

Experimental Investigation of Asphaltene Content Effect on Crude Oil/CO₂ Minimum Miscibility Pressure

Mehdi Ghorbani¹, Asghar Gandomkar^{2*}, Gholamhosein Montazeri¹, Bizhan Honarvar¹, Amin Azdarpour¹, Mohammad Rezaee³

¹ Department of Petroleum Engineering, Marvdasht Branch, Islamic Azad University, Marvdasht, P. O. B. 70528, Iran

² Department of Petroleum Engineering, Faculty of Chemical and Material Engineering, Shiraz Branch, Islamic Azad University, Shiraz, P. O. B. 71993, Iran

³ Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, P. O. B. 11155, Iran

* Corresponding author, e-mail: agandomkar@shirazu.ac.ir

Received: 19 March 2020, Accepted: 03 April 2020, Published online: 19 May 2020

Abstract

Minimum Miscibility Pressure (MMP) is regarded as one of the foremost parameters required to be measured in a CO₂ injection process. Therefore, a reasonable approximation of the MMP can be useful for better development of injection conditions as well as planning surface facilities. In this study, the impact of asphaltene content ranging from 3.84 % to 16 % on CO₂/heavy oil MMP is evaluated. In this respect, slim tube miscibility and Vanishing Interfacial Tension (VIT) tests are used. Regarding the VIT test, the Interfacial Tension (IFT) is measured by means of two methods including pendant drop and capillary apparatuses, and thereafter the MMP measurement error between slim tube and VIT methods are calculated. Based on the results, by increasing the asphaltene content, the measured MMP by slim tube method increases linearly while that by VIT follows no clear trend. The results also indicate that there is an asphaltene content range within which the MMP error between slim tube and VIT tests is minimized. IFT measurement by pendant drop and Capillary Glass Tube (CGT) methods show that by increasing asphaltene content up to 10.15 %, IFT declines, whereas for further increase in content, IFT increases because of the irregular dispersion of asphaltene in oil droplets.

Keywords

asphaltene content, Minimum Miscibility Pressure, Vanishing Interfacial Tension, slim tube, CO₂ injection, pendant drop, Capillary Glass Tube

1 Introduction

Carbon dioxide injection processes can improve oil recovery and reduce greenhouse gas emissions simultaneously via sequestration of CO₂ in oil reservoirs [1]. In fact, by CO₂ injection, a huge volume of gas is dissolved into oil phase, and thereby reducing Interfacial Tension (IFT) and oil viscosity [2]. One of the most fundamental parameters which should be taken into consideration is the Minimum Miscibility Pressure (MMP) which strongly depends on oil composition and temperature in CO₂/Oil systems [1–3]. It is generally known the heavy fraction of crude oil is mainly comprised of four groups including asphaltenes, saturated hydrocarbons, resins, and aromatics [4]. In particular, while the CO₂ injection process is performed, the phenomenon of asphaltene precipitation is one of the most challenging issues which should necessarily be addressed. This phenomenon causes many problems such as pore

blockage and wettability alteration within reservoir porous media and unfavorably affects the sweep efficiency [5–8]. Hence, measuring the effects of asphaltene content over the MMP is of paramount importance in CO₂/oil systems, specifically at high temperatures and pressures [9–11]. The most common MMP measurement method in industry is the slim tube miscibility test, which is proved to be relatively accurate and reliable according to previous studies [2], in which CO₂ meet oil in a long porous medium based on the multi-contact mechanism. However, despite its reliability, this method suffers from several shortcomings such as being almost expensive and time-consuming, particularly in the presence of heavy fractions such as asphaltenes. In addition, asphaltene precipitation can block its porous medium, yielding inaccurate results. To address the faults associated with the slim tube test, the Vanishing

Interfacial Tension (VIT) technique can be used as a satisfactory substitute since it is comparatively more cost-effective and time-saving [5, 12–14]. However, the MMP measured by VIT test is usually higher than that by the slim tube in a CO₂/light oil system. In fact, the VIT measurement is accompanied by error, and thus the MMP values obtained by this method needs to be corrected. In confirmation, regarding our previous works [13, 14], the measured MMP by VIT method (Pendant drop method) is distinguishably different from that by the slim tube test. Actually, it is typically overestimated by the VIT method, especially for light oils, and therefore the extrapolated MMP at which the IFT is zero does not match with the estimated MMP by the slim tube. This difference is mainly attributed to the media type where gas and oil contact with each other. In fact, the media related to slim tube is porous and a multiple contact miscibility process occurs in oil/gas system, whereas in VIT the gas and oil contact with each other in a bulk media, and represents a first contact miscibility. In order to correct the pressure at zero IFT in the IFT measurement approach, Ghorbani et al. [14] proposed a correlation. They also investigated the effects of several parameters on MMP such as oil components and temperature. Previously, numerous studies concerning the Interfacial Tension (IFT) of CO₂-asphaltic oil systems have been done [15–18]. In this respect, Zolghadr et al. [19] deals with evaluation of MMP for a number of oil samples and CO₂ using VIT technique (pendant drop method). Their results showed that the IFT slope is different for paraffinic hydrocarbons and diesel fuel. In another experimental study, they understood that the MMP corresponding to heavier components such as hexadecane and CO₂ was nearly identical to that related to diesel fuel and CO₂. In addition, they found that the IFT slope versus pressure obtained for the two paraffinic samples was virtually identical, regardless of the test temperature, while it was different for the diesel fuel when high pressures are tested. It should be noted that according to literature [15, 20], different linear slopes were observed at different temperatures. Besides, it is worth noting that the change in the slope of VIT curve starts at the beginning of the asphaltene precipitation [15]. Generally, the equilibrium IFT line changes both upwardly and downwardly versus the inverse of the equilibrium pressure for a medium oil type. Indeed, the IFT goes up abruptly, and afterward declines suddenly. The sudden increase can be owing to the existence of asphaltene, and fast separation of light components. Before this period, various light constituents may start separation from the oil sample. Thus, during

this period, the IFT measurement can be between CO₂ and heavy components of oil [21]. Kazemzadeh et al. [22] studied the asphaltene precipitation through estimating the interfacial tension between CO₂ and CH₄ in addition to CO₂ and different types of oil containing various asphaltene contents. Based on their results, asphaltene precipitation phenomenon happens provided that the coverage of surface beat a threshold value. In another study performed by Saini and Rao [23], the IFT was calculated for two different samples of live oil (both recombined) and CO₂ at various pressures higher than 17.87 MPa (bubble point) where the temperature was 142 °C. They applied the VIT measurement technique along with an equation of state to define the Minimum Miscibility Pressure (MMP). Besides, Wang et al. [20], and Wang and Gu [21] analyzed three oil samples from Canada in the presence of CO₂ using the VIT test. They realized that the equilibrium IFT generally declines linearly within three separate pressure ranges which can be justified by asphaltene precipitation as well as CO₂ solubility in the oil sample, which makes it noticeably light. It is worth noting that the swelling of oil sample occurs under low pressures although strong extraction of light constituents at the beginning is prevailing under high pressures. This action approves the conditions to reach MMP under a multiple contact miscibility process.

In addition, Mahdavi et al. [24] assessed the effects of type and content of asphaltene over the IFT behavior in an oil and CO₂ system. They understood that the IFT is directly proportional to the inverse of pressure, and the existence of asphaltene can affect the constant proportionality. Their results also demonstrated that both aromaticity and hydrogen deficiency of asphaltene molecules affects the IFT considerably. Khalaf and Mansoori [25] simulated asphaltene aggregation using molecular dynamics throughout the gas flooding process. According to their results, the start of the asphaltene aggregation strongly relies on its molecular structure. Zheng et al. [26] proposed a novel method for MMP measurement called ODVM standing for oil droplet volume measurement. They found out that there is a linear relationship between the temperature and the MMP of oil and CO₂ systems. Fathinasab et al. [27] determined the effect of water over the MMP at different conditions via VIT method. Their results indicated that the MMP goes up in the presence of water, and by increasing the water content, the MMP increases more notably. They also proposed different relationships to establish correlations between the IFT and MMP depending on pressure at specific temperatures. Zhang et al. [28] reviewed the experimental approaches

to find the MMP of oil/gas systems. Accordingly, the core flooding and slim tube tests are the most suitable experimental techniques to measure MMP, which are completed by VIT, rising-bubble apparatus and microfluidic tests. Chen et al. [29] developed a correlation in order to estimate the MMP in pure CO₂ injection processes and impure ones. They indicated that by increasing the impurities including yH₂S, xC₂-C₄, and xC₅-C₆, the MMP values decline, whereas by raising the temperature, presence of MW_{C7+}, yCO₂, and yC₁ contributes to MMP increase.

In this study, the effect of asphaltene content on the MMP during CO₂ injection process is examined for samples with asphaltene content between 3.84 % and 16 % by slim tube and VIT (Pendant drop method) tests. Moreover, a microscopic study and the capillary IFT measurement method are employed for further understanding of asphaltene content effect.

2 Experiment and materials

2.1 Fluids

In this study, heavy oil from the Middle East carbonate reservoir was selected to be analyzed. The oil composition is listed in Table 1. The crude oil has the American Petroleum Institute (API) of 18.2 and molecular weight of 340.7. The original oil asphaltene content was about 13.20 %, which was measured by IP143 method. The asphaltene particles were firstly separated from the original crude oil sample by centrifugation method. Following that, the diasphaltene oil was used as the base sample, and then in order to synthesize the intended oil samples, 3.84 to 16 % of asphaltene was added to the base.

Table 1 Composition of the dead oil

Component	Mole (%)
CO ₂	0
C1	0.14
C2	0.4
C3	1.92
iC4	0.65
nC4	2.39
iC5	1.34
nC5	1.71
C6	3.43
C7	5.76
C8	6.50
C9	5.04
C10	4.43
C11	3.14
C12+	63.15

Furthermore, highly pure CO₂ was injected to the prepared samples to conduct the experimental analyses involving IFT measurements and slim tube flooding.

2.2 Fluid preparation

For this purpose, 72 liter of the original crude oil was diasphaltene by the centrifugation method (using 6 L Beckman centrifuge (J6-MI High Capacity Centrifuge)) to purposefully collect solid asphaltene particles to utilize them for providing oil samples with different asphaltene contents. After running the centrifugation at the rotational speed of 5000 rpm for 72 hr, the separated liquid part was passed through a filter (Whatman™ 1442-125 Ashless Grade 42 Quantitative Filter Paper, Diameter: 12.5 cm, Pore Size: 2.5 μm) by Buchner funnel and vacuum separation to segregate the probable aggregated asphaltene particles in the oil sample. Afterward, the IP143 test was used in diasphaltene oil to measure the amount of its remained asphaltene content, which obtained to be about 3.84 %. Therefore, the sample containing 3.84 % of asphaltene was considered as the base to prepare the targeted samples by adding and mixing enough powder of separated solid asphaltene. In this regard, firstly, solid parts were mixed with n-heptane and allowed to stand for two days. Thereafter, the solution was passed through a filter to separate asphaltene particles. Since asphaltene can be dissolved in toluene, all separated solid particles were solved in toluene, and subsequently the solution was heated slowly, up to the point that only solid asphaltene particles were retained. The retained solid particles were then crushed to powder, and added to the reference oil.

Next, all synthesized samples were tested to check their asphaltene content. All the synthetic oils were allowed to stand for 3 days. Following that, the oil samples were examined visually in order to see any asphaltene deposition in containers. Above 16 % of asphaltene content was deposited, so synthesizing oil samples containing above 16 % asphaltene were not appropriate for this study. Also, asphaltene content related to seven samples of 3.84 %, 7 %, 10.15 %, 12 %, 13 %, 14 %, and 16 % was tested by IP143 to make sure that the samples contained exactly the same concentrations as the reported values. Before conducting IP143 test, mixers were allowed to stand for 1 day. After that, two samples were chosen to be examined in order to consider any asphaltene gradient; the first one was taken from the bottom and the second one from the top of the container. The corresponding results agreed very well with ±0.2 % error, suggesting no asphaltene content gradient after one day. The experiments were

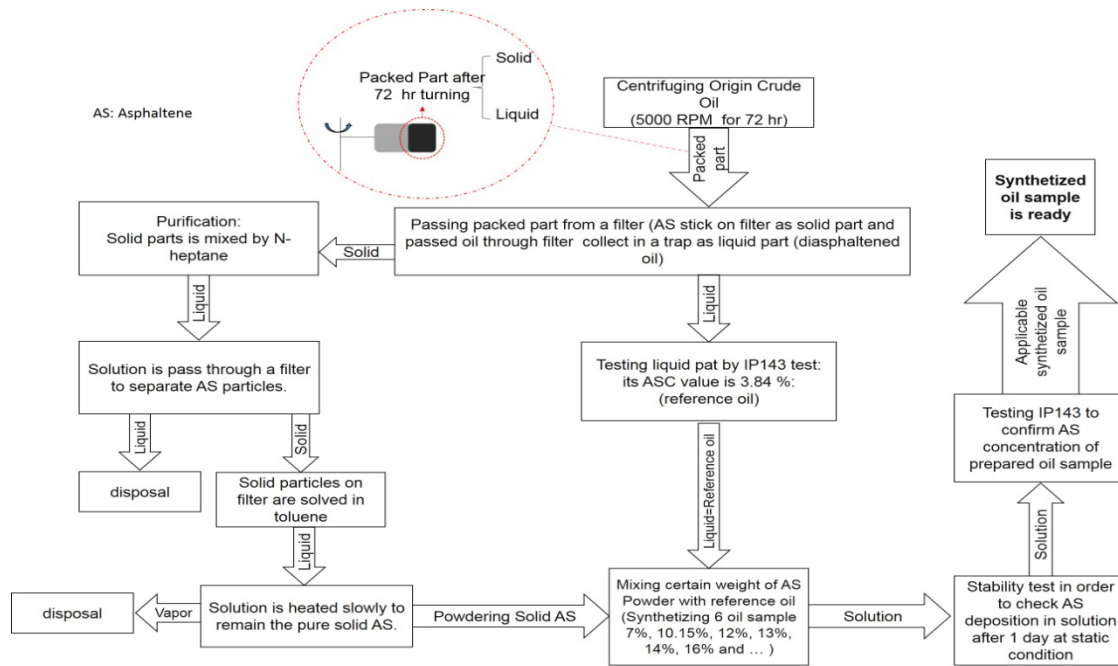


Fig. 1 Schematic of flow-work in order to synthesize oil sample for this study

performed twice for each sample. Fig. 1 illustrates schematically the procedure of preparing the synthesized oil samples with different asphaltene contents.

2.3 Slim tube test

Fig. 2 represents the schematic of the slim tube rig (DBR, 15000 psi and 180 °C, David Robinson under Schlumberger authority). This is mainly comprised of a filled tube with homogenous media (18 m), pump, gas meter, glass separator, high-pressure visual cell, and Back Pressure Regulator (BPR). The washing process was carried out using methanol and toluene. In order to clean the porous media, toluene was injected at the rate of 10 cc/hr (at 80 °C), and continued until transparent toluene could be observed in the outlet. Then, it was flooded by methanol at the rate of 15 cc/hr (at 80 °C) about 10 pore volumes to restore initial wettability of slim tube porous medium. To make it dry, air was flowed through porous medium for 24 hour and then it was vacuumed for 10 hour. Afterward, the dead oil along with CO₂ (1cc/hr for 1.2 pore volumes [13, 21]) were injected to the slim tube. The outlet pressure was kept constant by means of the back pressure regulator. This set of experiments was conducted at different pressures involving 13.78, 17.23, 24.13, 27.57, 31.02, 37.92 psi and the temperature of 80 °C. For each pressure, oil swelling factor was considered to obtain recovery, and the corresponding gas recovery and production rate were recorded [13]. The properties of slim tube rig are reported in Table 2.

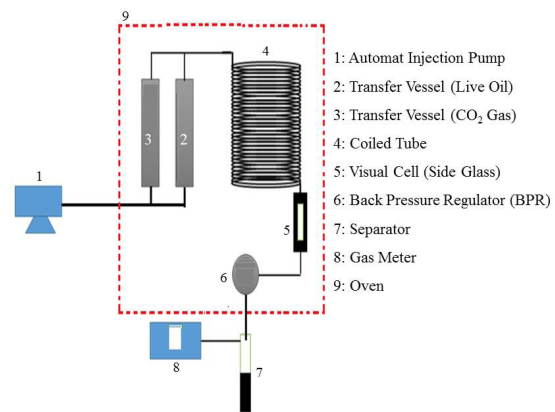


Fig. 2 Schematic of slim tube apparatus

Table 2 Dimensions and properties of the slim tube rig used in this study

Length (M)	Inner Diameter (cm)	Area (cm ²)	Pore Volume (cc)	Porosity %	Permeability (D)
18	0.516	0.209	120	33.4	6

2.4 IFT measurement apparatus

The employed experimental setup for the VIT measurement is depicted in Fig. 3 (DBR, produced by Datis Energy Company as MRezaeeAO6 Model, 6000 psi 180 °C).

The VIT measurement method relies on the interfacial tension between oil and gas phases, which gives the MMP where the IFT of both phases reach zero. The fundamental concept of zero IFT originates from the fact that two

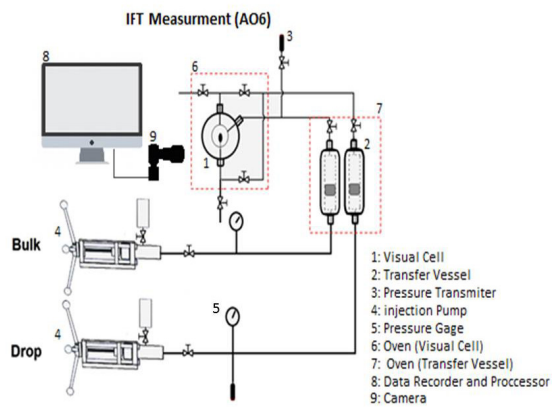


Fig. 3 Schematic of VIT

phases become totally miscible as the force which separates them weakens, up to the point that there is no interface between liquid and gas phases, and subsequently one phase is formed. As a result, by determining gas and oil IFT as a function of composition and pressure, and extrapolating the functions to the point at which the IFT is zero, the Minimum Miscibility Pressure (MMP) and Minimum Miscibility Composition (MMC) can be measured, correspondingly. In this respect, the VIT method can be adopted to calculate the gas/oil IFT using the pendant drop technique which is conducted by ADSA software by the Young Laplace equation at different temperatures and pressures of the reservoir [6, 7, 25].

The main parts of the HP-HT pendent-drop instrument (Fig. 3) are IFT visual cell, pump for injecting oil or gas, a vibration-free table, transfer cell, needle, system of controlling temperature, lamp, digitally displayed pressure transducers, and a totally automatic imaging system. The experiments associated with IFT measurement were carried out at the same conditions as the slim tube tests; i.e., at 80 °C and 6.89, 13.78, 20.68, 24.13, 27.57 and 31.02 MPa. Also, to check repeatability of results, all tests were conducted twice, yielding the same results.

2.5 Capillary method

This capillary technique is known as the oldest one regarding the measurement of the Interfacial Tension (IFT). This method is based on the transformation of liquid to a glass-made capillary tube arising from the appearance of surface tension at the interface of gas and liquid. Thus, to determine the surface tension of liquid, the capillary tube is dipped to the liquid sample. The capillary IFT measurement apparatus is illustrated in Fig. 4 (DBR, 8500 psi at 150 °C). The visual box had a glass-made

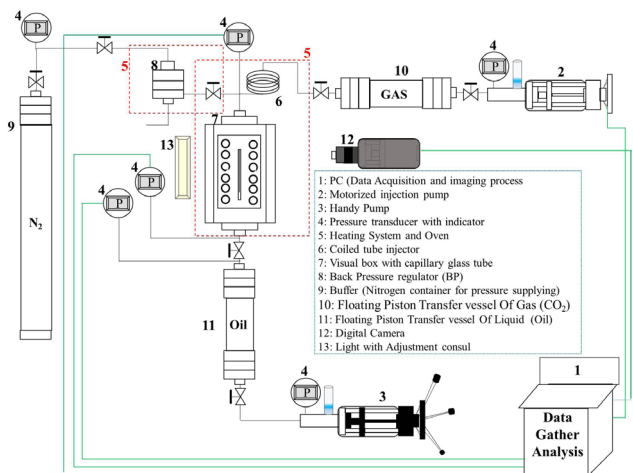


Fig. 4 Capillary glass tube IFT measurement schematic

capillary tube with 0.8 mm I.D, 3 mm O.D and 98 mm height and was located inside an oven which was insulated. The design rating of the optical cell was 58.60 MPa at 150 °C. VINCI Densitometer Anton Paar DMA HPM (68.94 MPa and 200 °C) was employed to calculate densities at high temperatures and pressures. Auto Displacement Pump (DBR model, 1 cc/hr accuracy, 10000 psi and ambient condition) and Handy pump were used to inject the targeted fluid rate accurately and supply the pressure needed to conduct the experiments. The pump was composed of a cylinder and piston, which was charged by distilled water and connected to two Transfer Vessels (TV). The first TV was connected to the top of Visual box and filled with pure CO₂, while the second one was connected to the bottom, and used to inject synthesized oil samples into the visual box. For all the tests, visual box was filled by CO₂, and then 10 cc of oil sample was injected into it. During oil sample injection, pressure was controlled by back pressure regulator which was linked to the top of visual box and CO₂ injection pump. IFT measurement by this method was performed and analyzed after 15 minutes of oil sample injection by measuring oil height in the capillary glass tube. All parameters including pressure, temperature and recording images (high resolution camera by focusing power of 500 times magnification) were stored in data acquisition system and analyzer. The capillary tube measurements were done twice at 13.78 MPa pressure and 80 °C temperature for each synthesized oil sample to assure the repeatability of the tests.

Also, the local asphaltene content related to top and bottom oil droplets was measured by capillary tube method. The procedure of local asphaltene content measurement is represented in Fig. 5.

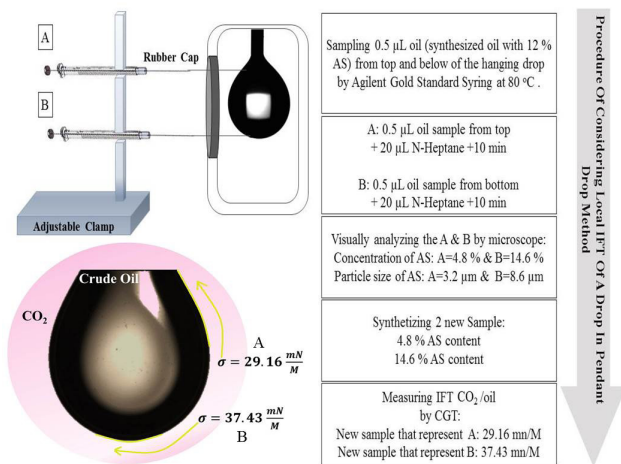


Fig. 5 Analyzing flow-chart of measuring local IFT for a drop

3 Results and discussion

After running slim tube experiments and VIT (pendant drop apparatus) for seven synthesized oil samples with different asphaltene contents, the corresponding results regarding MMP measurement are summarized in Figs. 6 to 8.

The data in Fig. 8 show the break in slopes of the recovery curves, at different pressures, for all the concentrations of asphaltene in the oil sample. There are distinguishable differences in recovery, which can presumably be the result of asphaltene precipitation in the homogeneous

porous medium of the slim tube. In fact, due to precipitation of asphaltene particles in the porous medium, the recovery declines.

Also, it should be noted that at the slim tube porous medium with the multi contact miscibility mechanism, light oil compositions are quickly separated and transferred into CO₂, and thus heavy components are left. These heavy compositions of crude oil reduce the solubility of CO₂ gas at a constant pressure for all slim tube experiments [30]. Therefore, it leads to a decrease in CO₂ solubility, and consequently an increase in the MMP. In this case, the VIT tests not only performed at PVT cell but also it is not recovery base, and however the VIT test were run to consider the asphaltene concentration effect on MMP by measuring IFT.

According to Fig. 8, for the slim tube test, the MMP value increases linearly by increasing the asphaltene content. The line passed through MMP-asphaltene content data obtained by slim tube tests can almost be divided into three separate straight lines with different slopes including Slope 1 for the asphaltene content of: 3.84 % to 7 %, slope 2: 7 % to 14 % and slope 3: 14 % to 16 %.

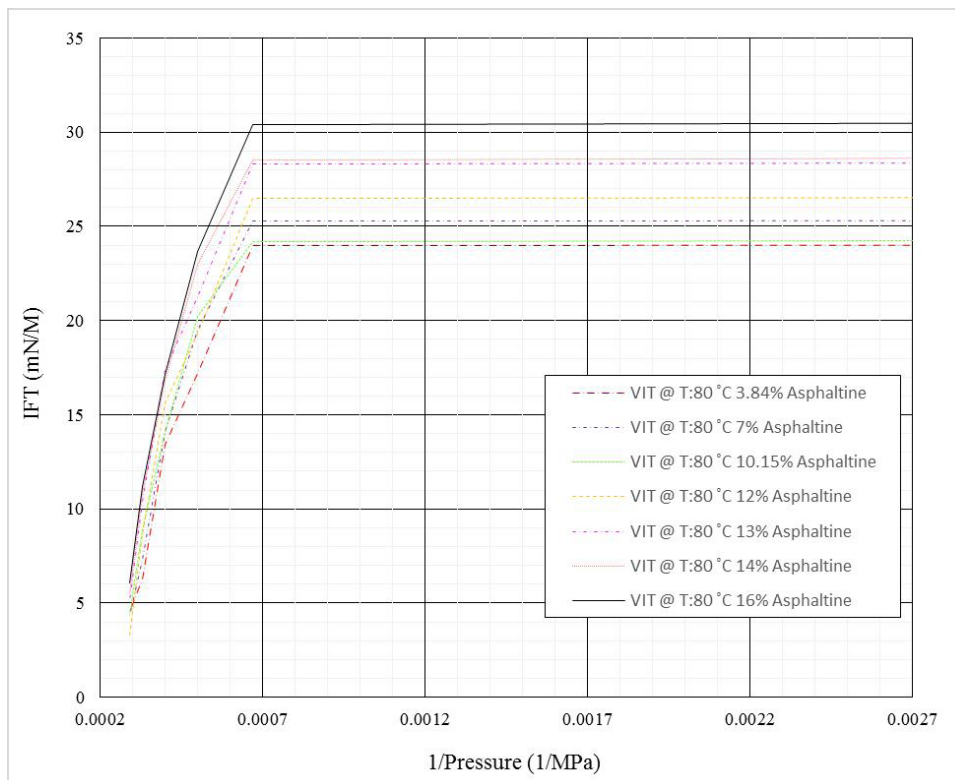


Fig. 6 VIT results for seven synthesized oil with asphaltene content in the range of 3.84 % to 16 % at 80 °C temperature, IFT was measured by pendant drop method

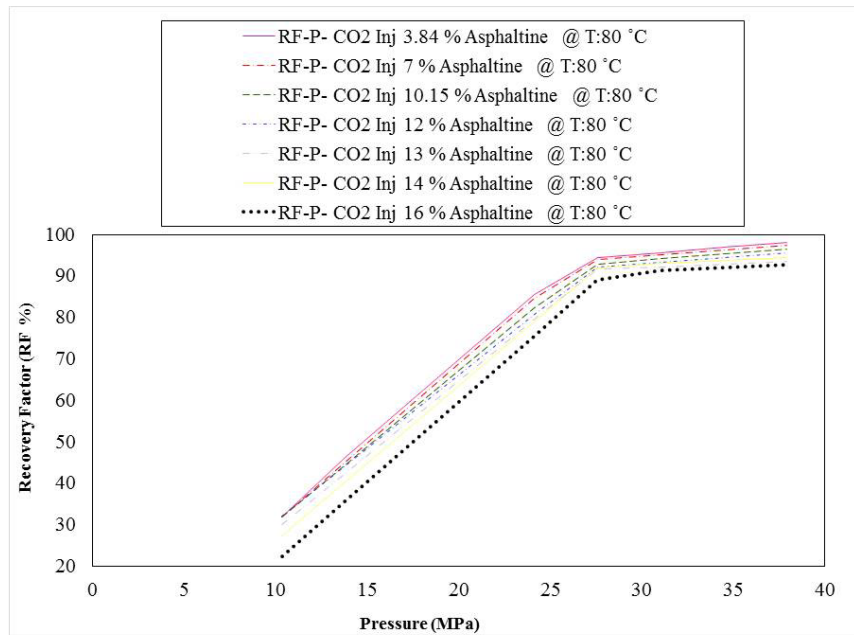


Fig. 7 Recovery factor Vs. pressure for each Slim tube saturated by synthesized oil samples with different asphaltene contents and MMP measurement of: 3.84 % MMP: 26.34, 7 % MMP: 26.54, 10.15 % MMP: 26.98, 12 % MMP: 27.31, 13 % MMP: 27.48, 14 % MMP: 27.73 and 16 % MMP: 28.04 MPa

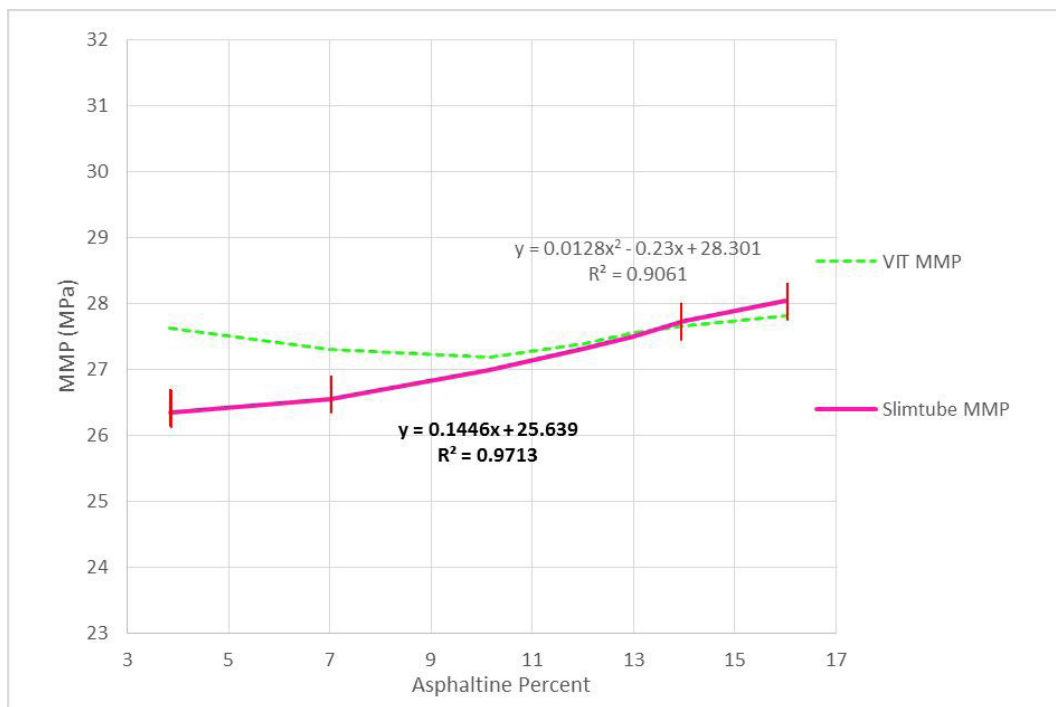


Fig. 8 MMP results for 3.84 %, 7 %, 10.15 %, 12 %, 13 %, 14 % and 16 % asphaltene content of synthesized oil samples which are measured by slim tube CO₂ flooding and VIT method (Pendant drop)

of asphaltene content (7–14 %) exerts a more significant effect over the MMP. This can actually be ascribed to the increase in heavy compositions of oil content, and thereby decreasing the solubility of CO₂. Asphaltene precipitation, which could happen during the slim tube flooding,

would raise the MMP value of the synthesized oil-CO₂ system. As mentioned previously, slim tube tests are strongly reliable, but they are very time-consuming and expensive rather than VIT method [9, 12–14]. However, VIT method has some drawbacks such as first contact

miscibility, lack of porous media and heavy oil component effect [9, 12–14]. In our previous study conducted by VIT method Ghorbani et al. [13], asphaltene content in the heavy oil exerted a different effect over the MMP relative to light oil. Hence, in this study, it is dealt with comparing MMP results measured by slim tube and VIT tests. Also, the measured MMP by VIT are obtained by extrapolating IFT/Pressure inverse line at zero IFT.

In addition, it is observed that the MMP calculated by VIT tests does not follow a clear trend towards increasing the asphaltene content. Based on Fig. 8, as the base oil becomes richer in asphaltene (up to 10.15 %), the MMP decreases, but by further increase in asphaltene, the MMP tends to follow an ascending trend. Besides, the MMP measurement error is depicted in Fig. 9, indicating that for the asphaltene concentration of above 10.15 %, the MMP measurement error tends to decline.

By comparing the results of Figs. 8 and 9, it can clearly be deduced that the effects of asphaltene content on MMP are more noticeable by VIT technique. The results of IFT value measured by Capillary Glass Tube (CGT) method at 13.78 MPa and 80 °C are illustrated in Fig. 10. Accordingly, the increasing trend of IFT versus asphaltene content by CGT method is thoroughly linear; however, this trend is not the same as the pendant drop method. In fact, it behaves as a second order polynomial which is nearly identical to the measured MMP by VIT

test (Fig. 11). By analyzing the oil droplet, it is revealed that the asphaltene particle distribution on the oil droplet surface is different for each point of oil drops (Fig. 12).

The oil samples have been taken with highly accurate needle sampler (Agilent Gold Standard Syringe, 0.5 μL total volume, 0.02 μL accuracy and Part No. 51885246-D03-A8390) from synthesized oil with 12 % AS content to measure the amount of local asphaltene content at 0.6894 MPa and 80 °C by CGT apparatus [31]. Also, 20 μL n-heptane was added to the samples and allowed to be in contact for 10 minutes prior to analysis with a microscope (see Fig. 13).

According to Fig. 12, microscopic images of asphaltene particles in oil samples from the top (Fig. 12 (A)) and bottom (Fig. 12 (B)) of oil droplet are not identical. Indeed, the top sample has less and smaller asphaltene particles in comparison with the bottom one. Accordingly, the average asphaltene particle size for top and bottom samples are about 3.2 and 8.6 μm , respectively. Also, the amount of local asphaltene content is obtained to be 4.8 % and 14.6 % for the top and bottom samples, correspondingly.

Following that, two samples are synthesized with exactly the same asphaltene content as the top and bottom samples (i.e., 4.8, and 14.6 %) to obtain the corresponding IFT values. As a result, IFT values measured by CGT method for 4.8 % and 14.6 % AS content are approximately 29.16 and 37.43 mN/m, respectively.

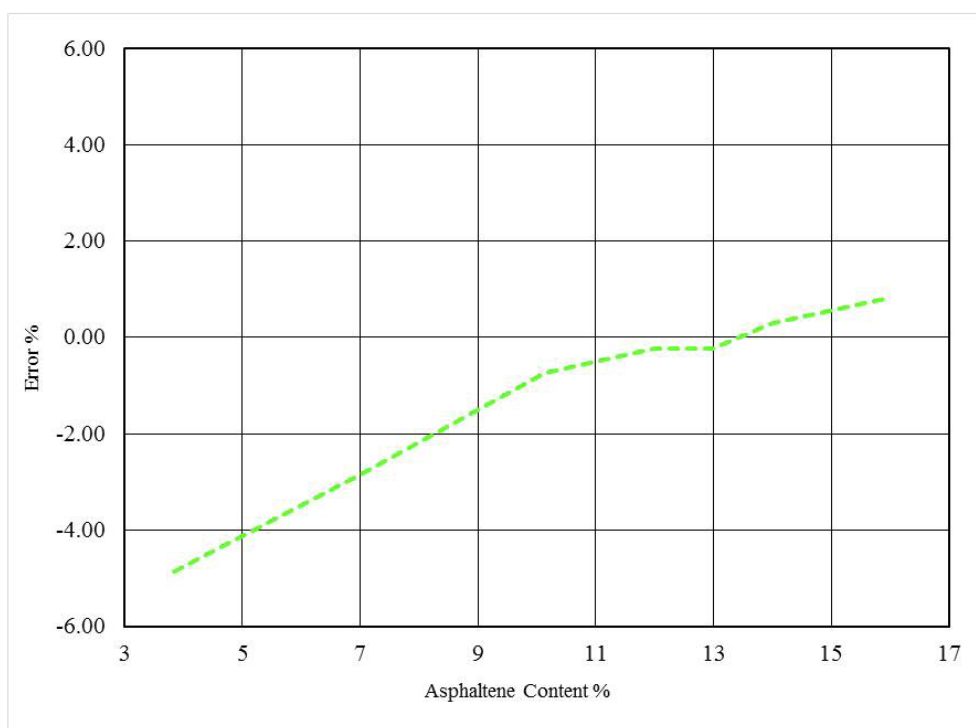


Fig. 9 Error of measured MMP by VIT (Pendant drop IFT measurement)

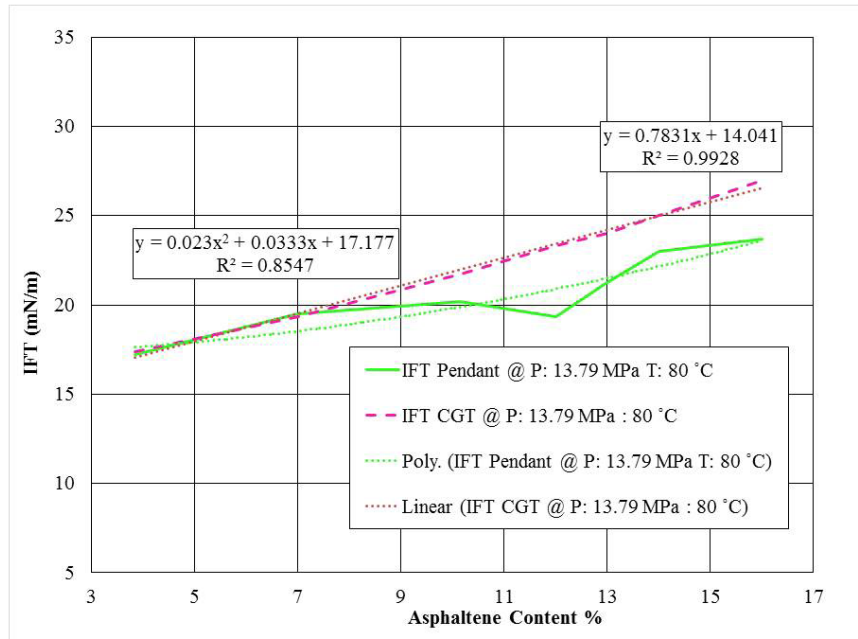


Fig. 10 IFT measurement with capillary glass tube and pendant drop for synthesized oil/CO₂ system. Synthesized oil samples with asphaltene content ranging from 3.84 to 16 %

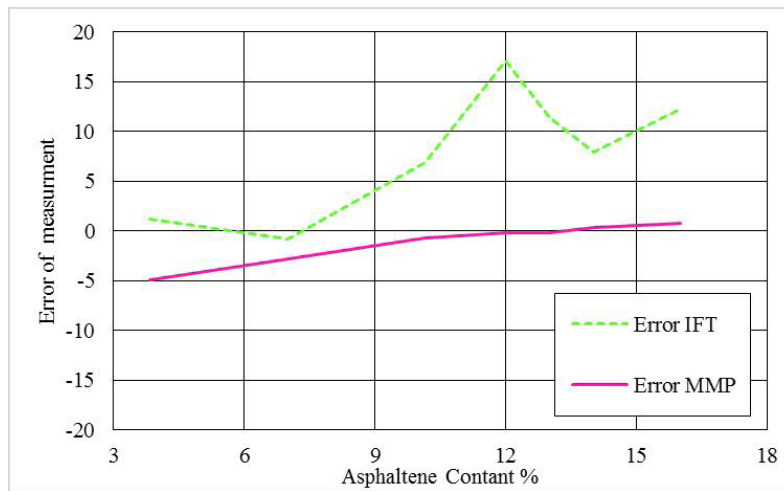


Fig. 11 Error of measured IFT by Pendant drop (Dash line) base on asphaltene content of oil samples for 13.78 MPa pressure and 80 °C temperature and stretch line shows MMP error of VIT test which vary with asphaltene content. It can be seen that the error of IFT measurement for lower asphaltene content (Less than 10.15 %) is greater than that of higher content, while this is reverse for the error associated with the MMP value.

These local IFT variations are in fact the main reasons for the difference in IFT value measured by CGT and pendant drop methods. This also clarifies why the MMP measurement error between VIT and slim tube for asphaltene content of above 10.15 % is lower. These local differential IFT in one oil drop in the existence of CO₂ at the pendant drop may accidentally compensate for the effect of porous medium in the slim tube on MMP measurement.

Typically, surface tension (σ) relies on chemical composition as well as temperature at the interface. As a consequence, either temperature or chemical composition

gradient can lead to IFT gradients, and thereby inducing Marangoni flows at an interface [32]. Here, since temperature is a constant parameter, heavy oil components can mainly contribute to the difference in the IFT associated with pendant drop by exerting an extra force on the oil droplet. The tangential stress balance can be calculated at a free surface according to the following equation:

$$n \cdot T \cdot t = -t \cdot \nabla \sigma,$$

where n denotes the unit outward normal to the surface, and t is connected with unit tangent vector. The hydrodynamic

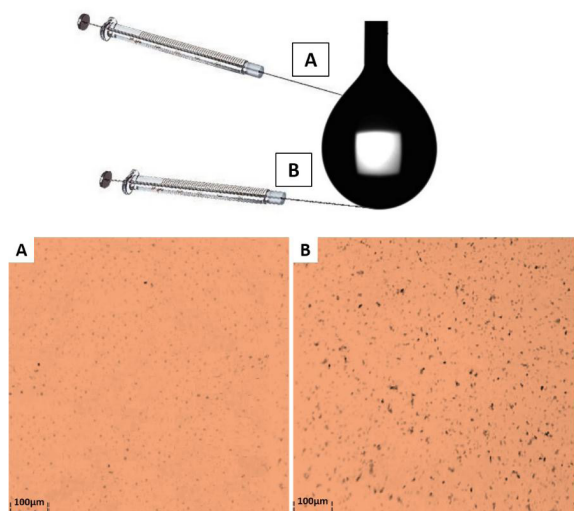


Fig. 12 Microscopic picture of two samples of the synthesized oil with 12 % asphaltene content/ CO_2 system at 80 °C which mixed by 20 μL n-heptane. A) Oil sample from the top of oil droplet which has less asphaltene particle (4.8 % AS) B) Oil sample from the bottom of oil droplet that has larger and denser asphaltene particles (14.6 % AS)

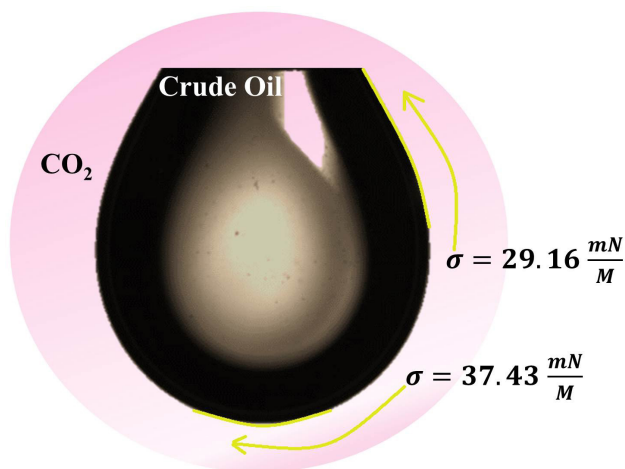


Fig. 13 Schematic diagram of synthesized oil droplet with 12 % asphaltene content and IFT gradient in the local points of oil droplet in pendant drop at the temperature of 80 °C.

stress over the surface derived by tangential component must be balanced by the tangential stress related to surface tension (σ) gradients. These Marangoni stresses can probably arise from the chemical composition gradients at the interface. If the system is static, because $n \cdot T \cdot t = 0$, $\nabla \delta$ becomes zero according to the balance equation of tangential stress [33]. Thus, this points to the conclusion that there is no surface tension gradient in a static system. Thus, the VIT approach using pendant drop method, which is based on static condition, is not an appropriate way to determine the sensitivity (it agrees with the study conducted by Orr and Jessen [12]) of the MMP to asphaltene concentration, while CGT can be more trustworthy for such evaluations.

4 Conclusions

In this experimental study with the main objective of determining the effect of asphaltene content over the MMP of oil/gas systems, generally the following results have been obtained:

- Based on slim tube results, the MMP increases linearly by increasing the asphaltene content of oil samples.
- Based on VIT approach by pendant drop method, the MMP related to oil samples with asphaltene content of above 10 % does not need correction, and thus the obtained results matches well with that of the slim tube method.
- The results of VIT (measuring by pendant drop) tests do not follow a significant trend towards increasing asphaltene content. The fitted line through the pendant drop data (MMP Vs. AS content) behaves as a second order polynomial.
- Results from the microscopic images of oil droplet and the Marangoni flows confirm that there is no surface tension gradient in a static system. As a result, VIT approach by pendant drop method is not an acceptable way to determine the effects of asphaltene content over the MMP; instead CGT can be more reliable for a sensitive analysis.

References

- [1] Maroto-Valer, M. M. (ed.) "Developments and Innovation in Carbon Dioxide (CO_2) Capture and Storage Technology", Woodhead Publishing Series in Energy, Boca Raton, FL, USA, 2010.
- [2] Green, D. W., Willhite, G. P. "Enhanced Oil Recovery", Henry L. Doherty Memorial Fund of AIME, Society of Petroleum Engineers, Richardson, TX, USA, 1998.
- [3] Andersen, S. I., Speight, J. G. "Thermodynamic models for asphaltene solubility and precipitation", Journal of Petroleum Science and Engineering, 22(1–3), pp. 53–66, 1999.
[https://doi.org/10.1016/S0920-4105\(98\)00057-6](https://doi.org/10.1016/S0920-4105(98)00057-6)
- [4] Mullins, O. C., Sheu, E. Y., Hammami A., Marshall, A. G. (eds.) "Asphaltenes, Heavy Oils and Petroleomics", Springer, New York, NY, USA, 2007.
<https://doi.org/10.1007/0-387-68903-6>
- [5] Kord, S., Miri, R., Ayatollahi, S., Escrochi, M. "Asphaltene Deposition in Carbonate Rocks: Experimental Investigation and Numerical Simulation", Energy Fuels, 26(10), pp. 6186–6199, 2012.
<https://doi.org/10.1021/ef300692e>

- [6] Mansoori, G. A., Elmi, A. S. "Remediation of Asphaltene and Other Heavy Organic Deposits in Oil Wells and in Pipelines", *Journal of Reservoir and Petroleum Engineering*, pp. 12–23, 2010. <https://doi.org/10.5510/OGP20100400039>
- [7] Roosta, A., Escrochi, M., Varzandeh, F., Khatibi, J., Ayatollahi, S., Shafiei, M. "Investigating the Mechanisms of Thermally Induced Wettability Alteration", In: *SPE Middle East Oil and Gas Show and Conference*, Manama, Bahrain, 2009, Article ID: SPE-120354-MS. <https://doi.org/10.2118/120354-MS>
- [8] Sayyad Amin, J., Nikooee, E., Ayatollahi, S., Alamdari, A. "Investigating wettability alteration due to asphaltene precipitation: Imprints in surface multifractal characteristics", *Applied Surface Science*, 256(21), pp. 6466–6472, 2010. <https://doi.org/10.1016/j.apsusc.2010.04.036>
- [9] Rao, D. N. "A new technique of vanishing interfacial tension for miscibility determination", *Fluid Phase Equilibria*, 139(1–2), pp. 311–324, 1997. [https://doi.org/10.1016/S0378-3812\(97\)00180-5](https://doi.org/10.1016/S0378-3812(97)00180-5)
- [10] Rao, D. N., Lee, J. I. "Application of the new vanishing interfacial tension technique to evaluate miscibility conditions for the Terra Nova Offshore Project", *Journal of Petroleum Science and Engineering*, 35(3–4), pp. 247–262, 2002. [https://doi.org/10.1016/S0920-4105\(02\)00246-2](https://doi.org/10.1016/S0920-4105(02)00246-2)
- [11] Rao, D. N., Lee, J. I. "Determination of gas-oil miscibility conditions by interfacial tension measurements", *Journal of Colloid and Interface Science*, 262(2), pp. 474–482, 2003. [https://doi.org/10.1016/S0021-9797\(03\)00175-9](https://doi.org/10.1016/S0021-9797(03)00175-9)
- [12] Orr, F. M., Jessen, K. "An analysis of the vanishing interfacial tension technique for determining minimum miscibility pressure", *Fluid Phase Equilibria*, 255(2), pp. 99–109, 2007. <https://doi.org/10.1016/j.fluid.2007.04.002>
- [13] Ghorbani, M., Gandomkar, A., Montazeri, G. H. "Describing a strategy to estimate the CO₂-heavy oil minimum miscibility pressure based on the experimental methods", *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 41(17), pp. 2083–2093, 2019. <https://doi.org/10.1080/15567036.2018.1549170>
- [14] Ghorbani, M., Momeni, A., Safavi, S., Gandomkar, A. "Modified vanishing interfacial tension (VIT) test for CO₂-Oil minimum miscibility pressure (MMP) measurement", *Journal of Natural Gas Science and Engineering*, 20, pp. 92–98, 2014. <https://doi.org/10.1016/j.jngse.2014.06.006>
- [15] Escrochi, M., Mehranbod, N., Ayatollahi, S. "The Gas-Oil Interfacial Behavior during Gas Injection into an Asphaltenic Oil Reservoir", *Journal of Chemical Engineering Data*, 58(9), pp. 2513–2526, 2013. <https://doi.org/10.1021/je400403y>
- [16] Jafari Behbahani, T., Ghotbi, C., Taghikhani, V., Shahrabadi, A. "Investigation on Asphaltene Deposition Mechanisms during CO₂ Flooding Processes in Porous Media: A Novel Experimental Study and a Modified Model Based on Multilayer Theory for Asphaltene Adsorption", 26(8), pp. 5080–5091, 2012. <https://doi.org/10.1021/ef300647f>
- [17] Zanganeh, P., Ayatollahi, S., Alamdari, A., Zolghadr, A., Dashti, H., Kord, S. "Asphaltene Deposition during CO₂ Injection and Pressure Depletion: A Visual Study", *Energy Fuels*, 26(2), pp. 1412–1419, 2012. <https://doi.org/10.1021/ef2012744>
- [18] Golkari, A., Riazi, M. "Experimental investigation of miscibility conditions of dead and live asphaltenic crude oil–CO₂ systems", *Journal of Petroleum Exploration and Production Technology*, 7(2), pp. 597–609, 2017. <https://doi.org/10.1007/s13202-016-0280-4>
- [19] Zolghadr, A., Escrochi, M., Ayatollahi, S. "Temperature and Composition Effect on CO₂ Miscibility by Interfacial Tension Measurement", *Journal of Chemical Engineering Data*, 58(5), pp. 1168–1175, 2013. <https://doi.org/10.1021/je301283e>
- [20] Wang, X., Zhang, S., Gu, Y. "Four Important Onset Pressures for Mutual Interactions between Each of Three Crude Oils and CO₂", *Journal of Chemical Engineering Data*, 55(10), pp. 4390–4398, 2010. <https://doi.org/10.1021/je1005664>
- [21] Wang, X., Gu, Y. "Oil Recovery and Permeability Reduction of a Tight Sandstone Reservoir in Immiscible and Miscible CO₂ Flooding Processes", *Industrial & Engineering Chemistry Research*, 50(4), pp. 2388–2399, 2011. <https://doi.org/10.1021/ie1016046>
- [22] Kazemzadeh, Y., Parsaei, R., Riazi, M. "Experimental study of asphaltene precipitation prediction during gas injection to oil reservoirs by interfacial tension measurement", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 466, pp. 138–146, 2015. <https://doi.org/10.1016/j.colsurfa.2014.10.053>
- [23] Saini, D., Rao, D. N. "Experimental Determination of Minimum Miscibility Pressure (MMP) by Gas/Oil IFT Measurements for a Gas Injection EOR Project", In: *SPE Western Regional Meeting*, Anaheim, CA, USA, 2010, Article ID: SPE-132389-MS. <https://doi.org/10.2118/132389-MS>
- [24] Mahdavi, E., Zebarjad, F. S., Ayatollahi, S., Taghikhani, V. "Experimental Investigation on the Effect of Asphaltene Types on the Interfacial Tension of CO₂-Hydrocarbon Systems", *Energy Fuels*, 29(12), pp. 7941–7947, 2015. <https://doi.org/10.1021/acs.energyfuels.5b02246>
- [25] Khalaf, M. H., Mansoori, G. A. "Asphaltenes aggregation during petroleum reservoir air and nitrogen flooding", *Journal of Petroleum Science and Engineering*, 173, pp. 1121–1129, 2019. <https://doi.org/10.1016/j.petrol.2018.10.037>
- [26] Zheng, L., Ma, K., Yuan, S., Wang, F., Dong, X., Li, Y., Du, D. "Determination of the multiple-contact minimum miscibility pressure of CO₂/oil system using oil droplet volume measurement method", *Journal of Petroleum Science and Engineering*, Article number: 106578, 2019. (In Press) <https://doi.org/10.1016/j.petrol.2019.106578>
- [27] Fathinasab, M., Ayatollahi, S., Taghikhani, V. "Minimum miscibility pressure and interfacial tension measurements for N₂ and CO₂ gases in contact with W/O emulsions for different temperatures and pressures", *Fuel*, 225, pp. 623–631, 2018. <https://doi.org/10.1016/j.fuel.2018.03.134>

- [28] Zhang, K., Jia, N., Zeng, F., Li, S., Liu, L. "A review of experimental methods for determining the Oil–Gas minimum miscibility pressures", *Journal of Petroleum Science and Engineering*, 183, Article number: 106366, 2019.
<https://doi.org/10.1016/j.petrol.2019.106366>
- [29] Chen, G., Gao, H., Fu, K., Zhang, H., Liang, Z., Tontiwachwuthikul, P. "An improved correlation to determine minimum miscibility pressure of CO₂–oil system", 5(1), pp. 97–104, 2020.
<https://doi.org/10.1016/j.gee.2018.12.003>
- [30] Ayirala, S. C., Xu, W., Rao, D. N. "Interfacial Behavior of Complex Hydrocarbons at Elevated Pressures and Temperatures", *The Canadian Journal of Chemical Engineering*, 84(1), pp. 22–32, 2006.
<https://doi.org/10.1002/cjce.5450840105>
- [31] Agilent "Agilent Syringe Specifications and Selection Guide: Part No. 51885246-D03-A8390", Agilent, Santa Clara, CA, USA, 2013.
- [32] Kohli, R., Mittal, K. L. (eds.) "Developments in Surface Contamination and Cleaning: Fundamentals and Applied Aspects", Elsevier: William Andrew, San Diego, CA, USA, 2016.
- [33] Rapp, B. E. "Microfluidics: Modeling, Mechanics and Mathematics: A volume in Micro and Nano Technologies", Elsevier: William Andrew, Kidlington, UK, 2017.
<https://doi.org/10.1016/C2012-0-02230-2>