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**
C7+,M (g/mol)	*196.0*		*215.1*		*231.0*	
C7+,ρ (g/mL)	*0.883*		*0.869*		*0.855*	
T (°C)	*92*		*79*		*99*	
MMP (bar)	*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**
C7+,M (g/mol)	*183.3*		*249.6*		*250.2*	
C7+,ρ (g/mL)	*0.827*		*0.827*		*0.870*	
T (°C)	*171*		*107*		*151*	
MMP (bar)	*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-CO_2 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).

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

$$R = 8.314472 \text{ J mol}^{-1}\text{K}^{-1} \tag{2}$$

$$b_i = 0.0777960739 \frac{RT_{c,i}}{P_{c,i}} \tag{3}$$

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

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

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 ai is dependent of temperature.

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

$$a = \sum_{i=1}^{N}\sum_{j=1}^{N} z_i z_k \sqrt{a_i a_j}\left(1 - k_{ij}(T)\right) \tag{5}$$

$$b = \sum_{i=1}^{N} z_i b_i \tag{6}$$

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).

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

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

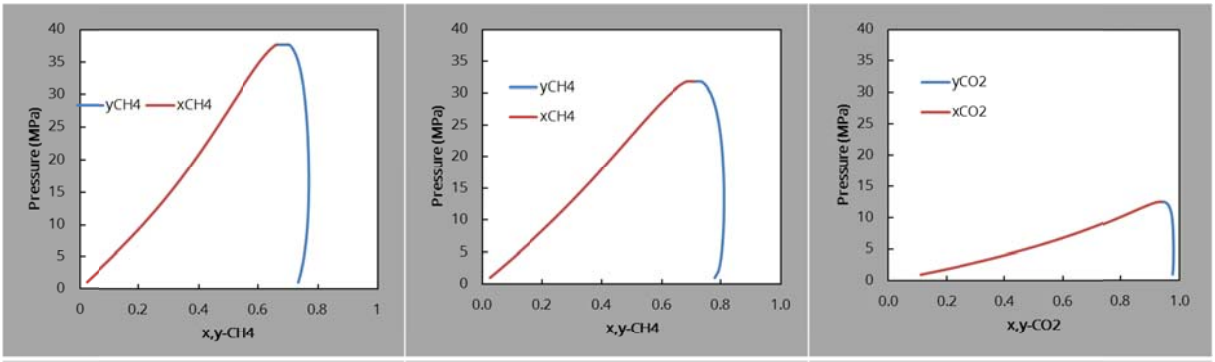
First-contact minimum miscibility pressure (FCMMP) was estimated by calculating the bubble and dew point pressure of the mixture using Honeywell® UNISIM Design. UCSP method was proven to be able to estimate MMP values with 9.40% of average error to slim-tube experiment results as shown in Table 5. The 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/mL). 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 CO_2 (~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%



Oil A-Gas A	Oil D-Gas D	Oil G-Gas G
Injection gas: 72% CH_4	Injection gas: 100% CH_4	Injection gas: 100% CO_2
T = 92 °C	T = 171 °C	T = 70 °C

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 CO_2) 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 CH_4) 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 CH_4's gas phase, thus decreasing the UCSP. Meanwhile,

the reverse phenomena happened in the CO_2 case. This might be caused by the steep decrease in CO_2 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 ^oC. The decrease in CO_2 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 CH_4 was higher than that of CO_2.

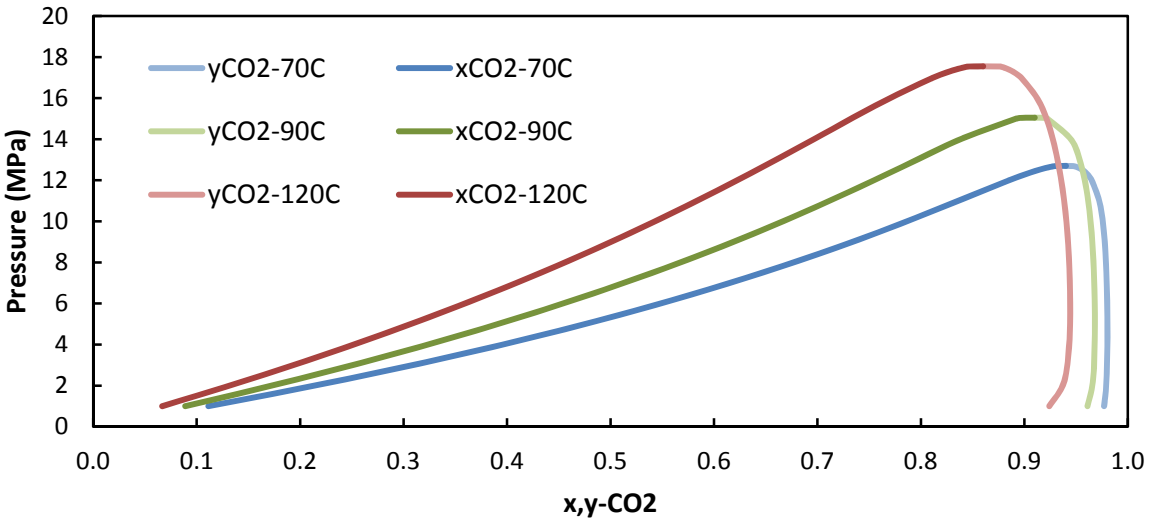


Figure 6 The effect of temperature to the MMP of Oil G-Gas G mixture

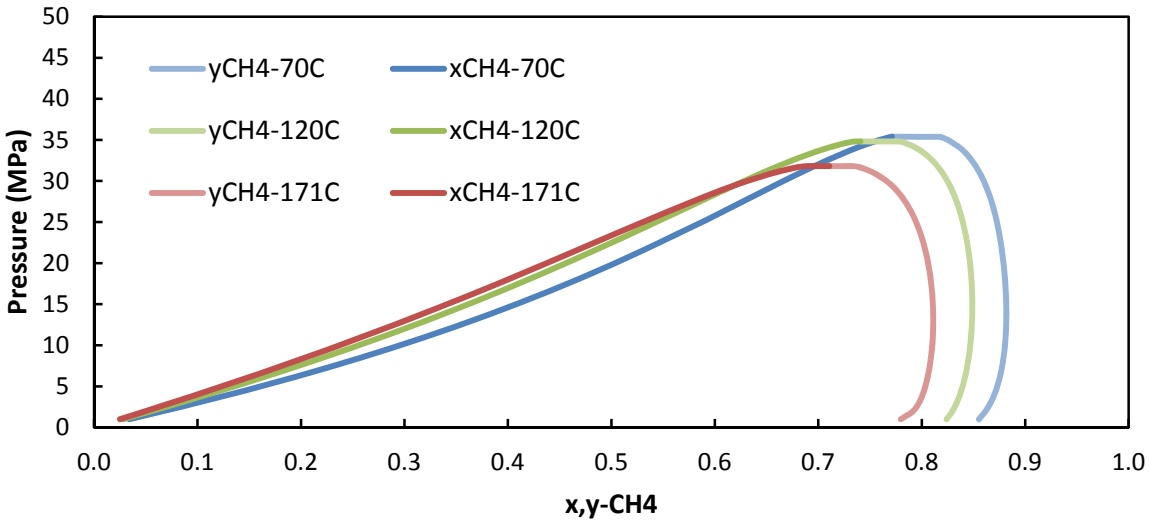


Figure 7 The effect of temperature to the MMP of Oil D-Gas D mixture

4. CONCLUSIONS

A computational method to estimate FCMMP for CO_2-EOR is developed based on thermodynamic calculations to describe phase behavior of CO_2-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 was 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.

REFERENCES

Elsharkawy, A.M., Poettman, F.H., and Christiansen, R.L. (1996), "Measuring CO2 Minimum Miscibility Pressures: Slim Tube or Rising Bubble Method?" *Energy & Fuels*, Vol. **10**, 443-449.

Honeywell (2013), *UNISIM Design Simulation Basis Reference Guide*, Honeywell, London. Ontario.

Koottungal, L. (2014), *2014 Worldwide EOR Survey*, Oil&Gas Journal, PennWell Corporation, Houston, TX.

Lake, L., Johns, R.T., Rossen, W.R., and Pope, G.A. (2014), *Fundamentals of Enhanced Oil Recovery*, Society of Petroleum Engineers, Richardson, TX.

Orr Jr., F.M. and Jessen, K. (2007) "An analysis of the vanishing interfacial tension technique for determination of minimum miscibility pressure" *Fluid Phase Equilibria*, Vol. **255**, 99-109.

Pedersen, K.S. and Christensen, P.L. (2007), *Phase Behavior of Petroleum Reservoir Fluids*, CRC Press, Boca Raton, FL.

Privat, R. Jaubert, J.-N., and Mutelet, F (2008), "Addition of the Nitrogen Group to the PPR78 Model (Predicive 1978, Peng-Robinson EOS with Temperature-Dependent kij Calculated through a Group Contribution Method), *Industrial & Engineering Chemistry Research*, Vol. **47**, 2033-2048.

Rahmatabadi, K.A. (2011), "Advances in Calculation of Minimum Miscibility Pressure", Ph.D dissertation. Austin, USA: The University of Texas at Austin

Rao, D.N., Lee, J.I. (2002) "Application of the new vanishing interfacial tension technique to evaluate miscibility condition for the Terra Nova Offshore Project" *Journal of Petroleum Science and Engineering*, Vol. **35**, 247-262

Vitu, S., Privat, R., Jaubert, J.-N., and Mutelet, F. (2008), "Predicting the phase equilibria of CO_2 + hydrocarbon systems with the PPR78 model (PR EOS and k_{ij} calculated through a group contribution method" *The Journal of Supercritical Fluids*, Vol. **45**, 1-26