

Research Article **A New Predictive Method for CO₂-Oil Minimum Miscibility Pressure**

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Gas injection processes are among the effective methods for enhanced oil recovery. Miscible and/or near miscible gas injection processes are among the most widely used enhanced oil recovery techniques. The successful design and implementation of a miscible gas injection project are dependent upon the accurate determination of minimum miscibility pressure (MMP), the pressure above which the displacement process becomes multiple-contact miscible. This paper presents a method to get the characteristic curve of multiple-contact. The curve can illustrate the character in the miscible and/or near miscible gas injection processes. Based on the curve, we suggest a new model to make an accurate prediction for CO_2 -oil MMP. Unlike the method of characteristic (MOC) theory and the mixing-cell method, which have to find the key tie lines, our method removes the need to locate the key tie lines that in many cases is hard to find a unique set. Moreover, unlike the traditional correlation, our method considers the influence of multiple-contact. The new model combines the multiple-contact process with the main factors (reservoir temperature, oil composition) affecting CO_2 -oil MMP. This makes it is more practical than the MOC and mixing-cell method, and more accurate than traditional correlation. The method proposed in this paper is used to predict CO_2 -oil MMP of 5 samples of crude oil in China. The samples come from different oil fields, and the injected gas is pure CO_2 -oil MMP is within 2%.

1. Introduction

Gas injection processes are among the effective methods for enhanced oil recovery [1–5]. In recent years, CO_2 injection has attracted the most attention because it not only reduces the greenhouse effect caused by CO_2 emissions but also greatly improves oil recovery. This is a win-win approach [5, 6]. A key parameter in the design of the CO_2 injection project is the MMP, whereas local displacement efficiency from the gas injection is highly dependent on the MMP [7, 8]. There are many different methods to determined MMP [9]. The commonly used prediction methods of MMP can be divided into empirical formula methods, experiment methods, and calculation methods [4, 10].

The usual empirical formulas are the NPC method, Johnson and Pollin correlation, and Yelling and Metcalfe correlation [11–13]. There is almost no need for calculation

resources when applying empirical formulas, which is quite convenient for the initial evaluation of oil reservoirs. However, due to the limited scope of application of the empirical formula, it is necessary to carefully select the appropriate formula for different reservoir conditions.

At present, the main experimental methods include the bubble rising method, surface tension method, and slimtube experiment [14–16]. During the experiment methods, the method that best accords with the field practice is to perform slim-tube displacement. Slim-tube test is the industry standard for measuring the MMP [17]; a key disadvantage is that there is no standard designed for the experimental set-up or operation, and difference may exist in experimental set-up or operation from one laboratory to next slim-tube test. Besides, the significant disadvantage of the thin tube experiment is that it is time-consuming. For practical reservoir suitability evaluation, it is impractical

The firs	st conta	ct				GAS +	OIL						
						↓ ↓	Ļ						
The second contact			GAS	$+X_1$	$Y_1 + 0$	OIL							
					ļ	↓ I	↓	Ļ					
The thi	rd cont	act		GAS+	X ₂₁	Y ₂₁ + 2	X ₂₂	$Y_{22}+0$	DIL.				
				ļ	ţ	ļĮ	ţ	ļ	Ļ				
The fou	The fourth contact GAS+		X ₃₁ Y ₃₁ + X ₃₂		$Y_{32} + X_{33}$ $Y_{33} + 0$		DIL						
			↓ ↓	Ļ	ļ	Ļ	↓	↓ ↓	↓	↓ I			
		GAS	+ X	Y+ .	X	Y +.	X	Y +.	X	Y+ (DIL .		
		↓ ↓	ŧ	↓	↓ I	↓	Ŧ	ļ	ŧ	ļ	ŧ		
	GAS	+ X _	Y +.	Χ.	Y +.	X	Y +.	X .	Y +.	X	Y+ (DIL	
	ļ	ţ	↓ ↓	ŧ	ļĮ	↓ I	↓	Ļ	ļ	Ļ	ļ	Ļ	
GAS+ X Y+X		Χ	Y +.	X	Y +.	X	Y +2	X	Y +2	X	Y +0	OIL	
	N's contact												

FIGURE 1: Mixing-cell processes.

N's	$ GAS + X \\ \downarrow \qquad \downarrow $	Y + X	 $\begin{array}{c} Y + X \\ \downarrow \\$	 Y + OIL	Y+ OIL ↓ ↓
contact	$X_1 Y_1$	X ₂ Y ₂	 X_n Y_n	 $X_{N-1} Y_{N-1}$	$X_N + Y_N$
n	1	2	 п	 N-1	Ν

FIGURE 2: Equilibrium composition of N contact.

to carry out slim-tube tests on all oil samples. Therefore, it is necessary to carry out calculation and simulation methods to predict MMP.

As for the calculation methods, more and more methods have been proposed in recent years to calculate MMP for real systems. There are mainly the following ways: methodsbased correlation [18-20], compositional simulation, mixing-cell models and analytical models [17, 21-23], and artificial neural network method [10, 24, 25]. Each of these methods, however, has advantages and disadvantages. Finegrid compositional simulations can suffer from numerical dispersion effects, and in compositional simulations, the number of pseudocomponents is usually much less than the crude oil, which can lead to the difference of phase behaviors. Analytical method of characteristic (MOC) considers the process of multiple-contact, and the approach for calculating MMP has been demonstrated clearly by Yun and Ahmadi [18, 26]. The validity of the model has been confirmed repeatedly. However, equations of crossover tie lines are a set of nonlinear equations and possible converged to a wrong set of tie lines. One method has been suggested to simplify the method of finding the key crossover tie lines for a dispersion-free displacement using the method of characteristic theory (MOC) [9]. But the system of equations is underdetermined because the number of unknowns exceeds the number of equations [9], which can also easily lead to a wrong set of tie lines. For the multiple mixing-cell methods [26], calculated for each cell the slope of the tie-line length as the function of cell number, a key line is developed when three successive cells have a slope of zero. However, when using this method, we found in many cases that the related



FIGURE 3: Characteristic curve of multiple-contact. The injection gas is $1\%CO_2$ +99%CH₄.



FIGURE 4: Characteristic curve of multiple-contact. The injection gas is $5\%CO_2+95\%CH_4$.



FIGURE 5: Characteristic curve of multiple-contact. The injection gas is $9\%CO_2+91\%CH_4$.



FIGURE 6: Characteristic curve of multiple-contact. The injection gas is $20\%CO_2+80\%CH_4$.

cells which satisfied these conditions cannot be obtained, and so the key tie lines cannot be found and the MMP cannot be determined. For the neural network method, the calculation speed is fast, and the reservoir can be screened on a large scale. However, due to the limitation of insufficient experimental data, the trained neural network is prone to overfitting, leading to insufficient generalization ability, and the error in actual use is often too large.

This paper suggests a new correlation for CO_2 -oil MMP. Unlike most of the traditional correlation, the model just considers some key factors (such as reservoir temperature, oil composition) affecting CO_2 -oil MMP. Besides, the model also considers the influence of the multiple-contact process. Based on multiple mixing-cell methods [26], we do not have to find the key tie lines (which in many cases cannot be found). We just use the minimum value of the characteristic curve of multiple-contact, after which a correlation from the change of the minimum value is obtained, and thus, the MMP is determined. This makes our new model to have both the advantage of correlation and multiple-contact so that more stable and accurate results can be obtained.

2. Method

2.1. Characteristic Curve of Multiple-Contact. To get the characteristic curve of multiple-contact, we still use the following mixing-cell processes [26] (see Figure 1).

At a fixed temperature and pressure, the injection GAS and OIL are mixed in a mole fraction, such as 1:1; this is



FIGURE 7: Characteristic curve of multiple-contact. The injection gas is 30%CO₂+70%CH₄.

the first contact. Thus, a flash can be performed, and this results in two equilibrium compositions, one for liquid X_1 and one for vapor Y_1 . For the second contact, GAS and X_1 are mixed. Meanwhile, Y_1 and OIL are mixed. Each of them can perform a flash and result in X_{21} , Y_{21} , X_{22} , and Y_{22} . For the third contact, analogously, GAS and X_{21} , Y_{21} and X_{22} , Y_{22} , and OIL are mixed.

According to the process, when the N contact (see Figure 2) will result in $N \times 2$ equilibrium composition, the equilibrium composition can be described as X_n , Y_n . The n is from 1 to N.

For the equilibrium composition X_n , Y_n , if the crude oil has been divided into K components, then the liquid phase mole fraction of component can be described as $X_n^k (k = 1 \cdots K)$. The vapor phase mole fraction of component can be described as $Y_n^k (k = 1 \cdots K)$. Next, we calculate f(n) according to Equation (1).

$$f(n) = \sqrt{\sum_{1}^{K} \left(\left(X_{n}^{K} \right)^{2} - \left(Y_{n}^{K} \right)^{2} \right)}, \qquad (1)$$

where X_n^k is the vapor phase mole fraction. Y_n^k is the liquid phase mole fraction.

Then we draw a f(n)-n curve $(n = 1 \dots N)$; here, we defined this curve as the characteristic curve of multiple-contact.

2.2. Character of Characteristic Curve of Multiple-Contact. Here, we use the following example to illustrate how our characteristic curve of multiple-contact reflects the influence of injection gas.

For a sample of crude oil, at a given pressure and temperature, the injection gas is $1\%CO_2+99\%CH_4$, and the characteristic curve of multiple-contact is shown in Figure 3. Figure 3 shows that the minimum value is located on the right side of the curve, and the change of the curve between the minimum value and the right endpoint is gentle. Although the left side of the curve decreases as the increase of *n*, it is always higher than the right side of the curve. This reflects that MMP is determined by the composition of the oil, and the miscibility is more likely a vaporizing drive



FIGURE 8: Characteristic curve of multiple-contact under different injection gas conditions.

Components	Mole fraction (%)	Pc (atm)	Tc (K)	ω
CO ₂	0.343	72.8	304.2	0.225
N_2	1.971	33.5	126.2	0.04
C_1	16.739	45.4	190.6	0.008
C ₂	5.901	48.2	305.4	0.098
C ₃	3.843	41.9	369.8	0.152
IC_4	20.401	36	408.1	0.176
NC_4	1.295	37.5	425.2	0.193
IC ₅	1.769	33.4	460.4	0.227
NC ₅	0.604	33.3	469.6	0.251
C ₆	1.576	30.473	546.686	0.296
C ₇ +	45.56	24.2231	637.54	0.414698

 $\underbrace{\underbrace{\begin{array}{c}c} 0.6 \\ 0.5 \\ 0.4 \\ 0.3 \\ 0.2 \\ 0.1 \\ 0 \\ 0 \\ 10 \\ 20 \\ 30 \\ 40 \\ 50 \\ 60 \\ n \\ \end{array}}}_{n}$

FIGURE 9: Characteristic curve of multiple-contact.

process. From the point of MOC, in this case, MMP is determined by the initial tie line.

By increasing CO_2 concentration in the injected gas (changing the inject gas to $5\% CO_2 + 95\% CH_4$), the characteristic curve of multiple-contact is shown in Figure 4, in which the curve is closed in Figure 3. The miscibility is still a vapor-



FIGURE 10: Minimum value decreases as the pressure increases.

TABLE 2: The predicted results of five samples.

Oil	Minimum value of character curve	Prediction of minimum value by Equation (2)	Predicted MMP
А	0.195136	0.201558	22.3
В	0.1867	0.190520	21.9
С	0.2129	0.206915	28
D	0.2038	0.206915	20.1
Е	0.1341	0.136969	19.55

izing drive process, and MMP is still determined by the composition of the oil.

By changing the inject gas to $9\%CO_2+91\%CH_4$, we can see a significant change in the characteristic curve of multiple-contact (Figure 5). This means the increase of CO_2 produces an obvious influence on the MMP. The miscibility has become a combined condensing and vaporizing displacement. From the point of MOC, in this case, the MMP is determined by crossover tie lines.

By changing the inject gas to $20\%CO_2+80\%CH_4$, the characteristic curve of multiple-contact is shown in Figure 6. The miscibility is still a combined condensing and vaporizing displacement, the minimum value moves leftward, this means

TABLE 1: Fluid character of oil A.

TABLE 3: The molar composition of oil samples A-E.

	Sample A	Sample B	Sample C	Sample D	Sample E
CO_2	0.34	0.83	0.00	0.02	0.25
N_2	1.97	0.76	0.36	1.33	3.71
C_1	16.74	30.12	30.27	10.79	53.52
C_2	5.90	5.94	2.39	3.39	3.11
C ₃	3.84	2.32	0.74	2.53	0.72
IC_4	20.40	0.88	0.08	1.02	0.28
NC_4	1.30	0.74	0.26	0.96	0.22
IC_5	1.77	2.77	2.09	3.43	0.12
NC_5	0.60	1.97	1.54	2.44	1.36
C ₆	1.58	3.56	3.49	4.71	2.07
C ₇	0.13	5.13	5.28	7.19	3.50
C ₈	0.06	5.76	6.25	7.74	4.20
C ₉	1.32	4.75	5.23	6.55	3.75
C ₁₀	2.24	4.04	4.52	5.43	3.82
C ₁₁	2.50	3.03	3.36	3.97	2.12
C ₁₂	4.18	4.17	4.71	5.53	2.98
C ₁₃	3.07	2.91	3.20	3.65	1.98
C_{14}	3.07	2.69	3.09	3.43	1.78
C ₁₅	2.18	1.94	2.18	2.36	1.24
C ₁₆	2.59	2.35	2.88	3.17	1.56
C ₁₇	2.38	1.95	2.39	2.61	1.29
C ₁₈	1.95	1.20	1.57	1.54	0.80
C ₁₉	1.59	0.86	1.18	1.04	0.64
C ₂₀	1.37	0.73	1.03	0.89	0.48
C ₂₁	1.31	0.73	1.00	0.93	0.48
C ₂₂	1.16	0.62	0.88	0.81	0.41
C ₂₃	1.11	0.57	0.81	0.74	0.37
C ₂₄	0.95	0.47	0.69	0.62	0.30
C ₂₅	0.93	0.43	0.65	0.59	0.29
C ₂₆	0.86	0.40	0.61	0.57	0.25
C ₂₇	0.89	0.41	0.66	0.61	0.25
C ₂₈	0.84	0.38	0.66	0.55	0.22
C ₂₉	0.82	0.34	0.64	0.48	0.19
C ₃₀	0.64	0.23	0.46	0.31	0.14
C ₃₁	0.52	0.17	0.34	0.22	0.10
C ₃₂	0.42	0.13	0.28	0.16	0.07
C ₃₃	0.40	0.12	0.26	0.15	0.06
C ₃₄	0.37	0.12	0.25	0.17	0.07
C ₃₅	0.43	0.15	0.31	0.24	0.09
C ₃₆₊	5.27	3.30	3.39	7.12	1.17
T/°C	98.9	97.3	108.4	76	71.56

the inject gas caused more influence to the MMP, and in all this case, the MMP is determined by crossover tie lines.

By changing the inject gas to 30%CO₂+70%CH₄, the characteristic curve of multiple-contact is shown in Figure 7. The minimum value continues to decrease, but the number of contacts does not change significantly.

Then the mole percentage of CO_2 continues to increase to 100%, and the curve does not change much.

TABLE 4: Comparison of MMP prediction results by different methods.

MMP\sample	А	В	С	D	Е
Our method	22.3	21.9	28	20.1	19.55
Slim-tube	22.0	22.1	27.9	19.8	19.5
Numerical simulation	22.4	21.2	26.6	20.3	18.9

But the minimum value becomes lower as CO_2 increases, as shown in Figure 8. This shows that MMP becomes lower as CO_2 increases.

2.3. MMP Predicted Method-Based Characteristic Curve of Multiple-Contact. In our paper, MMP prediction can be completed by the following method: Specify the reservoir temperature and pressure that is well below the MMP, get the characteristic curve of multiple-contact by the method described in the last, and find the minimum value, normally the value is above zero. Increase the pressure by a step, find the minimum value, repeat the step, and we can see the decrease of minimum value as the increase of pressure. From our calculation, and compared to the result of slim-tube, we find for most of the case, as the pressure reaches MMP, the minimum value of characteristic curve is below 0.23, and there is a change in a small scope (0.23-0.13). In fact, from the definition of f(n), we can see it has a similar meaning as the tie line, so, naturally, the minimum value of f(n) will decrease as the pressure increases. However, it does not reach zero. This can also be shown in multiple mixing-cell methods [26], only by power-law extrapolation, a zerolength tie line can be acquired, the minimum value is just near zero, and the extrapolation can also lead to the error of prediction. We find the main factor affecting the minimum value resembles the factor for the MMP, which is reservoir temperature and oil composition. By comparing with the result of slim-tube, we get a correlation, which is shown in Equation (2).

$$\begin{split} V_{\min} &= (-0.0017) \times T + (0.0057) \times C_{7-15} + (-0.0174) \\ &\times C_{16-26} + (0.0405) \times C_{27+}, \end{split}$$

where V_{\min} is the minimum value. *T* is reservoir temperature. C_{7-15} is mole fraction. C_{16-26} is mole fraction. C_{27+} is mole fraction.

Using Equation (2), we predict the minimum value of the characteristic curve of multiple-contact. If the value is below 0.23, we think the components system can become miscible, and then we calculate the characteristic curve of multiple-contact. When we increase the pressure, the minimum value will decrease, as it becomes smaller than the value calculating by Equation (2), the tolerance should be in 0.01, and then the related pressure is MMP.

3. Case Study

3.1. Example for MMP Predicted. The fluid character of oil A is shown in Table 1. When the inject gas is pure CO_2 , at temperature 98.9°C, pressure 10 MPa, after 50 numbers



FIGURE 11: Change of interfacial tension with displacement pressure.



FIGURE 12: Change of recovery factor with displacement pressure.

 TABLE 5: Comparison of the time consumption of different methods for MMP prediction.

Time\sample	А	В	С	D	Е
Our method	10 s	7 s	13 s	5 s	4 s
Slim-tube	5 d	5 d	7 d	5 d	5 d
Numerical simulation	3.5 m	3 m	6 m	2.5 m	3 m

of contact, the characteristic curve of multiple-contact is shown in Figure 9.

Using Equation (2), we make prediction that when the pressure reaches MMP, the minimum value is 0.201558, which is less than 0.23. This shows that the component system can become miscible. Increasing the pressure at a step, we can see the minimum value decreases as shown in Figure 10. When the minimum value is smaller than 0.201558, and the tolerance is in 0.01, the related pressure is 22.3 MPa, which is the prediction of MMP. This result is closed to the MMP from slim-tube (22.0 MPa). The minimum value of the characteristic curve at MMP from the slim-tube is 0.195136.

We use this method to predict 5 samples of crude oil in China. These samples come from different oil fields, and the injected gas is pure CO_2 . The molar composition of these crude oil samples is shown in Appendix A. The predicted results are shown in Tables 2 and 3.

3.2. Comparison of Different Prediction Methods. The methods in this paper, numerical simulation, and slimtube experiment were used to predict the CO_2 -oil MMP of 5 crude oils A, B, C, D, and E. The results are shown in Table 4. In the numerical simulation, by fitting the data of the constant composition expansion (CCE) experiment and differential liberation (DL) experiment to ensure the accuracy of the fluid model, a one-dimensional numerical simulation model with the same size as the slim-tube experiment was established to simulate the process of the slim-tube experiment.

Taking sample 1 as an example, the results of the numerical simulation experiment on the slim-tube are presented below. Figure 11 shows the change of interfacial tension with displacement pressure after CO_2 injection of 1.2PV. It can be seen that the interfacial tension decreases significantly with the increase of pressure. When the pressure increases from 20 MPa to 25 MPa, the interfacial tension changes suddenly to around 0, and there is no significant change in the interfacial tension after further increase in pressure. This shows that the minimum miscible pressure is between 20 MPa and 25 MPa. Based on these 6 sets of numerical experiments, the recovery factor versus pressure is drawn. As shown in Figure 12, it can be determined that the minimum miscible pressure is 22.4 MPa.

Compared with the slim-tube experiment, the average relative error of MMP predicted in this paper is 0.88%. For the numerical simulation method, the average relative error of predicting the MMP is 3.4% compared with the experimental method. The numerical simulation method can accurately simulate the experimental process of the slim-tube, but this is based on a good fitting of the PVT properties of the fluid. The method in this paper considers the influence of temperature and crude oil composition on MMP and the influence of the multiple-contact process. In addition, it also combines the advantages of correlation, which finally makes the prediction results accurate, and the calculation speed is faster. As shown in Table 5, the slim-tube experiment needs an average of 5.4 days, the numerical simulation needs an average calculation of 3.6 minutes, and the calculation time of the method in this paper is only 7.8 seconds on average.

4. Discussion

We make a comparison between our method of characteristic curve and the MOC method of characteristics [27]. MOC methods determine the MMP by the pressure at which one of the key tie-line becomes a line of zero length. From MOC, we can see a component missing sequence according to the *K*-value from big to small. And in our method of characteristic curve, from the equilibrium composition X_n , Y_n of f(n), when the *n* change from 1 to *N*, we can also get a component missing sequence, which is the same as the sequence of MOC. The results show these two methods agree with each other to some extent. But the values of equilibrium composition are different, so in these two methods, differences still exist.

In our method, the mix fraction of oil and gas will not influence the MMP prediction, which also shows that the MMP is independent of the fraction flow.

5. Conclusion

- (1) This paper illustrates a method to get a curve that shows the characteristics of multiple-contact. From the change of characteristic curve of multiple-contact, we can know the type of displacement, and the influence of injection gas (CO_2) to the MMP. We found as the pressure reaches MMP the minimum value of characteristic curve of multiple-contact changes in a very small scope near zero (0.23-0.13), and the main factors (reservoir temperature, oil composition) affecting the minimum value are similar to the factors for MMP. From these reasons, we get a correlation to predict the minimum value. Then, based on the process of multiple-contact, we increased the pressure, as the minimum value of the characteristic curve reaches the value predicted by our correlation, the MMP is determined; compared to the result of the slim-tube experiment, the error is in 0.3 MPa
- (2) MOC and mixing-cell models consider the process of multiple-contact. But for the MOC, equations of crossover tie lines are a set of nonlinear equations, and it is difficult to find a unique set of key tie lines for crude oil since there are many numbers of components. For mixing-cell models, the key tie lines also need to be found, which in many cases may not exist. But this problem does not exist in our method of characteristic curve, and we just find the minimum value of characteristic curve and do not have to find the key tie lines, so the MMP can get easier than MOC and mixing-cell models, more accurate than traditional correlation. We combined the process of multiple-contact with the main factor affecting (reservoir temperature, oil composition), which makes our correlation more accurate. Finally, testing on actual oil samples shows that the method in this paper has higher accuracy and faster calculation speed

7

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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