# Determination of Minimum Miscibility Pressure by Analytical Method

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**ABSTRACT:** The analytical theory of one dimensional, dispersion free miscible displacement of oil by injection gas with  $n_c$  component has shown that: the MMP is the lowest pressure at which any one of the initial oil, injection gas or crossover key tie lines becomes critical, which means that its length approaches to zero. In this paper, we propose a method for a solving multi component system based on analytical calculation of ternary systems, which simplifies and converts the multi component system into a pseudo ternary system and estimates the minimum miscibility pressure without solving complex and time consuming equations of crossover tie lines.

KEY WORDS: EOR, MMP, Gas injection, Miscible displacement by gas, Analytical solution.

#### INTRODUCTION

Miscible gas injection into an oil reservoir is among the most widely used enhanced oil recovery techniques, and its applications are increasingly visible in oil production worldwide. As the injected gas is initially at equilibrium with the reservoir oil, the contact between the phases results in mass transfer which subsequently it changes the properties of two phases. The displacement of oil by gas becomes highly efficient when the properties of the advancing gas and displaced oil become similar. In this situation, the two phases achieve complete miscibility and the vapor- liquid interface vanishes.

Two fluids are miscible when they can be mixed together in all proportions and all resulted mixtures remain as single phase. It is apparent from Fig.1 that if the interface tension between oil and displacing fluid is eliminated completely (i.e the capillary number becomes infinite), residual oil saturation can be reduced to its lowest possible value. This is the objective of miscible displacement. An important concept associated with the description of miscible gas injection processes is the minimum miscibility pressure (MMP). At this pressure, the injected gas and the initial oil, becomes multi-contact miscible, and the displacement process becomes very efficient.

The slim tube test is one of the most widely used techniques and is accepted as a standard means to measure MMP in the petroleum industry. The tube is initially filled with oil at reservoir temperature above the

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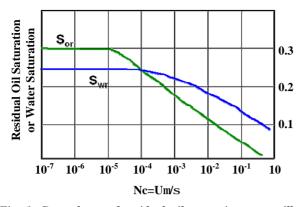


Fig. 1: Dependence of residual oil saturation on capillary number (Nc) [1].

bubble point pressure. The oil is then displaced by injecting gas into the tube at a constant inlet pressure or more often outlet pressure. The pressure is controlled by a back pressure regulator. The slim tube effluent is flashed at the atmospheric condition and pore volume recovery is measured. After plotting the ultimate recovery versus displacement pressure at several pressures, the MMP will be obtained. Based largely on slim tube test data, a number of empirical correlations have been developed. The earliest contribution to the development of MMP correlations was due to Benham et al. [2]. In general, MMP correlations can reproduce MMP predictions reasonably well for oil and gas composition ranges in which the correlations are developed. However, the MMP predictions by correlations, for oil and gas compositions that differ substantially from the conditions used to build the correlations, may not be reliable [3,4]. The other experimental test is called rising bubble. The observation of a gas bubble behavior, rising in a visual high pressure cell filled with the reservoir oil, has been suggested by Christiansen and Haines as a quick method of measuring MMP [5].

There are also two categories of numerical techniques that can be used to predict MMPs. One is direct numerical simulation. In this approach, the multi component conservation laws are solved numerically for one dimensional flow to obtain the oil recovery as a function of the displacement pressure for a given amount of injection (usually 1.2 PV). Then the MMP can be determined as the pressure at which the recovery curve levels off just as it would be in an experiment. Another approach is based on the idea of mixing cells. A mixing cell is a conceptualized container in which oil and gas are mixed and the equilibrium vapor and liquid phases are formed [6]. The MMP is taken to be the lowest of the pressure required to produce a critical mixture (vapor and liquid phase identical).

#### ANALYTICAL METHOD CALCULATION

Analytical method is the latest attempt for determination of minimum miscibility pressure. *Welge et al.* reported the first analytical solution for an oil displacement with a three components injecting gas [7]. Their analysis also included the effects of volume change upon mixing. The pioneering work by *Monroe et al.* extended the ternary theory to quaternary systems [8].

The subsequent work in 1990s continued the development of the analytical theory. The analytical theory of 1-D, dispersion free displacement of oil by injection gas with  $n_c$  components has shown that the behavior of the displacement is completely controlled by a sequence of key tie lines: those that extend through the initial oil composition (Initial tie line), injection gas composition (Injection tie line) and  $n_c$ -3 tie lines known as crossover tie lines. The theory also demonstrates that if any one of the key tie lines becomes a critical tie line, the dispersion-free displacement becomes piston-like, and multi contact miscibility develops. Therefore, the MMP is calculated as the lowest pressure at which any one of the key tie lines becomes a critical tie line.

# ANALYTICAL CALCULATION OF MMP FOR TERNARY SYSTEMS

According to analytical theory, there are two key tie lines (initial oil and injection gas) in ternary systems, which control the miscibility behavior. The pressure at which either one of them becomes a critical tie line (its length approaches to zero) is called MMP. *Wang* and *Orr* proposed the following procedure to find the MMP in a ternary system [9]:

1- Start calculation at a low pressure. For a proper initial guess, one can start by *Benham* curves or *Kuo* correlation and so on.

2- Find equilibrium values of the liquid and vapor phase  $(x_i, y_i)$  for initial oil and injection gas compositions by using one of the flash calculation methods (see next section).

3- Calculate key tie line lengths as:

$$L = \sqrt{\sum_{1}^{3} (y_i - x_i)^2}$$
(1)

4- Increase the pressure and to ensure convergence in the vicinity of the critical region, small pressure steps are taken so that the obtained key tie lines for the current pressure are a good approximation to the key tie lines of the next pressure step. In our calculations a typical pressure increment of 1 psia was considered.

5- Repeat steps 2-4 until either the initial tie line or the injection tie line becomes a critical tie line.

6- The pressure at which either the initial or the injection tie line becomes a critical tie line is the MMP.

# PROPOSED PROCEDURE FOR MULTI COMPONENT SYSTEMS

In addition to initial oil and injection gas tie lines, there are  $n_c$ -3 key tie lines known as crossover tie lines in a multi component system. The MMP is defined as the lowest pressure at which one of them becomes critical. A set of complex and time consuming equations must be solved by trial and error method to find the equation and the length of crossover tie line. In order to simplify the system and also decrease the time of calculations, the following procedure is proposed by the authors. Investigating of analytical calculation for ternary systems shows that MMP only depends on  $T_c$ ,  $P_c$  and  $\omega$ . These critical properties are listed in some tables for pure components. Therefore, we can use the previous procedure for multi component system, if it is converted into a pseudo ternary system. For this purpose, the pure components must be divided into Light, Intermediate and Heavy cuts. Then  $T_c$ ,  $P_c$  and  $\omega$  of the cuts are estimated by the following formulas:

1- For defined cuts (components are known) one can use molar average equations:

$$T_{c,m} = \Sigma Z_i T_{ci} \tag{2}$$

$$P_{c,m} = \Sigma z_i P_{ci} \tag{3}$$

$$\omega_{\rm m} = \Sigma z_i \omega_i \tag{4}$$

2- For undefined cuts (components are unknown), specific gravity and normal boiling point must be given. From *Win- Sim- Daubert* equation,  $T_{c,m}$  and  $P_{c,m}$  can be obtained [10]:

$$T_{c,m} = EXP(3.9934718 \times T_b^{0.08615} \gamma^{0.04614})$$
(5)

$$P_{c,m} = 3.48242 \times 10^9 \times T_b^{-2.3177} \gamma^{2.4853}$$
(6)

If  $T_b$  is not given, it can be calculated from *Riazi-Daubert* equation [11]:

$$T_{b} = 6.77857 MW^{0.401673} \gamma^{-1.58262} \times$$
(7)  

$$Exp(3.77409 \times 10^{-3} MW + 2.984036\gamma -$$

$$4.2588 \times 10^{-3} MW\gamma)$$

Where MW is the molecular weight.

To determine acentric factor,  $\omega$ , *Edmister* equation can be used [12]:

$$\omega_{\rm m} = \frac{3 \text{Log}(P_{\rm c,m}/14.70)}{7(T_{\rm c,m}/T_{\rm b}-1)} - 1$$
(8)

A subprogram is written for splitting  $C_{7+}$  cut in the main program. The *Katz* method is used for this purpose by the following equation:

$$z_n = 1.38205 z_{7+} \exp(-0.25903n)$$
(9)

Where n is the number of carbons. After calculating  $z_n$  up to desired cut ( $z_{16+}$  for example),  $z_{N+}$  is calculated by this equation:

$$z_{N+} = z_{7+} - \sum_{7}^{N^+ - 1} z_n$$
 (10)

Also  $MW_{N+}$  and  $\gamma_{N+}$  are obtained from the below equations:

$$\sum_{7}^{N+} [z_n M W_n] = z_7 + M W_{7+}$$
(11)

$$\sum_{7}^{N+} \frac{z_n M W_n}{\gamma_n} = \frac{z_{7+} N W_{7+}}{\gamma_{7+}}$$
(12)

Finally  $T_{cm}$ ,  $P_{cm}$  and  $\omega_m$  of the cut are calculated from equations (5)-(8). Then the MMP is estimated with a good accuracy from the ternary system procedure by using these mixture properties.

#### FLASH CALCULATIONS

The equation for the tie line is:

$$z_{i} = x_{i} [1 + (K_{i} - 1)S]$$
(13)

Where s is vapor phase mole fraction. Because of s value limitation in flash calculations (from 0 to 1) and subsequent errors, along with the inaccuracy of answers

in negative flash calculations for mixtures which lie far from two phase region, motivate us to use new method which is called "**modified negative flash**", proposed by *Wang- Orr* [13].

$$f(x_1) = \sum_{i=1}^{nc} \frac{z_i x_1 (K_1 - 1)(K_i - 1)}{(K_i - 1)z_1 + x_1 (K_1 - K_i)} = 0$$
(14)

Eq. (14) was solved for  $x_1$  for a set of K- values (initial guess for  $x_1$  was 0.5). We can use *Newton* iteration method to obtain final  $x_1$  value:

$$f(x_1) = \sum_{i=1}^{nc} \frac{Z_i Z_1 (K_1 - 1) (K_i - 1)^2}{[(K_1 - 1)Z_1 + x_1 (K_1 - K_i)]^2}$$
(15)

$$(x_1)_{j+1} = (x_1)_j - \frac{f(x_1)_j}{f'(x_1)_j}$$
(16)

Where j is the counter of iteration number.

Calculation is continued until below condition is satisfied.

$$\left| \left( x_1 \right)_{j+1} - \left( x_1 \right)_j \right| \le 10^{-4} \tag{17}$$

Then the mole fractions in the liquid and vapor are determined from the following equations:

$$S = \frac{z_1 - x_1}{x_1(K_1 - 1)}$$
(18)

$$x_{i} = \frac{z_{i}}{1 + (K_{i} - 1)S}$$
(19)

$$y_{i} = \frac{K_{i}z_{i}}{1 + (K_{i} - 1)S}$$
(20)

Then K-values are updated by calculating the fugacities from the PREoS or SRKEoS. In the last step, initial and injection tie line lengths will be calculated from eq.(1).

## JUSTIFYING THE PROPOSED PROCEDURE

In this section to illustrate the accuracy and reliability of mentioned method for multi component systems, two examples are solved and the obtained results are compared with the other methods. Note that slim tube test gives the most reliable results; therefore that is the base method of the MMP prediction.

#### Pseudo ternary system with lean gas injection

In this part, the described examples of *Hearn* and *Whitson* are considered. They reported results of slim tube experiments performed for lean and rich gas displacements of crude oil from Safah field, Oman at 212°F. In this work, it was assumed that oil is composed of 15 components [13]. The pure component properties and the initial oil and injection gas compositions are listed in tables 1 and 2.

Initial oil could be divided into different pseudo ternary systems as shown in table 3. Lean injected gas also was divided into two cuts:  $N_2$ -CO<sub>2</sub> -C<sub>1</sub> and C<sub>2</sub> to C<sub>4</sub>. Fig. 2 shows the tie line length versus pressure for oil no. 5, which is displaced by lean gas.

The calculated value of the MMP is 5178 Psia for this example. Note that the calculated MMP through solving complex and time consuming equations of crossover tie lines and slim tube test result reported by *Hearn* and *Whitson* are 5253 and 5215 Psia, respectively [14]. The differences are reasonably low and acceptable.

#### Pseudo ternary system with rich gas injection

In this example, the 15 component oil is displaced by rich gas with composition mentioned in the table 2.

The Rich gas can be divided into two fractions:  $N_2$ -CO<sub>2</sub>-C<sub>1</sub> and C<sub>2</sub>-C<sub>6</sub> or N2-CO2 and C<sub>1</sub>-C<sub>6</sub>.

Fig. 3 shows the tie line length versus pressure for oil no. 5, which is displaced by lean gas.

The determined MMP is 3123 Psia. Note that the calculated MMP by solving complex and time consuming equations of crossover tie lines and slim tube test result reported by *Hearn* and *Whitson* are 3115 and 3315 Psia respectively [14]. The differences are reasonably low and acceptable. The calculated MMP from different oils are listed in table 4.

Finally, the obtained results from this work are compared with the other methods in table 5. As we can see, the calculated MMP from this method gives relatively accurate and reliable results.

#### **RESULTS AND DISCUSSION**

In this paper, a new procedure is proposed for the prediction of the MMP of a multi component system with analytical theory basis by the authors. Two examples are solved and their results are compared with the results of the other MMP estimation methods. It can be conclude that:

Component Property		ty	
Comp.	Tc(°R)	Pc(Psia)	ω
N <sub>2</sub>	227.3	493	0.045
CO <sub>2</sub>	547.6	1070.6	0.231
C1	343	667.8	0.0115
C <sub>2</sub>	549.8	707.8	0.0908
C <sub>3</sub>	665.7	616.3	0.1454
IC <sub>4</sub>	734.7	529.1	0.1756
C <sub>4</sub>	765.3	550.7	0.1928
IC <sub>5</sub>	828.8	490.4	0.2273
C <sub>5</sub>	845.4	488.6	0.251
C <sub>6</sub>	913.4	436.9	0.2957
C7 <sup>+</sup> (1)	1026.1	409	0.3201
C7 <sup>+</sup> (2)	1141.1	352.9	0.4007
C7 <sup>+</sup> (3)	1300.6	247.3	0.560
C7 <sup>+</sup> (4)	1471.1	206.5	0.7825
C7 <sup>+</sup> (5)	1645.7	158.2	1.0468

Table 1: Components Properties of initial oil and injection gas[14].

### Table 2: Oil and gas composition [14].

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Comm	Oil and Gas Composition		
Comp.	Oil	Lean Gas	Rich Gas
N <sub>2</sub>	0.007	0.007	0.007
CO <sub>2</sub>	0.006	0.015	0.013
C1	0.334	0.840	0.639
C <sub>2</sub>	0.050	0.091	0.111
C <sub>3</sub>	0.055	0.036	0.103
$IC_4$	0.021	0.006	0.036
$C_4$	0.039	0.005	0.053
IC <sub>5</sub>	0.020	-	0.017
C <sub>5</sub>	0.028	-	0.014
C <sub>6</sub>	0.044	-	0.006
$C_{7(1)}^{+}$	0.096	-	-
C7 <sup>+</sup> (2)	0.099	-	-
C7 <sup>+</sup> (3)	0.087	-	-
C7 <sup>+</sup> (4)	0.068	-	-
C7 <sup>+</sup> (5)	0.046	-	- )

Table 3: Different categories to pseudo ternary systemconversion

Oil No.	Light	Intermed.	Heavy
1	$N_2$ , $CO_2$ , $C_1$	C <sub>2-6</sub>	C <sub>7+</sub> (1-5)
2	$N_2$ , $CO_2$ , $C_1$	C <sub>2-6</sub> , C <sub>7+</sub> (1)	C <sub>7+</sub> (2-5)
3	$N_2$ , $CO_2$ , $C_1$	C <sub>2-6</sub> , C <sub>7+</sub> (1,2)	C <sub>7+</sub> (3-5)
4	N <sub>2</sub> , CO <sub>2</sub>	C <sub>1-6</sub> , C <sub>7+</sub> (1)	C <sub>7+</sub> (2-5)
5	N <sub>2</sub> , CO <sub>2</sub>	$C_{1-6}, C_{7+}(1,2)$	C <sub>7+</sub> (3-5)
6	N <sub>2</sub> , CO <sub>2</sub>	C <sub>1-6</sub> , C <sub>7+</sub> (1-3)	C <sub>7+</sub> (4-5)

Table 4: Calculated MMP from different categories for leanand rich injection gas.

Oil No.	Minimum Miscibility Pressure (Psia)		
	Lean Gas	Rich Gas	
1	4791	3123	
2	4790	3123	
3	4701	3123	
4	5178	3123	
5	5178	3123	
6	5178	3123	

Table 5: Comparison of MMPs calculated by differentmethods [13].

Method	Minimum Miscibility Pressure (Psia)		
Withind	Lean Gas	Rich Gas	
Single Cell	5860	4540	
Numerical Sim.	5860	3225	
Slim Tube	5215 (+/-200)	3315 (+/-100)	
Analytical	5253	3115	
This Work	5178	3123	

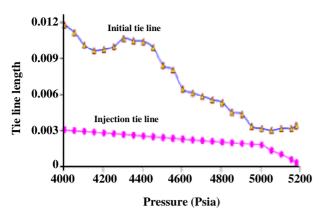


Fig. 2: Key tie line length for example 1.

1- If a multi component system with arbitrary number of components in initial oil and injection gas is converted into a pseudo ternary system (with a good engineering sense), the calculated MMP is in fair agreement with the estimated MMP by solving of complex and time consuming equations of crossover tie lines.

2- The presented method can be used to assess quickly the effects of designed injection gas composition changes on MMP, then the results will give the optimum injection gas composition.

3- This method can be used as a rapid and low cost method to evaluated performance and accuracy of the other MMP determination methods (To determine the MMP accurately by slim tube test, it is in general necessary to perform six displacements at six or seven different pressures. The time required to perform one displacement is about 8 h (a working day). This means one week of experimental work is necessary to measure one MMP).

#### Nomenclatures

L	Tie line length (ft,m)
Κ	Equilibrium constant (Dimensionless)
Nc	Capillary number (Dimensionless)
nc	No. of component in the system (Dimensionless)
Р	Pressure (psia)
S	Vapor phase mole fraction (Dimensionless)
Т	Temperature (R)
$T_b$	Normal boiling point (R)
U	Fluid Velocity (cm/s)
Х	Liquid mole fraction (Dimensionless)
у	Vapor mole fraction (Dimensionless)
Z	Overall mole fraction (Dimensionless)

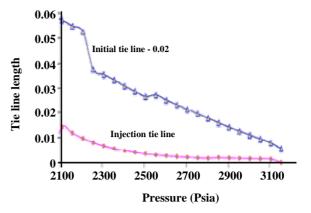


Fig. 3: Key tie line length for example 2.

# Subscripts

c	Critical property
i	Property of component i
m	Mixture property

#### **Greek letters**

γ	Specific Gravity (Dimensionless)
μ	Viscosity (cp)
σ	Interfacial tension (dyne/cm)
ω	Acentric factor (Dimensionless)

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#### REFERENCES

- Danesh, A., "PVT and Phase Behavior of Petroleum Reservoir Fluids", Academic Press., Elsevier Science, (1998).
- [2] Benham, A.L., Dowden, W.E. and Kunzman, W.J., Miscible Fluid Displacement Prediction of Miscibility, J. Pet. Tech., 219, p. 229 (1960).
- [3] Pedrood, P., "Prediction of Minimum Miscibility Pressure in Rich Gas Injection", M.Sc. Thesis, University of Tehran, Tehran, (1995).
- [4] Orr, F.M., Jr. and Silva, M.K., Effect of Oil Composition on Minimum Miscibility Pressure -Part 2: Correlation, *Soc. Pet. Eng. Res. Eng. J.*, 2, p. 479 (1987).
- [5] Christiansen, R.L. and Haines, H.k., Rapid Measurement of Minimum Miscibility Pressure with Rising Bubble Apparatus, *Soc. Pet. Eng. Res. J.*, 2, p. 523 (1987).
- [6] Metcalfe, R.S., Fussell, D.D. and Shelton, J.L., A Multicell Equilibrium Separation Model for the

Study of Multiple Contact Miscibility in Rich-Gas, *Soc. Pet. Eng. J.*, **13**, p. 147 (1973).

- [7] Welge, H.J., Johnson, E.F., Ewing, S.P. and Brinkman, F.H., The Linear Displacement of Oil from Porous Media by Enriched Gas, *J. Pet. Tech.*, 13, p. 787 (1961).
- [8] Monroe, W.W., Silva, M.K., Larsen, L.L. and Orr, F.M., Jr., Composition Paths in Four-Component Systems: Effect of Dissolved Methane on 1D CO<sub>2</sub> Flooding Performance, *Soc. Pet. Eng. Res. Eng. J.*, 5, p. 423 (1990).
- [9] Wang, Y. and Orr, F.M., Jr., Analytical Calculation of Minimum Miscibility Pressure, *Fluid Phase Equilibria J.*, **139**, p. 101 (1997).
- [10] Sim, W.J, Daubert, T.E, "Prediction of Liquid-Vapor Equilibria of Undefined Mixture, *Ind. Eng. Chem. Process J.*, **19** (3), p. 380 (1980).
- [11] Riazi, M. R. and Daubert, T. E., Characterization Parameters for Petroleum Fractions, *Ind. Eng. Chem. Res. J.*, **26** (24), p. 755 (1987).
- [12] Edmister W.C., "The Applied Hydrocarbon Thermodynamics," Part 4, Petroleum Refiner, **37**, pp 173-179 (1958).
- [13] Wang, Y. and Orr, F.M., Jr, Calculation of Minimum Miscibility Pressure, *Petroleum Science and Engineering*, **27** (3-4), p. 151 (2000).
- [14] Hearn, C.L. and Whitson, C., Evaluating Miscible and Immiscible Gas Injection in the Safah Field, Oman, paper SPE 29115 presented at the 13th SPE Symposium on Reservoir Simulation, San Antonio, TX, USA (1995).