

## Research Article

# An Improved CO<sub>2</sub>-Crude Oil Minimum Miscibility Pressure Correlation

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Received 25 August 2015; Accepted 11 October 2015

Academic Editor: Tomokazu Yoshimura

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Minimum miscibility pressure (MMP), which plays an important role in miscible flooding, is a key parameter in determining whether crude oil and gas are completely miscible. On the basis of 210 groups of CO<sub>2</sub>-crude oil system minimum miscibility pressure data, an improved CO<sub>2</sub>-crude oil system minimum miscibility pressure correlation was built by modified conjugate gradient method and global optimizing method. The new correlation is a uniform empirical correlation to calculate the MMP for both thin oil and heavy oil and is expressed as a function of reservoir temperature, C<sub>7+</sub> molecular weight of crude oil, and mole fractions of volatile components (CH<sub>4</sub> and N<sub>2</sub>) and intermediate components (CO<sub>2</sub>, H<sub>2</sub>S, and C<sub>2</sub>~C<sub>6</sub>) of crude oil. Compared to the eleven most popular and relatively high-accuracy CO<sub>2</sub>-oil system MMP correlations in the previous literature by other nine groups of CO<sub>2</sub>-oil MMP experimental data, which have not been used to develop the new correlation, it is found that the new empirical correlation provides the best reproduction of the nine groups of CO<sub>2</sub>-oil MMP experimental data with a percentage average absolute relative error (%AARE) of 8% and a percentage maximum absolute relative error (%MARE) of 21%, respectively.

## 1. Introduction

CO<sub>2</sub> injection is one of the most effective methods to enhance oil recovery [1]. Generally, the oil recovery of miscible flooding is higher than nonmiscible flooding. The minimum miscibility pressure (MMP) at which the crude oil and CO<sub>2</sub> become miscible is a key factor because, in general, the CO<sub>2</sub> is not miscible at first contact with reservoir oils but may achieve dynamic miscibility through multiple contact [2]. At present, prediction of the MMP commonly contains three methods: experiment [3], empirical correlation [4], and equation of state [5, 6]. The slim tube test is one of the most commonly used test methods [3]; in addition, there are rising-bubble apparatus (RBA) method [7], steam density method [8], multiple contact method [9], and interfacial tension vanish method [10]. The experimental method is the standard method, but it needs to consume large amounts of time and money. Equation of state is precise and fast, but the miscibility function is difficult to give a clear judgment standard, because

a characterization procedure of the plus-fraction must be used and such a characterization can have a huge influence on the calculated value. Thus, empirical correlation is usually used for predicting the MMP. Most the MMP empirical correlations are proposed based on the experimental data of CO<sub>2</sub>-oil system, while these MMP empirical correlations of CO<sub>2</sub>-oil system have certain constraints.

This study has two objectives. The first objective is to utilize the modified conjugate gradient and global optimization algorithm for establishing a four-parameter and improved MMP prediction model of CO<sub>2</sub>-oil system, which has a wider range of application, taking advantage of 210 groups of CO<sub>2</sub>-oil MMP experimental data tested by slim tube experiment in the literature. The second objective is to compare this model with the other eleven most popular and relatively high-accuracy CO<sub>2</sub>-oil MMP correlations presented in the previous literature by using other nine groups of CO<sub>2</sub>-oil MMP experimental data, which have not been used to develop the new correlation.

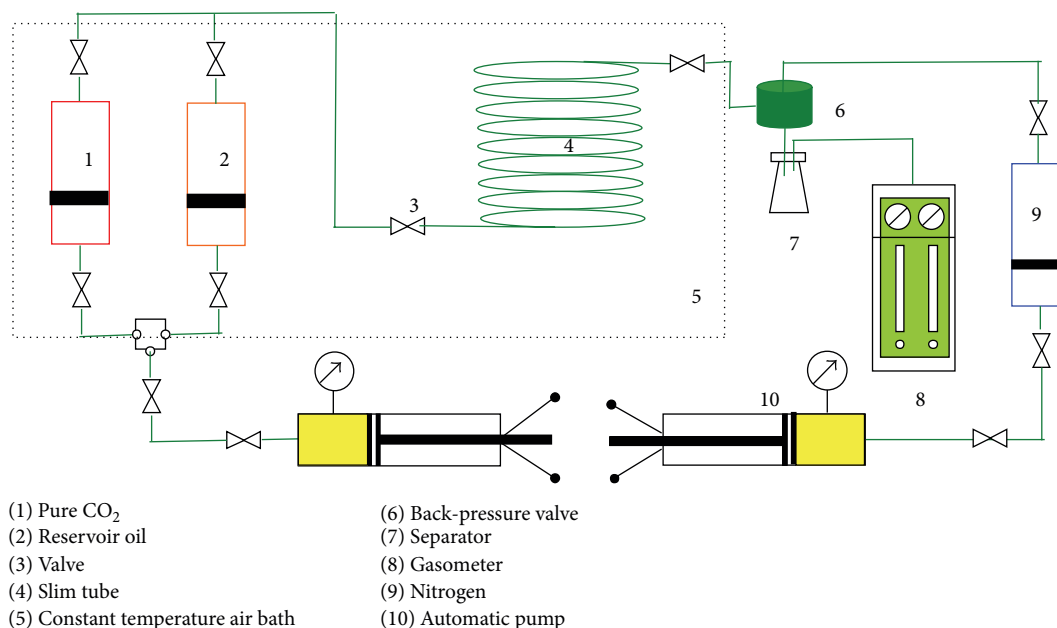


FIGURE 1: Schematic diagram of the slim tube experimental apparatus.

TABLE 1: Compositional analysis results of three oil samples with  $C_{7+}$  molecular weight in mole percentage.

Component	Oil sample 1	Oil sample 2	Oil sample 3
CO <sub>2</sub>	2.076	0.889	0.38
N <sub>2</sub>	0.887	1.962	0.56
C <sub>1</sub>	31.744	14.96	13.21
C <sub>2</sub>	8.217	8.545	2.55
C <sub>3</sub>	7.86	5.563	3.66
IC <sub>4</sub>	1.756	0.434	1.42
NC <sub>4</sub>	3.222	1.072	3.78
IC <sub>5</sub>	1.954	0.067	1.68
NC <sub>5</sub>	1.531	0.165	2.74
FC <sub>6</sub>	4.366	0	8.26
C <sub>7+</sub>	36.387	66.343	61.79
Total	100.00	100.00	100.00
$M_{C_{7+}}$	183.69	245.36	229.17

## 2. Experimental Section

The slim tube test has become a standard method to measure the MMP in the petroleum industry. In this study, the CO<sub>2</sub>-oil MMPs of three crude oil samples (i.e., oil 1, oil 2, and oil 3) are measured by using the slim tube test method. Table 1 shows the compositional analysis results of these three oil samples. It can be seen from the compositional analysis results that all these three oil samples used in this study have a large amount of volatile components (N<sub>2</sub> and CH<sub>4</sub>) and C<sub>7+</sub> fraction. The molecular weights of C<sub>7+</sub> fraction for oil 1, oil 2, and oil 3 are measured to be 183.69 g/mol, 245.36 g/mol, and 229.17 g/mol, respectively.

The slim tube apparatus used in this study is a stainless steel fine tube (length of 20 m, inner diameter of 4.4 mm, and a total pore volume of 92.75 cm<sup>3</sup>) filled with the 80~100 mesh quartz sand. Schematic diagram of the slim tube experimental apparatus is shown in Figure 1. The slim tube tests are performed on the recombined reservoir fluid with CO<sub>2</sub> at the given reservoir temperature. Once the slim tube is saturated with the crude oil sample, the CO<sub>2</sub> is introduced to displace the oil at an injection rate of 0.125 cm<sup>3</sup>/min.

CO<sub>2</sub> displacement experiments are carried out at several pressures with the temperature being maintained constant at the reservoir temperature. For each test pressure, the pore volume of CO<sub>2</sub> injected, produced oil volume, and produced gas volume are recorded. Figure 2 plots the oil recovery factors measured at 1.20 pore volume of CO<sub>2</sub> injected as a function of operating pressure for oil sample 1. The acknowledged criterion for determining slim tube test to achieve miscibility is the oil recovery greater than 90% when 1.20 pore volume of CO<sub>2</sub> or other gases is injected, and with the displacement pressure increased, the displacement efficiency is no longer increasing [11, 12]. The CO<sub>2</sub>-oil MMP at 130°C for oil sample 1 is determined to be 20.65 MPa by pinpointing the breakpoint of the oil recovery curve (see Figure 2). By applying the same methodology as for other temperature points (110°C, 90°C, and 70°C) for oil sample 1, the CO<sub>2</sub> flooding minimum miscibility pressure is 20.35 MPa, 19.95 MPa, and 19.3.8 MPa, respectively. As for oil sample 2 and oil sample 3 at 74.8°C and 89.7°C formation, the CO<sub>2</sub> flooding minimum miscibility pressure is 26.80 MPa and 22.65 MPa, respectively. A conservative error of 3% can be applied due to its complexity. Figures 2 and 3 indicate that crude oil recovery increases with injecting pressure and CO<sub>2</sub>-crude oil minimum miscible increases with temperature.

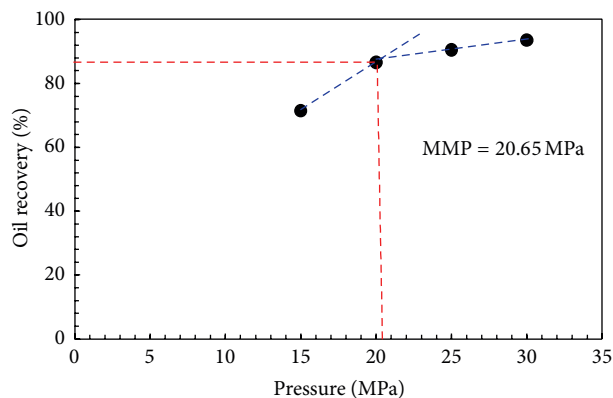


FIGURE 2: Variation of the oil recovery measured at 1.20 pore volume of CO<sub>2</sub> injected at various injection pressure for oil sample 1.

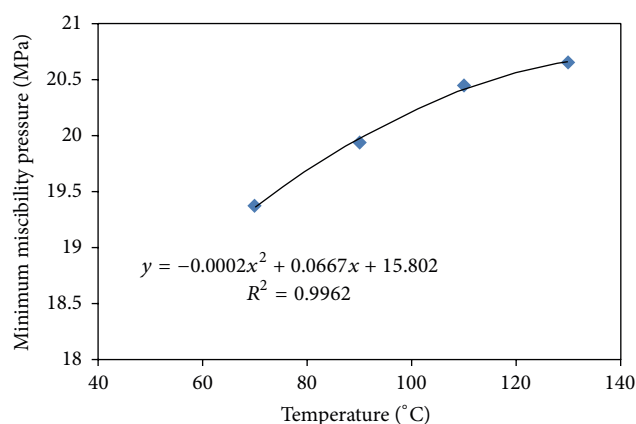


FIGURE 3: Variation of oil sample miscibility pressure with temperature.

### 3. Building of MMP Predicting Model

**3.1. Existing Methods.** Over the years, several empirical correlations have been developed for determining the MMP of CO<sub>2</sub>-oil system. The most popular and relatively high-accuracy correlations applied for prediction of CO<sub>2</sub>-oil MMP are those developed by Cronquist [4], Lee [13], Yelling-Metcalf [14], Orr-Jensen [15], Glaso [16], Alston [17], Emera-Sarma [18], Yuan [19], Shokir [20], Chen [21], and Ju [22]. Table 2 shows the expression of the above correlations and its application restrictions.

**3.2. Main Factors Influencing the MMP.** Reviewing published MMP slim tube test data and previously presented empirical models indicates the existence of the following [21, 22]:

- (1) The MMP of CO<sub>2</sub>-oil system is determined by the reservoir temperature, the components in the injected gas, and the components and properties of oil.
- (2) On the constant condition of the components in the injected gas and the components and properties of oil, the MMP increases with increasing the reservoir temperature.

- (3) On the constant condition of the components in the injected gas and the reservoir temperature, the higher the content of C<sub>2</sub>~C<sub>6</sub> and the lower the molecular weight in the crude oil, the smaller MMP. On the contrary, the more the heavy components in the crude oil are, the less favorable it will be for miscibility.
- (4) On the constant condition of the reservoir temperature and the components and properties of oil, the MMP decreases with increasing the content of intermediate components (CO<sub>2</sub>, H<sub>2</sub>S, and C<sub>2</sub>~C<sub>6</sub>) and increases with increasing the content of volatile components (CH<sub>4</sub> and N<sub>2</sub>) in the injected gas.

The paper is focused on building an improved MMP model of pure CO<sub>2</sub>-oil system, so the influence of injection gas components on MMP has been taken into account. Based on the shortages of the above empirical formula in Table 2 and the sensitive factors proposed in Section 3.2 influencing the MMP, we selected the four sensitive factors including reservoir temperature, relative molecular weight of C<sub>7+</sub>, the volatile components (CH<sub>4</sub> and N<sub>2</sub>), and intermediate components (CO<sub>2</sub>, H<sub>2</sub>S, and C<sub>2</sub>~C<sub>6</sub>) of crude oil to develop an improved MMP prediction correlation with four parameters by using the modified conjugate gradient and global optimization algorithm regression theory.

**3.3. Mathematical Model.** The determined MMP of CO<sub>2</sub>-crude oil system is the result of multiple factors interaction. Therefore, we should take full account of the sensitive factors in Section 3.2 and then maximize and utilize the experimental data. However, when the independent variable and dependent variable uncertainty or error is larger, prediction results by the traditional least squares linear regression method are very low. Thus, the optimization and regression algorithm can solve the problem well. In this paper we use the modified conjugate gradient and global optimization algorithm to establish a prediction model for the MMP of CO<sub>2</sub>-oil system.

And the prediction model, based on Emera-Sarma model, also consists of four affecting factors (reservoir temperature, C<sub>7+</sub> molecular weight of crude oil, mole fractions of volatile components (CH<sub>4</sub> and N<sub>2</sub>), and mole fractions of intermediate components (CO<sub>2</sub>, H<sub>2</sub>S, and C<sub>2</sub>~C<sub>6</sub>) in the crude oil) and four parameters; the following improved correlation was developed:

$$P_{m,\min,\text{pure}} = a [\ln(1.8T + 32)]^b [\ln(M_{C_{7+}})]^c \left(1 + \frac{x_{\text{VOL}}}{x'_{\text{MED}}}\right)^d \quad (1)$$

On the basis of Emera-Sarma model, reservoir temperature,  $M_{C_{7+}}$  in crude oil, mole content of volatile component (CH<sub>4</sub> and N<sub>2</sub>), and mole content ratio of intermediate components (CO<sub>2</sub>, H<sub>2</sub>S, and C<sub>2</sub>~C<sub>6</sub>) in crude oil were modified. The term  $\ln(1.8 \times T + 32)$  is used to suppress temperature effect on the hydrocarbon gas-oil MMP when the reservoir temperature is relatively high. The reason why  $M_{C_{7+}}$  instead of  $M_{C_{5+}}$  is used in the correlation is partially because  $M_{C_{7+}}$  is a routine measurement item in a typical compositional analysis

TABLE 2: Correlations for CO<sub>2</sub>-oil MMP.

Author	Published empirical correlation	Remarks
Cronquist [4]	(a) $P_{m,\min,pure} = 0.11027 (1.8T + 32)^{0.744206+0.0011038M_{C_5}+0.0015273x_{VOL}}$	(i) The tested oil gravity ranged from 23.7 to 44.8° API (ii) The tested $T$ ranged from 21.67 to 120.8°C (iii) The tested experimental MMP ranged from 7.4 to 34.5 MPa
Lee [13]	(b) $P_{m,\min,pure} = 7.3924 \times 10^{2.772-[1519/(492+1.8T)]}$	(i) Based on equating MMP with CO <sub>2</sub> vapor pressure when $T < \text{CO}_2$ critical temperature, while using the corresponding correlation when $T \geq \text{CO}_2$ critical temperature (ii) If MMP $< P_b$ , $P_b$ is taken as MMP
Yelling-Metcalf [14]	(c) $P_{m,\min,pure} = 12.6472 + 0.01553(1.8T + 32) + 1.24192 \times 10^{-4} (1.8T + 32)^2 - \frac{716.9427}{(1.8T + 32)}$	Limitations: $35.8 \leq T < 88.9^\circ\text{C}$ (i) If MMP $< P_b$ , $P_b$ is taken as MMP
Orr-Jensen [15]	(d) $P_{m,\min,pure} = 0.101386 \exp \left[ 10.91 - \frac{2105}{255.372 + 0.5556(1.8T + 32)} \right]$	(i) Based on extrapolated vapor pressure (EVP) method (ii) Used to estimate the MMP for low temperature reservoirs ( $T < 49^\circ\text{C}$ )
Glazo [16]	(e) $P_{m,\min,pure} = 5.8657 - 2.3477 \times 10^{-2} M_{C_{7+}} + 1.1725 \times 10^{-11} M_{C_{7+}}^{3.73} \exp^{786.8M_{C_{7+}}-1.058} (1.8T + 32)$ When $x'_{MED} < 18 \text{ mol}\%$ , When $x'_{MED} > 18 \%$ , (e2) $P_{m,\min,pure} = 20.33 - 2.3477 \times 10^{-2} M_{C_{7+}} + 1.1725 \times 10^{-11} M_{C_{7+}}^{3.73} \exp^{786.8M_{C_{7+}}-1.058} (1.8T + 32) - 0.836 \times x'_{MED}$ When $P_b \geq 0.345 \text{ MPa}$	Considers the effect of intermediates ( $C_2-C_6$ ) only when $x'_{MED} (C_2-C_6) < 18 \text{ mol}\%$
Alston [17]	(f) $P_{m,\min,pure} = 6.0536 \times 10^{-6} (1.8T + 32)^{1.06} (M_{C_{5+}})^{1.78} \left( \frac{x_{VOL}}{x_{MED}} \right)^{0.136}$ When $P_b < 0.345 \text{ MPa}$ (f2) $P_{m,\min,pure} = 6.0536 \times 10^{-6} (1.8T + 32)^{1.06} (M_{C_{5+}})^{1.78}$ When $P_b \geq 0.345 \text{ MPa}$	If MMP $< P_b$ , $P_b$ is taken as MMP
Emera-Sarma [18]	(g) $P_{m,\min,pure} = 5.0093 \times 10^{-5} (1.8T + 32)^{1.164} (M_{C_{5+}})^{1.2785} \left( \frac{x_{VOL}}{x_{MED}} \right)^{0.1073}$ When $P_b < 0.345 \text{ MPa}$ (g2) $P_{m,\min,pure} = 5.0093 \times 10^{-5} (1.8T + 32)^{1.164} (M_{C_{5+}})^{1.2785}$	Limitations: $40.8 < T < 112.2^\circ\text{C}$ ; $8.28 < P_{m,\min,pure} < 30.2 \text{ MPa}$ ; $166.2 < M_{C_{5+}} < 267.5 \text{ g/mol}$
Yuan [19]	(h) $P_{m,\min,pure} = a_1 + a_2 M_{C_{7+}} - a_3 x'_{MED} + \left( a_4 + a_5 M_{C_{7+}} + a_6 \frac{x'_{MED}}{M_{C_{7+}}^2} \right) (1.8T + 32)$ + $(a_7 + a_8 M_{C_{7+}} - a_9 M_{C_{7+}}^2 - a_{10} x'_{MED}) (1.8T + 32)^2$ $a_1 = -9.8912$ ; $a_2 = 4.5588 \times 10^{-2}$ ; $a_3 = -3.1012 \times 10^{-1}$ ; $a_4 = 1.4748 \times 10^{-2}$ $a_5 = 8.0441 \times 10^{-4}$ ; $a_6 = 5.6303 \times 10^{-1}$ ; $a_7 = -8.4516 \times 10^{-4}$ ; $a_8 = 8.8825 \times 10^{-6}$ $a_9 = -2.7684 \times 10^{-8}$ ; $a_{10} = -6.3830 \times 10^{-6}$	Limitations: $21.7 < T < 148^\circ\text{C}$ ; $P_{m,\min,pure} < 70 \text{ MPa}$ ; $139 < M_{C_{7+}} < 319 \text{ g/mol}$

TABLE 2: Continued.

Author	Published empirical correlation	Remarks
Shokir [20]	(i1) $P_{m,\min,\text{pure}} = -0.068616Z^3 + 0.31733Z^2 + 4.9804Z + 13.432$	Limitations: $32.2 < T < 112.2^\circ\text{C}$ ; $6.9 < P_{m,\min,\text{pure}} < 30.28\text{ MPa}$ ; $185 < M_{C_{5+}} < 268\text{ g/mol}$
	(i2) $Z = \sum_{i=1}^4 Z_i$	
	(i3) $Z_i = a_i + b_i x_i + c_i x_i^2 + d_i x_i^3$	
	$a_1 = -2.9182$ ; $a_2 = -3.1227 \times 10^{-1}$ ; $a_3 = -4.9485 \times 10^{-2}$ ; $a_4 = 25.430$	
	$b_1 = 7.5340 \times 10^{-2}$ ; $b_2 = -7.9169 \times 10^{-3}$ ; $b_3 = 4.2165 \times 10^{-2}$ ; $b_4 = -3.9750 \times 10^{-1}$	
Chen [21]	$c_1 = -5.5996 \times 10^{-4}$ ; $c_2 = 1.3644 \times 10^{-3}$ ; $c_3 = -2.7853 \times 10^{-3}$ ; $c_4 = 1.9860 \times 10^{-3}$	Limitations: $32.2 < T < 118.3^\circ\text{C}$ ; $6.9 < P_{m,\min,\text{pure}} < 28.17\text{ MPa}$ ; $185 < M_{C_{7+}} < 249\text{ g/mol}$
	$d_1 = 2.3660 \times 10^{-6}$ ; $d_2 = -1.3721 \times 10^{-5}$ ; $d_3 = 3.5551 \times 10^{-5}$ ; $d_4 = -3.1604 \times 10^{-6}$	
	(j) $P_{m,\min,\text{pure}} = 3.9673 \times 10^{-2} T^{0.8293} (M_{C_{7+}})^{0.5382} (x_{C_1+N_2})^{0.1018} (x_{C_2-C_6})^{-0.2316}$	
	(kl) $P_{m,\min,\text{impure}} = -0.04562S^3 + 0.33399S^2 + 4.9811S + 13.569$	
	(k2) $S = \sum_{i=1}^8 S_i$	
Ju [22]	(k3) $S_i = a_i + b_i x_i + c_i x_i^2 + d_i x_i^3$	Limitations: $P_{m,\min,\text{pure}} < 40\text{ MPa}$
The detailed parameters refer to [18]		

TABLE 3: Regression parameters.

Parameters	Value
$a$	$8.3397 \times 10^{-5}$
$b$	3.9774
$c$	3.3179
$d$	$1.7461 \times 10^{-1}$

report, while  $M_{C_{5+}}$  normally need to be calculated from  $M_{C_{7+}}$ . In addition, it is found in this study that the use of  $M_{C_{7+}}$ , rather than  $M_{C_{5+}}$ , even leads to a slightly better performance of (1) in terms of the correlation coefficient  $R^2$ . Meanwhile,  $M_{C_{7+}}$  is replaced by  $\ln(M_{C_{7+}})$  to reduce the influence of  $M_{C_{7+}}$  on the MMP of CO<sub>2</sub>-oil system when  $M_{C_{7+}}$  is larger. And  $x_{VOL}/x'_{MED}$  is replaced by  $(1 + x_{VOL}/x'_{MED})$  to avoid the fact that  $x_{VOL}/x'_{MED}$  approaches to zero because of too fewer volatile components in heavy oil which result in great differences between the parameters.

The objective optimization function contains four parameters ( $m = (m_1, m_2, m_3, m_4)$ ). The CO<sub>2</sub>-oil MMP database used in this study includes a total of 210 MMP measurements from the literature, among which the temperature has a range of 21.67°C~191.97°C and  $C_{7+}$  molecular weights range from 130 g/mol to 402.7 g/mol [2, 20–37]. In addition, it should be noted that 176 out of the 210 measurements are obtained from overseas data in the literature, while the remaining 34 measurements are obtained from domestic data in the literature. The CO<sub>2</sub>-oil MMP database is used to determine the tuned coefficients ( $m = (m_1, m_2, m_3, m_4)$ ) in (1) by regression fitting using the modified conjugate gradient and global optimization algorithm. The regression fitting has been conducted by using the Matlab programming. The tuned coefficients are given in Table 3 and (1) generates a fit with  $R^2 = 0.9488$  (Figure 4).

*Step 1.* Given the constant  $\sigma_1 \in (0, 1/2)$ ,  $\sigma_1 < \sigma_2 < 1$ ,  $\varepsilon > 0$ , pick the initial point  $m_0 \in R^4$ ,  $d_0 = -g_0$ , and place  $k = 0$ .

*Step 2.* If  $\|g_k\| < \varepsilon$ , algorithm stops and  $m_k$  in  $f(m)$  is to be obtained; otherwise, algorithm turns to Step 3.  $g_k$ , the conjugate gradient of  $f(m)$  at  $m_k$ , represents  $g_k = \beta_k \times f'(m_k)$ , in which  $\|g_k\|$  is the norm of  $g_k$  and  $\beta_k$  is the parameter. Generally, two expression forms include  $\beta_k^{FR} = \|g_k\|^2 / \|g_{k-1}\|^2$  and  $\beta_k^{PR} = g_k^T (g_k - g_{k-1}) / \|g_{k-1}\|^2$  [22]. In this paper,  $\beta_k = \max\{0, \beta_k^{FR} + \min\{0, g_k^T g_{k-1} / g_{k-1}^T d_{k-1}\}\}$ , in which  $g_k^T$  is the transposed conjugate gradient.

*Step 3.* Step length  $\alpha_k$  is determined by 1D linear search.

*Step 4.* Place  $m_{k+1} = m_k + \alpha_k d_k$ , in which  $d_k$  is the conjugate gradient search direction and is determined as follows:

$$d_k = \begin{cases} -g_k & k = 0, \\ -\theta_k g_k + \beta_k d_{k-1} & k \geq 1, \end{cases} \quad (2)$$

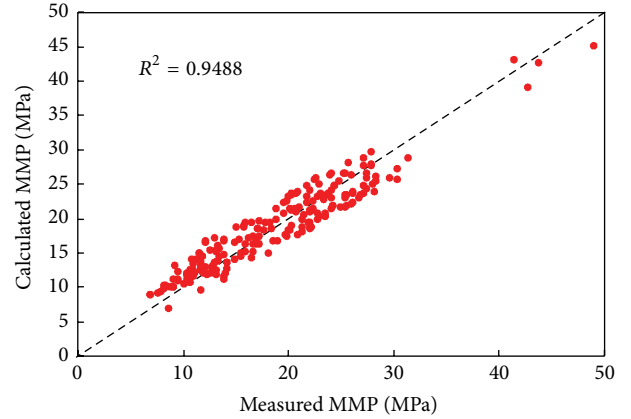


FIGURE 4: Resulted CO<sub>2</sub>-oil MMP from the new correlation versus the experimental measurements.

in which  $\theta_k = 1 + (g_k^T d_{k-1} / \|g_k\|^2) \beta_k$ . It can be inferred that  $d_k = -g_k - (g_k^T d_{k-1} / \|g_k\|^2) \beta_k g_k + \beta_k d_{k-1}$ , where  $g_k^T$  is to be multiplied at both sides to obtain the following expression:

$$\begin{aligned} g_k^T d_k &= -\|g_k\|^2 - \frac{g_k^T d_{k-1}}{\|g_k\|^2} \beta_k \|g_k\|^2 + \beta_k g_k^T d_{k-1} \\ &= -\|g_k\|^2 < 0. \end{aligned} \quad (3)$$

It is obvious that  $g_k^T d_k$  is always less than 0 and  $g_k^T$  is greater than 0, which results in downward search direction. Moreover, if  $\beta_k \neq 0$ ,  $-g_k^T g_{k-1} / g_{k-1}^T d_{k-1} \geq 0$ ,  $\beta_k = \beta_k^{FR}$ , the modified conjugate gradient method is FR conjugate gradient method [38]. Otherwise, combining correlation ((c), see Table 2), we can draw that

$$\begin{aligned} \beta_k &= \beta_k^{FR} + \frac{g_k^T g_{k-1}}{g_{k-1}^T d_{k-1}} = \frac{\|g_k\|^2}{\|g_{k-1}\|^2} - \frac{g_k^T g_{k-1}}{\|g_{k-1}\|^2} \\ &= \frac{g_k^T (g_k - g_{k-1})}{\|g_{k-1}\|^2} = \beta_k^{PR}. \end{aligned} \quad (4)$$

It is called FR conjugate gradient method. It is indicated that the FR conjugate gradient method takes in excellent global convergence of FR algorithm and excellent numerical result of PR algorithm.

*Step 5.*  $d_k$  is determined, and place  $k = k + 1$ . Process turns to Step 2.

Finally, the modified MMP correlation of CO<sub>2</sub>-crude oil is as follows:

$$\begin{aligned} f(m) &= P_{m, \min, \text{pure}} = 8.3397 \\ &\times 10^{-5} [\ln(1.8T + 32)]^{3.9774} [\ln(M_{C_{7+}})]^{3.3179} \\ &\cdot \left(1 + \frac{x_{VOL}}{x'_{MED}}\right)^{0.17461}. \end{aligned} \quad (5)$$



TABLE 4: The nine oil samples components, properties, and MMP data for the new correlation validation.

$T$ ( $^{\circ}\text{C}$ )	$M_{C_{7+}}$	$M_{C_{5+}}$	$x_{\text{MED}}$	$x'_{\text{MED}}$	$x_{\text{VOL}}$	Experimental data (MMP) (MPa)	Reference
60.00	149.690	136.470	39.370	46.160	24.680	11.138	[39]
80.00	149.690	136.470	39.370	46.160	24.680	14.152	[39]
137.22	149.690	136.470	39.370	46.160	24.680	18.379	[39]
100.00	151.740	138.530	26.760	37.950	13.530	14.634	[40]
80.00	170.080	160.590	2.630	7.100	12.150	16.062	[41]
130.00	183.690	165.262	23.131	30.982	32.631	20.650	Current work
74.80	245.690	229.085	16.501	16.733	16.922	26.800	Current work
89.70	229.170	211.213	11.790	24.470	13.770	22.630	Current work
53.00	205.740	182.800	12.933	25.333	18.706	13.090	[42]

Compared with the other 11 correlations in Table 2, the correlation has broader application (pressure range: 0~70 MPa, temperature range: 21.67~191.97 $^{\circ}\text{C}$ , and relative molecular weight of  $C_{7+}$ : 130~402.7 g/mol).

#### 4. Calculation Results and Analysis

Generally, the absolute error (6), the absolute relative error (7), and the average absolute relative error (8) are used to express the deviation between the calculated MMP by the empirical correlation and optimize the most appropriate empirical correlation for predicting the MMP of  $\text{CO}_2$ -oil system:

$$\text{AE} = \text{Cal} - \text{Exp}, \quad (6)$$

$$\text{ARE} (\%) = \sum_{i=1}^N \left| \frac{\text{Cal} - \text{Exp}}{\text{Exp}} \right| \times 100, \quad (7)$$

$$\text{AARE} (\%) = \frac{1}{N} \sum_{i=1}^N \left| \frac{\text{Cal} - \text{Exp}}{\text{Exp}} \right| \times 100. \quad (8)$$

A new correlation validation is performed with more MMP data (Table 4). These MMP data have not been used to develop the new correlation. The comparative results of the calculated MMP by the correlation proposed in this study and the other eleven most popular and relatively high-accuracy correlations presented in the previous literatures are shown in Figure 5 and Table 5. The average absolute relative errors (AARE) for the correlation proposed in this study, Cronquist's correlation, Lee's correlation, Yelling-Metcalf's correlation, Orr-Jensen's correlation, Glaso's correlation, Alston's correlation, Emera-Sarma's correlation, Yuan's correlation, Shokir's correlation, Chen's correlation, and Ju's correlation are 8%, 16%, 37%, 20%, 32%, 19%, 20%, 13%, 27%, 21%, 14%, and 29%, respectively. The maximum absolute relative errors (MARE) for the proposed correlation in this study, Cronquist's correlation, Lee's correlation, Yelling-Metcalf's correlation, Orr-Jensen's correlation, Glaso's correlation, Alston's correlation, Emera-Sarma's correlation, Yuan's correlation, Shokir's correlation, Chen's correlation, and Ju's correlation are 21%, 31%, 73%, 46%, 78%, 50%, 39%, 25%, 58%, 52%, 28%, and 57%, respectively. These results indicate that the proposed correlation in this study is significantly more precise than the other correlations. The results of the calculated MMP by

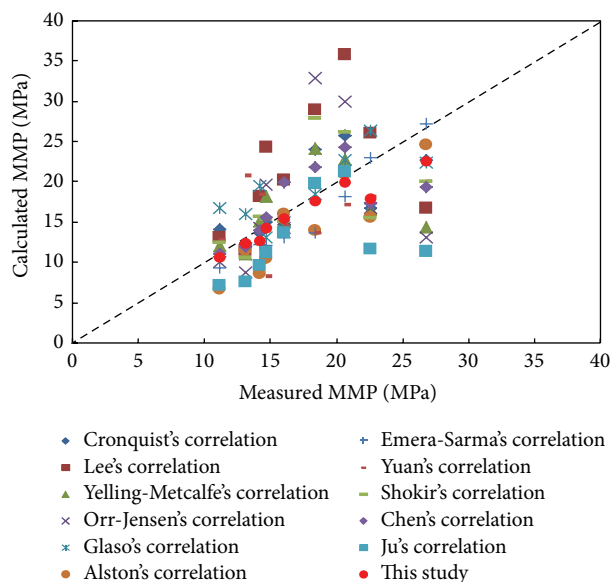


FIGURE 5: The resulted nine-oil-sample MMP from the new correlation proposed in this study versus the calculated nine-oil-sample MMP from Cronquist's correlation, Lee's correlation, Yelling-Metcalf's correlation, Orr-Jensen's correlation, Glaso's correlation, Alston's correlation, Emera-Sarma's correlation, Yuan's correlation, Shokir's correlation, Chen's correlation, and Ju's correlation.

the correlation proposed in this study, the measured MMP by slim tube test, and the absolute error (AE) are shown in Figures 5 and 6. From Table 5, it is clearly seen that the absolute errors (AE) of the calculated MMP by the model proposed in this study of many oil samples are less than 1.5 MPa, which are very close to the experimental data.

#### 5. Conclusions

(1) Four sensitive factors are determined for affecting the MMP of  $\text{CO}_2$ -oil system, which includes the reservoir temperature,  $C_{7+}$  molecular weight of oil, mole fractions of volatile components ( $\text{CH}_4$  and  $\text{N}_2$ ), and mole fractions of intermediate components ( $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{C}_2\sim\text{C}_6$ ) of oil. Based on the above sensitive factors, a four-parameter and improved MMP prediction model of  $\text{CO}_2$ -oil system is

TABLE 5: Comparison of predicted MMPs for nine oil samples by the correlation proposed in this study and other eleven literature correlations.

Exp. (MMP) (MPa)	Correlation proposed in this study		Cronquist's correlation		Lee's correlation		Yelling-Metcalf's correlation	
	MMP (MPa)	ARE, %	MMP (MPa)	ARE, %	MMP (MPa)	ARE, %	MMP (MPa)	ARE, %
11.138	10.594	4.881	14.062	26.251	13.055	17.214	12.135	8.947
14.152	12.619	10.833	13.693	3.241	18.143	28.201	15.154	7.080
18.379	17.548	4.522	24.043	30.816	28.968	57.614	24.077	31.004
14.634	14.243	2.673	15.050	2.844	24.340	66.325	18.139	23.954
16.062	15.387	4.203	14.645	8.820	20.143	25.408	15.154	5.654
20.650	19.990	3.196	25.722	24.561	35.810	73.416	22.870	10.752
26.800	22.551	15.853	22.616	15.613	16.716	37.627	14.381	46.338
22.630	17.864	21.060	16.765	25.919	26.007	14.921	16.594	26.673
13.090	12.399	5.278	12.419	5.129	11.525	11.959	11.014	15.860
AARE, %		8.055		15.910		36.965		19.585
MAARE, %		21.060		30.816		73.416		46.338
Exp. (MMP) (MPa)	Orr-Jensen's correlation		Glaso's correlation		Alston's correlation		Emera-Sarma's correlation	
	MMP (MPa)	ARE, %	MMP (MPa)	ARE, %	MMP (MPa)	ARE, %	MMP (MPa)	ARE, %
11.138	10.002	10.196	16.679	49.746	6.756	39.342	9.362	15.945
14.152	14.306	1.087	19.472	37.593	8.611	39.155	12.214	13.695
18.379	32.845	78.712	18.464	0.462	14.032	23.650	13.738	25.251
14.634	19.691	34.556	13.128	10.290	10.462	28.512	12.071	17.513
16.062	14.306	10.934	14.973	6.779	15.941	0.751	13.032	18.863
20.650	29.963	45.097	22.617	9.525	20.944	1.423	18.150	12.105
26.800	13.087	51.170	22.328	16.687	24.636	8.074	27.222	1.575
22.630	16.777	25.863	26.327	16.337	15.512	31.454	23.042	1.820
13.090	8.734	33.279	16.029	22.452	11.524	11.963	12.102	7.550
AARE, %		32.321		18.874		20.481		12.702
MAARE, %		78.712		49.746		39.342		25.251
Exp. (MMP) (MPa)	Yuan's correlation		Shokir's correlation		Chen's correlation		Ju's correlation	
	MMP (MPa)	ARE, %	MMP (MPa)	ARE, %	MMP (MPa)	ARE, %	MMP (MPa)	ARE, %
11.138	12.775	14.699	12.549	12.669	11.002	1.218	7.091	36.332
14.152	18.512	30.809	15.783	11.522	13.967	1.309	9.539	32.598
18.379	13.735	25.266	27.908	51.845	21.849	18.878	19.767	7.554
14.634	8.304	43.255	15.366	5.004	15.543	6.210	11.280	22.921
16.062	14.568	9.302	15.191	5.420	19.961	24.274	13.697	14.727
20.650	17.164	16.879	26.111	26.445	24.313	17.739	21.215	2.734
26.800	20.033	25.250	20.132	24.881	19.328	27.879	11.409	57.428
22.630	18.113	19.960	15.509	31.468	17.374	23.226	11.615	48.674
13.090	20.738	58.425	10.647	18.664	11.973	8.531	7.577	42.116
AARE, %		27.094		20.880		14.363		29.454
MAARE, %		58.425		51.845		27.879		57.428

established by using the modified conjugate gradient and the global optimization algorithm.

(2) The nine groups of CO<sub>2</sub>-oil MMP experimental data, which have not been used to develop the new correlation, were calculated by the empirical correlation proposed in this study and other eleven most popular and relatively high-accuracy empirical correlation presented in the literature to

validate the new correlation. It can be seen from the comparative results that the accuracy of the empirical correlation proposed in this study is significantly more precise than the other eleven most popular and relatively high-accuracy empirical correlations presented in the literature. The range of the absolute error is less than 1.5 MPa, which corresponds to the requirement of engineering design of CO<sub>2</sub> displacement.



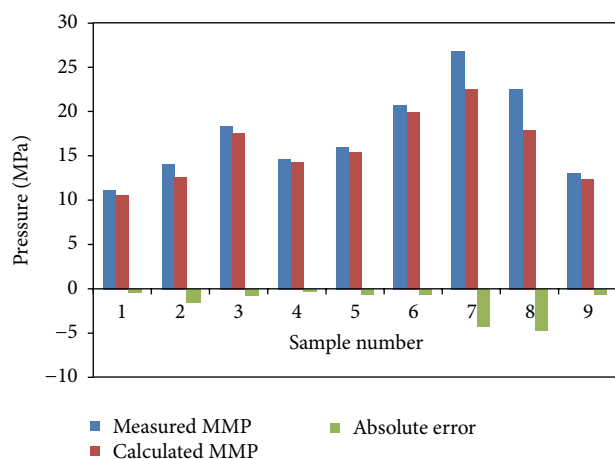


FIGURE 6: The MMPs of the system of nine CO<sub>2</sub>-oil samples and their errors predicted by the correlation proposed in this paper.

## Nomenclature

$M_{C_{5+}}$ :	Molecular weight of C <sub>5+</sub> in the crude oil, g/mol
$T$ :	Reservoir temperature, °C
$M_{C_{7+}}$ :	Molecular weight of C <sub>7+</sub> in the crude oil, g/mol
$x_{VOL}$ :	Mole fraction of volatile components (CH <sub>4</sub> + N <sub>2</sub> ) in the crude oil, mol%
$x_{MED}$ :	Mole fraction of intermediate components (CO <sub>2</sub> , H <sub>2</sub> S, and C <sub>2</sub> ~C <sub>4</sub> ) in the crude oil, mol%
$x'_{MED}$ :	Mole fraction of intermediate components (CO <sub>2</sub> , H <sub>2</sub> S, and C <sub>2</sub> ~C <sub>6</sub> ) in the crude oil, mol%
$P_{m,min,pure}$ :	Minimum miscibility pressure by pure CO <sub>2</sub> injection, MPa
$P_{m,min,impure}$ :	Minimum miscibility pressure by impure CO <sub>2</sub> injection, MPa
$x_1$ :	Reservoir temperature, °C
$x_2$ :	Mole fraction of volatile components (CH <sub>4</sub> + N <sub>2</sub> ) in the crude oil, mol%
$x_3$ :	Mole fraction of intermediate components (CO <sub>2</sub> , H <sub>2</sub> S, and C <sub>2</sub> ~C <sub>6</sub> ) in the crude oil, mol%
$x_4$ :	Molecular weight of C <sub>5+</sub> in the crude oil, g/mol
$x_5$ :	Mole fraction of volatile components (C <sub>1</sub> ) in the injection gas, mol%
$x_6$ :	Mole fraction of intermediate components (C <sub>2</sub> ~C <sub>4</sub> ) in the injection gas, mol%
$x_7$ :	Mole fraction of volatile components (N <sub>2</sub> ) in the injection gas, mol%
$x_8$ :	Mole fraction of volatile components (H <sub>2</sub> S) in the injection gas, mol%
$x_{C_1+N_2}$ :	Mole fraction of volatile components (CH <sub>4</sub> + N <sub>2</sub> ) in the crude oil, mol%
$x_{C_2-C_6}$ :	Mole fraction of intermediate components (C <sub>2</sub> ~C <sub>6</sub> ) in the crude oil, mol%

AE: Absolute error  
 %ARE: Percentage absolute relative error  
 %AARE: Percentage average absolute relative error  
 %MARE: Percentage maximum average absolute relative error.

## Conflict of Interests

Here, all the authors solemnly declare that there is no conflict of interests regarding the publication of this paper.

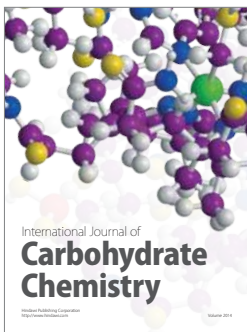
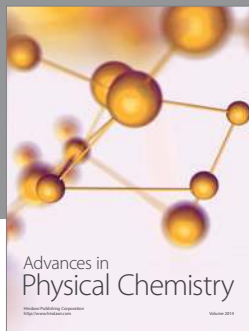
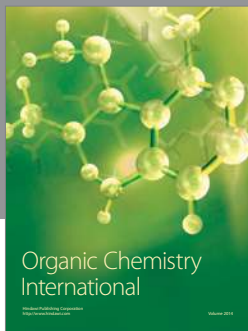
## Acknowledgment

This work was supported by a Grant from the National Natural Science Foundation of China (no. 51374044).

## References

- [1] T. W. Teklu, S. G. Ghedan, R. M. Graves, and X. Yin, "Minimum miscibility pressure determination: modified multiple mixing cell method," in *Proceedings of the SPE EOR Conference at Oil and Gas West Asia*, Paper SPE 155454-MS, Muscat, Oman, April 2012.
- [2] H. Z. Li, J. S. Qin, and D. Y. Yang, "An improved CO<sub>2</sub>-oil minimum miscibility pressure correlation for live and dead crude oils," *Industrial and Engineering Chemistry Research*, vol. 51, no. 8, pp. 3516–3523, 2012.
- [3] A. M. Amao, S. Siddiqui, and H. Menouar, "A New Look at the minimum miscibility pressure (MMP) determination from slimtube measurements," in *Proceedings of the SPE Improved Oil Recovery Symposium*, SPE-153383-MS, Tulsa, Okla, USA, April 2012.
- [4] C. Cronquist, "Carbon dioxide dynamic miscibility with light reservoir oils," in *Proceedings of the 4th Annual U.S. DOE Symposium*, Tulsa, Okla, USA, August 1977.
- [5] T. Ahmed, "Minimum miscibility pressure from EOS," in *Proceedings of the Canadian International Conference*, Paper SPE 2000-001, Calgary, Canada, June 2000.
- [6] Y. Wang and M. Franklin, "Calculation of minimum miscibility pressure," in *Proceedings of the SPE/DOE Improved Oil Recovery Symposium*, Paper SPE 39683-MS, Tulsa, Okla, USA, April 1998.
- [7] R. K. Srivastava and S. S. Huang, "New interpretation technique for determining minimum miscibility pressure by rising bubble apparatus for enriched-gas drives," in *Proceedings of the SPE India Oil and Gas Conference*, Paper SPE 39566-MS, New Oethi, India, February 1998.
- [8] R. A. Harmon and R. B. Grigg, "Vapor-density measurement for estimating minimum miscibility pressure," in *Proceedings of the SPE Annual Technical Conference and Exhibition*, Paper SPE 15403-PA, New Orleans, La, USA, October 1986.
- [9] W. N. Razak, W. A. Daud, A. H. Faisal et al., "Multi-component mass transfer in multiple contact miscibility test; forward and backward method," in *Proceedings of the SPE/EAGE Reservoir Characterization and Simulation Conference*, Paper SPE 125219-MS, Abu Dhabi, UAE, October 2009.
- [10] M. Nobakht, S. Moghadam, and Y. A. Gu, "Determination of CO<sub>2</sub> minimum miscibility pressure from measured and predicted equilibrium interfacial tensions," *Industrial and Engineering Chemistry Research*, vol. 47, no. 22, pp. 8918–8925, 2008.

- [11] P. M. Jarrell, C. E. Fox, M. H. Stein et al., *Practical Aspects of CO<sub>2</sub> Flooding*, vol. 22 of *SPE Monograph Series*, Society of Petroleum Engineers, Richardson, Tex, USA, 2002.
- [12] F. L. Yang, G.-B. Zhao, H. Adidharma, B. Towler, and M. Radosz, "Effect of oxygen on minimum miscibility pressure in carbon dioxide flooding," *Industrial and Engineering Chemistry Research*, vol. 46, no. 4, pp. 1396–1401, 2007.
- [13] J. I. Lee, "Effectiveness of carbon dioxide displacement under miscible and immiscible conditions," Report RR-40, Petroleum Recovery Institute, Calgary, Canada, 1979.
- [14] W. F. Yellig and R. S. Metcalfe, "Determination and prediction of CO<sub>2</sub> minimum miscibility pressures," *Journal of Petroleum Technology*, vol. 32, no. 1, pp. 160–168, 1980.
- [15] F. M. Orr Jr. and C. M. Jensen, "Interpretation of pressure-composition phase diagrams for CO<sub>2</sub>/crude-oil systems," *Society of Petroleum Engineers Journal*, vol. 24, no. 5, pp. 485–497, 1984.
- [16] O. S. Glaso, "Generalized minimum miscibility pressure correlation," *Society of Petroleum Engineers journal*, vol. 25, no. 6, pp. 927–934, 1985.
- [17] R. B. Alston, G. P. Kokolis, and C. F. James, "CO<sub>2</sub> minimum miscibility pressure: a correlation for impure CO<sub>2</sub> streams and live oil systems," *Society of Petroleum Engineers Journal*, vol. 25, no. 2, pp. 268–274, 1985.
- [18] M. K. Emera and H. K. Sarma, "Use of genetic algorithm to estimate CO<sub>2</sub>-oil minimum miscibility pressure—a key parameter in design of CO<sub>2</sub> miscible flood," *Journal of Petroleum Science and Engineering*, vol. 46, no. 1-2, pp. 37–52, 2005.
- [19] H. Yuan, R. T. Johns, A. M. Egwuenu, and B. Dindoruk, "Improved MMP correlations for CO<sub>2</sub> floods using analytical gasflooding theory," *SPE Reservoir Evaluation and Engineering*, vol. 8, no. 5, pp. 418–425, 2005.
- [20] E. M. E.-M. Shokir, "CO<sub>2</sub>-oil minimum miscibility pressure model for impure and pure CO<sub>2</sub> streams," *Journal of Petroleum Science and Engineering*, vol. 58, no. 1-2, pp. 173–185, 2007.
- [21] B. L. Chen, H. D. Huang, Y. Zhang et al., "An improved predicting model for minimum miscibility pressure (MMP) of CO<sub>2</sub> and crude oil," *Journal of Oil and Gas Technology*, vol. 35, no. 2, pp. 126–130, 2013.
- [22] B. S. Ju, J. S. Qin, Z. P. Li, and X. Chen, "A prediction model for the minimum miscibility pressure of the CO<sub>2</sub>-crude oil system," *Acta Petrolei Sinica*, vol. 33, no. 2, pp. 274–277, 2012.
- [23] J. L. Shelton and L. Yarborough, "Multiple phase behavior in porous media during CO<sub>2</sub> or rich-gas flooding," SPE 5827, Society of Petroleum Engineers, 1976.
- [24] R. K. Srivastava, S. S. Huang, and M. Dong, "Laboratory investigation of Weyburn CO<sub>2</sub> miscible flooding," *Journal of Canadian Petroleum Technology*, vol. 39, no. 2, pp. 41–51, 2000.
- [25] J.-N. Jaubert, L. Auvallee, and J.-F. Souvay, "A crude oil data bank containing more than 5000 PVT and gas injection data," *Journal of Petroleum Science and Engineering*, vol. 34, no. 1–4, pp. 65–107, 2002.
- [26] Z. L. Gao, T. M. Yang, J. F. Zhang et al., "CO<sub>2</sub> miscible displacement and reservoir numerical simulation in block wen 184," *Journal of Jiangnan Petroleum Institute*, vol. 22, no. 4, pp. 61–62, 2000.
- [27] G. J. Yuan, J. A. Wang, Z. L. Zhou et al., "The indoor experimental study for CO<sub>2</sub> flooding," *Inner Mongolia Petroleum Chemical industry*, vol. 4, no. 8, pp. 94–96, 2005.
- [28] P. Zhao, *Study on CO<sub>2</sub> Flooding for Enhancing Oil Recovery in Pucheng Shayixia Reservoir*, China University of Petroleum, 2011.
- [29] S. Yang and R. Bao, "Research on increasing recovery efficiency in Shayixia oil reservoir by CO<sub>2</sub> miscible displacement agent," *Advances in Fine Petrochemicals*, vol. 13, no. 10, pp. 20–22, 2012.
- [30] P. Li, *Study on injection-production system in low permeability reservoirs in Jilin [Ph.D. thesis]*, Daqing Petroleum Institute, Heilongjiang, China, 2009.
- [31] Y. Zhang, *Study on CO<sub>2</sub>-EOR and geological storage in Caoshe reservoir in Jiangsu [Ph.D. thesis]*, China University of Petroleum, Beijing, China, 2009.
- [32] Y. M. Hao, Y. M. Chen, and H. L. Yu, "Determination and prediction of minimum miscibility pressure in CO<sub>2</sub> flooding," *Petroleum Geology and Recovery Efficiency*, vol. 12, no. 6, pp. 64–66, 2005.
- [33] Y. Xiong, L. Sun, S. L. Li, L. T. Sun, F. L. Zhang, and Y. Wu, "Experimental evaluation of carbon dioxide injection for enhanced oil recovery in Liaohe light oil district," *Journal of Southwestern Petroleum Institute*, vol. 23, no. 2, pp. 30–32, 2001.
- [34] X. L. Li, P. Guo, H. C. Li et al., "Determination of minimum miscibility pressure between formation crude and carbon dioxide in Fan 124 block of Daluhu oilfield," *Petroleum Geology and Recovery Efficiency*, vol. 9, no. 6, pp. 62–63, 2002.
- [35] X. Yang, *Study on the MMP in gas-injection oil reservoirs [Ph.D. thesis]*, Southwest Petroleum Institute, Chengdu, China, 2003.
- [36] K. Zhang, *Interfacial Characteristics and Application Research on CO<sub>2</sub>-Formation Oil System*, Institute of Porous Flow and Fluid Mechanics, Chinese Academy of Sciences, 2011.
- [37] Q. Zheng, L. S. Cheng, S. J. Huang et al., "Prediction of the minimum miscibility pressure of CO<sub>2</sub>-flooding for low permeability reservoir," *Special Oil and Gas Reservoirs*, vol. 17, no. 5, pp. 67–69, 2010.
- [38] C. Guo, H. Tang, and L. Zhang, "Global convergence for a class of conjugate gradient methods," *Journal of Operational Research*, vol. 3, no. 2, pp. 46–49, 1999.
- [39] J. Bon, H. K. Sarma, and A. M. Theophilos, "An investigation of minimum miscibility pressure for CO<sub>2</sub>-rich injection gases with pentanes-plus fraction," in *Proceedings of the SPE International Improved Oil Recovery Conference in Asia Pacific*, SPE-97536-MS, Kuala Lumpur, Malaysia, December 2005.
- [40] J. Bon, M. K. Emera, and H. K. Sarma, "An experimental study and genetic algorithm (GA) correlation to explore the effect of nC<sub>5</sub> on impure CO<sub>2</sub> minimum miscibility pressure (MMP)," SPE 101036, Society of Petroleum Engineers, 2006.
- [41] H. Zhou, *Experimental study on CO<sub>2</sub> miscible flooding in ultra low permeability reservoir [Ph.D. thesis]*, Daqing Petroleum Institute, Heilongjiang, China, 2008.
- [42] C. Peng, *Feasibility assessment on CO<sub>2</sub> miscible flooding for enhancing oil recovery in Gbeibe oil reservoirs [Ph.D. thesis]*, Southwest Petroleum University, Chengdu, China, 2012.



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