Effect of Impurities in Industrial Flue Gas on Minimum Miscibility Pressure in CO_2 Flooding

Fu-lin Yang(✉), Peng Yu, Xue Zhang, and Meng Fan

College of Petroleum and Chemical Engineering, Beibu Gulf University, Qinzhou, China
Fulinyang@sina.com

Abstract. Understanding the effect of impurities (non-CO_2 gases) in industrial flue gas on the minimum miscibility pressure (MMP) is necessary for the design and implementation of a cost-effective flue gas enhanced oil recovery process. Slim tube experiments of effect of O_2 concentration in CO_2 on MMP are carried out on the model oil (n-C_5H_{12}/n-$C_{16}H_{34}$) and Jiangsu crude oil with three types of gases having various O_2 contents. The results indicated that the MMPs for these oils increase with increasing O_2 contents in the CO_2 streams. The experimental results and the case are also supported by our modeling work using a new multiple-mixing-cell model, which is found to be a robust and more accurate method with a tie-line length for determining the MMP. The calculation results indicated that MMPs decrease with increasing H_2S and SO_2 impurity contents, and increase with increasing O_2, CO and N_2 impurity concentrations in the CO_2 streams.

Keywords: MMP · Industrial flue gas · Multiple-mixing-cell model · Slim tube · Enhanced oil recovery

1 Introduction

CO_2 miscible flooding has become one of the most widely applied non-thermal EOR techniques [1–3]. The process development efforts have also been escalated, partly due to an increasing global awareness of the detrimental effects of industrial flue gases on

J. Lin (Ed.): *Proceedings of the International Field Exploration and Development Conference 2019*, SSGG, pp. 3105–3116, 2020.
https://doi.org/10.1007/978-981-15-2485-1_287

the environment [4, 5]. Industrial flue gas from power plants, which contains high CO_2 concentrations, is an attractive option. However, extracting CO_2 from the industrial flue gas will increase project costs due to requiring expensive gas separation facilities. And it is often the remaining low percentages of non-CO_2 component gases (H_2S, SO_2, N_2, CO, and O_2) that are more difficult and costly to remove [6–9]. A promising cost-effective process is thus to inject flue gas directly.

One important consequence is the need to understand the effects of the impurities (non-CO_2 gases) on minimum miscibility pressure (MMP), which is critical to the design and implementation of a flue gas flooding. A lot of effort has been made toward investigating the effects of contaminants in CO_2, i.e., H_2S, SO_2, N_2, and C_1-C_4 on MMP [9–16]. In general, the existence of H_2S, SO_2, and C_2-C_4 or intermediate hydrocarbons can decrease the CO_2-MMP, while the presence of methane or N_2 in CO_2 can substantially increase the CO_2-MMP.

Although O_2 and carbon monoxide are the most common components in flue gas, a few studies has been reported on the effect of O_2 and carbon monoxide on CO_2-MMP [16, 17]. Therefore, the objective of this study is to investigate systematically the effect of non-CO_2 component gases, i.e., H_2S, SO_2, N_2, CO, and O_2, on MMP in detail. In this work, slim tube experiments of effect of O_2 concentration in CO_2 on MMP are carried out on the model oil (n-C_5H_{12}/n-$C_{16}H_{34}$) and Jiangsu crude oil with three types of gases having various O_2 contents. To verify the accuracy of our algorithm determining MMP, the experimental results and the case published in the literature are compared with the MMPs calculated by using a new multiple-mixing-cell model with a tie-line length for determining the MMP [18–21]. And then the MMPs of model oils with non-CO_2 components are predicted.

2 Experiment

2.1 Materials

The crude oil samples with a viscosity of 12.3 mPa·s at 50 °C, studies are from Block L6 in the Jiangsu Oilfield, China. The model oil is a mixture of n-C_5H_{12}/n-$C_{16}H_{34}$ with a mole fraction ratio of 0.43/0.57. The n-pentane and n-hexadecane were purchased from Sinopharm Chemical Reagent Co. Ltd. And used without further treatment. The CO_2 gas (99.5%) and O_2 contaminated gases (94.81% and 90.01% CO_2) were purchased from Linde Industrial Gas (China), and used without further purification or adjustment.

2.2 Slime Tube Apparatus and Procedure

The slim-tube tests for determining oil recovery by displacing hydrocarbon fluids with pure CO_2 or contaminated CO_2 gases were conducted in a coiled, stainless tube of 0.46 cm ID packed with 50/70-mesh glass beads. The column length of the tube was 14.6 m. The porosity of the slim-tube column was 35.3% and the permeability 11.0 Darcy. The pore volume of the slim tube was 86.0 cm^3.

Both the reservoir fluid and the injection gas were transferred to the slim tube from vessels with a floating piston; the piston was activated with distilled water driven by a high-pressure Syringe pump. A backpressure regulator was placed close to the slim-tube outlet to control the system pressure.

Prior to each run, the apparatus is carefully cleaned with toluene followed by distilled acetone and dried with N_2 at a temperature of 100 °C. And then the slim tube is heated to the operating temperature. The oil sample is injected into the slime tube at the desired operating pressure to saturate the slim tube. The gas is injected into the slim tube to displace oil using a positive displacement pump at a rate of 12.0 cm^3/h. The following data are collected during the slim-tube experiment: the pore volume of injected gas, the volume of oil produced, and the volume of gas produced. Data are taken every ten minutes. The experiments continued until 1.2 PV of gas was injected into the slim tube. The recovery of oil plotted vs. different displacement pressures at 1.2 PV CO_2 gas injected determined the MMP at the prevailing temperature.

In this work, the MMPs of six systems were measured, which are the model oil (a mixture of 43/0.57*n*-C_5H_{12}/*n*-$C_{16}H_{34}$) and Jiangsu crude oil with three types of gases having various O_2 contents (pure CO_2, 5.19 mol% O_2, and 9.99 mol% O_2). The experiments are conducted at five different pressures for each system. The operating temperatures used are 50 °C for the model oil and 60 °C for the Block L6 crude oil, respectively.

3 Multiple-Mixing-Cell Modeling

In this paper, a multiple-mixing-cell model is used in order to compute key tie length and then the MMP. The multiple-mixing-cell model is a discrete model of a continuous gas injection process in the slim tube experiment. A packed slim tube is discretized into a series of constant volume cells and the continuous gas injection process is discretized into a series of constant volume batches (shown in Fig. 1).

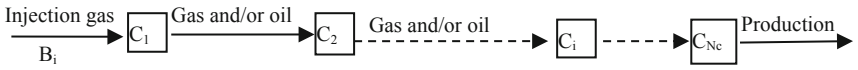

Fig. 1. Schematic diagram of cell-to-cell simulation

By assuming constant temperature and pressure in each cell, no physical dispersion among cells, no capillary force in each cell and among cells, and perfect mixing in each cell, this multiple-mixing-cell model is converted into a pure thermodynamic *P/T* flash calculation. A block-algebra simultaneous flash algorithm coupled with the Peng-Robinson (PR) cubic equation of state (EOS) is used in this work. The binary interaction parameters (k_{ij}) used and the parameters of the model are given in Table 1. We also set k_{ij}'s involving O_2, H_2S, SO_2 and CO to zero.

The parameters of our multiple-mixing-cell model are listed in Table 2. The total number of cells (N_c) is chosen to ensure that a steady-state compositional path of the process can be achieved. The cell volume, gas oil ratio (GOR), and fraction flow

Table 1. Binary interaction parameters [22]

Component	N_2	CO_2	CH_4	C_4H_{10}	C_5H_{12}-$C_{16}H_{34}$
N_2	0				
CO_2	0.0000	0			
CH_4	0.0311	0.1070	0		
C_4H_{10}	0.0711	0.1333	0.0133	0	
C_5H_{12}	0.1000	0.1400	0.0236	0.0170	0
$C_{10}H_{22}$	0.1550	0.0145	0.0500	0.0100	0.0000
$C_{14}H_{30}$	0.1550	0.0145	0.0500	0.0100	0.0000
$C_{16}H_{34}$	0.1550	0.0145	0.0600	0.0100	0.0000
$C_{20}H_{42}$	0.1550	0.0145	0.0700	0.0150	0.0000

Table 2. Parameters of the multiple-mixing-cell model

Total number of cells	1000
Total batch number	4000
GOR	0.3
Cell volume, cm^3	1.0
Fractional flow function	1.0

function do not affect the determination of the key tie lines, thus they do not affect the MMP calculation. The total batch number of gas injection can be calculated from.

$$N_b = N_c \frac{1.2}{GOR} \tag{1}$$

Where the value of 1.2 is an extensively accepted criterion; i.e., the required amount of gas injected for oil recovery calculation from the slim tube experiment is 1.2 PV.

A multi-contact miscibility process is controlled by a sequence of (nc − 1) key tie lines: the initial tie line, the injection tie line, and (n_c − 3) crossover tie lines, where n_c is the number of components [19, 22–28]. The MMP is defined as the lowest pressure at which one of the key tie lines becomes a critical tie line. There are many criteria that can be used to determine the MMP, but Zhao et al. found that zero key tie-line length is a robust criterion for this purpose [18]. Since all of the key tie lines can be robustly found through our multiple-mixing-cell model, our MMP calculation can be robustly based on the determination of tie-line length (TL), which is defined as

$$TL = \sqrt{\sum_i (x_i - y_i)^2} \tag{2}$$

where x_i and y_i are the equilibrium mole fractions of component i in the liquid and vapor phases, respectively. At the MMP, the tie-line length of one of the key tie lines reaches zero.

The calculation procedure of the gas displacement process in the slim tube experiment is summarized as follows [18–21]:

In a first step, the program simulates a number of cells of equal volume in a series. All the cells contain initially the same fluid (the reservoir oil). A specified amount of gas is added to cell 1. After mixing of the injected gas and the cell fluid, assuming perfect mixing, vapor fraction in the cell (v) can be determined from a *P/T* flash calculation. If $v \geq 1$, the mixture is at or above its dew point and the total gas volume must be larger than the cell volume. The excess gas is then moved into cell 2. If $v \leq 0$, the mixture is at or below its bubble point. The excess oil is moved into cell 2. If $0 < v < 1$, the mixture is in the two-phase region. The excess fluid moved from cell 1 to cell 2 is determined by the fractional flow function, i.e., Eq. (3).

$$\begin{cases} f_g = \dfrac{S_g^2/\mu_g}{S_g^2/\mu_g + (1-S_g)^2/\mu_o} \\ f_o = \dfrac{(1-S_g)^2/\mu_o}{S_g^2/\mu_g + (1-S_g)^2/\mu_o} \end{cases} \tag{3}$$

The liquid saturation (So) is defined as

$$S_o = \frac{V_l}{V_l + V_v} \tag{4}$$

where V_l and V_v are volumes of liquid and vapor phases after flash calculation, respectively.

In a second step, the excess volume formed in cell 2 is transferred to cell 3 and so on until production is obtained from the last cell. When one batch calculation has been completed, a new injection into cell 1 can take place and the cell to cell transfer calculation is resumed. If all key tie lines on current pressure are located, the calculation of next pressure should be processed.

It is important to mention that although the multiple-mixing-cell model [17] is somewhat similar to a one-dimensional compositional flood simulator, it offers an important advantage over the latter, i.e., the determination of key tie lines, and thus the MMP is not affected by the size of the mixing cell and the numerical dispersion induced by GOR and fractional flow. As also previously explained, the total number of cells we choose: as long as the steady-state compositional path can be achieved, all of the key tie lines can be determined.

4 Results and Discussion

4.1 Slim Tube Experiments

To interpret the experiments, oil recovery factors (ORF) at 1.2 pore volume (PV)s of injected gas are often plotted as a function of injection pressure. The MMP criteria were used to determine MMP as the pressure when ORF is 90% or 95%. Figure 2 shows

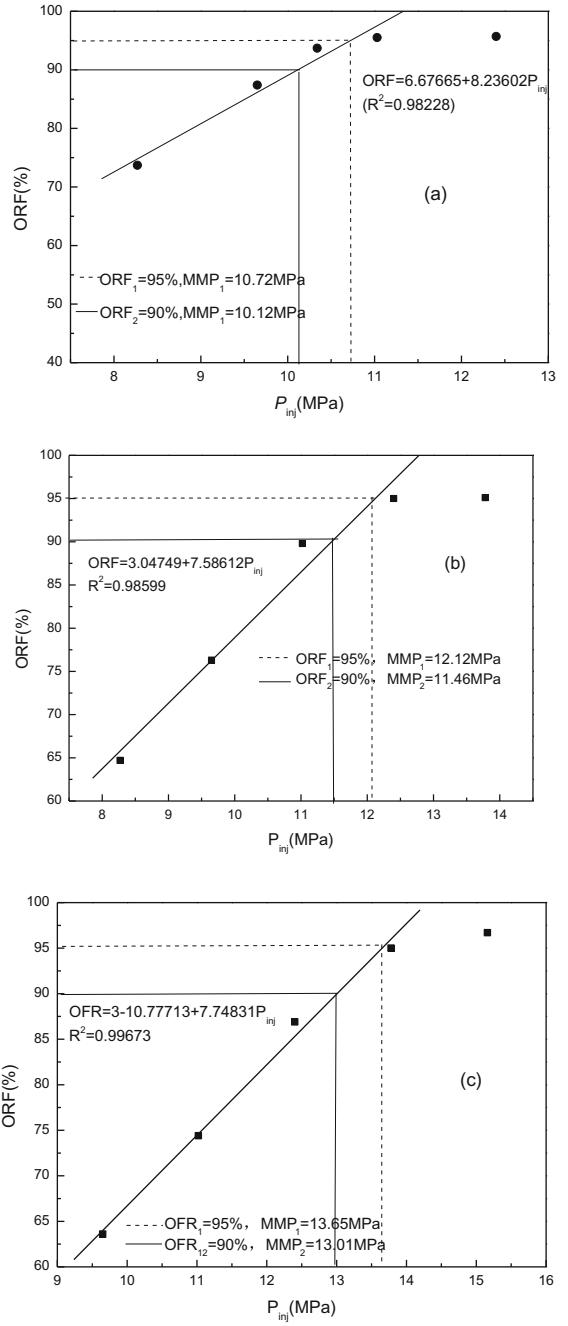

Fig. 2. ORF versus injection pressure for the model oil with three different gas injections at 50 °C. (a) pure CO_2, (b) 5.19 mol% O_2 in CO_2 gas, (c) 9.99 mol% O_2 in CO_2 gas

plots of ORF versus injection pressure for the model oil with three different gas injections at 50 °C. When ORF is 95%, the MMPs of the model oil with pure CO_2 is 10.72 MPa. This is in better agreement with that for the same system reported in the literature [29], indicating that the MMP determined in our slim tube experiment is reliable. As expected, the MMP varied depending on the criterion used. The results in Table 3 and Fig. 2 show that a slim tube oil recovery criterion of 90% will usually yield MMPs lower than that from 95% criterion. The results indicated that the effect of O_2 impurity in CO_2 is to increase the MMP.

Table 3. Slim tube experimental MMP

Gas	MMP_a, MPa		MMP_b, MPa	
	Jiangsu crude oil at 60 °C	Model oil at 50 °C	Jiangsu crude oil at 60 °C	Model oil at 50 °C
Pure CO_2	17.67	10.12	18.46	10.72
5.19 mol% O_2 in CO_2	21.55	11.46	22.97	12.12
9.99 mol% O_2 in CO_2	28.15	13.01	30.12	13.65

MMP_a defined as pressure at 90% oil recovery factor, MMP_b defined as pressure at 95% oil recovery factor.

Figure 3 shows plots of ORF versus injection pressure for the Jiangsu crude oil with three different gas injections at 60 °C. The MMPs for these systems are also summarized in Table 1. Similar to the model oil, O_2 impurity in CO_2 increases the MMP for the Jiangsu crude oil.

4.2 Multiple-Mixing-Cell Modeling

4.2.1 Validity of the Algorithm

In this study, the accuracy of our algorithm determining MMP was verified and compared with a case. The required oil and gas composition of the case was taken from the published literature [23]. The case is a six-component oil consisting of 20% CH_4, 5% CO_2, 5% C_4H_{10}, 40% $C_{10}H_{22}$, 10% $C_{14}H_{30}$, and 20% $C_{20}H_{42}$ with pure CO_2 as the injection gas. The tie-line length calculations are illustrated in Fig. 4. For this six-component system, there are five key tie lines and the crossover tie-line1 reaches zero at the MMP. As noted in the figure, the calculation is stopped at a pressure close to the MMP; the length of the crossover tie-line1 would be exactly zero at the MMP. This is due to the common difficulty encountered when one tries to do flash calculation in the critical region. We determine the MMP to be 16.02 MPa by extrapolation, which is in excellent agreement with the calculated MMP (16.4 MPa) reported in the literature [23].

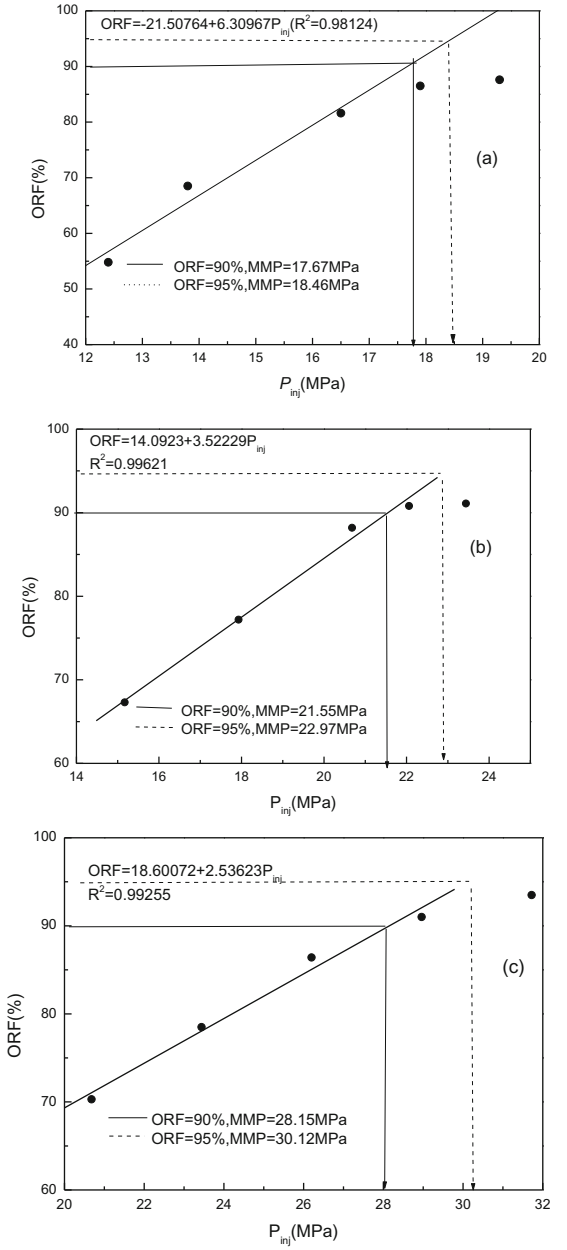

Fig. 3. ORF versus injection pressure for the Jiangsu crude oil with three different gas injections at 60 °C. (a) pure CO_2, (b) 5.19 mol% O_2 in CO_2 gas, (c) 9.99 mol% O_2 in CO_2 gas

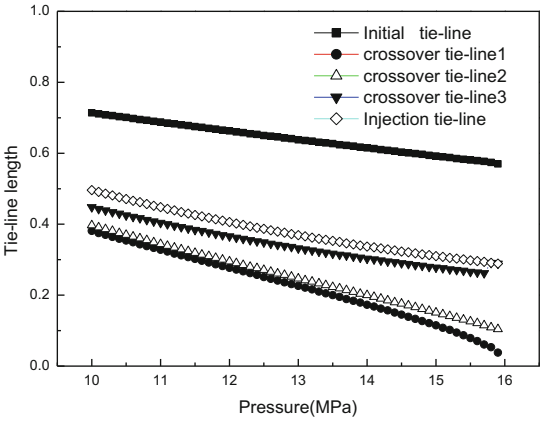

Fig. 4. Key tie-line lengths in the simulation of a six-component oil with pure CO_2 as the injection gas at 71.1 °C. crossover tie-line1 becomes a critical tie line at 16.02 MPa.

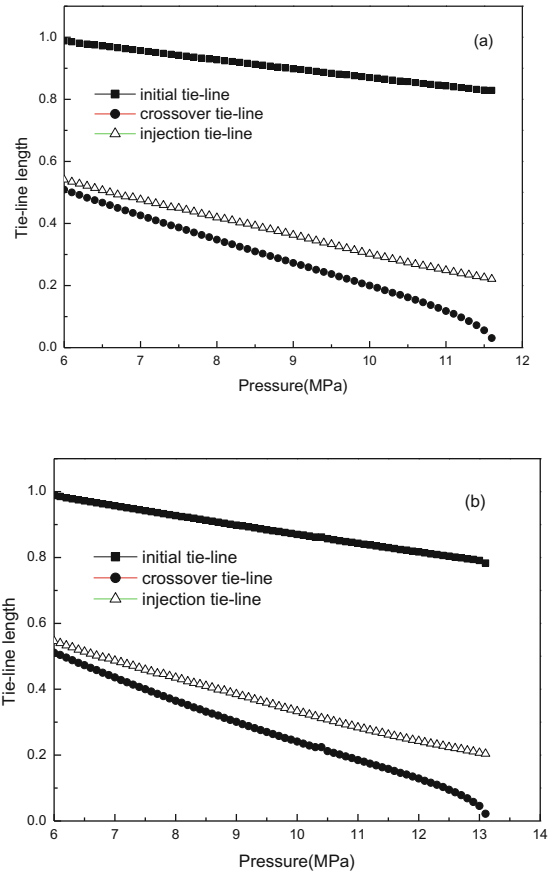

Fig. 5. Key tie-line length versus injection pressure for the model oil with three different gas injections at 50 °C. (a) 5.19 mol% O_2 in CO_2, (b) 9.99 mol% O_2 in CO_2. crossover tie-line becomes a critical tie line at 11.76 MPa and 13.24 MPa, respectively.

Table 4. Comparison of measured and calculated MMPs for model oil

Gas	MMP, MPa		Absolute relative deviation of calculated MMP, %
	Measured MMP_b	Predicted MMP	
Pure CO_2	10.72	10.29	4.18
5.19 mol% O_2	12.12	11.76	3.06
9.99 mol% O_2	13.65	13.24	3.10
5.19 mol% H_2S	–	9.43	–
9.99 mol% H_2S	–	9.04	–
5.19 mol% N_2	–	12.63	–
9.99 mol% N_2	–	15.26	–
5.19 mol% SO_2	–	9.08	–
9.99 mol% SO_2	–	8.54	–
5.19 mol% CO	–	12.24	–
9.99 mol% CO	–	14.26	–

The MMPs of model oils with O_2-contaminated CO_2 are then predicted. As showed in Fig. 5, MMP was determined to 11.76 MPa and 13.24 MPa by extrapolation, respectively, which are found to be reliable within the experimental error (4.18%–3.06%) in Table 4. This indicates our modeling has higher accuracy to determine MMP.

4.2.2 Effect of Non-CO_2 Components on MMP

In this study, the MMPs of model oils with non-CO_2 components (N_2, H_2S, O_2, CO, and SO_2) are predicted. Table 4 summarizes our predictions. The content of N_2, CO and O_2 in CO_2 increases the MMP, and the effect of H_2S and SO_2 in CO_2 is to decrease the MMP. This is because an improvement in the solubility of contaminated CO_2 in the model oil due to the higher critical temperatures of H_2S and SO_2 than that of CO_2. On

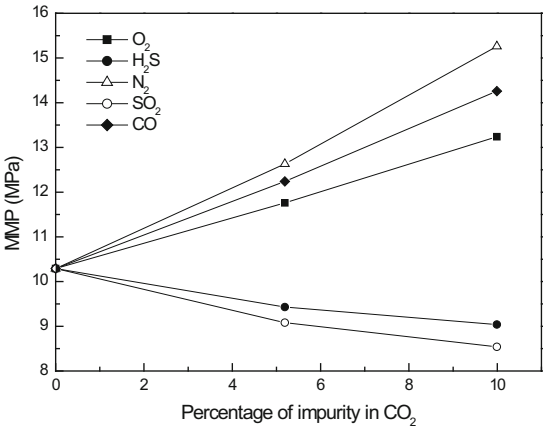

Fig. 6. MMPs for model oils with impurity in CO_2 gases at 50 °C.

the other hand, the existence of the components (i.e., N_2, CO and O_2) with lower critical temperatures causes a reduction in solubility of contaminated CO_2 in the model oil and has the opposite effect. From our prediction, the effect of impurity in CO_2 stream on MMP is found to $N_2 > CO > O_2 > H_2S > SO_2$ in order, as depicted in Fig. 6.

5 Conclusion

In this study, lab experiments of effect of O_2 concentration in CO_2 on MMP are carried out on the model oil (n-C_5H_{12}/n-$C_{16}H_{34}$) and Jiangsu crude oil with three types of gases having various O_2 contents. The results indicated that the MMPs for these oils increase with increasing O_2 contents in CO_2 gas. The experimental results and the case are also supported by our modeling work using a new multiple-mixing-cell model, which is found to be a robust and more accurate method for determining the MMP. The calculation results indicated that MMPs decrease favorably as the H_2S and SO_2 contents in CO_2 stream increase, and increase unfavorably as an increase of O_2, CO and N_2 impurity in the CO_2 streams, and the effect of impurity in CO_2 stream on MMP is found to $N_2 > CO > O_2 > H_2S > SO_2$ in order.

Acknowledgments. The project is supported by Guangxi Province Natural Science Foundation (2018JJA120001, 2017GXNSFAA198105, 2016GXNSFBA380180) and Beibu Gulf University High-level Talent Foundation (18KYQD52).

References

1. Moritis, G.: CO_2 miscible, steam dominate enhanced oil recovery processes. Oil Gas J. **101** (14), 36–40 (2010)
2. Kahrobaei, S., Li, K., Vincent-Bonnieu, S., et al.: Effects of compositional variations on CO_2 foam under miscible conditions. AIChE J. **64**(2), 758–764 (2018)
3. Huang, F., Huang, H.D., Wang, Y.Q., et al.: Assessment of miscibility effect for CO_2 flooding EOR in a low permeability reservoir. J. Petrol. Sci. Eng. **145**, 328–335 (2016)
4. Zhao, H.L., Chang, Y.W., Feng, S.L.: Oil recovery and CO_2 storage in CO_2 flooding. Pet. Sci. Technol. **34**(13/16), 1151–1156 (2016)
5. Bender, S., Akin, S.: Flue gas injection for EOR and sequestration: case study. J. Petrol. Sci. Eng. **157**, 1033–1045 (2017)
6. Porter, R.T.J., Fairweather, M., Pourkashanian, M., et al.: The range and level of impurities in CO_2 streams from different carbon capture sources. Int. J. Greenhouse Gas Control **36**, 161–174 (2015)
7. Wei, N., Li, X.C., Wang, Y., et al.: Geochemical impact of aquifer storage for impure CO_2 containing O_2 and N_2: Tongliao field experiment. Appl. Energy **145**(1), 198–210 (2015)
8. Bian, X.Q., Han, B., Du, Zh.M., et al.: Integrating support vector regressing with genetic algorithm for CO_2-oil minimum miscibility pressure (MMP) in pure and impure CO_2 streams. Fuel **182**(15), 550–557 (2016)
9. Shokoya, O.S., Mehta, S.A., Moore, R.G., et al.: An environmentally-friendly process for improved recovery from light oil reservoirs. JCPT **44**(8), 49–54 (2005)

10. Kovarik, F.S.: A minimum miscibility pressure study using impure CO_2 and West Texas oil system: data base, correlations and compositional simulation. In: SPE, no. 14689, pp. 1–8 (1985)
11. Zhang, P.Y., Huang, S., Sayegh, S., Zhou, X.L.: Effect of CO_2 impurities on gas injection EOR process. In: SPE, no. 89477, pp. 1–10 (2004)
12. Zuo, Y.X., Chu, J.Z., Ke, Sh.L., Guo, T.M.: A study on the minimum miscibility pressure for miscible flooding systems. J. Pet. Sci. Eng. **8**, 315–328 (1993)
13. Bon, J., Sarma, H.K., Theophanous, A.M.: An investigation of minimum miscibility pressure for CO_2 – rich injection gases with pentanes-plus fraction. In: SPE, no. 97536, pp. 1–12 (2005)
14. Yellig, W.F., Metcalfe, R.S.: Determination and prediction of CO_2 minimum miscibility pressures. J. Pet. Technol. **32**(01), 160–170 (1980)
15. Alston, R.B., Kokolis, G.P., James, C.F.: CO_2 minimum miscibility pressure: a correlation for impure CO_2 streams and live oil systems. SPE J. **25**(02), 268–274 (1985)
16. Dong, M.Z., Huang, S., Steve, B.D., Mourits, F.M.: A comparison of CO_2 minimum miscibility pressure determinations for Weyburn crude oil. J. Pet. Sci. Eng. **31**, 13–22 (2001)
17. Yang, F., Zhao, G.-B., Adidharma, H., et al.: Effect of oxygen on minimum miscibility pressure in carbon dioxide flooding. Ind. Eng. Chem. Res. **46**(4), 1396–1401 (2007)
18. Zhao, G.B., Adidharma, H., Towler, B., et al.: Using a multiple-mixing-cell model to study minimum miscibility pressure controlled by thermodynamic equilibrium tie lines. Ind. Eng. Chem. Res. **45**(23), 7913–7923 (2006)
19. Jaubert, J.-N., Wolff, L., Neau, E., Avaullee, L.: A very simple multiple mixing cell calculation to compute the minimum miscibility pressure whatever the displacement mechanism. Ind. Eng. Chem. Res. **37**(12), 4854–4859 (1998)
20. Jaubert, J.-N., Arras, L., Neau, E., Avaullee, L.: Properly defining the classical vaporizing and condensing mechanisms when a gas is injected into a crude oil. Ind. Eng. Chem. Res. **37** (12), 4860–4869 (1998)
21. Jaubert, J.-N., Avaullee, L., Pierre, C.: Is it still necessary to measure the minimum miscibility pressure? Ind. Eng. Chem. Res. **41**(2), 303–310 (2002)
22. Danesh, A.: PVT and Phase Behavior of Petroleum Reservoir Fluids. Elsevier Science B.V., New York (1998)
23. Wang, Y., Orr, F.M.: Analytical calculation of minimum miscibility pressure. Fluid Phase Equilib. **139**(1–2), 101–124 (1997)
24. Jessen, K., Michelsen, M.L., Stenby, E.H.: Global approach for calculation of minimum miscibility pressure. Fluid Phase Equilib. **153**(2), 251–263 (1998)
25. Ahmadi, K., Johns, R.T.: Multiple mixing-cell method for MMP calculations. In: SPE Annual Technical Conference and Exhibition, Denver, Colorado, 21–24 September 2008. SPE 116823
26. Teklu, T.W., Ghedan, S.G., Graves, R.M., et al.: Minimum miscibility pressure determination: modified multiple mixing-cell method. In: SPE EOR Conference at Oil and Gas West Asia, Muscat, Oman, 16–18 April 2012. SPE 155454
27. Fazlali, A., Nikkokar, M., Mohammadi, A.H.: Computational procedure for determination of minimum miscibility pressure of reservoir oil. Fuel **106**, 707–711 (2013)
28. Fazlali, A., Nikkokar, M., Agha-Aminiha, A., et al.: Prediction of minimum miscibility pressure in oil reservoirs using a modified SAFT equation of state. Fuel **108**, 675–681 (2013)
29. Elsharkawy, A.M., Poettmann, F.H., Christiansen, R.L.: Measuring CO_2 minimum miscibility pressures: slim-tube or rising-bubble method? Energy Fuels **10**(2), 443–449 (1996)