

# Reduction of MMP Using Oleophilic Chemicals

C. L. Voon, M. Awang

**Abstract**—CO<sub>2</sub> miscible displacement is not feasible in many oil fields due to high reservoir temperature as higher pressure is required to achieve miscibility. The miscibility pressure is far higher than the formation fracture pressure making it impossible to have CO<sub>2</sub> miscible displacement. However, by using oleophilic chemicals, minimum miscibility pressure (MMP) could be lowered. The main objective of this research is to find the best oleophilic chemical in MMP reduction using slim-tube test and Vanishing Interfacial Tension (VIT). The chemicals are selected based on the characteristics that it must be oil soluble, low water solubility, have 4 – 8 carbons, semi polar, economical, and safe for human operation. The families of chemicals chosen are carboxylic acid, alcohol, and ketone. The whole experiment would be conducted at 100°C and the best chemical is said to be effective when it is able to lower CO<sub>2</sub>-crude oil MMP the most. Findings of this research would have great impact to the oil and gas industry in reduction of operation cost for CO<sub>2</sub>EOR which is applicable to both onshore and offshore operation.

**Keywords**—Enhanced Oil Recovery, Oleophilic Chemical, Minimum Miscibility Pressure, CO<sub>2</sub> Miscible Displacement.

## I. INTRODUCTION

CO<sub>2</sub> miscible displacement is a type of multi-contact miscible displacement where when CO<sub>2</sub> is injected into the reservoir, it would first react with light oil components which has 2 to 6 carbon atoms to form single phase solution. Then, the solution would move forward in the reservoir to react with heavier oil components. The cycle continues until the solution is fluid enough to be pumped out [1]. As the flooding front advances through the reservoir, the composition of the fluid slowly changes from crude oil to carbon dioxide.

In order for CO<sub>2</sub> to become miscible with crude oil, it would need to achieve zero interfacial tension with crude oil. For CO<sub>2</sub> and crude oil's interfacial tension to reach nil, a certain pressure which is known as Minimum Miscibility Pressure (MMP) must be achieved. MMP is a function of reservoir temperature, oil composition, and CO<sub>2</sub> impurities [2].

Currently, there are a few problems with CO<sub>2</sub> flooding which is high MMP, gravity override, and viscous fingering phenomenon [3]. In Malaysia, the typical MMP for CO<sub>2</sub>-crude oil ranges from 2300psi to 4380psi [4] where MMP above 2000psi is considered high. High MMP caused the oil in some reservoirs unable to be recovered due to impracticality and lack of economic feasibility [5].

C. L. Voon is a master Candidate at Universiti Teknologi PETRONAS, 31750 Tronoh, Perak, Malaysia (phone: +6016-875 8393; email: choonlin.voon@gmail.com).

M. Awang is a professor and MOR EOR director at Universiti Teknologi PETRONAS, 31750 Tronoh, Perak, Malaysia (e-mail: mariyamni\_awang@petronas.com.my).

This research focuses on lowering the MMP using oleophilic chemicals. Oleophilic chemicals that are shortlisted are semi-polar, which includes alcohol where its hydroxyl group is polar while the hydrocarbon chain is non-polar [6]. Crude oil and CO<sub>2</sub> are non-polar and are miscible with the hydrocarbon chain of alcohol. This could be easily explained using the theory of "Like Dissolve Like" [7]. Apart from that, due to the unique structure of oleophilic chemicals, they are able to lower CO<sub>2</sub>-crude oil MMP by enhancing the solvating power and polarity of CO<sub>2</sub> caused by formation of special interaction between solute and co-solvent molecules [5].

Having said all that, this research represents a possible solution to decrease the operating cost of miscible CO<sub>2</sub>EOR by adding oleophilic additives. One of the recent breakthroughs in this field is the application of alcohol with CO<sub>2</sub> to lower CO<sub>2</sub>-crude oil MMP [5]. Hence, this research might even open new doors of possibilities by offering alternatives to alcohol to reduce CO<sub>2</sub>-crude oil miscibility. More oil could be recovered to fulfil world oil demand by using these additives in CO<sub>2</sub>EOR.

The problem with CO<sub>2</sub> is that it has no polarity and do not have the ability to form specific solvent-solute interactions in order to be miscible. The CO<sub>2</sub>-crude oil MMP would be very high which would be expensive to operate and may cause formation fracture [8], [9]. This, however, could be solved using oleophilic chemicals.

The CO<sub>2</sub>-crude oil MMP is measured using VIT where the MMP is estimated by extrapolation of the line until IFT=0 and the corresponding pressure would be the MMP. The procedure is repeated by injecting carboxylic acid, alcohol, and ketone with CO<sub>2</sub>. Another technique used in this research is slim-tube test. The principle behind both VIT and slim-tube test are different however the change in MMP with addition of oleophilic chemicals should be the same. The chemical with the highest polarity is expected to reduce the MMP the most [5].

This research would be valuable in the field of miscible CO<sub>2</sub> displacement by having more alternative chemicals to decrease CO<sub>2</sub>-crude oil MMP. The best chemical functional group can be used in future research to understand more about them.

The objectives that are aimed to be achieved are as follow:

- Investigate the ability of oleophilic chemicals to lower CO<sub>2</sub>-crude oil MMP.
- Comparison of different functional group in effectiveness in lowering CO<sub>2</sub>-crude oil MMP.
- Modify existing correlations to predict MMP based on the oleophilic chemicals added.

In the research, the scope of the chemicals is narrowed

down to carboxylic acid, alcohol, and ketone.

Most Malaysian fields are already in the mature stage and require EOR to maintain production. One of the promising EOR techniques would be miscible  $\text{CO}_2$  displacement and oleophilic chemicals can lower the MMP, making miscible  $\text{CO}_2$  displacement method much more economically feasible.

## II. MATERIALS AND METHODS

### A. Material

Oil: Dulang crude oil, medium synthetic oil, and heavy synthetic oil. Dulang crude oil is selected to observe oleophilic chemicals' effect on  $\text{CO}_2$ -crude oil MMP. Besides that, medium and heavy synthetic oil is to see the effect of oil composition on oleophilic chemicals' effectiveness in lowering MMP.

Gas: Carbon Dioxide. Carbon dioxide with purity of 99.99% is used to eliminate any other external factors that might affect the result of the experiment.

### B. Methods

#### Vanishing Interfacial Tension (VIT)

The interfacial tension between the oil,  $\text{CO}_2$ , and oleophilic chemicals are measured at various pressures. At each point, the interfacial tension between the oil and  $\text{CO}_2$  is measured. The pressure is then increased and measured continuously until the interfacial tension is zero. The final pressure would be the MMP of crude oil- $\text{CO}_2$ . The test would be conducted at  $100^\circ\text{C}$ , similar to the reservoir temperature of Dulang.

#### Slim-tube Test

The crude oil is pumped into the slim tube which acts like a core, followed with the displacement of oil using carbon dioxide. The experiment runs at various pressures and the oil recovered is recorded. Then, a graph with percentage recovery versus pressure is drawn to find the MMP. This test would also be conducted at  $100^\circ\text{C}$ .

## III. RESULTS AND DISCUSSION

### A. Initial Measurements

The first phase of the experiment involves the measurement of  $\text{CO}_2$ -crude oil MMP with alcohol using VIT. Concentration of 2.5%, 5.0%, and 10.0% of alcohol is added to observe their impact on MMP.

ALFOL 1214, ISO FOL 12, ISO FOL 16, ISO FOL 28, LIAL 123A, LIAL 167, and Marlupal 013 were selected for initial testing in reduction of  $\text{CO}_2$ -crude oil MMP. All these alcohols are just brand names and they are mixtures of various straight or branched alcohol. Test results shows that by introducing oleophilic chemicals into the system, the MMP is significantly reduced as shown in Figs 1-3. However, it is also found that increase of concentration has no clear trends in either increasing or decreasing the MMP as shown in Fig. 4.

Based on the knowledge in this early stage of the study, the next phase of the research would include various functional

groups to understand the relationship between polarity and reduction of MMP.

## IV. CONCLUSION

Important findings from early study include:

1. The introduction of oleophilic chemicals into crude oil- $\text{CO}_2$  system reduces the MMP.
2. The change in concentration of oleophilic chemicals does not have a clear effect on the MMP.

### APPENDIX

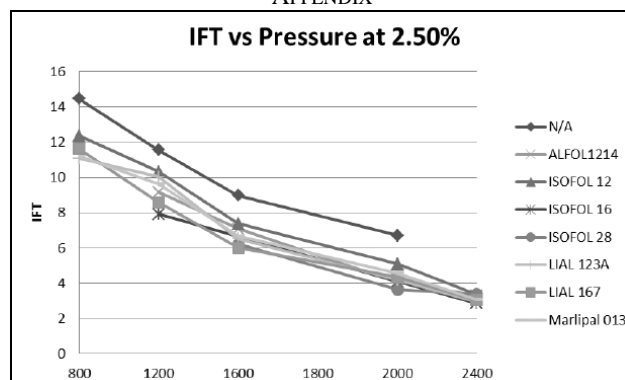


Fig. 1 Result of VIT at concentration of 2.50%

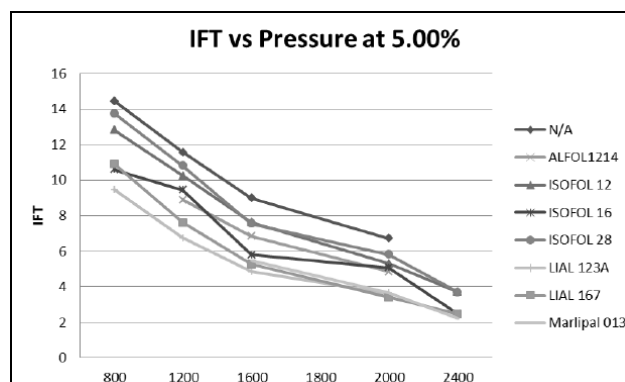


Fig. 2 Result of VIT at concentration of 5.00%

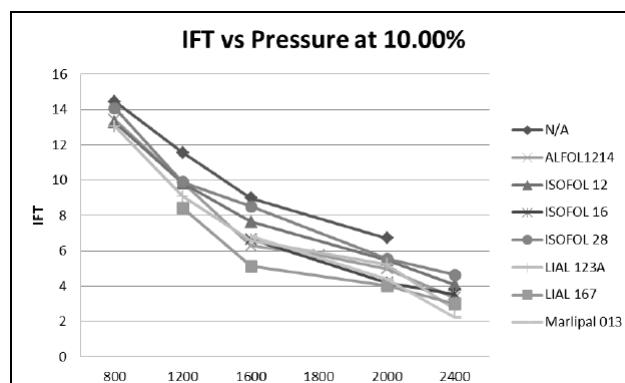


Fig. 3 Result of VIT at concentration of 10.00%

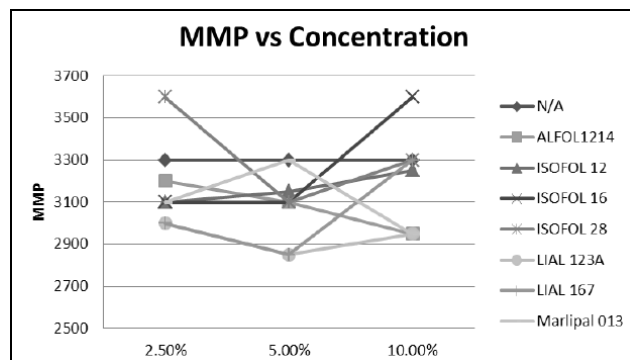


Fig. 4 Change in MMP with different concentration

#### ACKNOWLEDGMENT

The author would like to thank Universiti Teknologi PETRONAS for the equipment provided and extend gratitude to Ministry of Higher Education of Malaysia for their financial support on this project via MyRA Grant.

#### REFERENCES

- [1] Wu, Y., et al., *A Study of Branched Alcohol Propoxylate Sulfate Surfactants for Improved Oil Recovery*. Society of Petroleum Engineers.
- [2] Ahmed, T., *Minimum Miscibility Pressure from EOS*. Petroleum Society of Canada.
- [3] Gardner, J.W. and J.G.J. Ypma, *An Investigation of Phase Behavior-Macroscopic Bypassing Interaction in CO<sub>2</sub> Flooding*.
- [4] Hui, L.H., *Penganggaran dan penentuan MMP CO<sub>2</sub> untuk lapangan minyak Malaysia*, in *Petroleum Engineering*. 1995, Universiti Teknologi Malaysia: Skudai, Johor, Malaysia.
- [5] Djabbarah, N.F., *Miscible oil recovery process using carbon dioxide and alcohol*. 1990, Google Patents.
- [6] Li, Q., et al., *Solubility of solid solutes in supercritical carbon dioxide with and without cosolvents*. *Fluid Phase Equilibria*, 2003. **207**(1-2): p. 183-192.
- [7] Montes, I., C. Lai, and D. Sanabria, *Like Dissolves Like: A Guided Inquiry Experiment for Organic Chemistry*. *Journal of Chemical Education*, 2003. **80**(4): p. 447.
- [8] Jarrell, P.M. and S.o.P. Engineers, *Practical Aspects of CO<sub>2</sub> Flooding*. 2002: Society of Petroleum Engineers.
- [9] Martin, D.F. and J.J. Taber, *Carbon Dioxide Flooding*.