

Experimental and Theoretical Investigation of the CO₂ Minimum Miscibility Pressure for the Omani Oils for CO₂ Injection EOR Method

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Abstract—In Oman there are still large remaining oil reserves that require implementation of Enhanced Oil Recovery processes such as CO₂ injection, for light oil.

CO₂-Oil Minimum Miscibility Pressure (MMP) is the key parameter for the design and operations of successful CO₂ flood. This study is based on developing a method of calculating the MMP for Omani oil reservoirs. Part-1 of the study is the experimental work based on the Rising Bubble Apparatus (RBA) measurement of MMP and part-2 is the examination of the existing models for MMP predictions and the adjustment of parameters for obtaining the most accurate predictions by the equation of state fluid PVT modeling simulator PVTPro5.2.1 software.

The RBA system set-up was successfully developed for the first time at Sultan Qaboos University. CO₂ MMP measurements were carried out for three different oil samples using the RBA. For the RBA experiments, the PVTPro5.2.1 simulator was used to adjust the best setting parameters for CO₂ MMP predictions. Very good agreement between the experimental MMP and the software predictions were achieved within the range of 2.27% error maximum. Moreover, some existing well-known models have been examined for CO₂-Oil MMP predictions with the observed errors of up to 43.55%.

Index Terms—CO₂ injection, Equation of state simulator software, Minimum Miscibility Pressure, and Rising Bubble Apparatus

I. INTRODUCTION

Oil reservoirs in the Sultanate of Oman; have currently been developed mostly by either primary or secondary recovery methods. However, there are still large remaining oil reserves that require implementation of the technically more challenging applications such as Enhanced Oil Recovery (EOR) processes. One EOR method, for light oil, that has proven success in different parts of the world is CO₂ injection.

Determining CO₂-Oil Minimum Miscibility Pressure (MMP) is the key parameter for the design and operations of successful CO₂ miscible flood project. This research study is based on developing a method of calculating the CO₂-Oil MMP for different Omani oil reservoirs. The study involves experimental work by using the Rising Bubble Apparatus (RBA) to measure the CO₂-Oil MMP for different Omani Oils and determining, from the existing literature, a mathematical model for predicting CO₂-Oil MMP based on the obtained CO₂-Oil MMP experimental results.

II. LITERATURE REVIEW

Enhanced Oil Recovery is the oil recovery method at which stage is applied to the depleted oil reservoir after secondary recovery that either involves waterflooding or gas injection [1]. The EOR methods can be classified by three main categories chemical, thermal, and Miscible.

Given Oman challenges of increasing oil production levels, CO₂ injection could be a plausible solution providing sources of additional oil production. CO₂ injection is intended to reduce residual oil saturations after all secondary oil displacement processes have been exhausted. Miscible CO₂ injection would contribute towards more oil reserves and maintain production levels for years to come.

The first CO₂-EOR application was patented in 1952 for Whorton, Brownscombe, and Dyes of Atlantis Refining Company [2]. The field application was first tested in 1964 at the Mead Strawn Field in the U.S.A [2]. The results showed that 53% to 82% of incremental oil was produced by CO₂ flooding. The main reasons behind the high ultimate oil recovery are the low CO₂-oil single phase viscosity and low surface tension of miscible CO₂-Oil fluids that are more easily displaced.

In 1986, Christiansen and Kim [3] invented the rising bubble apparatus (RBA). The Minimum miscibility pressure is determined by observing the configuration of the gas bubble as it rises through an oil column at different pressure levels at a given temperature. The bubble rises through the oil column confined in a glass tube.

In the literature review CO₂-Oil system MMP correlations are available for pure and impure CO₂ gas. Those correlations are based on a unique set of oil reservoir conditions. As it is well known that CO₂-Oil system MMP greatly depends on the CO₂ purity, reservoir oil composition, and reservoir temperature and pressure. Thus, using the CO₂-Oil system MMP correlations from the literature for the Omani oil reservoirs can lead to an invalid estimate of MMP. Accurate estimation of MMP is vital in the CO₂ flooding project. In case of using a high operating CO₂ injection pressure based a highly estimated MMP, can lead to over inflated operation or facility costs and HSE (health, safety, and environment) issues.

The first attempt to develop a correlation for reservoir oil fluid and rich gas to predict the MMP, was in 1960 by Benham, A. L. [4]. This correlation was developed by Benham, A. L., Dowden, W. E., and Kunzman, W. J to predict the approximate miscible condition for the displacement of reservoir fluid by rich gas for the pressure range of 3447 kPa to 20684 kPa and temperature range of 70 °F and 260 °F. This correlation involved using pseudo ternary

diagrams with limiting tie in lines for various reservoir fluid and rich gas mixtures.

In 1964 R. Simon and D. J. Graue developed correlations for predicting the solubility, swelling and viscosity behavior of CO₂-Oil systems [5]. The correlations were based on experimental data obtained by the authors for nine different oils. The experiments conditions for the CO₂-Oil mixtures covered the pressure of up to 15858 kPa and a temperature range of 100 °F and 250 °F.

III. CO₂ GAS PROPERTIES

Carbon Dioxide (CO₂) is one of the leading solvents for miscible EOR methods. Other solvents such as; N₂, Liquefied petroleum gas (LPG), Natural gas, liquefied Natural Gas (LNG), air, exhaust gas, flue gas, can be used for miscible EOR methods [6]. To reiterate, CO₂ miscible flooding is applied to light oil and comes at a later stage after primary and secondary drive mechanisms have recovered oil down to residual oil.

The Carbon Dioxide (CO₂) is composed of two Oxygen atoms and one Carbon atom [7]. The CO₂ can be described as a colorless, odorless, and none combustible gas. The calculated molecular weight of CO₂ is 44.01 g/mole. The density of CO₂ is higher than that of air and it is closer to typical light oil density. At a reservoir pressure of 17237 kPa and temperature of 65.55 °C, the density of CO₂ is 0.69 g/cm³. It is noted that for typical reservoirs conditions the CO₂ viscosity ranges from 0.04 cP to 0.06 cP.

The Thermodynamic behavior of CO₂ is illustrated in the phase diagram in Fig. 1 [8]. The three different phases of CO₂ vapor, liquid and solid are clearly shown in Fig. 1.

The triple point at the pressure of 518 kPa and at a temperature of -56.6°C is defined as the point at which the three phases exit in equilibrium. The CO₂ supercritical region exists above the critical point that has a pressure of 7370 kPa and a temperature of 31.0 °C. For most oil reservoirs CO₂ will be supercritical fluid.

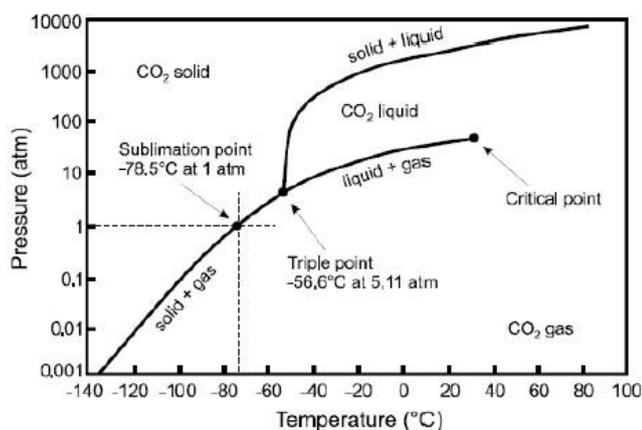


Fig. 1. CO₂ phase diagram [8]

IV. CO₂ IN CRUDE OIL PROPERTIES

The CO₂ is highly soluble in crude oil and causes the swelling of oil. In addition, it reduces the oil viscosity, increases the oil density and the interfacial tension to be reduced [6]. All these CO₂ – Oil mixture properties greatly

help to significantly reduce the CO₂-Oil Mobility ratio and consequently enhances the volumetric sweep efficiency and allow the oil to flow more easily in the reservoir rock that is beneficial for the CO₂ flooding in the EOR method.

V. METHODOLOGY

CO₂ injection in an oil reservoir is an EOR method that is widely known for its higher oil ultimate recovery and for its use in the Carbon Capture and Storage (CCS) that leads to desirable benefits on the environment (reducing CO₂ content in the atmosphere).

In the CO₂ flooding method, favorable conditions of reservoir pressure, temperature, and oil composition are required to achieve the dynamic or multiple-contact miscibility displacement of injected CO₂ and oil reservoir. The multiple-contact miscibility can be defined as the thermodynamic equilibrium between the CO₂ gas and the reservoir oil fluid [6]. In other words a complete mass transfer of the CO₂ gas into the reservoir oil fluid, which is a condensing process, and of the components of the reservoir oil to the CO₂ gas, which is a vaporizing process. It is worthwhile mentioning that the miscibility with the oil at injection pressure of MMP occurs at CO₂ supercritical conditions, which is the optimum condition to become an efficient solvent.

Accurate prediction of CO₂-oil MMP is the most important key step required for the design of CO₂ miscible flood. Therefore, it is advisable to determine the CO₂-oil MMP for the correct specific candidate oil field based on the representative reservoir pressure, temperature, and oil composition [6]. In other words, the oil producing company should not rely on the various empirical correlations found in the literature that are not based on the Omani oil reservoirs. This could lead to inaccurate estimate of the MMP.

In this research study the Rising Bubble method is considered for the measurement of the CO₂-Oil MMP. The advantages of RBA Apparatus are; visible miscibility, smaller Oil sample volume, bubble results recorded on video camera, less time consuming and more cost effective.

The methodology adopted in this research study involves two parts; part-1, includes the experimental work based on the Rising Bubble experiments to measure CO₂-Oil MMP for selected Omani oils from different reservoirs in Oman, and in Part-2, of the research study contains the examination of the existing mathematical correlations for MMP predictions as well as the necessary adjustments on the oil parameters in the simulation software to achieve the most accurate results compared to the experimental MMP values.

VI. CONSTRUCTION OF THE RISING BUBBLE APPARATUS

In the start-up of the research project during the initiation process the Gas-Oil Miscibility equipments were not available in the research laboratory. Thus, tremendous effort and engineering thinking was made for the construction of the Rising Bubble Apparatus.

For limited cases the equipment sapphire visual cell and the oven were purchased from outside. The assembly of the RBA system was made from adapted equipment and devices

such as the high pressure PVT Cell, the ISCO digital positive displacement pump and Ruska positive displacement pump.

The high pressure PVT Cell was adapted for the purpose of the storage and supply high pressure source of CO₂. The ISCO digital positive displacement pump was connected to the high pressure PVT Cell for the CO₂ injection to the sapphire cell. The Ruska positive displacement pump was used for the liquids (oil and water) transfer to the sapphire cell. The SQU Rising Bubble Apparatus System is shown in Fig. 2.



Fig. 2. SQU rising bubble apparatus system

An accurate digital pressure and temperature measurements recording devices accompanied by the computer software installed to the RBA system. The constructed RBA system is rated for a maximum pressure and temperature of 40,000 kPa and 200 °C respectively. Successfully assembled and used the RBA system at SQU research laboratory for the CO₂-Oil MMP study.

VII. EXPERIMENTAL PROCEDURE

In the SQU laboratory, the RBA system has been constructed and the step by step experimental procedure below is used to perform the CO₂-Oil miscibility experiments on the Omani oil samples.

- 1) Fill the sapphire visual cell with distilled and deionized water until air is removed.
- 2) Inject reservoir oil downward in the sapphire visual cell and displace the distilled water till the oil-water interface is slightly above the injection point of the CO₂ bubble.
- 3) Increase the pressure of the sapphire visual cell to just lower than the desired reservoir pressure (considering effect of temperature) by adding or removing the water (by using Ruska pump).
- 4) Increase the oven temperature to the desired reservoir temperature.
- 5) After the reservoir pressure and temperature are set, inject a bubble of CO₂ in the bottom of the sapphire visual cell.
- 6) Allow the CO₂ bubbles to rise through the water phase and oil.
- 7) Record the CO₂ bubbles that rise through the water phase and oil by using the video camera.
- 8) Remove the contaminated oil by the water phase and replace by fresh reservoir oil.
- 9) Repeat steps 2 to 8 till the MMP (final pressure) is reached.

VIII. PVTPro5.2.1 SOFTWARE

The PVTPro5.2.1 equation of state (EOS) is the state of

the art fluid PVT modeling behavior simulator software by Schlumberger. The PVTPro5.2.1 software can help predict the Minimum Miscibility Pressure, the First contact miscibility solvent, the Multiple contact Minimum Miscibility, Multiple contact mixing and flashing and the Swelling curve.

For the experimental part, the PVTPro5.2.1 software was used to simulate the mixing of CO₂ gas with the oil compositional components and the MMP was calculated. This helped in the planning and designing of the CO₂-Oil miscibility experiment and it provided a guide about the expected measured MMP.

IX. OIL SAMPLES FLUID CHARACTERISATION

The crude oil samples that used for this study were collected from different oil fields from Petroleum Development Oman and Daleel Petroleum companies in Oman. The oil fields contain light oil and they are located in the North of Oman. The oil samples were obtained from the test separator and thus they are at surface conditions. A summary of the oil samples properties is shown in the Table I below:

TABLE I: CRUDE OIL SAMPLES PROPERTIES

Crude Oil Samples	Density, g/cc	°API Gravity	Viscosity*, cP
UFUQ	0.828	39.40	0.468
L	0.837	37.60	0.715
MZE	0.808	43.60	0.498

* At reservoir conditions

X. CO₂ - OIL MMP PREDICTION

The CO₂-Oil MMP can be calculated from the existing correlations available in the literature. The most commonly used correlations selected for the calculation of the MMP are; Cronquist [9], Lee [10] and Yellig & Metcalfe [11] and are written in the equations (1), (2) and (3) respectively;

$$MMP = 0.11027 \times (1.8T_R + 32)^y \quad (1)$$

$$y = 0.744206 + 0.0011038 \times MW_{C5+} + 0.0015279 \times Vol$$

$$MMP = 7.3942 \times 10^b \quad (2)$$

$$b = 2.772 - \left(\frac{1519}{(492 + 1.8T_R)} \right)$$

$$MMP = 12.6472 + 0.015531 \times (1.8T_R + 32) + 1.24192 \times 10^{-4} \times (1.8T_R + 32)^2 - \frac{716.9427}{(1.8T_R + 32)} \quad (3)$$

XI. RESULTS AND DISCUSSION

The experimental runs on the oil samples UFUQ, L, and MZE were performed by using the RBA apparatus. Each experimental run included four stages. These stages are pre-experimental clean up, CO₂ gas and liquid transfer; such as water and oil, to the visual sapphire cell, experimental run

and the post-experimental clean up. All CO₂ – Oil MMP experiments were run at reservoir pressure and temperature and each one lasted for about 5 hours.

Fig. 3 shows the CO₂ bubble behavior at or close to MMP. It can be observed at the time-step-3 the CO₂ changes its shape, does not rise upward and finally disappears in the crude oil column.

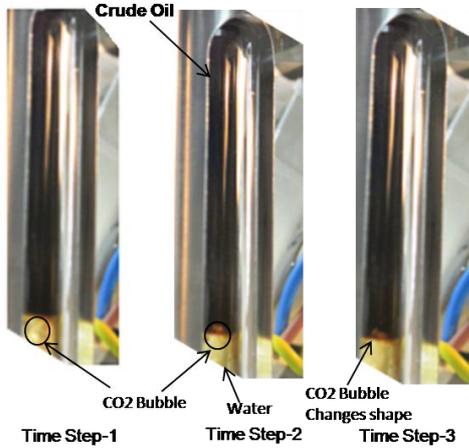


Fig. 3. CO₂ Bubble behavior at MMP

The RBA experimental results of the measured CO₂ – Oil MMP for the oil samples used for the research study are summarized in Table II:

TABLE II: EXPERIMENTAL RESULTS OF MMP

Oil Samples	Reservoir	Reservoir	RBA System
	Pressure	Temperature	
	kPa	°C	MMP*
			kPa
UFUQ	14700.31	80.00	14450.03
L	13779.86	63.00	14250.01
MZE	15058.15	75.60	14550.01

* The accuracy of pressure gauge is 0.25% × MMP Pressure

The CO₂ – Oil MMP was calculated by different methods to compare between the experimental results with the predicted ones. The software PVT Pro 5.2.1 was used to calculate the CO₂ – Oil MMP. The input into the software was the reservoir pressure and temperature, oil properties and the oil compositions of the three oil samples. The resultant calculations of the CO₂ – Oil MMP values are shown in Table III.

The CO₂ – Oil MMP correlations mentioned earlier were used to estimate the MMP. The results of the calculation of the CO₂ – Oil MMP by using the correlations equations 1, 2 and 3 for the three oil samples are shown in Table III.

TABLE III: PREDICTED MMP

Oil Samples	PVTPro 5.2.1	Cronquist	Lee	Yellig& Metcalfe
	MMP	MMP	MMP	MMP
	kPa	kPa	kPa	kPa
UFUQ	14121.84	9000.00	17887.00	15154.10
L	14230.09	8043.50	13546.00	12600.10
MZE	14259.05	9702.60	16688.00	14500.70

In Table III, it can be seen that the calculated CO₂ – Oil MMP values from the PVT Pro 5.2.1 and the literature correlations. This is done for comparison between the different methods and consequently to be able to determine the method that best estimates the CO₂ – Oil MMP based on the three oil samples experimental results.

The % differences between the experimental and the calculated MMP values from the different methods are summarized in Table IV.

TABLE IV: % DIFFERENCES BETWEEN EXPERIMENTAL AND PREDICTED MMP

Oil Samples	PVT Pro 5.2.1	Cronquist	Lee	Yellig& Metcalfe
	% Difference	% Difference	% Difference	% Difference
UFUQ	2.27	37.72	-23.79	-4.87
L	0.14	43.55	4.94	11.58
MZE	2.00	33.32	-14.69	0.34

It can be deduced from Table IV that CO₂ – Oil MMP values obtained by PVT Pro 5.2.1 are the ones that are the closest to the experimental results for all the pressure and temperature ranges of the crude Omani oil samples. Thus, PVT Pro 5.2.1 software provides the most accurate calculations of the CO₂ – Oil MMP compared to the literature correlations. This is due to the fact that there are more detailed oil properties and oil composition data that are inputted in the PVT Pro 5.2.1 software to better simulate the oil sample phase behavior.

XII. CONCLUSIONS

The technical contributions of the CO₂-Oil MMP study are concluded below:

- 1) Developing and constructing successfully the first RBA system in Oman in the most cost effective way.
- 2) The newly constructed RBA Apparatus allowed visible miscibility, consumed smaller Oil sample volumes and was less time consuming for the experimental runs.
- 3) PVT Pro 5.2.1 software provides the most accurate model prediction of CO₂ – Oil MMP for Omani light Oil reservoirs.
- 4) Using the PVT Pro 5.2.1 software Provide a cost effective and less time consuming method for the oil companies to predict CO₂ - Oil MMP.
- 5) This study helps oil companies to evaluate the economic viability of the potential CO₂ flooding for effective EOR method in Oman in a fast and less time consuming technique.

It is recommended to extend this study for further experimental runs on more oil samples to cover more Omani light oil reservoirs.

NOMENCLATURE

- EOR: Enhanced Oil Recovery
- EOS: Equation of State
- MMP: Minimum Miscibility Pressure
- MW_{C5+}: Molecular Weight of C₅₊ fractions
- RBA: Rising Bubble Apparatus
- T_R: Reservoir Temperature, °C

VIT: Vanishing Interfacial Tension
Vol.: Volatiles (C₁ and N₂) mole percentage, %

ACKNOWLEDGMENT

Petroleum and Chemical Engineering Department at Sultan Qaboos University acknowledges and appreciates all who helped in the construction of the Rising Bubble Apparatus system, in the collection of the oil samples from the Omani fields, in the Oil PVT compositional data gathering and in the experimental work. Their cooperation and support was greatly beneficial.

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