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Research Article

CO_2 Minimum Miscibility Pressure Determination of Pure Hydrocarbons in Different Temperatures Using Slimtube Simulations

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Abstract: Slimtube experiments are used as a determination of Minimum Miscibility Pressure (MMP) for different Enhanced Oil Recovery (EOR) techniques. It is the most reliable technique available for MMP determination. Since slimtube experiments are time consuming, simulation of the process is highly beneficial for fast determination of MMP. This article presents a new set of slimtube simulations to obtain MMP of pure hydrocarbons by CO_2. Pure hydrocarbons are subjected to CO_2 flooding in slimtube simulationsat different temperatures. Pure hydrocarbons MMP cannot be determined by present correlations used in petroleum industry. At the end, CO_2 MMP for each pure hydrocarbon up to C8 is obtained in temperatures varying from 15 to 70°C. As liquid CO_2 is also used in these simulations, it showed that by using liquid CO_2, the dependency of MMP to molecular weight of hydrocarbon will be decreased and usage of liquid CO_2 will yield almost same result for all pure hydrocarbons used in this research.

Keywords: CO_2 injection, liquid CO_2, MMP, pure hydrocarbons, slimtube simulation

INTRODUCTION

MMP measurement is of high importance in petroleum industry especially in EOR. Over decades, several experimental methods have been proposed to measure MMP including rising bubbles (Christiansen and Haines, 1987), Vanishing Interfacial Tension (VIT) (Rao, 1997) and slimtube experiments (Yellig and Metcalfe, 1980). Also several analytical methods (Wang and Jr. Orr, 1997) as well as empirical methods (Emera and Sarma, 2005, 2006) have been used widely to determine the MMP of crude oil. Furthermore, numerical simulations have been done and modified to represent slimtube experimental procedure (Cook *et al*., 1969; Metcalfe *et al*., 1973; Neau *et al*., 1996).

Currently, slimtube method is the most accepted procedure in the industry. Slimtube is a tube with small diameter (<0.25") but with high length up to 75 ft, packed with glass beads or sand representing a one dimensional reservoir (Amao *et al*., 2012). For controlling the temperature of the slimtube, oven or water bath is normally used. Slimtube is saturated with crude oil and by gas flooding; then, the miscibility conditions are determined by applying different injection pressures. Each pressure of injection corresponds to a recovery factor resulted by 1.2 Pore Volume (PV) of injected gas. Finally, the oil recovery vs. pressure is plotted and interpretation is conducted to determine the MMP. MMP is determined as the breakthrough point in the recovery vs. pressure plot.

Since using single component hydrocarbons in different temperatures are hard and too much time consuming to be conducted with slimtube experiments, this research develops simulations of the exact slimtube experiment using Eclipse software package to obtain accurate MMP of some pure hydrocarbons in different temperatures.

LITERATURE REVIEW

Gas flooding is widely used as successful tertiary method for EOR. During gas flooding, other than viscosity reduction and swelling of the oil, miscibility is achieved by component exchange of the injected gas and crude oil. Miscibility is an improving and desired factor for design of gas flooding. Thermodynamic miscibility of two or more fluids is defined as thermodynamic conditions where the fluids exist in a single phase and they are mixed in any proportion with each other. In this case, the interfacial tension becomes zero. MMP is defined as the minimum pressure that the fluids in contact achieve miscibility. In pressures higher than MMP, the recovery is expected to reach 100% in microscopic scale (Yan *et al*., 2012).

Miscibility can be either in form of first contact (FCM) or multi contact (MCM). FCM refers to when the fluids reach miscibility with the first contact between them; while MCM refers to the state which fluids reach miscibility after several contacts.

In slimtube experiments, the aim is to find MCM of an injected gas and a crude oil. MMP depends on the composition of the crude oil and injected gas, pressure and temperature of the fluids (Gardner *et al*., 1981;

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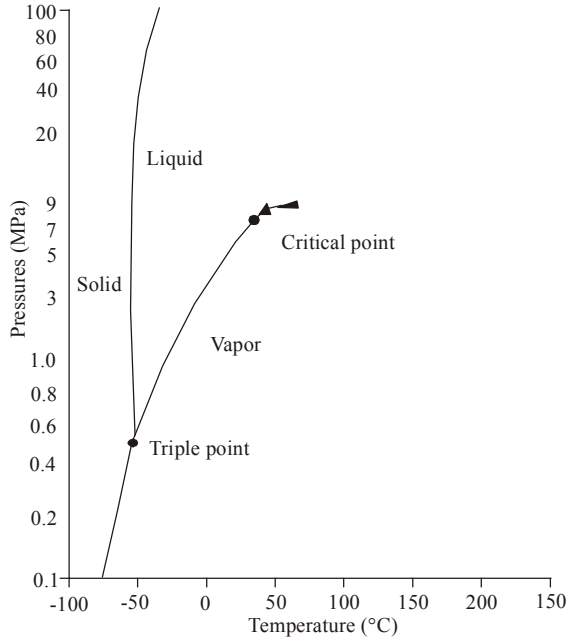

Fig. 1: CO_2 phase diagram (Baviere, 1980)

Table 1: Dunyushkin and Namiot (1978) available MMP correlations

	Temperature (°C)		
Component	30	50	70
C7	72	94	112
C8	72	97	119

Table 2: Glass MMP correlations

	Temperature (°C)			
Component	15.000	30.000	50.000	70.000
C7	258.67	295.87	345.48	395.08
C8	234.90	262.71	299.79	336.87

Holm and Josendal, 1982; Harmon and Grigg, 1988; Turek *et al*., 1988; Creek and Sheffield, 1993).

CO_2 flooding is used in EOR as well as sequestration. CO_2 flooding can be in form of liquid or gas depending on pressure of injection and temperature as shown in Fig. 1. Generally, CO_2 floods have been used for reservoirs with pressures above MMP (Stalkup Jr., 1983; Hadlow, 1992). So determination of MMP can determine the aspect of CO_2 usage for EOR.

Temperature is assumed to be constant in slimtube experiments. However this assumption is not true as previous studies showed that if injected gas and reservoir has different temperatures, a local equilibrium temperature may be formed in different parts of the reservoir (Hamdi and Awang, 2013). This will cause different MMP values in crude oil inside a reservoir. Therefore, several temperatures are taken into account to evaluate the effect of temperatures on MMP of different hydrocarbons.

Previous correlations of MMP were not obtained based on single hydrocarbons and usually C5+ or C7+ is taken as the main component for determination of MMP and C1-C4 were not considered individually (Holm and Josendal, 1974; Cronquist, 1978; Yellig and Metcalfe, 1980; Alston *et al*.,1985). This study will determine each hydrocarbon MMP in different temperatures so that the MMP of crude oil or mixed hydrocarbons may be investigated based on each pure hydrocarbons.

Previous correlations: The equations and correlations used so far cannot cover the range used in this study. Holm and Josendal (1974) MMP correlation from CO_2 flooding used C5+ with minimum molecular weight of 180 that is not in the range of study. Mungan (1981) is later extended their work by increasing the upper limit of molecular weight to 340, while leaving molecular weight less than 180 with no correlation. Dunyushkin and Namiot (1978) presented a graph for MMP correlation which covered only a part of the study presented in Table 1. Cronquist (1978) correlation for CO_2 MMP was based on C5+. Glass correlation for CO_2 MMP was based on C2-6 and C7+ composition in total which leads to uncertain values for pure hydrocarbons (Glass, 1985). The results of hydrocarbons that can be obtained with Glass correlation is presented in Table 2. As we can compare with Dunyushkin correlation, there is a large gap between the values. Our simulations suggest that Glass correlation is not suitable for pure hydrocarbons. Furthermore, Yuan's CO_2 MMP correlation is not usable as no pure hydrocarbon can be fit into the correlation (Yuan *et al*., 2005).

Since no correlation can validate the work, a C7+ component is tested in our simulations in order to validate our methodology and to check if slimtube results are acceptable. MMP of C7+ is calculated using previous correlations and the results presented in Table 3.

Table 3: C7+ MMP determination by different correlations

	Temperature (°C)				
MMP Correlations	15.0	30.000	50.000	70.000	Remarks
Dunyashkin (Dunyushkin and Namiot, 1978)	-	-	165.00	200.00	-
Holm (Holm and Josendal, 1974)	-	95.000	123.13	164.63	-
Cronquist (1978)	60.3	87.420	123.36	159.14	Assumed that C1 and N2 is present that increase the calculated MMP
Glass (1985)	200	223.68	254.51	286.33	It is assumed that C2-4 is present that can cause up to 150 atm reduction

Table 4: Initial data used in simulation

Parameter	Amount
Slimtube length-m	10
Slimtube cross section-cm	1
Solution method	Fully implicit
Equation of State (EOS)	Peng-robinson
Grid dimensions	200×1×1
Porosity (%)	10
Permeability-D	2
Compressibility of rock (1/atm)	0.000004 at 136 atm
Initial hydrocarbon saturation (%)	100
Gas saturation (%)	$S_{gas} = 1-S_{oil}$
Initial hydrocarbon saturation (%)	100
Total pore volume (mL)	100
Injection rate-PV per hour	0.1
Duration of injection (h)	12
Capillary pressure (atm)	0

Table 5: Properties of CO_2 and hydrocarbons used in the simulations

Name	Molecular weight	Critical temperature (°C)	Critical pressure (atm)
CO_2	44.0100	31.55000	72.90000
C1	16.0430	-82.5500	45.44000
C2	30.0700	32.28000	48.20000
C3	44.0970	96.65000	42.10000
iC4	58.1240	134.9500	36.00000
nC4	58.1240	152.0500	37.47000
iC5	72.1510	187.2500	32.90000
nC5	72.1510	196.4500	33.31000
C6	84.0000	238.8500	32.96000
nC7	100.210	275.5037	31.48673
nC8	114.231	307.5218	29.15231
C7+	218.000	471.7747	16.84718

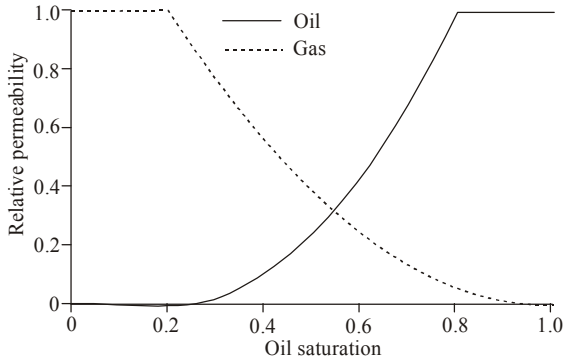

Fig. 2: Relative permeability curves vs. oil saturation

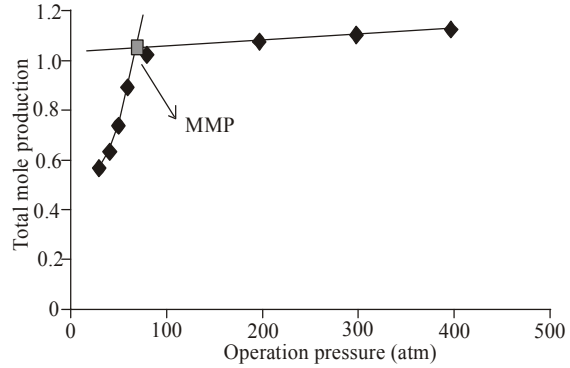

Fig. 3: Example of slimtube simulation result

METHODOLOGY

To obtain the PVT properties of different hydrocarbons, PVTi software is used. Based on available Equation of State (EOS) parameters for each pure hydrocarbon, critical temperature, specific gravity, acentric factor and other data can be made to use in the slimtube model. Then, the PVT data is added to the main simulator for the slimtube experiment, i.e., Eclipse 300 as the simulation software package.

Different temperatures are used to perform these simulations. 15, 30, 50 and 70°C are chosen to perform the experiments. In 15 and 30°C, CO_2 is liquid according to its phase behavior.

For each temperature, the simulations are performed with pressures 30 to 90 atm with a 5 atm interval and then from 100 to 600 atm with 100 atm interval.

The initial data used for the simulations are presented in Table 4.

Different pure hydrocarbons are used to perform slimtube simulations. Also, a C7+ sample is added to the simulation, representing heavy component.The properties of CO_2 and the hydrocarbon used in this simulation are shown in Table 5. Also, the relative permeability curves used in slimtube simulation is shown in Fig. 2.

Because in different temperatures different hydrocarbons may be gas or liquid, choosing total oil recovery may lead to wrong interpretation of MMP. Therefore, instead of recovery factor, the total mole of each hydrocarbon produced is taken into the consideration.

Based on each component and for each temperature, a simulation is performed. Then, the total mole of hydrocarbon produced vs. pressures is plotted for respective component and temperature. The breakthrough point is then determined and considered as MMP of specific hydrocarbon at the indicated temperature (Fig. 3).

RESULTS AND DISCUSSION

Because 44 plots are not possible to be presented in this study, only the calculated MMP is presented as in Table 6. Since the previous correlations and methods were not built on the basis that the crude oil can be pure hydrocarbon, any comparison was not possible. But the validation is made through the comparison of previous correlation with the C7+ component. A sample plot is shown in Fig. 3 to present the trend of hydrocarbon production in different operating pressures. Also the MMP is plotted based on extrapolation of lines connecting the results.

The results seem to be valid for all the hydrocarbons except C1. There is no breakthrough of the plot in any of operating temperatures. In Fig. 4 the slimtube simulations for C1 in 50°C is shown. As it can be realized, MMP cannot be determined. The reason is

Table 6: MMP values calculated for different temperatures (atm)

	Temperature (°C)			
Component	15	30	50	70
C1 (not valid)	346.6001	352.8258	381.8939	393.875600
C2	56.26267	71.82837	98.83110	143.243425
C3	51.91211	71.29087	75.59448	76.3606200
iC4	50.92321	69.92521	74.94124	78.8150000
nC4	50.65779	72.26347	76.61120	86.3303100
iC5	50.52278	71.78257	83.05838	89.6197800
nC5	50.44509	72.31052	82.15326	93.7615700
C6	50.31336	75.46238	85.90020	110.320000
nC7	50.15092	75.34349	98.25993	125.503400
nC8	50.14613	80.43694	112.2868	138.937700
C7+	50.34290	84.21965	155.2369	213.973500

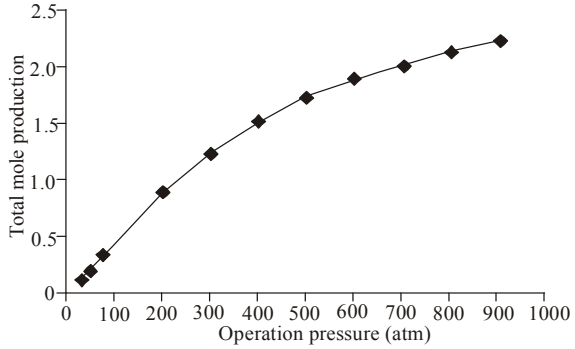

Fig. 4: Methane slimtube simulation results in T = 50 °C

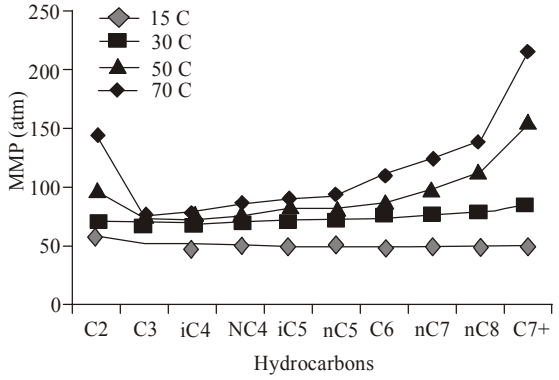

Fig. 5: MMP of pure hydrocarbons in different temperature

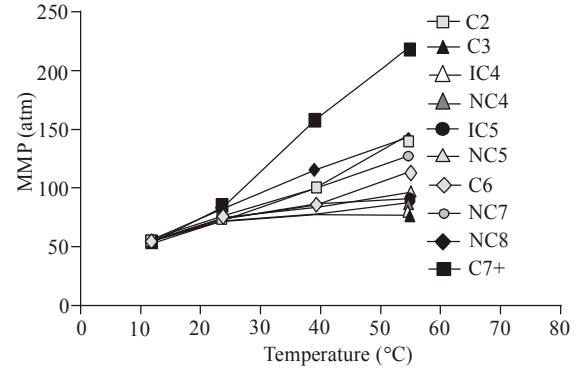

Fig. 6: MMP vs. temperature of slimtube for each pure hydrocarbon

that because of very low molecular weight of C1, injection of CO_2 will not cause single phase system and therefore, C1 has to be injected into CO_2 in order to achieve miscibility.

Figure 5 and 6 represent the MMP calculated from slimtube simulations. In Fig. 5, we can see that in high temperatures, other than C2, by increasing the molecular weight MMP is also increasing steadily. But in low temperatures, MMP does not change significantly. This suggests that when CO_2 is liquid, MMP of pure hydrocarbons remain low and independent from molecular weight of the hydrocarbon.

In Fig. 6, MMP is plotted vs. temperature of slimtube for each pure hydrocarbon. Increase in MMP by increase in temperature is as expected. The figure also shows that when CO_2 is liquid, MMP is decreased steadily but with slower rate. The reason is that according to Miller, solubility of CO_2 into hydrocarbons reaches almost a constant amount and cannot cause earlier miscibility between CO_2 and hydrocarbon (Miller and Jones, 1981). As the temperature increases, dependency of solubility to temperature is also increasing, causing higher rate of MMP increase.

By comparing iC4 and iC5 with nC4 and nC5, respectively, it is realized that in temperatures 50°C and below, same molecular weight will cause almost same MMP value. This suggests that by knowing molecular weight of a hydrocarbon, miscibility can be determined without knowing actual component of hydrocarbon.

The MMP values of C7+ are compared with previous correlation results. Cronquist correlation seems to be the nearest match to our results that can be interpreted as successful simulation of C7+ as well as other pure hydrocarbons.

CONCLUSION

In this research several slimtube simulations were done with pure hydrocarbon using CO_2 as injection gas. The MMP of each hydrocarbon is determined and presented based on slimtube simulation in different temperatures.

For temperatures below 50°C, MMP of each hydrocarbon can be reflected on its molecular weight and not its nature. It means that each molecular weight can produce one MMP that can be used for other hydrocarbons with same molecular weight.

Liquid CO_2 MMP simulation results are published for the first time and the results suggest that using liquid CO_2 will cause the MMP to be independent from molecular weight. MMP will still decrease by decreasing temperature and the reduction rate is constant for all components used in this research. This opens a new look for usage of liquid CO_2 in different tertiary recovery methods.

This research opens an opportunity for further studies to analyze and determine the miscibility of crude oil based on each hydrocarbon component.

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