## CHAPTER VI

## Results and Discussion

In the pressure decay experiment, $\mathrm{CO}_{2}$ pressure from 500 psi to 900 psi was applied to condensate (API 63.9), oil sample and $n$-decane. The pressure decay curves and total pressure drop curves were plotted to determine MMP. The MMP is maximum total pressure drop from total pressure drop curve. The pressure decay curve is the curve which is a plot of pressure against time as shown in Figure 4.1 Figure 4.3 to determine equilibrium time of each samples.


Figure 4.1 Pressure decay curve of condensate API 63.9 at $20^{\circ} \mathrm{C}$.


Figure 4.2 Pressure decay curve of oil sample at $20^{\circ} \mathrm{C}$.


Figure 4.3 Pressure decay curve of n -decane at $20^{\circ} \mathrm{C}$.

After injecting $\mathrm{CO}_{2}$ gas into the reactor, $\mathrm{CO}_{2}$ diffuses into the oil. It can be observed by the pressure inside the reactor decreasing at the initial time and slightly decreasing to the equilibrium. Equilibrium time of condensate (API 63.9) is around 30 minutes at $20^{\circ} \mathrm{C}$ temperature. In the case of oil sample and n -decane, the equilibrium time are 20 min and 45 min , respectively.

### 4.1 MMP Determination From Pressure Decay Curve

The pressure drop curve is plotted between total pressure drop against initial pressure. At below the MMP, the total pressure drop is slightly increased with increasing the initial pressure and it increases to the ultimate point. After that it will decrease. The MMP point is the ultimate point of the total pressure drop curve. The results of MMP measured by the pressure decay technique of condensate, oil sample and $n$-decane are shown in Figure 4.4 - Figure 4.6. At $20^{\circ} \mathrm{C}$, the MMP point of condensate API 63.9 is 775 psi . The MMP point of oil sample is 725 psi and MMP point of $n$-decane is 825 psi. At below the MMP point, the pressure drop of the system is increase with increasing initial pressure. At above the miscible condition, the total pressure drop is increase again with initial pressure that shows in Figure 4as for oil sample at $20^{\circ} \mathrm{C}$


Figure 4.4. Pressure drop curve of condensate at $20^{\circ} \mathrm{C}$.


Figure 4.5 Pressure drop curve of oil sample at $20^{\circ} \mathrm{C}$.


Figure 4.6 Pressure drop curve of $n$-decane at $20^{\circ} \mathrm{C}$.

### 4.2 Effect of Molecular Weight on MMP

Effect of molecular weight on MMP is determined in three different samples (condensate, oil sample and n -decane) at temperature $20^{\circ} \mathrm{C}$. The molecular weight on MMP are shown in Table 4.1. Figure 4.7 shows the MMP of the three different samples.
$\qquad$

Table. 4.1 Effect of molecular weight on MMP in condensate, oil sample and $n$ decane at $20^{\circ} \mathrm{C}$

| Sample | Molecular Weight | MMP from Experiment |
| :---: | :---: | :---: |
| Condensate API 63.9 | 113.64 | 775 psi |
| Oil sample | 107.15 | 725 psi |
| n-decane | 142.28 | 825 psi |



Figure 4.7 Effect of molecular weight on MMP in condensate, oil sample and $n$ decane at $20^{\circ} \mathrm{C}$.

Figure 4.7 shows the results showed that increase of molecular weight increases the MMP between $\mathrm{CO}_{2}$ and samples (Rao and Lee, 2003) because viscosity of the sample is increase and it has low amount of light hydrocarbon component. Thus, it is difficult for $\mathrm{CO}_{2}$ to diffuse in the samples. Hence, it requires higher pressure to achieve the miscibility. At $20^{\circ} \mathrm{C}$, n -decane has the highest MMP, because n -decane has highest molecular weight (144). Oil sample has the lowest MMP because oil sample has the lowest molecular weight (107.32).

### 4.3 Effect of Temperature on MMP

Effect of temperature on equilibrium time and MMP at two different temperature $\left(20^{\circ} \mathrm{C}\right.$ and $\left.30^{\circ} \mathrm{C}\right)$ was determined shown in Table 4.2 and Table 4.3, respectively. The pressure decay curves are shown in Figure 4.8-4.10. The total pressure drop curves are shown in Figure 4.10 for crude oil and in Figure 4.11 for the oil sample.

Table. 4.2 Effect of temperature on equilibrium time in condensate and oil sample

| Sample | Temperature $\left({ }^{\circ} \mathbf{C}\right)$ | Equilibrium Time |
| :---: | :---: | :---: |
| Condensate | $20.1 \pm 0.12$ | 30 minute |
|  | $30.16 \pm 0.09$ | 20 minute |
| Oil sample | $20.15 \pm 0.13$ | 20 minute |
|  | $30.32 \pm 0.34$ | 15 minute |

Table. 4.3 Effect of temperature on MMP in crude oil and oil sample


Figure 4.8 Pressure decay curve of condensate API 63.9 at $30^{\circ} \mathrm{C}$.


Figure 4.9 Pressure decay curve of oil sample at $20^{\circ} \mathrm{C}$.


Figure 4.10 Effect of temperature on MMP on $\mathrm{CO}_{2}$ and condensate system at $20^{\circ} \mathrm{C}$ and $30^{\circ} \mathrm{C}$.


Figure 4.11 Effect of temperature on MMP on $\mathrm{CO}_{2}$ and oil sample system at $20^{\circ} \mathrm{C}$ and $30^{\circ} \mathrm{C}$.

The effect of temperature on equilibrium time which high temperature (30 ${ }^{\circ} \mathrm{C}$ ) has lower equilibrium time than low temperature $\left(20^{\circ} \mathrm{C}\right)$ in Table 4.2 because oil viscosity is decreased at high temperature. It is faster for $\mathrm{CO}_{2}$ to diffuse into condensate than low temperature. The MMP of condensate (API 63.9) is 775 psi at $20^{\circ} \mathrm{C}$ and 850 psi at $30^{\circ} \mathrm{C}$ (Figure 4.10 ) and 725 psi at $20^{\circ} \mathrm{C}$ and 800 psi at $30^{\circ} \mathrm{C}$ (Fig. 4.11) fcr oil sample system. The results of MMP at two different temperatures are shown; the MMP at $30^{\circ} \mathrm{C}$ is higher than the MMP at $20^{\circ} \mathrm{C}$. The increase of temperature of the system increases the MMP because the solubility of $\mathrm{CO}_{2}$ in the samples is decreased with increasing the system temperature which required higher pressure to achieve the miscibility (Cao and $\mathrm{Gu}, 2013$ ).

### 4.4 Effect of Impurity Gas on MMP

Effect of impurity gas (Nitrogen gas) on MMP at two different percent of nitrogen gas ( $1 \%$ and $3 \%$ ) in $\mathrm{CO}_{2}$ was determined at $20^{\circ} \mathrm{C}$ as shown in Table 4.4 and the total pressure drop curve in Figure 4.12. The MMP of $\mathrm{CO}_{2}{ }^{-}$oil sample system is 725 psi for pure $\mathrm{CO}_{2}$ injection, 750 psi for the $1 \% \mathrm{~N}_{2}$ in $\mathrm{CO}_{2}$ injection, and 850 psi for the $3 \% \mathrm{~N}_{2}$ in $\mathrm{CO}_{2}$ injection. For comparison of the pure $\mathrm{CO}_{2}$ injection with $\mathrm{CO}_{2}$ injection containing $1 \% \mathrm{~N}_{2}$, nitrogen gas has lower critical temperature than $\mathrm{CO}_{2}$ which is more difficult to achieve miscibility than pure $\mathrm{CO}_{2}$. Thus, the $\mathrm{CO}_{2}$ injection containing $1 \% \mathrm{~N}_{2}$ in the oil sample required higher pressure to achieve miscibility (Belhaj et al., 2013). The effect of percent $\mathrm{N}_{2}$ impurity gas was varied between $1 \%$ and $3 \% \mathrm{~N}_{2}$ in $\mathrm{CO}_{2}$ stream with oil sample at $20^{\circ} \mathrm{C}$. The MMP of the 3 $\% \mathrm{~N}_{2}$ in the $\mathrm{CO}_{2}$ stream is higher than that of $1 \% \mathrm{~N}_{2}$ because higher pressure is required which can substantially increase with the amount of $\mathrm{N}_{2}$ present in the $\mathrm{CO}_{2}$ stream to achieve miscibility (Dong et al., 2001).

Table. 4.4 Effect of gas impurity on MMP of $\mathrm{CO}_{2}$-oil sample system at $20^{\circ} \mathrm{C}$

| Sample | MMP from Experiment |
| :---: | :---: |
| Pure $\mathrm{CO}_{2}$ injection | 725 psi |
| $1 \%$ of $\mathrm{N}_{2}$ in $\mathrm{CO}_{2}$ injection | วิทยาลัย |
| $3 \%$ of $\mathrm{N}_{2} \mathrm{CO}_{2}$ injection | 750 psi |



Figure 4.12 Effect of gas impurity on MMP of $\mathrm{CO}_{2}$ - oil sample at $20^{\circ} \mathrm{C}$, pure $\mathrm{CO}_{2}$ injection, with $1 \%$ of $\mathrm{N}_{2}, 3 \%$ of $\mathrm{N}_{2}$ in $\mathrm{CO}_{2}$ stream.

### 4.5 MMP Calculation

To evaluate the results of MMP measured from the pressure decay technique, the MMP values was also calculated using Li et al. correlation (2013) in Equation 2.18. It requires $\mathrm{MW}_{\mathrm{C7}}, \mathrm{X}_{\mathrm{VOL}}, \mathrm{X}_{\text {INT }}$ and $\mathrm{T}_{\mathrm{R}}$ as shown in Table 4.5 which $\mathrm{MW}_{\mathrm{C7}}, \mathrm{X}_{\text {VoL }}, \mathrm{X}_{\text {INT }}$ were found from GC-TOFMS in Table 12.1. However it could not be obtained in this work due to the limitation of the experimental capacity. This prediction was far from the experimental value because in the literature, Li et al. correlation was testing at the high temperature (around $100^{\circ} \mathrm{C}$ ). This correlation wasn't accuracy enough for the prediction at low temperature. This equation should improve the accuracy for calculation in low temperature. The correlation factor for impure $\mathrm{CO}_{2}$ streams ( $\mathrm{F}_{\mathrm{imp}}$ ) was used to find MMP in the effect of impurity gas which it was determined from Alston et al. correlation in Equation 2.4-2.6. Nevertheless, $\mathrm{F}_{\text {imp }}$ is calculated from the critical temperature of the stream. The pseudo-critical temperature of the stream is calculated using the weight-fraction mixing rule as follows in Equation 2.4, and used Equation 2.5 to find MMP.

Table 4.5 Comparison of MMPs from this work with Li et al. correlation

| Sample | $\begin{gathered} \mathrm{T}_{\mathrm{R}} \\ \left({ }^{\circ} \mathrm{C}\right) \end{gathered}$ | $\mathbf{M W}_{\text {C7+ }}$ | $\mathbf{X}_{\mathrm{VOL}}$ | XINT | MMP (psi) |  | \%AD (\%) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | This Work | Li et al. |  |
| Pure $\mathrm{CO}_{2}$ <br> in <br> condensate <br> API 63.9 | 20.10 | 113.64 | 0 | 0.275 | 775 | 594 | 23.36 |
|  | 30.16 | 113.64 | 0 | 0.275 | 850 | 763 | 10.24 |
| Pure $\mathrm{CO}_{2}$ <br> in oil sample | 20.15 | 107.15 | 0 | 0,383 | 725 | 580 | 20 |
|  | 30.32 | 107.15 | 0 | 0.383 | 800 | 776.24 | 2.97 |
| $\mathrm{CO}_{2}$ with 1 <br> $\% \mathrm{~N}_{2}$ in oil <br> sample $\left(\mathrm{F}_{\mathrm{imp}}=1.08\right)$ | 20.17 | 107.15 | 0 | 0.383 | 750 | 625.66 | 16.58 |
|  | 30.24 | 107.15 | 0 | $0.383$ | 850 | 835.44 | 1.7 |
| $\mathrm{CO}_{2}$ with 3 <br> $\% \mathrm{~N}_{2}$ in oil <br> sample $\left(\mathrm{F}_{\text {imp }}=1.29\right)$ | 20.18 | 107.15 | 0 | 0.383 | $850$ | 747.22 | 12.1 |
| Pure $\mathrm{CO}_{2}$ <br> in n -decane | 19.97 | 142.28 | 0 | 0 | 825 | 651.12 | 21.08 |

