

New empirical correlations for predicting Minimum Miscibility Pressure (MMP) during CO₂ injection; implementing the Group Method of Data Handling (GMDH) algorithm and Pitzer's acentric factor

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Abstract. Miscible injection of carbon dioxide (CO₂) with ability to increase oil displacement as well as to reduce greenhouse effect has become one of the pioneering methods in Enhanced Oil Recovery (EOR). Minimum Miscibility Pressure (MMP) is known as a key indicator to ensure complete miscibility of two phases and maximum efficiency of injection process. There are various experimental and computational methods to calculate this key parameter. Experimental methods provide the most accurate and valid results. However, such methods are time consuming and expensive leading researchers to use mathematical methods. Among computational methods, empirical correlations are the most straight-forward and simple tools to precisely estimate MMP, especially for gases with impurities.

Furthermore, in predicting the miscibility state of oil-gas system, phase behavior is a vital issue which should be taken into account to achieve reliable results. In this regard, equations of state have an indisputable role in predicting the phase behavior of reservoir fluids. Remarkable improvements have been introduced to elevate performance of equations of state, based on Pitzer's acentric factor. Hereupon, this study aims to enumerate acentric factor of injected gas (impure CO₂) as a correlating parameter alongside conventional parameters including reservoir temperature, oil constituents (molecular weight of C₅₊, ratio of volatiles to intermediates) and critical properties of injected gas (pseudo-critical pressure & temperature).

Thus, in this study an effective empirical correlation is created, implementing the Group Method of Data Handling (GMDH) algorithm along with including the acentric factor of injected gas, which eventuated to precise predictions of MMP for impure CO₂ injection. The GMDH is one of the most robust mathematical modeling methods for predicting physical parameters using linear equations.

A comparison with well-known correlations, demonstrated at least 2% improvement in average absolute error with enumerating the acentric factor and the final error was equal to 12.89%.

1 Introduction

Minimum Miscible Pressure (MMP) is the minimum pressure at which first or multi-contact miscible displacement takes place. This parameter plays an important role in selecting miscible flooding method for Enhanced Oil Recovery (EOR) process according to the type and characteristics of oil reservoirs. An accurate estimation of MMP results in appropriate surface facilities design for gas injection, management of costs, and optimized injection pattern.

Various gases are utilized for the injection purpose, including natural gas, flue gas, nitrogen, and supercritical CO₂ resulting in various levels of success in operational and economic aspects [1, 2]. Among mentioned gases, high

solubility of CO₂ in oil reservoir results in an extreme mass transfer between the phases [1, 2], interfacial tension reduction which increase oil sweep by reducing viscosity between the phases [3] and final recovery up to 90% [4, 5]. Injecting CO₂ as a greenhouse gas and removing it from atmosphere has also environmental benefits by storing this detrimental gas under the ground [4, 6–8]. Another advantage of CO₂ injection is the considerable reduction of MMP and higher number of potential strategies for CO₂ flooding, in comparison to other gases [2]. This is caused because of CO₂'s higher molecular weight in comparison to other usually used hydrocarbon gases such as Methane and Ethane and also no corrosion problems in comparison to H₂S [3].

To obtain MMP, different experimental and computational methods are available. Experimental methods include slim tube test, Vanishing Interfacial Tension

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(VIT) technique, multi-contact mixing-cell experiment and rising bubble apparatus [1]. Computation methods contain two main groups: (1) Equation of State (EoS), (2) empirical correlations. For multicomponent injections, semi-analytical and multiple-mixing-cell methods implementing EoS would be appropriate. However, lots of steps for calibrating the EoS with respect to laboratory data must be carried out, which would be complicated. For pure gas injection or injection with small degree of impurities, empirical correlations would perform properly.

One of the most accurate experimental methods for determining MMP is the slim tube test where the oil and gas displacement process in porous medium is simulated. Due to horizontal position of slim tube and low pressure drop across the tube surface because of its small diameter, fingering phenomena and gravitational effects are eliminated. This will result in more accurate MMP measurements. On the other hand, performing slim tube experiment is substantially time and money consuming [1, 9]. Therefore, application of this in miscible injection design where a great number of MMPs should be determined would not be feasible. In fact, the major application of slim tube test is to calibrate EoS for phase equilibria calculations and to develop empirical correlations for MMP prediction in pure and impure gas injections.

In this study, we focused on empirical correlations applied for predicting MMP in pure and impure gas injections. Empirical correlations are mathematical models developed with respect to experimental data. In empirical correlations, MMP is correlated to physical parameters of oil, gas and thermodynamic conditions. Application of these models has eliminated the need for repeating time-consuming and costly experiments for each injection [10, 11].

Cronquist [12] considered reservoir temperature, C_{5+} molecular weight, and light components mole fraction as the key parameters of MMP prediction. Although, Lee [13], Yellig and Metcalfe [14] and Orr and Jensen [15] considered reservoir temperature (T) as the key parameter of MMP prediction.

To account for impurities in MMP calculations, correction factors were applied to MMPs obtained for pure gases. Various correction factors were introduced by researchers. Sebastian *et al.* [16] presented the molar average critical temperature of the mixture (T_{cm}) as the most accurate parameter to correlate impure MMP.

Alston *et al.* [5] presented a correlation for pure MMP based on reservoir temperature, C_{5+} molecular weight, and the ratio of light to intermediate components of the reservoir oil. Impure MMP was calculated by multiplying a correction factor based on pseudo-critical temperature. Emera and Sarma [17] presented a correlation using genetic algorithm based on reservoir temperature, C_{5+} molecular weight, and the ratio of light to intermediate components, similar to Alston *et al.* [5]. Liao predicted MMP for low permeable reservoirs. In addition, impure MMP was obtained by a parameter called the relative MMP, which was the ratio of impure to pure MMP.

Fathinasab and Ayatollahi [1] introduced a correlation for MMP prediction combining genetic programming with the multivariate search method based on reservoir

temperature, C_{5+} molecular weight, injected gas pseudo-critical temperature, and the ratio of light to intermediate components. Using gene expression programming, Ahmadi *et al.* [4] predicted MMP based on parameters proposed by Fathinasab and Ayatollahi [1], Liao *et al.* [18], and Alston *et al.* [5] (T , T_{cm} , light to intermediate components ratio, and C_{5+} molecular weight). However, implementing these implicit methods in operational applications would be complex.

The above mentioned empirical correlations have significant errors for high-temperature reservoirs. Furthermore, applying correction factors to pure MMP in order to predict impure MMP would be very erroneous, since the error of pure MMP calculation can also affect impure MMP results and causes additional error.

This study aims to provide an accurate, explicit and simple empirical correlation with less computational errors compared to prior correlations for MMP prediction. The necessity to present correction factors for impure MMP prediction have been also eliminated and two separate correlations were developed to predict pure and impure CO_2 MMP using multi-variable optimization algorithms. Furthermore, as a unique feature of this study, two new parameters considering the ratio of reservoir temperature to pseudo critical temperature as one parameter and acentric factor (ω) for the other one, have been implemented in impure MMP correlation. These two parameters can effectively determine the impact of injected gas impurities on MMP predictions.

A large data bank of oil reservoirs collected from authenticated articles [5, 7, 16–24] as well as two Iranian oil fields (Darkhovin and Yadavaran) were collected and applied to develop the new correlations.

2 Data analysis/Experimental

2.1 Data analysis

Data are divided in two categories. The first category includes 126 data points which will be used to develop the correlation for pure CO_2 injection. The second category includes 126 data points which will be used to develop the correlation for impure CO_2 injection.

Most part of data that are used in this study have been collected from the literature [5, 7, 16–24]. It is worth mentioning that previous correlations had also been developed based on these set of data [5, 7, 16–24]. Therefore, a unique and new dataset is not considered to develop the correlation, except for some data points, which are added from Iranian oil fields in both pure CO_2 injection (two points) and impure CO_2 injection (four points). The reason to add Iranian oil fields dataset was to increase the range of temperature and because Iranian oil fields are involved with relatively high-temperature deep reservoirs.

2.2 Experimental

Iranian datasets are obtained through slim tube experimental result. Tables 1 and 2 represent the oil properties of these reservoirs.

Table 1. Properties of field oil Darkhovin.

Composition	Mole percent (%)
H ₂ S	0.00
N ₂	0.36
CO ₂	0.51
C ₁	25.24
C ₂	7.91
C ₃	5.48
IC ₄	1.07
NC ₄	3.39
IC ₅	1.42
NC ₅	1.73
C ₆	4.98
C ₇₊	2.6
$T = 107.22$ (°C)	
$Mw_{C5+} = 162.3$ g/gmole	

Table 2. Properties of field oil Yadavaran.

Composition	Mole percent (%)
N ₂	0.04
CO ₂	2.23
H ₂ S	0.25
C ₁	50.74
C ₂	8.59
C ₃	5.66
IC ₄	1.06
NC ₄	2.94
IC ₅	1.21
NC ₅	1.67
C ₆	2.77
C ₇	2.60
C ₈	2.10
C ₉	2.22
C ₁₀	2.25
C ₁₁	1.69
C ₁₂₊	11.98
$T = 143$ (°C)	
$Mw_{C5+} = 186.7$ g/gmole	

The characteristics of the slim tube used in this study are presented in Table 3.

Slim tube is a stainless steel, packed with glass beds that fairly simulates one-dimensional flow through pore geometry. Before starting the test, toluene is injected in the slim tube in order to clean it and after that N₂ is injected to remove the remaining amount of toluene. Moreover, a vacuum pump evacuates the porous media for several hours.

At the beginning of the fluid displacement tests, the slim tube system is saturated by the oil (reservoir fluid) at the

Table 3. Slim-tube features.

Parameter	Value
Pipe length	13000 cm
Pipe height	1 cm
Porosity	0.1
Permeability	2000 mD

reservoir temperature and a pressure above the bubble pressure. Then the gas with a constant flow rate is injected into the tube (1.2 pore volume) by an injection pump for miscibility process to occur. This process is repeated in several pressures and a sight glass is imbedded for the flow/process observation. There are also an accumulator and measuring systems at the end of the tube to measure gas breakthrough through, checking the producing gas–oil ratio and composition as functions of the injected volume. The schematic diagram of the slim-tube test used in this study is shown in Figure 1.

The common experimental procedure for determining MMP of CO₂/Crude oil system, once the injection CO₂ becomes miscible with crude oil, an inflection point is observed in the curve of recovery factor with respect of displacement pressure and the recovery will not improve as much above with a step change in pressure (Fig. 2).

Table 4 represents the experimental MMP data obtained in this study. As can be seen in this table, three experimental points were obtained for each fluid sample using the slim-tube testing.

3 Theory

The Group Method of Data Handling (GMDH) was developed by a Russian cybernet specialist, Prof. Alexey Ivakhnenko, in 1966. In standard regression models, the only criterion is the least squared error, and thus it cannot be determined whether the final model is simple or complex. However, using in the Ivakhnenko polynomials, one can obtain a polynomial with optimal complexity [25, 26].

The GMDH algorithm is robust and gives unique answers and produce linear and explicit correlations. This method is very suitable for solving complex and multi-dimensional problems with limited data [27] as with the case we have encountered in this article.

The GMDH algorithm creates a process for developing higher order polynomials as in equation (1):

$$y = a + \sum_{i=1}^m a_i u_i + \sum_{i=1}^m \sum_{j=1}^m a_{ij} u_i u_j + \sum_{i=1}^m \sum_{j=1}^m \sum_{k=1}^m a_{ijk} u_i u_j u_k + \sum_{i=1}^m \sum_{j=1}^m \sum_{k=1}^m \sum_{l=1}^m a_{ijkl} u_i u_j u_k u_l + \dots, \quad (1)$$

which relates m input parameters u_1, u_2, \dots, u_m to a single target parameter called y . In the GMDH algorithm, it is not necessary to use all formats of the summations (dou-

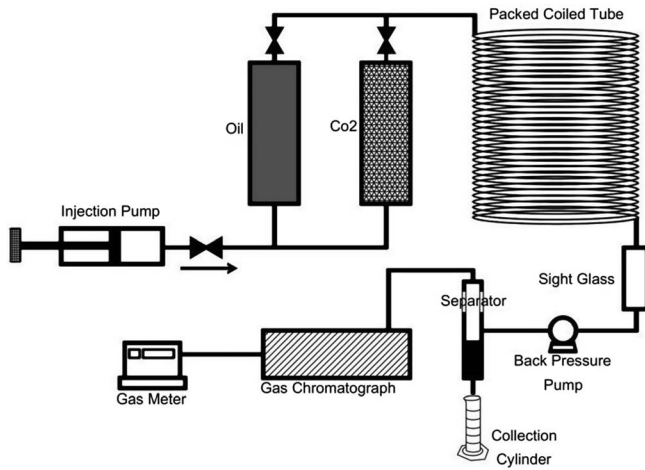


Fig. 1. Schematic of slim-tube apparatus.

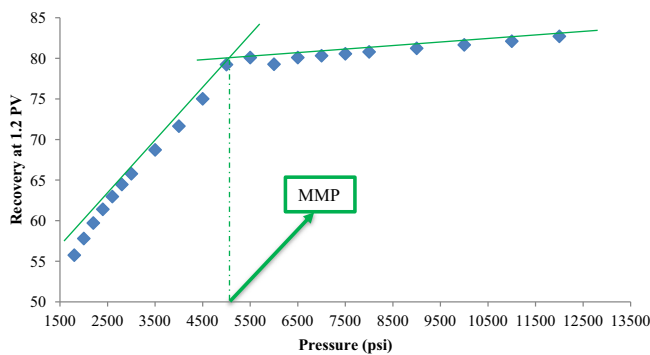


Fig. 2. Schematic graph of oil recovery versus injection pressure obtained from slim-tube test.

ble, triple, quadruple, etc.) in equation (1). In fact, it depends on the difficulties involved in modeling of a system. In systems with more variables involved, a higher order summation might be essential for accurate modeling. In this study we intended to make the correlations as simple (consisting of less constants) as possible while keeping a significant accuracy. In this regard, based on the optimization process, some variables from the regular and double summation terms are utilized for the modeling purpose as can be seen for pure CO₂ MMP system (Sect. 4.1) and for impure CO₂ MMP system (Sect. 4.2). Hence, implementing the triple and quadruple summations makes the correlation more complex while not improving its accuracy noticeably here.

We have divided the data into training and testing datasets. Training datasets will be implemented in developing the correlation and testing datasets will be applied for validation. To this end, 70% of data are randomly used for training and 30% of data are assigned to the test subset.

In the first step, all possible first-order polynomials are created for all existing input parameters. In this case, the constants are determined in such a way that the resulting polynomials have the least sum of squared error compared to the training data. For example, assuming only linear

Table 4. Experimental obtained data from slim-tube testing.

Field name	Temperature (°C)	Injection gas composition		Measured MMP (Mpa)
		CO ₂ mole fraction	C ₁ mole fraction	
Darkhovin	107.22	1	0	23.34
		0.9	0.1	24.132
		0.8	0.2	25.03
Yadavaran	143	1	0	24.04
		0.9	0.1	24.13
		0.8	0.2	26.89

relationship, the following polynomials are constructed for a three-parameter function as can be seen in equation (2):

$$\begin{aligned}
 y_1 &= a_0^{(1)} + a_1^{(1)} u_1 \\
 y_2 &= a_0^{(2)} + a_2^{(2)} u_2 \\
 y_3 &= a_0^{(3)} + a_1^{(3)} u_1 + a_2^{(3)} u_2 \\
 y_4 &= a_0^{(4)} + a_3^{(4)} u_3 \\
 y_5 &= a_0^{(5)} + a_1^{(5)} u_1 + a_2^{(5)} u_2 \\
 y_6 &= a_0^{(6)} + a_2^{(6)} u_2 + a_3^{(6)} u_3 \\
 y_7 &= a_0^{(7)} + a_1^{(7)} u_1 + a_2^{(7)} u_2 + a_3^{(7)} u_3.
 \end{aligned} \tag{2}$$

where y_k is the estimated output of k th unit, $k = 1, 2, \dots, 7$; and $a_i^{(k)}$, $i = 0, 1, 2, 3$ are their weight constants. In general, $M = (2^m - 1)$ polynomials are constructed for m input parameters.

In the second step, for each of these polynomials, the sum of least squared error is calculated for the test data as mentioned in equation (3):

$$d_j^2 = \sum_{i=1}^{\text{Number of data}} (y_{ij} - z_i)^2 \quad j = 1, 2, \dots, 2^m - 1, \tag{3}$$

where z_i represents the i th test data and y_{ij} represents the i th corresponding prediction of the j th equation. d_j is the sum of least squared error of the j th polynomial. In the third step, the polynomial with least squared error is selected as the solution. If the solution is undesired, other modes such as the division or multiplication of the current parameters can be selected as new parameters to be added to the previous parameters. Thus, the number of parameters varies and therefore the number of equations. Then the process starts again from the first step.

4 Result and discussion

4.1 Empirical correlation for pure CO₂ MMP

Initial input parameters for pure MMP determination are reservoir temperature (T), Mw_{C5+} and volatile to

Table 5. Range of oil properties for pure CO₂ injection.

Parameter	Max	Min	Average
T (°C)	143	31.11	68.87
x	13.607	0	2.08
Mw _{C₅₊} (g/gmole)	350.3	154	204.87
MMP (MPa)	30	7	17

Notes: T , Temperature; x , volatile to intermediate ratio; Mw_{C₅₊}, Molecular weight of C₅₊ fraction of the oil; MMP: Minimum Miscibility Pressure.

intermediate oil fraction (x) which is defined in equation (4) (mol stands for mole fraction of each component). Table 5 shows the range of changes in reservoir temperature (T) in °C, molar ratio of volatile (C₁, N₂) to intermediate components (C₂, C₃, C₄, CO₂, H₂S), average molecular weight of components heavier than pentane (Mw_{C₅₊}), and pure MMP in MPa:

$$x = \frac{\text{mol}_{C_1} + \text{mol}_{N_2}}{\text{mol}_{C_2} + \text{mol}_{C_3} + \text{mol}_{C_4} + \text{mol}_{CO_2} + \text{mol}_{H_2S}}. \quad (4)$$

The proposed correlation for pure CO₂-MMP is shown in equation (5):

$$\begin{aligned} \text{MMP}_{\text{pure}} = & A_1 + A_2 \frac{x}{\text{Mw}_{C_5+}} + A_3 \frac{\text{Mw}_{C_5+}}{T} \\ & + A_4 \text{Mw}_{C_5+} e^x + A_5 \ln(T) + A_6 \frac{e^x}{\ln(T)}. \end{aligned} \quad (5)$$

A1–A6 are constants shown in Table 6.

In this study, Mean Squared Error (MSE) is used for estimating absolute deviation. Average Absolute Percentage Relative Error (AAPRE) is applied for estimating error precisely. These deviation and error measurement methods are defined as follows:

$$E_{\text{MSE}} = \frac{\sum_{i=1}^n (\text{MMP}_i^{\text{observed}} - \text{MMP}_i^{\text{calculated}})^2}{n}, \quad (6)$$

$$E_{\text{AAPRE}} = \frac{\sum_{i=1}^n \left(\left| \frac{\text{MMP}_i^{\text{observed}} - \text{MMP}_i^{\text{calculated}}}{\text{MMP}_i^{\text{calculated}}} \right| \right)}{n} \times 100, \quad (7)$$

where $\text{MMP}_i^{\text{observed}}$ is the i th observed (experimental) MMP value. $\text{MMP}_i^{\text{calculated}}$ is the i th calculated MMP value and n is the number of data points.

For pure CO₂, 126 data points were available. 70% of these data (including 88 data points) were used to develop the corresponding correlation. The remaining 30% of data set (including 38 data points) were used to evaluate and test the obtained correlation. Performance of the proposed correlation is evaluated based on each dataset (train, test and total data) as presented in Table 7 which provides results of simulation based on AAPRE and MSE.

On the other hand, there is no certainty if the previous authors have selected a specific part of data for test or if

Table 6. Correlating parameters for pure CO₂-MMP prediction.

Coefficient	Value
A_1	−83.9439
A_2	329.928
A_3	2.99863
A_4	0.0000400011
A_5	21.0968
A_6	−0.0351046

Table 7. Performance evaluation of proposed pure MMP correlation.

Data	Number of data points	AAPRE (%)	MSE
Train	88	7.44	2.89
Test	38	10.47	3.55
Total	126	8.35	3.07

Table 8. MSE and AAPRE error for pure MMP.

Correlation	MSE	AAPRE (%)
Liao <i>et al.</i> [18]	322.7	99.28
Orr and Jensen [15]	26.022	18.05
Yellig and Metcalfe [14]	27.68	17.98
Lee [13]	23.32	17.22
Alston <i>et al.</i> [5]	32.33	17.05
Ahmadi <i>et al.</i> [4]	17.7	13.6
Emera and Sarma [17]	17.71	13.33
Fathinasab and Ayatollahi [1]	7.01	11.07
Proposed correlation	3.07	8.35

they do, which part of data have been used for test. Therefore, it would be reasonable to compare the performance of developed correlation with other correlations based on total data points available, not just the test data.

Thus, MSE and AAPRE calculated based on total pure data points for well-known correlations in predicting pure MMPs are given in Table 8. This table is sorted based on descending values of AAPRE.

As seen in, Liao correlation [18] shows the highest error. In contrast, the correlation presented in this study has the lowest error, reducing error by at least 3.3% compared to other existing correlations.

In Figure 3 the experimental MMP graphs for three correlations with higher accuracy and minimum Error Fathinasab and Ayatollahi [1], Ahmadi *et al.* [4] and Emera and Sarma [17], are compared with the proposed correlation in this paper. In these graphs, the vertical and horizontal axes show the experimental MMP and the corresponding calculated MMP, respectively. Accumulation of data

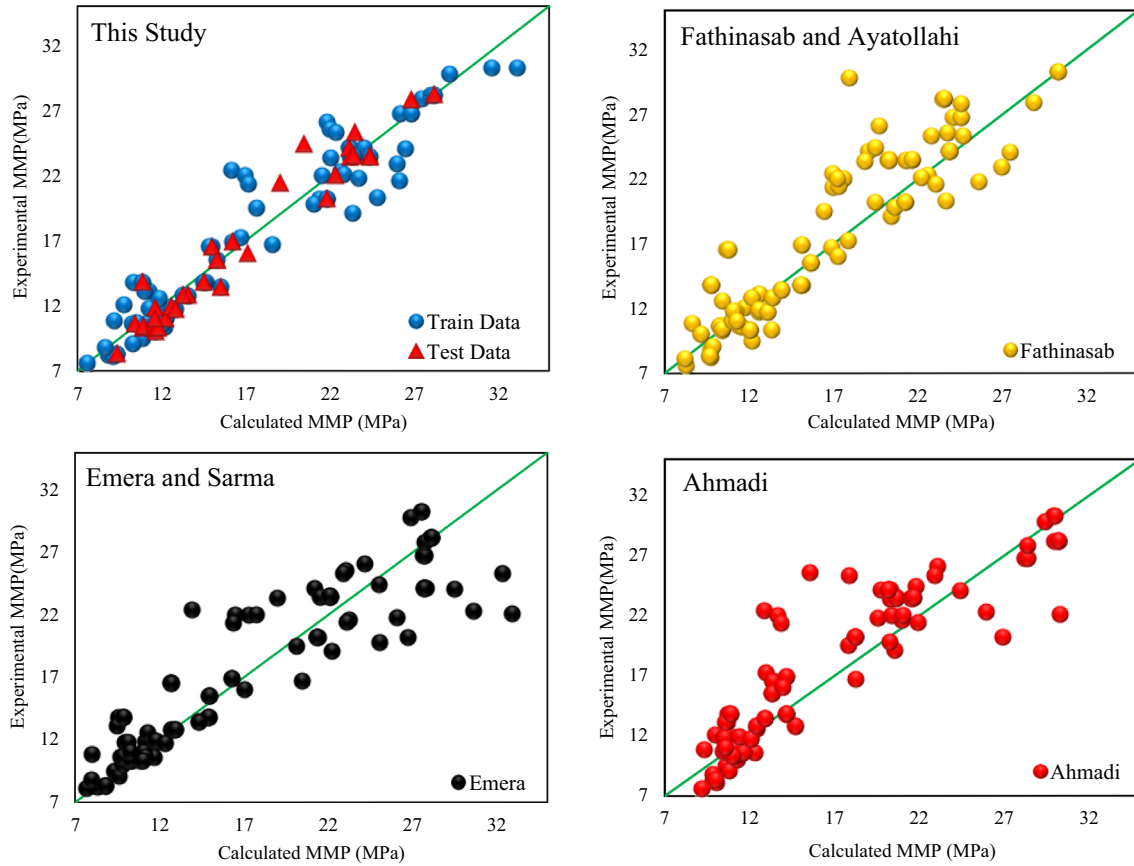


Fig. 3. Comparison of experimental versus calculated MMP graphs for three correlations with minimum error.

around the diagonal line in these graphs indicates the accuracy of each correlation in prediction of MMP. As can be seen, the graph plotted for the present study shows the best accumulation around the diagonal line $y = x$.

4.2 Empirical correlation for impure CO₂ MMP

Input parameters for impure MMP determination include C_{5+} molecular weight ($Mw_{C_{5+}}$) of the oil, volatile to intermediate ratio (Eq. (4)), pseudo-critical pressure of the injected gas (P_{pc}), relative pseudo-reduced temperature (reservoir temperature to pseudo critical temperature ratio) (T_{pr}) and average acentric factor of the injected gas (ω). Where the parameters T_{pc} , P_{pc} are defined in equations (8) and (9) in accordance with the Kay's rule [28]:

$$T_{pc} = \sum_i^n y_i T_{ci}, \quad (8)$$

$$P_{pc} = \sum_i^n y_i P_{ci}. \quad (9)$$

T_{pr} is also defined in equation (10):

$$T_{pr} = \frac{T}{T_{pc}}. \quad (10)$$

ω is molar averaged based on equation (11) [29]:

$$\omega = \frac{\sum_i^n y_i \omega_i}{\sum_i^n y_i}, \quad (11)$$

where y_i stand for the i th component mole fraction in the gas in equations (8)–(11). T_{ci} and P_{ci} represent critical temperature and pressure of the i th component, respectively. As mentioned earlier, 126 data points were used to develop the impure CO₂ MMP empirical correlation. Range of data used for developing this correlation is given in Table 9.

It is noteworthy saying that while the temperature of the published data mostly ranged from 32.2 to 118.3 °C, utilizing Iran's data in this paper increased the temperature range according to the higher depth and temperature of these reservoirs (up to 143 °C). Moreover, the range of molecular weight of components heavier than pentane was in former studies Liao *et al.* [18] and Alston *et al.* [5], was extended between 154 and 350.3 g/gmole range of C_{5+} molecular weight is extended considerably using the Iran's data. Amount of injected gas impurities for impure MMP dataset is given in Table 10.

It is worth noting that in previous studies [1, 4], T and T_{pc} were considered as correlating parameters. In this

Table 9. Range of oil properties for impure CO₂ injection.

Parameter	Max	Min	Average
T_{pr}	1.478	0.926	1.13
x	7.714	0	1.15
Mw _{C₅₊} (g/gmole)	261.64	136.264	176.76
ω	0.224	0.126	0.2
P_{pc} (MPa)	5.753	8.172	7.15
MMP (MPa)	26.89	6.536	14.71

Notes: T , Temperature; T_{pc} , Pseudo critical temperature of injection gas; T_{pr} , relative pseudo reduced temperature of injection gas; x , volatile to intermediate ratio; Mw_{C₅₊}, Molecular weight of C₅₊ fraction of oil; ω , average acentric factor of injected gas; P_{pc} , Pseudo reduced pressure; MMP, Minimum Miscibility Pressure.

Table 10. Range of impurities along with injected CO₂.

Parameter	Maximum mole fraction (%)	Minimum mole fraction (%)
CH ₄ (mole %)	40	4.78
C ₂ H ₆ (mole %)	25	0
C ₃ H ₈ (mole %)	20	0
C ₄ H ₁₀ (mole %)	12	0
H ₂ S (mole %)	50	0
N ₂ (mole %)	808	0

study, a ratio of these parameters called relative pseudo-reduced temperature is chosen as a correlating parameter. This choice was due to higher observed coefficient of determination between T_{pr} and MMP relative to MMP and T_{pc} or T .

A higher linear coefficient of determination can be measured as a representative of the correlation between the target parameter and the input parameters. It can be observed that the data correlation for T_{pr} and MMP is the highest, compared to T_C and T (Fig. 4). Therefore, it is more suitable to develop the correlation based on T_{pr} (Eq. (10)).

The Pitzer's acentric factor [30] was introduced in 1955 with the aim of developing the corresponding states theorem; increasing its reliability and accuracy in fluid properties modeling and prediction. This coefficient is defined as follows:

$$\omega = -\log_{10}(P_r^{\text{sat}}) - 1 \text{ at } T_r = 0.7, \quad (12)$$

where $T_r = \frac{T}{T_c}$ is the reduced temperature and $P_r^{\text{sat}} = \frac{P^{\text{sat}}}{P_c}$ is the reduced saturation vapor pressure.

Employment of acentric factor has significantly ameliorated the prediction of fluid phase behavior and calculation of reservoir fluid properties [31–34].

In evolutionary process of equations of state, Soave [31] proposed a correction factor as a function of acentric factor on the attractive term of Redlich and Kwong [35] EoS which was previously introduced merely as function of

temperature. The proposed format of attractive term temperature dependency is subsequently incorporated in development of equations of state. Moreover, Pitzer's acentric factor has also played an important role in developing three-parameter equations of state, which led to significant improvements in prediction of fluid volumetric data. This impact can be clearly observed in equations of state such as Schmidt and Wenzel [33], Esmailzadeh and Roshanfekr [32] and Patel and Teja [34].

Success of foregone applications of acentric factor in phase behavior predictions, gave an idea to use this parameter as a correlating parameter to predict MMP alongside other previously alluded parameters.

The GMDH-based MMP function is presented as follows (Eq. (13)):

$$\begin{aligned} \frac{\text{MMP}_{\text{impure}}}{P_{pc}} = & A_1 + A_2 T_{pr} + \frac{A_3}{T_{pr} \ln(T_{pr})} + A_4 \frac{\omega}{\text{Mw}_{C_{5+}}} \\ & + A_5 \omega x + A_6 \frac{x}{\omega} + A_7 \text{Mw}_{C_{5+}} x + A_8 \\ & \times \frac{\text{Mw}_{C_{5+}}}{\ln(T_{pr})} + A_9 \frac{x}{\text{Mw}_{C_{5+}}}. \end{aligned} \quad (13)$$

Constants A1–A8 are also listed in Table 11.

It is worth noting that, the reason for presenting two separate correlations for pure CO₂ and impure CO₂ is to achieve the ultimate goal to adhere simplicity and accuracy, and to avoid using correction factors for impure MMP predictions which would lead up to additional errors. As with the importance and prevalence of impure CO₂ injection scenario in oil and gas industry (since pure CO₂ can be hardly accessible), it is preferred to develop a separate correlation for impure CO₂ injection to properly handling the simultaneous presence of accuracy and simplicity.

Moreover, using a dimensionless relative temperature (T_{pr}), a dimensionless pressure ratio MMP/ P_{pc} , relative molar ratio (x) and molecular weight of C₅₊ (Mw_{C₅₊}) which could be considered dimensionless despite its unit, all result in a semi-dimensionless correlation, and also reduce the number of correlation parameters.

For impure CO₂, 126 data points were available. It should be emphasized that these 126 data points are completely distinct from 126 data points which were used for pure CO₂. 70% of these data (including 88 data points) were used to develop the corresponding correlation. The remaining 30% of dataset (including 38 data points) were used to evaluate and test the obtained correlation. Performance of the proposed correlation is evaluated based on each dataset (train, test and total data) and presented in Table 12 which provides results of simulation based on AAPRE and MSE.

Again, there is no certainty if the previous authors have selected a specific part of data for test or if they do, which part of data have been used for test. Therefore, it would be reasonable to compare the performance of developed correlation with other correlations based on total data points available, not just the test data.

Thus, AAPRE (Eq. (7)) and MSE (Eq. (6)) errors for the above equation (13) based on total impure data points, is shown and compared with former studies in Table 13.

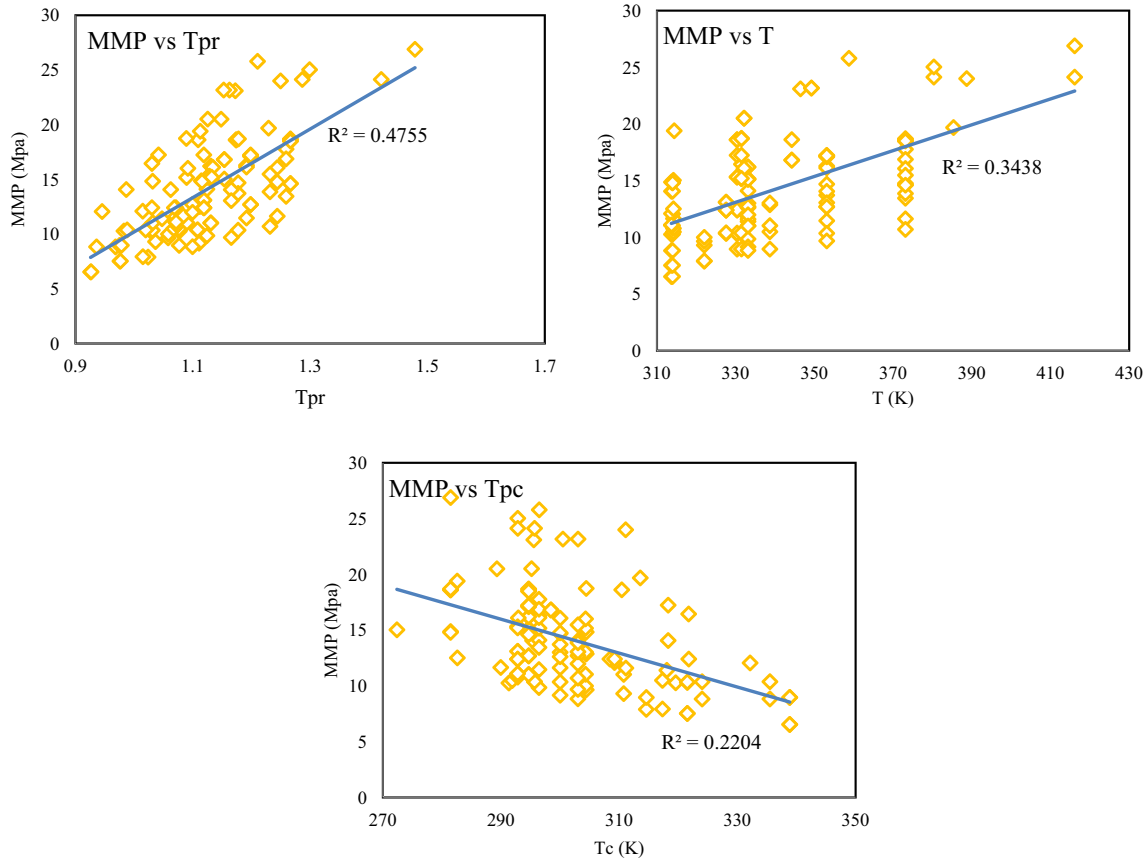


Fig. 4. Comparison of data correlations for T , T_{pc} , T_{pr} .

Table 11. Correlation parameters for impure MMP.

Coefficient	Value
A_1	-1.12058
A_2	6.21956
A_3	0.282895
A_4	-3180.89
A_5	-32.3245
A_6	-1.51449
A_7	0.0364995
A_8	-0.00149903
A_9	1324.94

Table 13 is sorted based on descending values of the AAPRE. It should be noted that in this study, correlations proposed by Emera and Sarma [17], Yellig and Metcalfe [14], Orr and Jensen [15], and Lee [13] were applied using the Sebastian correction factor [16] to predict the impure MMP.

Experimental MMP graphs in terms of calculated MMP for three correlations with the least error from Table 13 along with the correlation of this study were compared in Figure 5. In the present study data points are

Table 12. Performance evaluation of proposed for impure correlation.

Data	Number of data points	AAPRE (%)	MSE
Train	88	12.20	4.08
Test	38	14.49	6.32
Total	126	12.89	4.77

well-accumulated around the diagonal line. This indicates the higher accuracy of the correlation provided for MMP calculation.

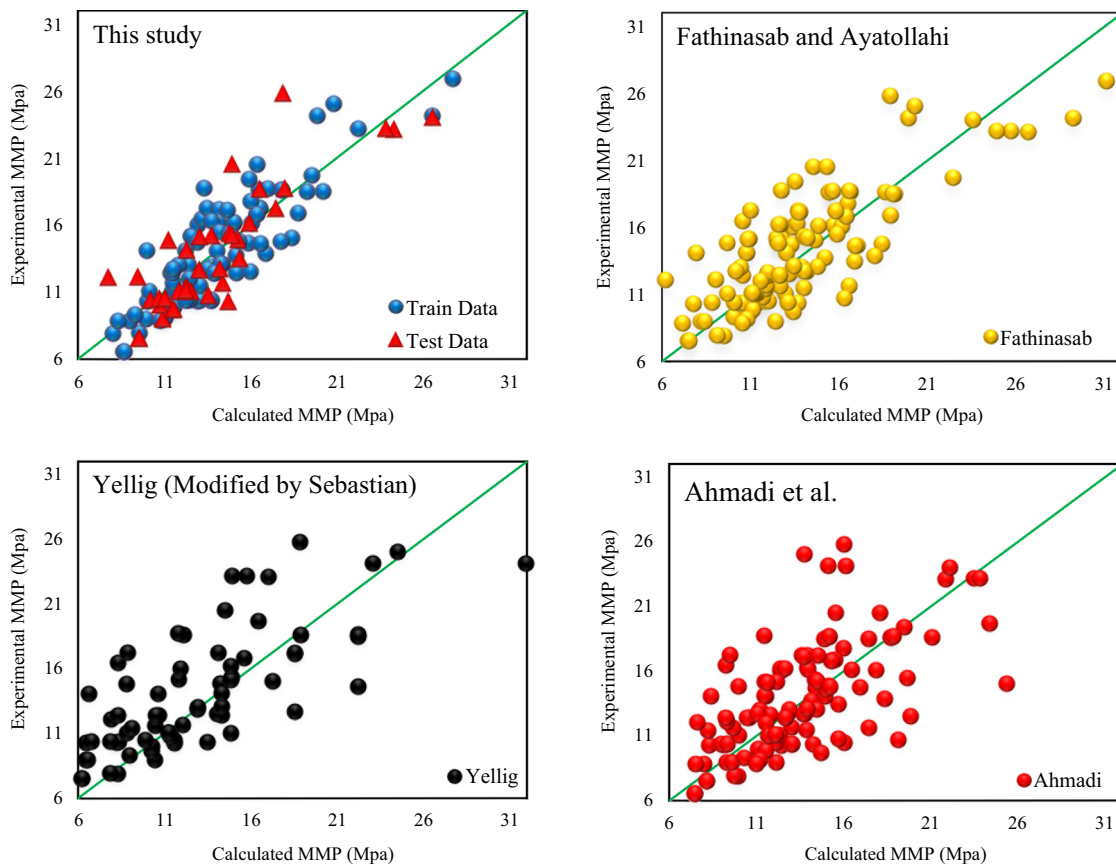
5 Sensitivity analysis

In this study, the sensitivity analysis was performed on parameters affecting both pure and impure correlations using the relevancy factor:

$$r_{(\text{input}_{k,i}, \text{MMP})} = \frac{\sum_{i=1}^n (\text{input}_{k,i} - \text{input}_{\text{ave},k}) (\text{MMP}_i - \text{MMP}_{\text{ave}})}{\sqrt{\sum_{i=1}^n (\text{input}_{k,i} - \text{input}_{\text{ave},k})^2 \sum_{i=1}^n (\text{MMP}_i - \text{MMP}_{\text{ave}})^2}} \quad (14)$$

Table 13. MSE and AAPRE error for impure MMP.

Correlation	MSE	AAPRE (%)
Alston <i>et al.</i> (impure) [5]	142386.1	289.75
Liao <i>et al.</i> (impure) [18]	508.23	96.60
Emera and Sarma (Modified by Sebastian) [17, 16]	34.05	27.17
Orr and Jensen (Modified by Sebastian) [15, 16]	59.05	33.23
Lee (Modified by Sebastian) [13, 16]	49.35	31
Yellig and Metcalfe (Modified by Sebastian) [14, 16]	21.26	21.26
Ahmadi <i>et al.</i> [4]	16.42	18.26
Fathinasab and Ayatollahi [1]	7.45	14.87
Proposed correlation	4.76	12.89

**Fig. 5.** Comparison of experimental versus calculated MMP graphs for three correlations with minimum error.

In equation (14), $\text{input}_{k,i}$ and $\text{input}_{\text{ave},k}$ are the i th value and the average value of the k th input, respectively. The index k refers to each enumerating parameter, e.g. Temperature, volatile to intermediate ratio, etc; MMP_i stands for the i th value of predicted MMP and MMP_{ave} is the arithmetic average of predicted MMP values. r shows the effect of each parameter (each input_k) on the correlation output (MMP in this study). If $r > 0$, then the associated parameter has a positive effect; in contrast, if r is negative ($r < 0$), the associated parameter has a negative effect. The parameter r ranges from -1 to 1 , indicating the highest negative or positive effect.

The results of sensitivity analysis on pure MMP correlation are depicted in Figure 6. As can be seen, all parameters (including x , $\text{Mw}_{\text{C}_{5+}}$, T) have a positive effect on predicted MMP. Temperature has the largest effect and C_{5+} molecular weight of components has the smallest effect. The impact of these parameters in this study is consistent with the results of foregone studies [7, 18, 36].

The results of sensitivity analysis are rendered for the correlation of impure MMP parameters (ω , P_{pc} , $\text{Mw}_{\text{C}_{5+}}$, x and T_{pr}) in Figure 7 (T_{pr} consists of two parameters, T and T_{pc}). Previous researchers reported direct relation of T [7, 18, 36] and inverse relation of T_{pc} [7]. Consequently,

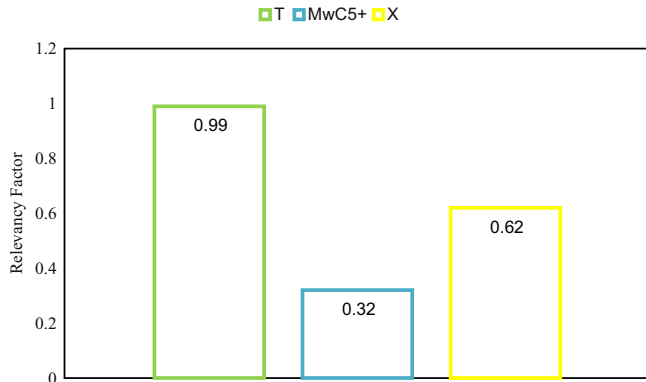


Fig. 6. Relevancy factor for pure MMP.

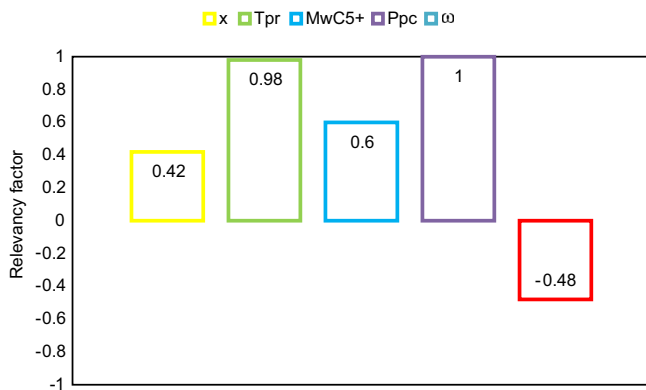


Fig. 7. Relevancy factor for impure MMP considering acentric factor.

the effect of their ratio (T/T_{pc}) reported as T_{pr} is ultimately deduced to have a direct relation with MMP. The effect of the parameter x and C_{5+} molecular weight is similar to pure MMP. Sensitivity analysis on correlating parameters in this study confirms these results.

A gas with high molecular weight has a lower P_{pc} . As a result, one can assume that increasing the molecular weight of gas has the same effect as decreasing P_{pc} . By increasing the molecular weight of gas, P_{pc} and hence the MMP decreases. The results of the sensitivity analysis also confirm this conclusion.

In general, with increasing the gas molecular weight, the acentric factor (ω) increases and accordingly, MMP decreases. Therefore, inverse relation of the acentric factor on MMP can also be explained and interpreted. Among the parameters mentioned above, T_{pr} , P_{pc} , and ω showed the most while x and MW_{C5+} showed the least impact.

6 Conclusion

Reviewing experimental data in foregone studies and data from two Iranian reservoirs, a database with a higher temperature range was collected. Then, to predict MMP

in pure and impure CO_2 injection operations, correlations were provided using the GMDH algorithm.

1. The correlation proposed to predict pure MMP is an explicit correlation based on MW_{C5+} , x , and T parameters. This correlation ameliorates the results compared to other previous correlations and reduces the computational error by at least 2.5%. Remarkable decrease of computational error corroborates robustness of the GMDH algorithm approach.
2. The correlation proposed to predict impure MMP is presented explicitly without using the correction factor. The effective parameters in this correlation include T_{pr} , x , Mw_{C5+} and ω . Using the dimensionless temperature and presenting the correlation as MMP/P_{pc} , this correlation is developed in a semi-dimensionless form. It should be noted that such non-dimensionalization not only shortens the correlation but also provides its applicability for many reservoirs. Employing the GMDH algorithm approach along with implementing the gas acentric factor, eventuated in at least 2% decrease in computational error compared to previous studies.
3. Since the data from Iranian reservoirs were used to develop new correlations in this study, they can be used as means for predicting CO_2 -MMP in reservoirs with high depth and temperatures such as some Middle East reservoirs.

References

- 1 Fathinasab M., Ayatollahi S. (2016) On the determination of CO_2 -crude oil minimum miscibility pressure using genetic programming combined with constrained multivariable search methods, *Fuel* **173**, 180–188.
- 2 Shaw J., Bachu S. (2002) Screening, evaluation, and ranking of oil reservoirs suitable for CO_2 -flood EOR and carbon dioxide sequestration, *J. Can. Pet. Technol.* **41**, 51–61.
- 3 Rahimi V., Bidarigh M., Bahrami P. (2017) Experimental study and performance investigation of miscible water-alternating- CO_2 flooding for enhancing oil recovery in the Sarvak formation, *Oil Gas Sci. Technol. - Rev. IFP Energies nouvelles* **72**, 35.
- 4 Ahmadi M.A., Zendehboudi S., James L.A. (2017) A reliable strategy to calculate minimum miscibility pressure of CO_2 -oil system in miscible gas flooding processes, *Fuel* **208**, 117–126.
- 5 Alston R., Kokolis G., James C. (1985) CO_2 minimum miscibility pressure: A correlation for impure CO_2 streams and live oil systems, *Soc. Pet. Eng.* **25**, 268–274.
- 6 Huang Y., Huang G., Dong M., Feng G. (2003) Development of an artificial neural network model for predicting minimum miscibility pressure in CO_2 flooding, *J. Pet. Sci. Eng.* **37**, 83–95.
- 7 Kamari A., Arabloo M., Shokrollahi A., Gharagheizi F., Mohammadi A.H. (2015) Rapid method to estimate the minimum miscibility pressure (MMP) in live reservoir oil systems during CO_2 flooding, *Fuel* **153**, 310–319.
- 8 Sun L., Hao X., Dou H., Adenutsi C.D., Li Z., Zhang Y. (2018) Co-optimization of oil recovery and CO_2 storage for

- cyclic CO₂ flooding in ultralow permeability reservoirs, *Oil Gas Sci. Technol. - Rev. IFP Energies nouvelles* **73**, 42.
- 9 Glaso O. (1985) Generalized minimum miscibility pressure correlation (includes associated papers 15845 and 16287), *Soc. Pet. Eng.* **25**, 927–934.
 - 10 Danesh A. (1998) *PVT and phase behaviour of petroleum reservoir fluids*, Elsevier, The Netherlands.
 - 11 Kharrat R., Asadollahi M., Namani M. (2008) *Enhanced oil recovery*, Bahr Danesh, Tehran, Iran.
 - 12 Cronquist C. (1978) Carbon dioxide dynamic miscibility with light reservoir oils), in: *Proc. Fourth Annual US DOE Symposium, Tulsa*.
 - 13 Lee J. (1979) *Effectiveness of carbon dioxide displacement under miscible and immiscible conditions*, Report RR-40, Pet. Rec. Inst. Calg, Canada.
 - 14 Yellig W., Metcalfe R. (1980) Determination and prediction of CO₂ minimum miscibility pressures (includes associated paper 8876), *J. Pet. Technol.* **32**, 160–168.
 - 15 Orr F. Jr, Jensen C. (1984) Interpretation of pressure-composition phase diagrams for CO₂/crude-oil systems, *Soc. Pet. Eng.* **24**, 485–497.
 - 16 Sebastian H., Wenger R., Renner T. (1985) Correlation of minimum miscibility pressure for impure CO₂ streams, *J. Pet. Technol.* **37**, 2,076–072,082.
 - 17 Emera M.K., Sarma H.K. (2005) Use of genetic algorithm to estimate CO₂-oil minimum miscibility pressure – A key parameter in design of CO₂ miscible flood, *J. Pet. Sci. Eng.* **46**, 37–52.
 - 18 Liao C., Liao X., Chen J., Ye H., Chen X., Wang H. (2014) Correlations of minimum miscibility pressure for pure and impure CO₂ in low permeability oil reservoir, *J. Energy Inst.* **87**, 208–214.
 - 19 Yuan H., Johns R., Ekwuenu A., Dindoruk B. (2004) Improved MMP correlations for CO₂ floods using analytical gas flooding theory, in: *SPE/DOE Symposium on Improved Oil Recovery*, Society of Petroleum Engineers.
 - 20 Shokir E.M.E.-M. (2007) CO₂-oil minimum miscibility pressure model for impure and pure CO₂ streams, *J. Pet. Sci. Eng.* **58**, 173–185.
 - 21 Bon J., Emera M.K., Sarma H.K. (2006) An experimental study and genetic algorithm (GA) correlation to explore the effect of nC₅ on impure CO₂ minimum miscibility pressure (MMP), in: *SPE Asia Pacific Oil & Gas Conference and Exhibition*, Society of Petroleum Engineers.
 - 22 Eakin B., Mitch F. (1988) Measurement and correlation of miscibility pressures of reservoir oils, in: *SPE Annual Technical Conference and Exhibition*, Society of Petroleum Engineers.
 - 23 Moosazadeh M., Keshavarzi B., Ghotbi C. (2017) Investigation of the minimum miscibility pressure for injection of two different gases into two Iranian oil reservoirs: Experimental and theory, *Cad. J Chem. Eng.* **95**, 1014–1020.
 - 24 Zuo Y.-X., Chu J.-Z., Ke S.-L., Guo T.-M. (1993) A study on the minimum miscibility pressure for miscible flooding systems, *J. Pet. Sci. Eng.* **8**, 315–328.
 - 25 Farlow S.J. (1981) The GMDH algorithm of Ivakhnenko, *Am. Stat.* **35**, 210–215.
 - 26 Madala H.R., Ivakhnenko A.G. (1994) *Inductive learning algorithms for complex systems modeling*, CRC Press, Boca Raton, FL.
 - 27 Ivakhnenko A. (1970) Heuristic self-organization in problems of engineering cybernetics, *Automatica* **6**, 207–219.
 - 28 Kay W. (1936) Density of hydrocarbon gases and vapors at high temperature and pressure, *Ind. Eng. Chem.* **28**, 1014–1019.
 - 29 Joergensen M., Stenby E. (1995) *Optimization of pseudo-component selection for compositional studies of reservoir fluids*, Society of Petroleum Engineers.
 - 30 Curl R., Pitzer K. (1958) Volumetric and thermodynamic properties of fluids – enthalpy, free energy, and entropy, *Ind. Eng. Chem.* **50**, 265–274.
 - 31 Soave G. (1972) Equilibrium constants from a modified Redlich-Kwong equation of state, *Chem. Eng. Sci.* **27**, 1197–1203.
 - 32 Esmaeilzadeh F., Roshanfekar M. (2006) A new cubic equation of state for reservoir fluids, *Fluid Phase Equil.* **239**, 83–90.
 - 33 Schmidt G., Wenzel H. (1980) A modified van der Waals type equation of state, *Chem. Eng. Sci.* **35**, 1503–1512.
 - 34 Patel N.C., Teja A.S. (1982) A new cubic equation of state for fluids and fluid mixtures, *Chem. Eng. Sci.* **37**, 463–473.
 - 35 Redlich O., Kwong J.N. (1949) On the thermodynamics of solutions. V. An equation of state. Fugacities of gaseous solutions, *Chem. Rev.* **44**, 233–244.
 - 36 Chen G., Fu K., Liang Z., Sema T., Li C., Tontiwachwuthikul P., Idem R. (2014) The genetic algorithm based back propagation neural network for MMP prediction in CO₂-EOR process, *Fuel* **126**, 202–212.