

Co-Injection of Carbon Dioxide and Non-Polar Chemical Modifiers using Micro-model System at Immiscible Conditions for Enhancing Oil Recovery

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ABSTRACT In order to improve extraction capability of carbon dioxide (CO₂) in the chemistry industry, a joint application of supercritical CO₂ with some chemical modifiers such as alcohols is usually employed. Polar chemical modifiers such as methanol, is well known for its capability in extracting polar components of crude oil such as asphaltic. Most of the components in crude oils are, however, non-polar. This paper investigates the influence of non-polar chemical modifiers' addition with CO₂ on improving the crude oil extraction at immiscible conditions by using a micro-model system. From the experiments, it was found that extraction of crude oil improved with the addition of non-polar solvent with the highest oil recovery of 52.54% achieved by co-injection of gaseous CO₂ and toluene, as compared to oil recovery of 27.4% by gaseous CO₂ alone after 20 Pore Volume Injected (PVI).

KEYWORDS: carbon dioxide; non-polar chemical modifiers; micro-model system; immiscible condition; enhanced oil recovery

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INTRODUCTION

In the face of declining oil production and at a time where recovering hydrocarbon is becoming more difficult, effective techniques is the key in recovering more oils in a mature oilfield. The average oil recovery of mature oilfields around the world is estimated to be somewhere between 20 to 40% (US Department of Energy, 2006; Sandrea, 2007 ; International Energy Agency, 2008) leading to large amount of discovered oil to be left behind in the reservoir despite the existing production well.

It has been estimated that only one third of the original oil in-place (OOIP) is produced by the traditional primary and secondary oil recovery stages in a conventional oil field (Alagorni, Yaacob, and Nour, 2015), with only around 5 to 15% of oil in the reservoir extracted at the primary oil recovery stage and additional 30% of the oil in the well reserve can be extracted at the secondary oil recovery stage (Petro Online, 2014).

By applying EOR process, oil production in a conventional oil well could reach up to 40 to 60% of oil in the reservoir (Alagorni, Yaacob, and Nour, 2015). Hence, there has been more emphasis, in the recent years, with the different methods used on optimizing the recovery of crude oil by using the final oil recovery stage, the EOR stage, to extract more of the original in-place oil left in the oil reservoirs (Donaldson, Chilingarian, and Yen 1989; Romero-Zeron 2012; Akintunji *et al.* 2013; Alagorni, Yaacob, and Nour 2015).

CO₂ has been used for decades in enhanced oil recovery (EOR) to liberate residual oil, including water-alternating-gas (WAG) operations (Sohrabi *et al.*, 2004; Dijke *et al.*, 2010; Robin *et al.*, 2012). It

has been approximated that CO₂ flooding would produce an additional 7 to 15% of the initial oil in place (Mathiassen, 2003).

In order to improve extraction capability of CO₂, in the chemistry industry, joint application of supercritical CO₂ with some chemical modifiers such as alcohols is usually employed. Polar chemical modifiers such as methanol, is well known for its capability in extracting polar components of crude oil such as asphaltic. However, most of the components in crude oils are non-polar, so there is a possibility for the significant influence of the addition of non-polar chemical modifiers with CO₂ on improving the extraction capability of CO₂ with crude oil, with regards to the solvents rule of 'like dissolves like', where polar solvents would dissolve polar solutes, and vice versa (Dobbs *et al.*, 1986). In previous studies, it was found that CO₂ extraction accompanied with chemical modifiers can yield crude oil extracts almost 3 times over the CO₂ extraction only (Hwang and Ortiz, 2000).

CO₂ can either be totally or partially miscible with crude oil in an oil reservoir at certain temperature and pressure. In theory, miscibility between CO₂ and crude oil increases while pressure increases. The miscibility of CO₂ with crude oil would lead to expansion of crude oil volume, decrease of crude oil density and reduction of crude oil viscosity. As a result, recovery of crude oil can be improved greatly (Al-Netaifi, 2008).

However, not all oilfields are operating at miscible condition. In Malaysia, the minimum miscible pressure (MMP) for crude oil-CO₂ system in the oil reservoirs, is in the range of approximately 2300 psi to 4380 psi (Hui, 1995) which is equivalent to 158 bar to 300 bar. On the other hand, the critical pressure and temperature of CO₂ where CO₂ would be in supercritical phase is 73.9 bar and 31.0°C, respectively (Wikipedia, 2018). Similarly, not all reservoirs are able to maintain CO₂ in supercritical phase as it requires reservoir pressure to be at least 73.9 bar and has to be operating at temperature of at least 31°C.

Thus, in this paper, enhanced oil recovery technique of non-polar chemical modifiers assisted-CO₂ injection where CO₂ was in gaseous phase was studied in detail by using a micromodel system at immiscible conditions.

Research on the utilization of non-polar chemical modifiers in carbon dioxide injection for enhanced oil recovery has not been done yet by any other researchers by using a micro-model system, and in this paper, the utilization of nonpolar chemical modifiers in carbon dioxide injection for enhanced oil recovery can be studied in great detail at the pore scale. This is important because the flow on the pore scale decides the large scale flow patterns in the oil reservoirs, and thus by optimizing oil recovery at the pore scale in this research, the ultimate oil recovery can be achieved.

The findings of this paper will indicate the possibility of implementing this technique in Malaysian oil reservoirs.

BACKGROUND THEORY

Oil Recovery

Oil recoveries were analyzed by the method of image analysis using Adobe Photoshop CC 2017 software.

During co-injection of CO₂ and non-polar chemical modifiers, at the experimental temperature of 25°C and pressure of 20 bar, with flow rate of 3 ml/min, time lapse images were captured by camera in video mode, until 20 Pore Volume Injected (PVI) was achieved.

The Adobe Photoshop CC 2017 software was then used to differentiate the colours from the images captured by contrasting the colours in the image. The software also counted the pixels of the colour and displays the sum of counts, which were used for calculating oil saturation and oil recovery.

The following is the formula for calculating oil saturation:

$$S_o = \frac{A_o}{A_o + A_c} \quad (1)$$

where, S_o is saturation of oil, A_o is area of oil and A_c is area of CO₂ or chemicals.

The formula for calculating final oil recovery is as follows:

$$\text{Oil recovery} = \frac{S_I - S_F}{S_I} \quad (2)$$

where, S_I is initial oil saturation and S_F is final oil saturation.

METHODOLOGY

Materials

The 99.99% purified CO₂ gas was supplied by Linde Malaysia Sdn. Bhd. Toluene, dimethyl carbonate (DMC), and diethyl carbonate (DEC) were analytically pure and supplied by Merck & Co. The dewatered, degassed and stabilized crude oil was supplied by PETRONAS with API Gravity Value of 36.5 (light crude).

Apparatus description

The experiments were carried out by using a micromodel system as shown in Figure 1 fabricated by Dixon Engineering Company.



Figure 1. Micro-model system in the UMS laboratory.

The system comprised of micromodel reactor, high pressure injection pump, accumulator, motors, storage tank, gas booster, pressure indicator, and heater as shown in the Piping and Instrumentation Diagram (P&ID) in **Figure 2**. It was controlled by using an online system which was accessed by using a personalized Lenovo laptop with Indusoft software and licence. Pressure, temperature and flow rate in the system was monitored and controlled using the online system.

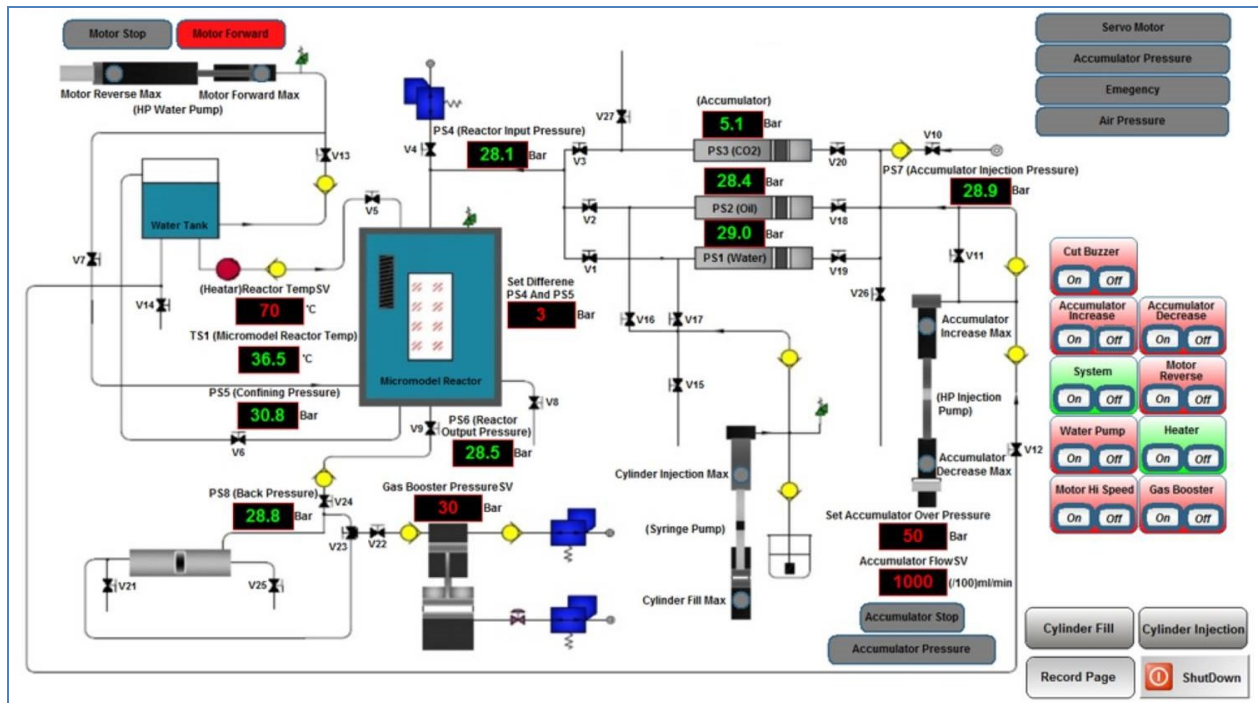


Figure 2. P&ID of the micromodel system.

The micro model system in Universiti Malaysia Sabah (UMS) laboratory was constructed with a combination of different type of materials with the construction techniques of glass core sample developed by Hornbrook *et. al.* (1991). It is suitable for experimental study of flow in porous media at the pore scale, the smallest scale relevant to petroleum recovery. The glass core sample used contains enclosed pore networks where flow can be observed visually using a camera or microscope, making it possible to study how pore scale events affect flow patterns and displacement efficiency at larger scales.

The glass core sample used in the experiment has the length of 22.9 cm, width of 9 cm, pore volume of 0.799 cm³ and porosity of 40.1%, and is shown in Figure 3.



Figure 3. Glass core sample used in the experiment.

The camera used for recording time lapse images was a Panasonic Lumix Camera (Model No. DMC-GM1K) high-definition colour camera and was installed about 1 feet above the micro model reactor. It is a 16-megapixel Digital camera that can capture images of up to 4592 x 3448 pixels with 16 bit RGB pixel depth and a capture rate of 1 frame per second could be achieved during image sequence capturing for images of 1280 x 960 pixels with 8bit RGB pixel depth.

Experimental procedure

Three different non-polar chemical modifiers which were toluene, and dimethyl carbonate (DMC), diethyl carbonate (DEC) were tested in the experiments. To differentiate the colours between crude oil and chemical modifiers during experiment, crude oil was dyed red using Sudan red dye, while the chemical modifiers were dyed blue with blue coloured oil-based dye.

The experiments were conducted at immiscible pressure of 20 bar and at ambient temperature of 25°C, where the CO₂ was in gaseous phase.

As a controlled variable in the experiment, a test of flooding of CO₂ gas only was conducted. Initially, in the experiment, crude oil was flooded at the flow rate of 3ml/min, until fully saturated and fully occupied the glass core sample. Subsequently, the injection for the crude oil was stopped. Gaseous CO₂ was then injected into the glass core sample at the rate of 3ml/min until 20 PVI of CO₂ was reached which was approximately 16 cm³ or 16 ml in volume, as 1 pore volume is equivalent to 0.8mL.

For the test of co-injection of CO₂ gas with the non-polar chemical modifiers, the same procedure as the above were carried out except that gaseous CO₂ was injected simultaneously with chemical modifier, into the glass core sample at the rate of 3ml/min until 20 PVI of CO₂ and chemical modifier was reached.

For each test, the experiments were repeated two times, to get a precise value from the experiments.

Image processing procedures

The procedures for image processing are given below:

- i. Image selection: File-Open
- ii. Colour Adjustment: Image-Adjustments-Brightness/Contrast-Adjust contrast to 100.
- iii. Colour range selection: Select-Colour Range-Select the colour on the image
- iv. Pixel count measurement: Image-Analysis-Record Measurements

An example of the image analysis process is discussed in detail below:

Firstly, image to be analyzed is shown in Figure 4, which is the image of the glass after co-injection of CO₂ and toluene. After going through step i and ii in the above procedure, step iii, which is selection of red and blue coloured area is carried out as shown in Figure 5 and Figure 6, respectively.

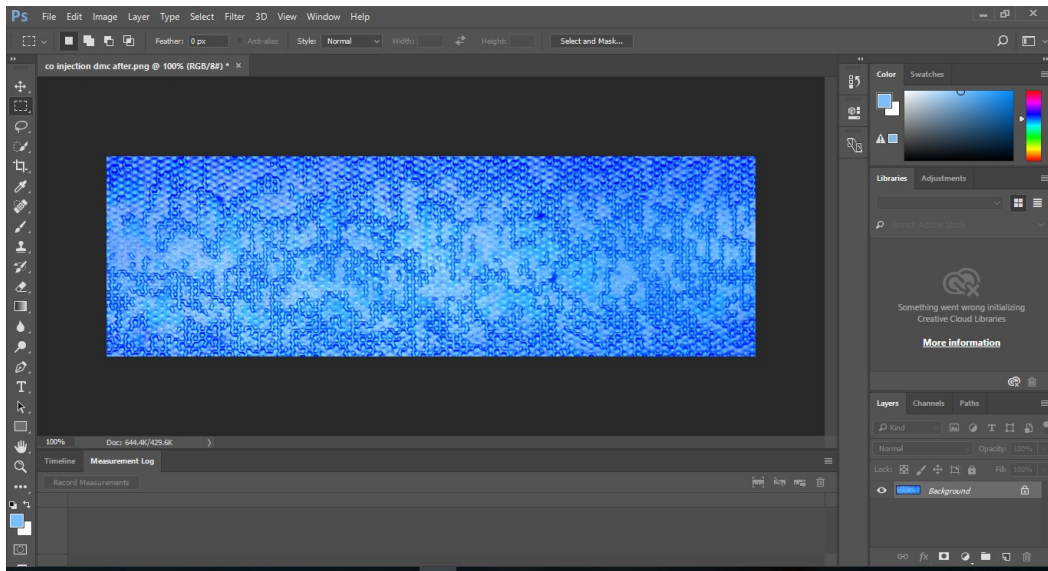


Figure 4. Image of glass core sample after co-injection of toluene and CO₂ in Photoshop software.

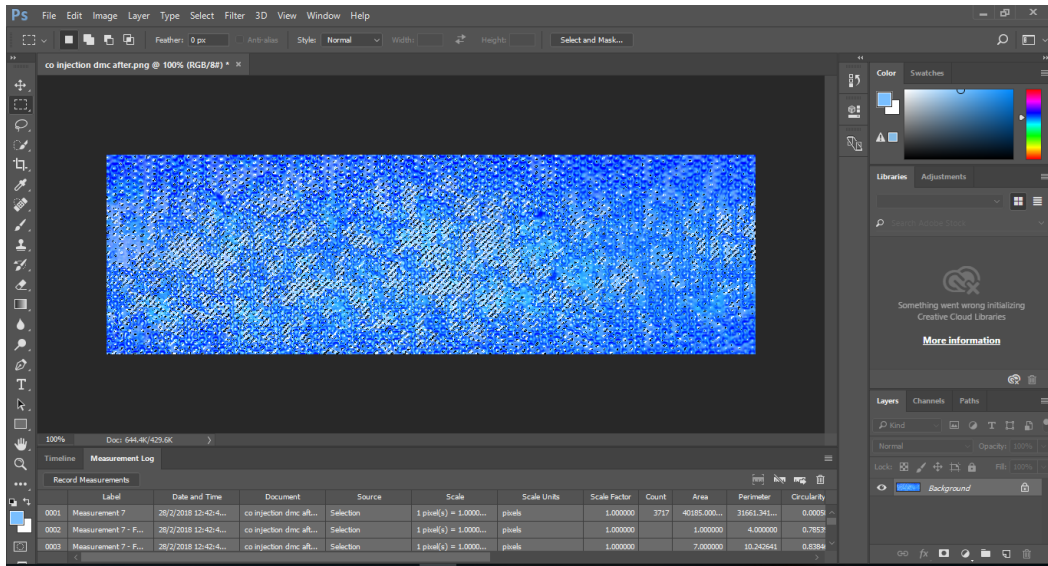


Figure 5. Selection of red-coloured area in the image representing crude oil area.

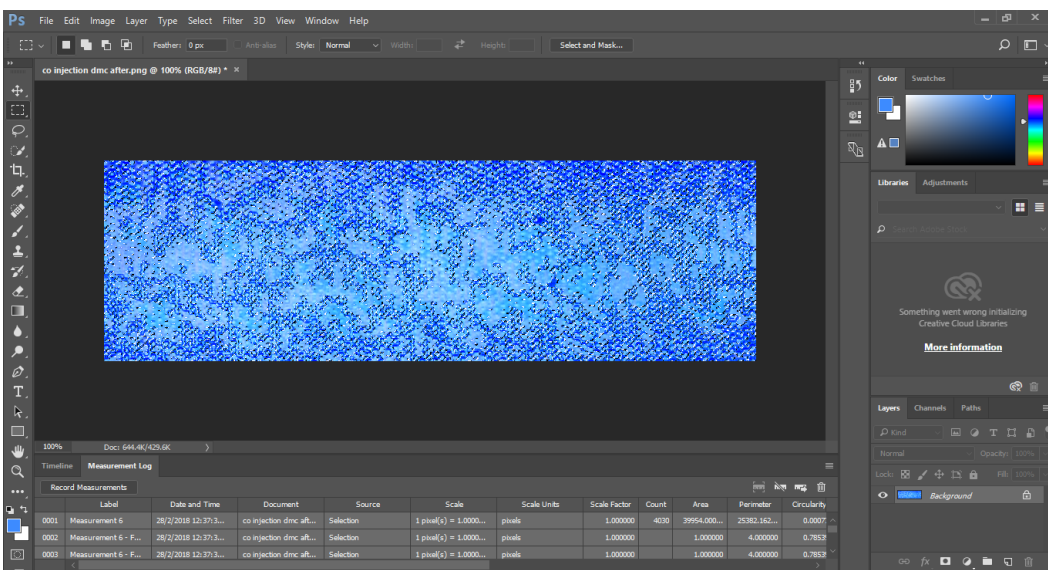


Figure 6. Selection of blue-coloured area in the image representing CO₂ and toluene.

Using equation (1) and using the values of pixel count from the software, the saturation of crude oil and other fluids can be calculated and plotted as shown in **Figure 7**, which is fluid saturation graph for the test of flooding of CO₂ gas only.

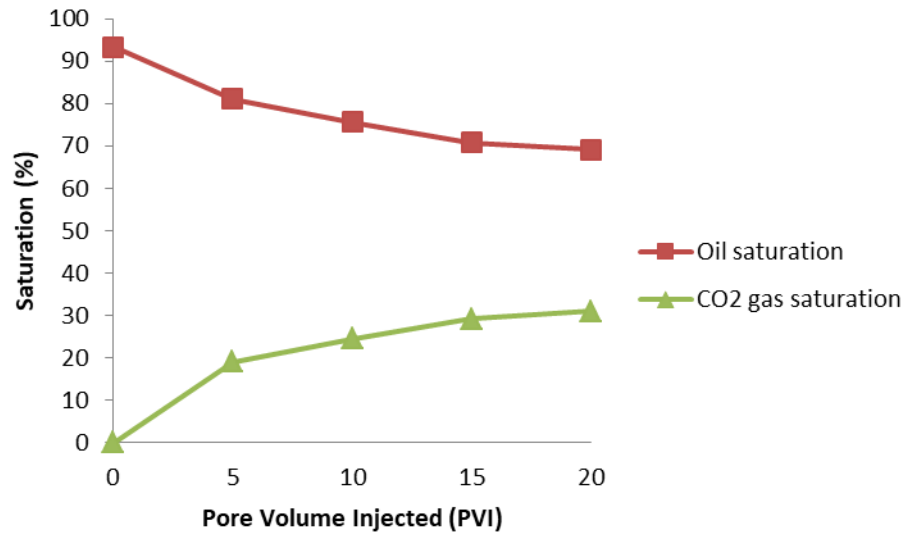


Figure 7. Plot of oil saturation and CO₂ gas saturation (%) against pore volume injected (PVI)

Finally, using the saturation value of crude oil from previous step as well as initial saturation value of the crude oil before the CO₂ flooding was carried out, using equation (2), oil recovery can be calculated and plotted as shown in Figure 8.

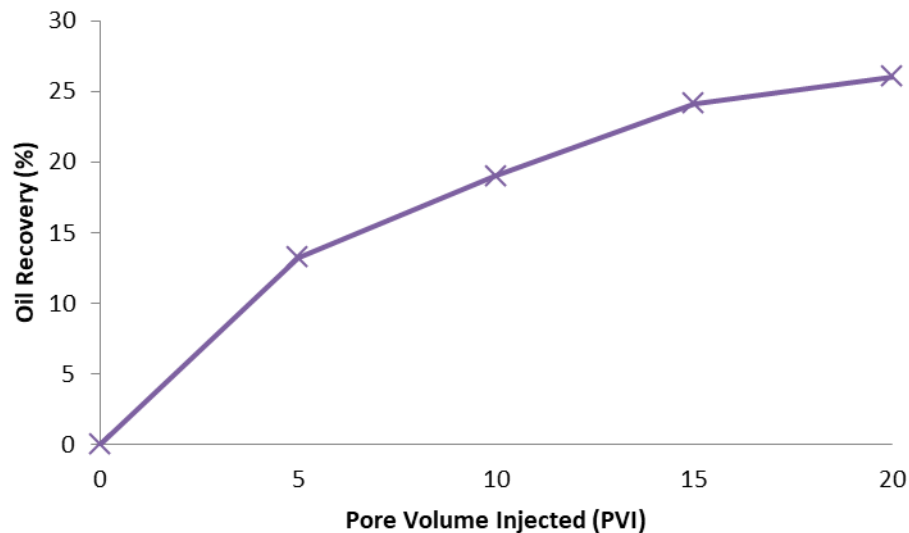


Figure 8. Graph of oil recovery (%) against pore volume injected (PVI) for flooding of CO₂ gas only.

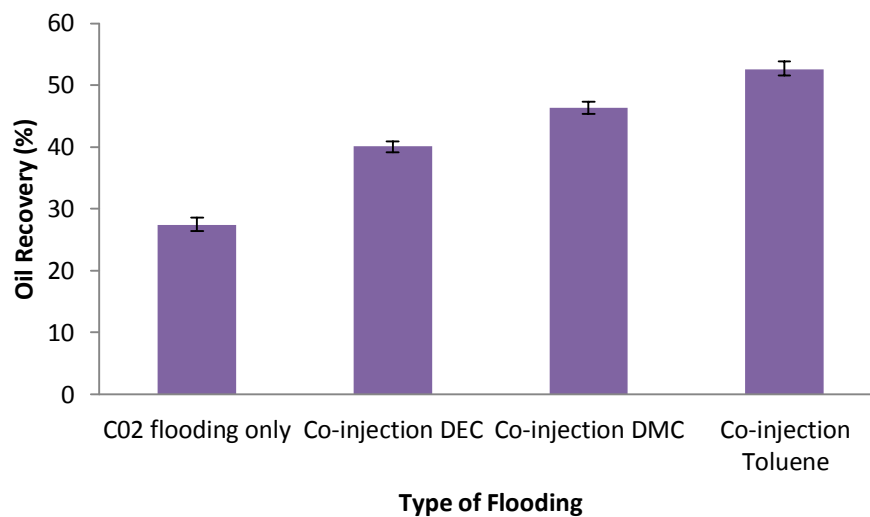
RESULTS AND DISCUSSION

The results of the different EOR flooding types and the final oil recovery after 20 PVI are shown in Table 1.

Table 1. Table of oil recovery (%) of different types of flooding.

Type of EOR flooding	Oil Recovery (%)			Average Value (Mean)	Standard Deviation
	Test 1	Test 2	Test 3		
CO ₂ flooding only	26.05	28.86	27.29	27.40	1.15
Co-injection DEC	41.12	39.97	39.36	40.15	0.73
Co-injection DMC	45.26	47.61	46.12	46.33	0.97
Co-injection Toluene	51.13	54.40	52.10	52.54	1.37

From the result in Table 1, a graph of oil recovery of the different types of flooding was plotted as shown in Figure 9.

**Figure 9.** Graph of oil recovery (%) of different types of EOR flooding.

In this result, it can be seen that the flooding tests of co-injection of non-polar chemical modifiers with CO₂ significantly improves oil recovery as compared to flooding of CO₂ gas alone as shown in the graph Figure 9.

The highest oil recovery of 52.54% was achieved by co-injection of CO₂ and toluene, followed by co-injection of DMC with CO₂ with oil recovery of 46.33% and co-injection of DEC with CO₂ with oil recovery of 40.15%, with the lowest oil recovery of 27.4% by flooding of CO₂ gas alone.

Co-injection of CO₂ with toluene yielded the highest oil recovery as compared to the other chemical modifiers. This is probably due to the ability of toluene in improving the miscibility of crude oil and CO₂ is considered best as compared to the other chemicals. This finding is consistent with the research by Yang *et al.* (2016) where toluene showed the best ability of improving the miscibility of crude oil and CO₂ by having the highest vaporization-enhancing indicator (VI) and solubilization-enhancing indicator (SI) values as compared to other chemicals, as can be seen in Table 2, which was the same chemicals used in this research, by using a pressure-volume-temperature (PVT) phase equilibrium device.

Table 2. Vaporization-enhancing indicator (VI) and solubilization-enhancing indicator (SI) values of different chemical modifiers from Yang *et al.* (2016).

Name of chemical	VI (%)	SI (%)
Toluene	251.0	64
DMC	7.6	4.6
DEC	4.0	3.1

Although the tests were done at immiscible conditions with the experimental pressure of 20 bar and at ambient temperature, 25°C, it can be seen that oil recovery significantly improved as compared to injection of CO₂ gas alone. This indicates that there is a possibility for the co-injection flooding of non-polar chemical modifiers and CO₂ to show promising result if being implemented in the existing Malaysian oil reservoirs operating at immiscible conditions as EOR's effort in retrieving more crude oil.

It can also be speculated that at miscible conditions where supercritical CO₂ and MMP of CO₂-crude oil system can be maintained, the co-injection flooding of non-polar chemical modifiers and CO₂ will show a significantly better result due to the improved miscibility of CO₂, crude oil and non-polar chemical modifiers (Dobbs, Wong, and Johnston 1986; Hwang and Ortiz 2000; Yang *et al.* 2016).

CONCLUSION

In conclusion, the co-injection of CO₂ and non-polar chemical modifiers significantly improves oil recovery with the highest oil recovery of 52.54% achieved by co-injection of gaseous CO₂ and toluene, as compared to oil recovery of 27.4% by gaseous CO₂ alone after 20 Pore Volume Injected (PVI) at immiscible conditions using a micro-model system.

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REFERENCES

- [1] Akintunji, Folami, Tor Austad, Lewis Brown, Harry L. Chang, Birol Dindoruk, Bradley Govreau, Russell T. Johns, et al. 2013. "Contributors." In *Enhanced Oil Recovery Field Case Studies*, xxi. Boston: Gulf Professional Publishing. <https://www.sciencedirect.com/science/article/pii/B9780123865458000300>.
- [2] Alagorni, H. Abubaker, Zulkefli Bin Yaacob, and Abdurahman H. Nour. 2015. "An Overview of Oil Production Stages: Enhanced Oil Recovery Techniques and Nitrogen Injection." *International Journal of Environmental Science and Development* 6 (9): 693–701. <https://doi.org/10.7763/IJESD.2015.V6.682>.
- [3] Al-Netaifi, Ali Suleman. 2008. "Experimental Investigation of CO₂-Miscible Oil Recovery at Different Conditions." MasterThesis. King Saud University, Saudi Arabia.

http://fac.ksu.edu.sa/sites/default/files/experimental_investigation_of_co2_-_miscible_oil_recovery_at_different_conditions.pdf.

- [4] Dijke, Van, Marinus I.j, Morten Lorentzen, Mehran Sohrabi, and Kenneth S. Sorbie. 2010. "Pore-Scale Simulation of WAG Floods in Mixed-Wet Micromodels." *SPE Journal* 15 (1): 238–47. <https://doi.org/10.2118/113864-PA>.
- [5] Dobbs, Joseph M., Joseph M. Wong, and Keith P. Johnston. 1986. "Nonpolar Co-Solvents for Solubility Enhancement in Supercritical Fluid Carbon Dioxide." *Journal of Chemical & Engineering Data* 31 (3): 303–8. <https://doi.org/10.1021/je00045a014>.
- [6] Donaldson, E.C., G.V. Chilingarian, and T.F. Yen. 1989. *Enhanced Oil Recovery, II*. 1st ed. Vol. 17B. Elsevier Science. <https://www.elsevier.com/books/enhanced-oil-recovery-ii/donaldson/978-0-444-42933-9>.
- [7] Hornbrook, J. W., L. M. Castanier, and P. A. Pettit. 1991. "Observation of Foam/Oil Interactions in a New, High-Resolution Micromodel." In . Society of Petroleum Engineers. <https://doi.org/10.2118/22631-MS>.
- [8] Hui, H.L. 1995. "Penganggaran Dan Penentuan MMP CO2 Untuk Lapangan Minyak Malaysia." Master's Thesis, Petroleum Engineering, UTM, Malaysia.
- [9] Hwang, R. J, and J Ortiz. 2000. "Mitigation of Asphaltics Deposition during CO2 Flood by Enhancing CO2 Solvency with Chemical Modifiers." *Organic Geochemistry* 31 (12): 1451–62. [https://doi.org/10.1016/S0146-6380\(00\)00082-6](https://doi.org/10.1016/S0146-6380(00)00082-6).
- [10] International Energy Agency. 2008. *World Energy Outlook*. Paris, France. <https://www.iea.org/media/weowebiste/2008-1994/WEO2008.pdf>.
- [11] Mathiassen, Odd Magne. 2003. "CO2 as Injection Gas for Enhanced Oil Recovery." Master's Thesis. Norwegian University of Science and Technology.
- [12] *Petro Online*. 2014. "What Is the Difference between Primary, Secondary & Enhanced Recovery for Oil Extraction?," August 26, 2014.
- [13] Robin, Michel, Varvara Sygouni, and Jolle Behot. 2012. "CO2 Injection in Porous Media : Observations Un Glass Micromodels Under Reservoir Conditions (PDF Download Available)." In *SPE 154165-PP*. Tulsa, Oklahoma. <https://doi.org/10.2118/154165-MS>.
- [14] Romero-Zeron, Laura B. 2012. "Advances in Enhanced Oil Recovery Processes, Introduction to Enhanced Oil Recovery (EOR) Processes and Bioremediation of Oil-Contaminated Sites." In *InTech*, 43. <http://www.intechopen.com/books/introduction-to-enhanced-oil-recovery-eor-processes-and-bioremediation-of-oil-contaminated-sites/advances-in-enhanced-oil-recovery>.
- [15] Sandrea, I. 2007. "Recovery Factors Leave Vast Target for EOR Technologies." *Oil & Gas Journal*, no. 105: 44–47.
- [16] Sohrabi, M., D. H. Tehrani, A. Danesh, and G. D. Henderson. 2004. "Visualization of Oil Recovery by Water-Alternating-Gas Injection Using High-Pressure Micromodels." *SPE Journal* 9 (3): 290–301. <https://doi.org/10.2118/89000-PA>.
- [17] "Supercritical Carbon Dioxide." 2018. *Wikipedia*. https://en.wikipedia.org/w/index.php?title=Supercritical_carbon_dioxide&oldid=828544076.
- [18] US Department of Energy. 2006. "Undeveloped Domestic Oil Resources: The Foundation for Increased Oil Production and a Viable Domestic Oil Industry." Advanced Resources International. http://www.fossil.energy.gov/programs/oilgas/publications/eor_co2/Undeveloped_Oil_Document.pdf.
- [19] Yang, Yong, Xiangliang Li, Ping Guo, Yayun Zhuo, and Yong Sha. 2016. "Improving Oil Recovery in the CO2 Flooding Process by Utilizing Nonpolar Chemical Modifiers." *Chinese Journal of Chemical Engineering* 24 (5): 646–50. <https://doi.org/10.1016/j.cjche.2015.12.002>.