value, the mixture of Oil G-Gas G (pure CO₂) was simulated under different temperatures, i.e. 90 and 120 °C, as shown in **Figure 6**. It can be seen that as the temperature increased, MMP value increased. However, when the mixture of Oil D-Gas D (pure CH₄) was simulated under different temperatures (120 and 70 °C) as shown in **Figure 7**, the reverse trend was observed, whereas the temperature increased, MMP value decreased.

Increase in temperature was hypothesized to help increasing the fraction of the crude oil evaporating to the CH₄'s gas phase, thus decreasing the UCSP. Meanwhile,

the reverse phenomena happened in the CO₂ case. This might be caused by the steep decrease in CO₂ density as the temperature increased, i.e. 0.51 g/mL to 0.28 g/mL as the temperature was raised from 70 to 120 °C. The decrease in CO₂ density will disrupt its miscibility with the crude oil, thus increasing the UCSP. However, in the observed temperature range, the average UCSP value of the crude oil injected with CH₄ was higher than that of CO₂.

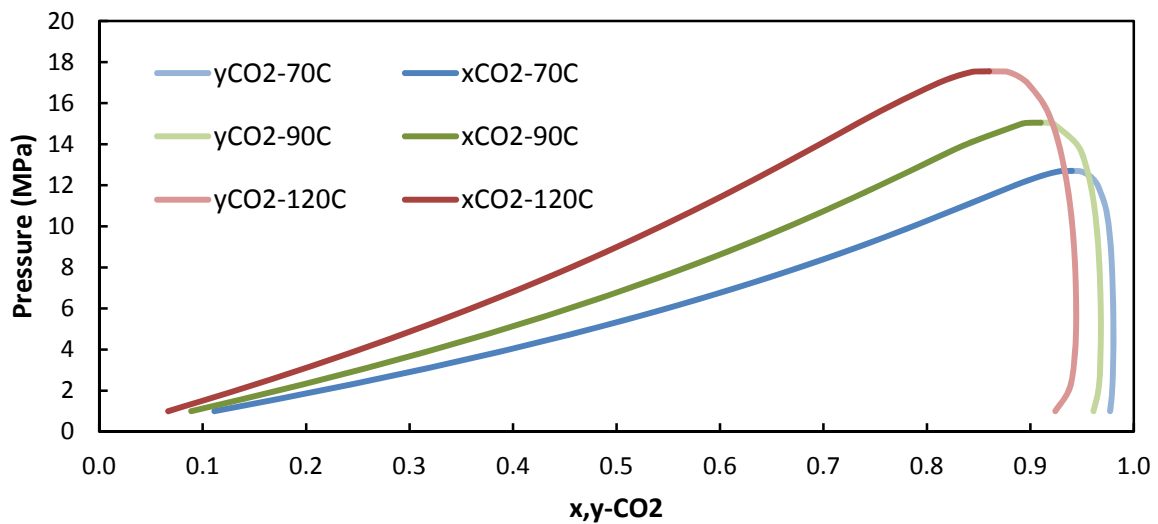


Figure 6 The effect of temperature to the MMP of Oil G-Gas G mixture

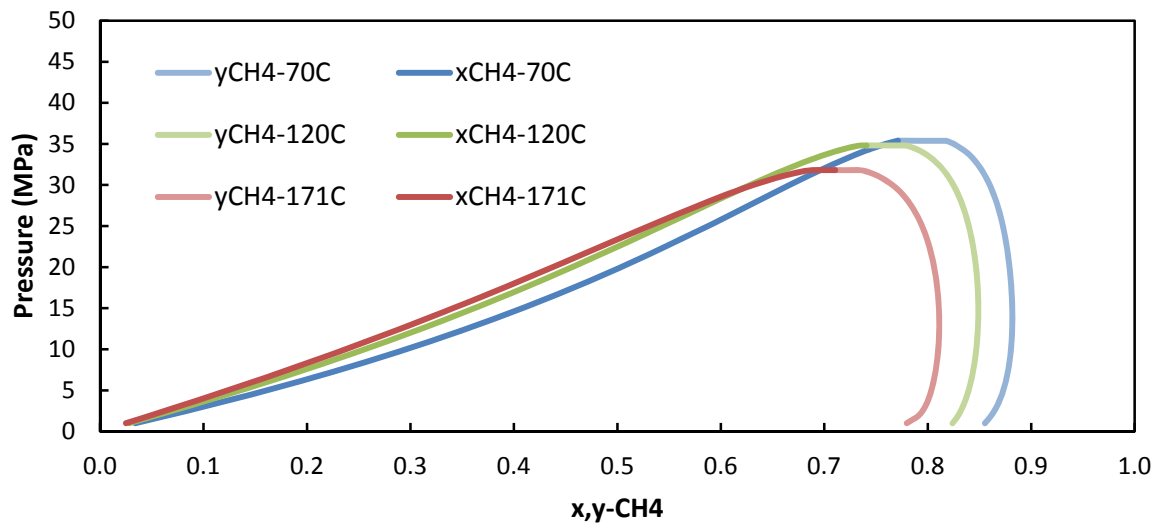


Figure 7 The effect of temperature to the MMP of Oil D-Gas D mixture

4. CONCLUSIONS

A computational method to estimate FCMMP for CO₂-EOR is developed based on thermodynamic calculations to describe phase behavior of CO₂-crude oil multicomponent mixture. Thermodynamic calculation gives an alternative to the

otherwise time-consuming experimental methods. In this study, Predictive Peng-Robinson 1978 (PPR78) EOS was used, where binary interaction parameter (k_{ij}) is set to be dependent on the temperature.

The initial assumption of FCMMP as identical to the upper critical solution pressure (UCSP) at the given temperature was proven, with the average error of 9.40% compared to the experimental slim tube results. There are some MMP values that were predicted far above the actual MMP, raising questions in the possibility of miscibility development under other mechanism (multi-contact miscibility).

The MMP values of the crude oil injected with CH_4 were significantly higher than the one injected with CO_2 . However, as the temperature increased, for mixture with CO_2 as the injection gas, the MMP decreased while for mixture with CH_4 as the injection gas, the MMP increased.

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