Effect of oil composition on minimum miscibility pressures using mixtures of CO_2, N2 and lean gas.

by

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ABSTRACT

In gas flooding projects where miscibility is the desired displacement mechanism, carbon dioxide (CO_2) is the best performing gas due to its ability to be miscible with oil at low pressures compared to other gases. This minimum miscibility pressure (MMP) is of high importance because it represents the first limiting factor in the feasibility of a miscible flooding project. However, when it comes to other limiting factors such as availability and cost, lean gas and nitrogen (N2) sometimes offer a larger degree of freedom compared to CO_2. Mixing CO_2 with lean gas or with nitrogen can allow the design of an injection gas that will satisfy the availability and cost constraints while also having a reasonable and reachable miscibility pressure. The objectives of this paper are to investigate the effect of adding nitrogen or lean gas to CO_2 on MMP, and to study the effect of oil composition in the MMP.

The MMP estimation method used in this study is the numerical simulation method, so the first step is to validate it. Comparing the results from actual experiments and correlations with the results from the numerical simulation, it is shown that the numerical simulation method successfully captures the miscibility mechanism during oil displacement and provides trustable MMP results. The effect of oil composition is observed by varying the molar fraction of each of the grouped components which are the light weight components, the intermediate weight components, and the heavy weight components, as well as the heptane plus molecular weight.

It is observed that when injecting pure CO_2, the main factor is the molecular weight, followed by the intermediate weight component molar fraction. When mixing CO_2 with lean gas or nitrogen, the ratio of light to heavy component fractions becomes the third parameter affecting the MMP. In this paper, the effectiveness of nitrogen or lean gas is expressed as the additional MMP per percent of solvent added to the pure CO_2 injection gas. It is also observed that lean gas is at least twice as effective as nitrogen in terms of effectiveness. This effectiveness is also used to determine the maximum solvent fraction in the injection gas in order to satisfy a maximum allowable pressure. It is shown that this number can vary greatly depending on the maximum pressure constrain.

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CHAPTER I

Introduction

After an oilfield is discovered, the initial mechanism that allows production from that field is classified as primary recovery mechanism, which is driven by the natural energy of the reservoir. Natural driving mechanisms are rock and liquid expansion, solution gas drive, gas cap drive, water drive, gravity drainage drive. With these primary recovery mechanisms, only 5 to 25 percent of the original oil in place can be recovered. Additional recovery can be obtained using secondary recovery, in which artificial energy is added to the reservoir by the injection of water or immiscible gas. In that context, water or immiscible gas are used to increase or maintain the pressure in the reservoir, or act as a displacing fluid to push oil into the production wellbore. When applied, secondary recovery methods are reported to extend the recovery to a maximum of 35 to 45 percent. The third recovery mechanism, which is called tertiary recovery or enhanced oil recovery (EOR), aimed at the considerable amount of residual oil at the end of the secondary recovery. EOR methods can be grouped into three categories: thermal methods, in which oil temperature is changed; chemical methods, in which chemicals such as polymers or surfactants are injected into the pores; miscible displacement methods, in which hydrocarbon, carbon dioxide, nitrogen or inert gases are injected at miscible condition.

Miscible displacement methods are processes where the effectiveness of the displacement results primarily from miscibility between the oil in place and the injected fluid. By achieving miscibility, interfacial tension is somewhat eliminated, which allows more oil to be displaced. The gases commonly used in this process are carbon dioxide (CO_2), nitrogen (N_2) and hydrocarbon gas. Carbon dioxide is by far the most efficient due to its ability to be miscible with oil at relatively low pressures ant temperatures. Since the first commercial flooding in Scurry County, Texas, in 1972, CO_2 flooding has proved to be efficient compared to other methods. With a quarter million barrels of incremental oil per day, it is about 5% of the total US production. Looking at the evolution of active EOR projects within the United States shown in Figure 1-1, the production from carbon dioxide has increased continuously compared to the production from other EOR methods.

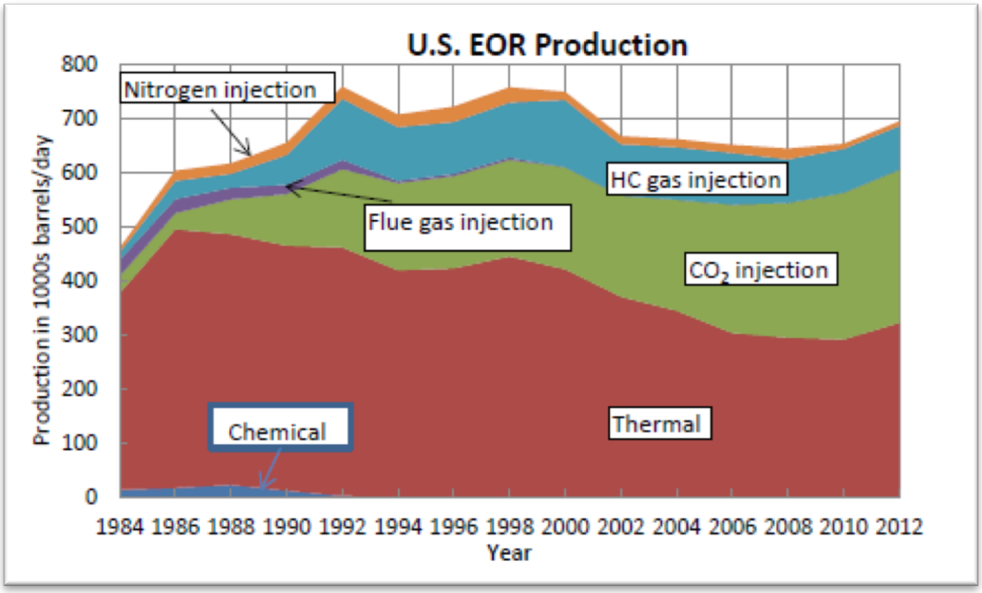

Figure 1-1: U.S production associated with various EOR methods

The use of CO_2 does not come without limitations. The major limitation with CO_2 is the availability of a low-cost source. Figure 1-2 shows a map of all CO_2 operations and sources in North America. Natural and industrial sources are limited, and the pipelines network only feeds big major fields. The cost to extend pipelines to smaller fields is most of the time not economical. The cost of buying, transporting and recycling carbon dioxide is significant. According to the National Energy Technology Laboratory, "it costs \$0.25-0.75 per thousand cubic feet to transport CO2 to West Texas fields from the sources to the north". In some cases, the amount of carbon dioxide needed for a project is so important that the cost of storing it makes the project uneconomical. Figure 1-3 shows an illustrative table of cost for an EOR project. The total cost for buying and recycling CO_2 is between 25 to 50% of the total cost per barrel of oil produced.

An alternative to CO_2 is hydrocarbon gases and nitrogen. Nitrogen is cheaper, easily obtainable (contained in the air), and less corrosive than carbon dioxide. The inconvenient of nitrogen is its relatively high miscibility pressure conditions (as high as 9000 psi). In many cases, the minimum miscibility pressure (MMP) of nitrogen is too close or even higher than the fracture pressure of the reservoir. It is often used at lower pressures for immiscible displacements. Hydrocarbon can be obtained from the field production itself, or nearby fields. Especially where there is no commercial use production gas, hydrocarbon gases can be reinjected into the pores for a miscible displacement, instead of being flared. Hydrocarbon gases can reach miscibility at pressure lower than the nitrogen but still higher than CO_2.

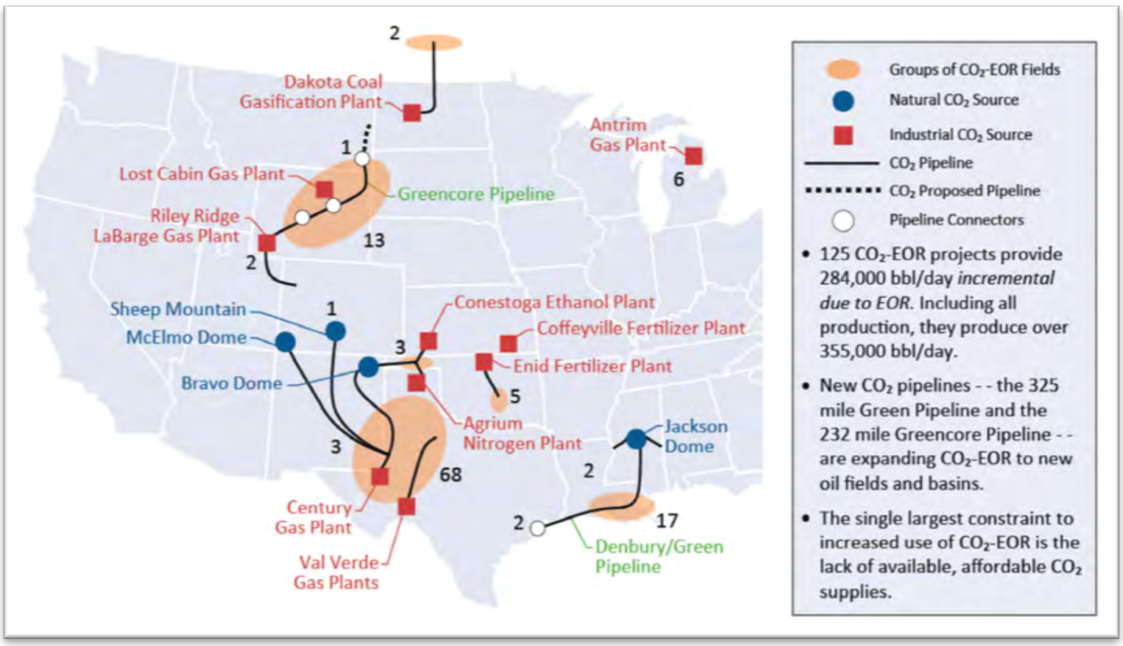

Figure 1-2: North America CO2 EOR operations and sources

One of the solutions to these issues with individual uses of injection gas is to mix them in a proportion that will eliminate or at least reduce most of the constraints. A CO_2-N_2 mixture can reduce the amount of CO_2 needed, reduce the high MMP of pure nitrogen to a more reasonable MMP or even cause less corrosion. A CO_2-Lean gas mixture can reduce the amount of both CO_2 and lean gas needed while still having a low MMP. Mixture of injection gases can be a game changer and make a previously uneconomical project economical.

Oil Price ($/Barrel)	**$70**
Gravity/Basis Differentials, Royalties and Production Taxes	($15)
Net Wellhead Revenues ($/Barrel)	**$55**
Capital Cost Amortization	($5 to $10)
CO_2 Costs (@ $2/Mcf for purchase; $0.70/Mcf for recycle)	($15)
Well/Lease Operations and Maintenance	($10 to $15)
Economic Margin, Pre-Tax ($/Barrel)	**$15 to $25**

Figure 1-3: Illustrative cost of CO2 EOR project

The main factor of miscible displacement effectiveness being the MMP, what is the change in MMP we can expect by mixing injection gases? Does reservoir oil composition influence gas mixtures MMP? Can we predict the performance of mixing injection gases knowing the reservoir oil composition?

Scope and Objective

This project has for main objective to develop a relationship between a reservoir oil composition and the expected MMP using mixtures of injection gases.

1. Determine the effect of oil composition on MMP using mixtures of injection gases composed of carbon dioxide (CO_2), nitrogen (N_2) and lean gas (98% methane + 2% ethane).
2. Determine the effect of nitrogen and lean gas added to pure CO_2 on MMP.
3. Propose ways to predict the performance of injection gas mixtures based on oil composition.

CHAPTER 2

Literature Review

2.1 Miscible gas injection mechanism

During an immiscible displacement process such as water flood, the microscopic displacement efficiency is less than 100% due to the oil left behind trapped as isolated drops, stringers, or pendular rings, depending on the wettability. Because of the capillary pressure, oil cannot pass through small pores and the displacing fluid can no longer displace the oil and flows around it. In a miscible displacement, the interfacial tension between the displacing and the displaced fluids is eliminated and a single phase is formed. Depending on how miscibility is reached, this process may be classified as first-contact miscible displacement (FCM) or multi-contact miscible displacement (MCM), which are discussed in this section. To illustrate the miscibility mechanisms, ternary diagrams are used. The ternary diagram describes the phase behavior of a three-component or three-pseudo-component system at constant temperature and pressure. In this project, the top point represents 100% of lighter component or the injected fluid, the bottom right point represents 100% of intermediate pseudo-component (C_2-C_6), and the bottom left represents the heavy pseudo-component (C_{7+}). The curve inside the triangle represents the 2-phase region and composition point of the fluids will determine the miscibility process (See Figure 2-1).

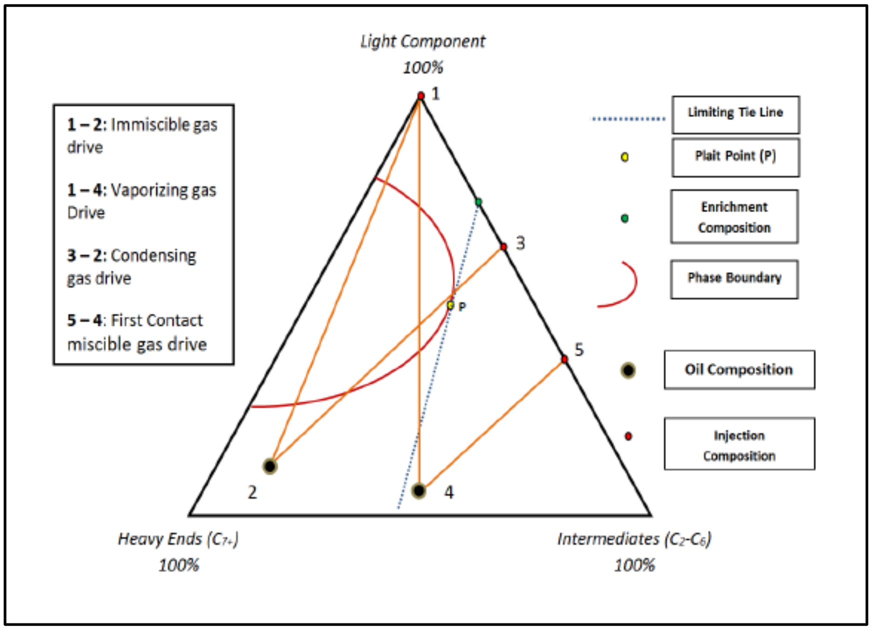

Figure 2-1: Ternary diagram for miscible displacements

2.1.1 First Contact Miscibility

First contact miscibility implies that miscibility is reached between the injected fluid and the oil upon the first contact when mixed in all proportions at a certain pressure and temperature. This process can be illustrated using a ternary diagram show in Figure 2-2. The shaded blue areas represent the two phase envelops at different pressures: the bigger area is for the case of pressure equal to P1 and the smaller area for pressure equal to P2, where P2 is greater than P1. Point E represents the reservoir fluid. Points A, B, C and D represent different injection fluids. If the line between the reservoir oil and the injection fluid crosses the 2-phase region, then there are some combinations of composition that will yield to a two-phase product. When this line is outside the two-phase region, the product of mixing the two fluids is a single-phase fluid for all proportions, which defines the concept of first contact miscibility. In Figure 2-2, mixing solvents A, B or C are first-contact miscible with the reservoir oil when the pressure if above P1. Solvent D is first-contact miscible with the reservoir oil when the pressure is above P2.

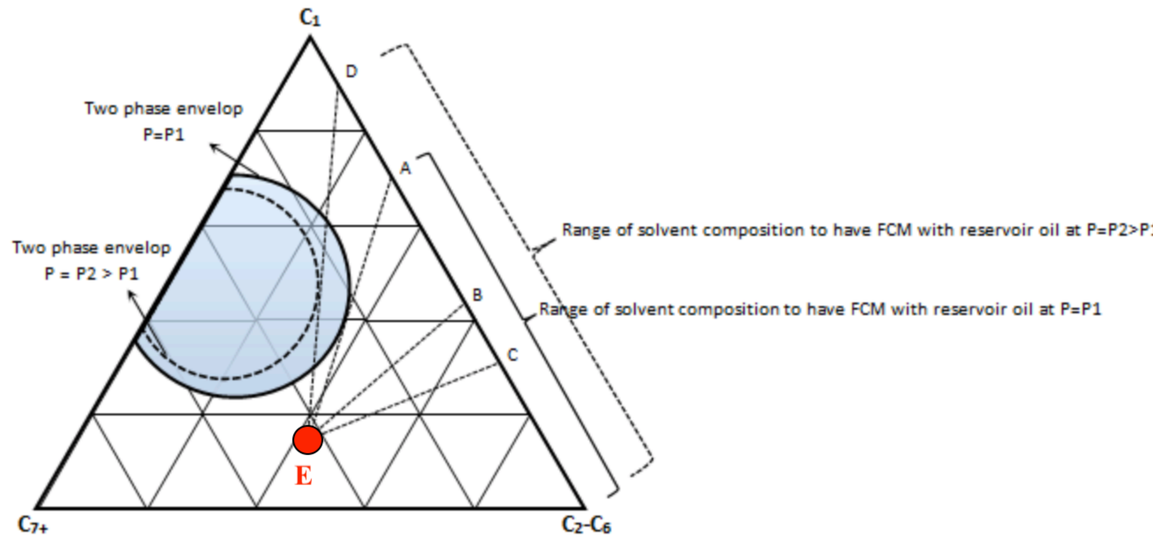

Figure 2-2: Ternary diagram for First Contact Miscibility

2.1.2 *Multi-Contact Miscibility (MCM)*

Multi-contact miscibility implies that miscible condition is developed through composition alteration of the oil or the injected fluid as it advances in the reservoir. Upon first contact, the composition of the oil or the injected gas starts to change, and as more surface is contacted, composition change continues until miscibility is reached. For example, an injected gas that is not miscible in all proportion with oil, might exchange some component with the oil as it flows through the reservoir until miscibility is reached. This is a dynamic miscible process. There are three main MCM categories: the vaporizing-gas displacement, the condensing-gas process, and the CO_2 displacement.

2.1.2.1 Vaporizing-Gas Displacement:

During this process, the injected fluid is a generally composed of low molecular weight components or inert gas (methane or nitrogen). The injected fluid is enriched in composition by the vaporization of intermediate components from the oil into the injected gas. As injection continues, the enrichment of the injected gas continues until miscibility is reached. Figure 2-3 illustrates this process using a ternary diagram. Point S represents the initial injected gas composition and point O the initial oil composition. The mixture of S and O leads to point ‘M1’, which falls in the 2-phase region. The vapor phase of that mixture can be represented by point V1. Now we have a gas of composition V1 mixing with the newly contacted oil of original composition O. The gas composition will continue to change the same way until the mixture fall into the single-phase region outside the 2-phase envelop. We can notice that the vapor phase volume fraction of the mixture (represented by the distance from M1 to V1) increases as the process continues while the liquid phase volume fraction decreases. This indicates that the intermediate components of the oil are vaporizing into the injected gas.

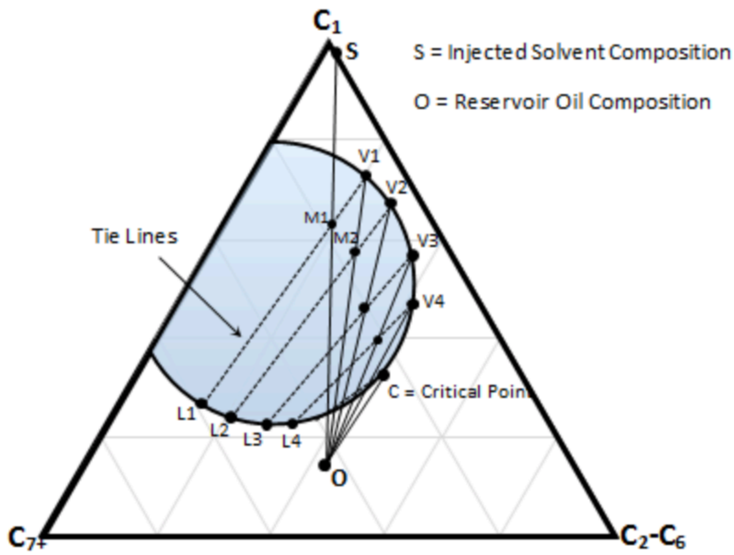

Figure 2-3: Ternary Diagram for Vaporizing Gas Displacement

2.1.2.2 Condensing-Gas Displacement:

During this process, the injected fluid is generally composed of intermediate molecular weight components. The oil is enriched in composition by the condensation of these intermediate components from the injected gas into the oil. As injection continues, the enrichment of the oil continues until miscibility is reached. Figure 2-4 shows a ternary diagram illustrating this process. This process develops the same manner as Figure 2-4 previously explained in the vaporizing process. The difference is that the vapor phase of the mixture V1 moves ahead of the liquid phase L1, which is now exposed to injected gas with the original composition A. This composition changes until miscibility is reached. We can notice that the vapor phase volume fraction of the mixture decreases as the process continues while the liquid phase volume fraction increases. This indicates that the intermediate components of the injected gas are vaporizing into the oil.

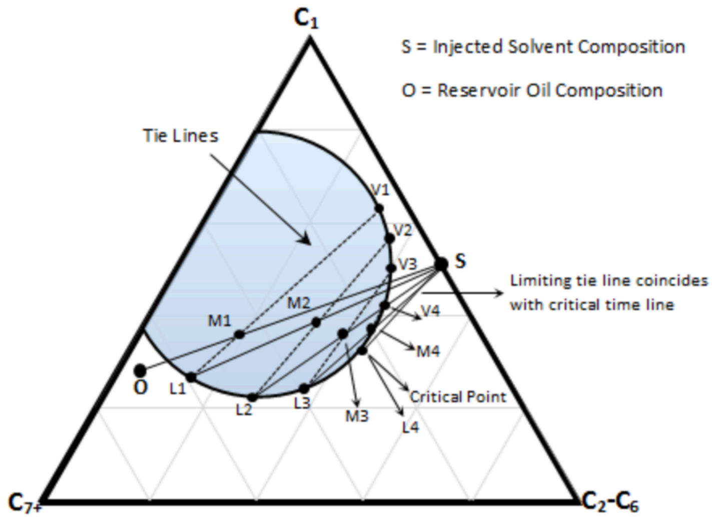

Figure 2-4: Ternary diagram for Condensing Gas Displacement

2.1.2.3 CO2 Displacement:

Carbon dioxide displacement is similar to the vaporizing-gas process. At temperature below 120°F, the ternary diagrams with methane as injected gas and the one with carbon dioxide as injected gas are the same. However, above 120°F, the 2-phase envelop when using carbon dioxide is much smaller than the one when using methane. Also, the tie-lines are more parallel. (See Figure 2-5). These differences imply that miscibility using CO_2 as injection gas is reached a lower pressure that when using CH_4.

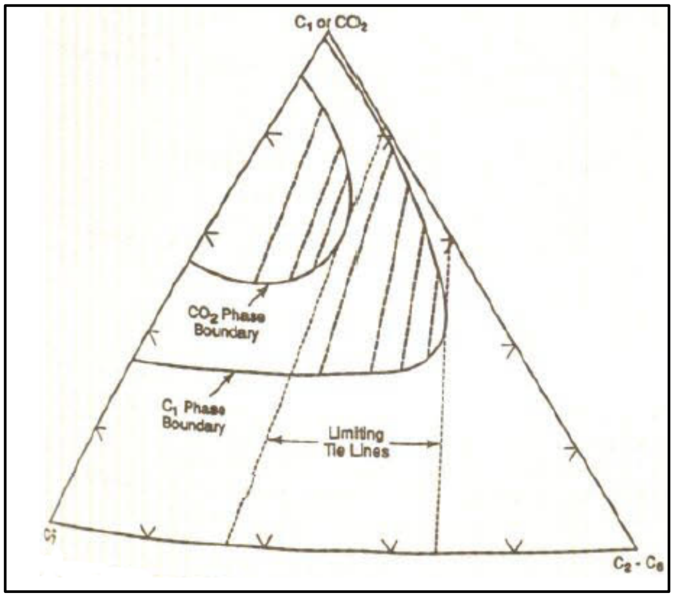

Figure 2-5: Ternary diagram for CO_2 displacement

2.2 Minimum Miscibility Pressure (MMP) determination.

There are many methods to estimate the minimum miscibility pressure. These methods can be experiments, correlations or numerical simulations. MMP may be experimentally estimated by conducting displacement tests under conditions that are not always ideal. Some common experiments are the slim-tube test, the rising bubble method (RBA) and the vanishing interfacial tension technique. These different techniques can result in different values and one is not necessarily more accurate than the other. The most common experiment is the slim-tube test, which can also be simulated using numerical methods. Many empirical correlations are developed and available in the literature. Although using correlations is the least accurate method, they are a quick and easy way to estimate MMP. Finally, numerical methods use tools with integrated EOS characterization to simulate laboratory experiments. They are usually used to match an experiment that can be repeated it at different conditions.

2.2.1 Slim-tube Test

Slim-tube is a generally accepted procedure in which the flushing efficiency and fluid mixing during a miscible displacement is examined. Figure 2-6 is a schematic diagram of a slim-tube experiment apparatus. The slim-tube equipment consists of a 20 to 80 ft stainless steel tube with a very small inside diameter ranging from 0.15 to 0.78 inches. The tube is uniformly packed with fine grade sand of glass beads that represent the porous medium for the displacement test. The small ratio diameter to length of the slim-tube column creates an environment that attempts to suppress viscous fingering by transverse dispersion. The tube is coiled to simulate a horizontal flow while eliminating the gravity effect. The tube is attached to a pumping system that forces fluids inside the porous medium. The inside pressure is controlled by a backpressure regulator and the temperature is usually set with a constant temperature air bath. A collection system and a measurement system is placed at the end of the tube and provide the data necessary to evaluate the experiment.

At the start of the test, the tubing is saturated with hydrocarbon simulating the displaced fluid. Because reservoir oil is hard to get at surface conditions, recombined oil or deal oil from the stock tank are generally used. The temperature is set to reservoir condition and the back pressure to the desired pressure. If correlations or other methods provide an estimate of the MMP, the back pressure is generally set bellow and above the anticipated MMP. The injection fluid is then injected into the tubing at constant rate and constant pressure and the displacement is simulated. Depending on the definition of ultimate recovery, either the recovery factor at 1.2 PV of fluid injected or the recovery factor at breakthrough is recorded.

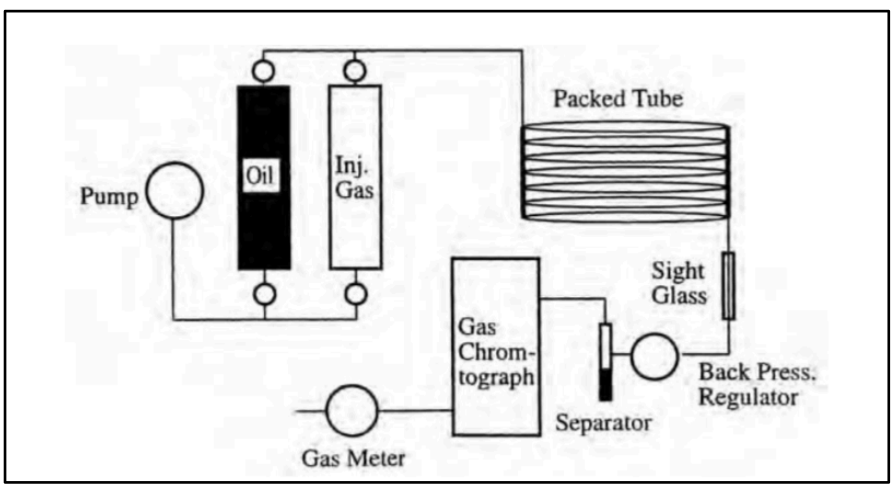

Figure 2-6: Slim-tube set-up diagram

This process is repeated several times at pressures bellow and above the anticipated miscible pressure while all other parameters are kept constant. A plot of pressure versus ultimate recovery is generated as seen in Figure 2-7. There is no definite criteria to determine the MMP from this test. The most common definitions of MMP are the pressure at which a sharp slope change in the plot occurs or the pressure at which 95% of the oil in place is recovered.

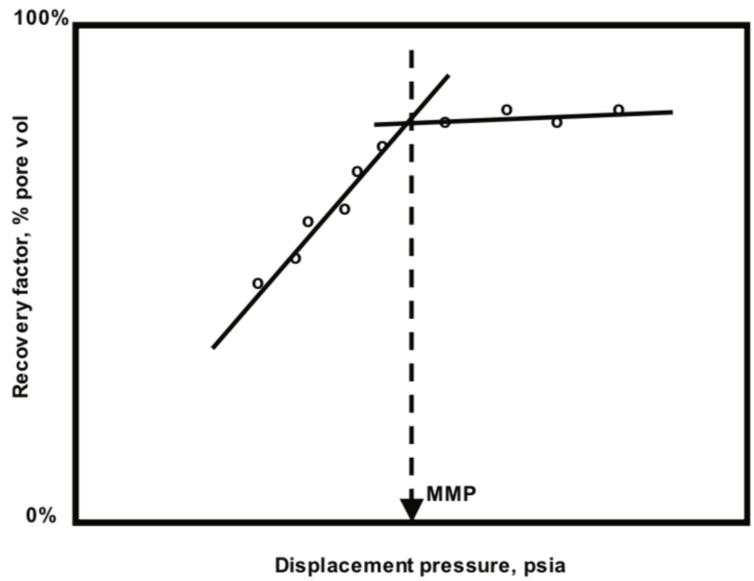

Figure 2-7: Illustration of MMP determination

2.2.2 MMP Correlations

The need for MMP correlations becomes crucial when time and energy are limited. Many correlations are developed and published in the literature as an attempt to estimate the MMP as accurately as possible. These correlations relate the MMP to the physical properties of the oil and the displacing gas. The parameters that are known to affect MMP are:

- Reservoir temperature
- Oil characteristics and properties
- Concentration of intermediate components (C2-C6) in the oil
- Concentration of C1 and N2 in the oil

- Oil molecular weight
- Injection gas composition

Correlations are a good way of quickly and easily estimate MMP when experiments are not possible. The disadvantage is that most of them are derived from regression of slim-tube data from a particular area or setting and that are not necessarily accurate themselves. Some use fewer input data than others and some are more specific to a certain type of oil. Bellow are presented two types of MMP correlations: correlations for pure CO_2 MMP, and correlations for nitrogen and lean gas correlations.

2.2.2.1 CO2 MMP correlations

Petroleum Recovery Institute:

Function of temperature only.

$$\text{MMP} = 1071.82893(10b)$$

$$b = [2.772 - (1519/\text{T})]$$

Yellig and Metcalfe

Function of temperature only.

$$\text{MMP} = 1833.7217 + 2.2518055(T - 460) + 0.01800674(T - 460)^2 - \frac{103949.93}{T - 460}$$

Alston's

Function of temperature, pentane plus molecular weight, mole fraction of intermediate oil components and mole fraction of the volatile oil components.

$$\text{MMP} = 0.000878(T-460)^{1.06}(M_{C_{5+}})^{1.78}\left[\frac{X_{\text{vol}}}{X_{\text{int}}}\right]^{0.136}$$

where

T = system temperature, °R
$M_{C_{5+}}$ = molecular weight of pentane and heavier fractions in the oil phase
X_{int} = mole fraction of intermediate oil components (C_2–C_4, CO_2, and H_2S)
X_{vol} = mole fraction of the volatile (C_1 and N_2) oil components

Cronquist

Function of temperature, pentane plus molecular weight, and volatile components molar fraction.

$$\text{MMP} = 15.988(T-460)^{A}$$

$$A = 0.744206 + 0.0011038M_{C_{5+}} + 0.0015279y_{C_1\text{–}N_2}$$

Yuan

Function of temperature, heptane plus molecular weight, and molar fraction of the intermediate components.

$$(\text{MMP})_{\text{pure CO}_2} = a_1 + a_2 M_{C_{7+}} + a_3 C_M + \left[a_4 + a_5 M_{C_{7+}} + \frac{a_6 C_M}{(M_{C_{7+}})^2}\right](T-460) + (a_7 + a_8 M_{C_{7+}} + a_9 (M_{C_{7+}})^2 + a_{10} C_M)(T-460)^2$$

with the coefficients as follows:

$a_1 = -1463.4$ $a_6 = 8166.1$
$a_2 = 6.612$ $a_7 = -0.12258$
$a_3 = -44.979$ $a_8 = 0.0012283$
$a_4 = 21.39$ $a_9 = -4.052(10^{-6})$
$a_5 = 0.11667$ $a_{10} = -9.2577(10^{-4})$.

$$\frac{(\mathrm{MMP})_{\mathrm{impure}}}{(\mathrm{MMP})_{\mathrm{pure\,CO_2}}} = 1 + m(y_{\mathrm{CO_2}} - 100)$$

with

$$m = a_1 + a_2 M_{\mathrm{C_{7+}}} + a_3 \mathrm{C}_M + \left[a_4 + a_5 M_{\mathrm{C_{7+}}} + \frac{a_6 \mathrm{C}_M}{(M_{\mathrm{C_{7+}}})^2} \right](T - 460)$$
$$+ [a_7 + a_8 M_{\mathrm{C_{7+}}} + a_9 (M_{\mathrm{C_{7+}}})^2 + a_{10} \mathrm{C}_M](T - 460)^2$$

with the coefficients as follows:

$a_1 = -0.065996$	$a_6 = -0.027344$
$a_2 = -1.524(10^{-4})$	$a_7 = -2.6953(10^{-6})$
$a_3 = 0.0013807$	$a_8 = 1.7279(10^{-8})$
$a_4 = 6.2384(10^{-4})$	$a_9 = -43.1436\ (10^{-11})$
$a_5 = -6.7725(10^{-7})$	$a_{10} = -1.9566\ (10^{-8})$

2.2.2.2 Lean-Gas and Nitrogen MMP correlations

Firoozabadi and Aziz

Function of temperature, heptane plus molecular weight, and intermediate components molar fraction.

$$\mathrm{MMP} = 9433 - 188\ (10^3)F + 1430(10^3)F^2$$

with

$$F = \frac{I}{M_{\mathrm{C_{7+}}}(T - 460)^{0.25}}$$

$$I = x_{\mathrm{C_2-C_5}} + x_{\mathrm{CO_2}} + x_{\mathrm{H_2S}}$$

where

I = concentration of intermediates in the oil phase, mol%
T = temperature, °R
$M_{\mathrm{C_{7+}}}$ = molecular weight of $\mathrm{C_{7+}}$

Hudgins

Function of temperature, heptane plus molecular weight, and intermediate components molar fraction.

$$\text{MMP} = 5568\ \text{e}^{R1} + 3641\ \text{e}^{R2}$$

with

$$R1 = \frac{-792.06 x_{C_2-C_5}}{M_{C_{7+}} T^{0.25}}$$

$$R2 = \frac{-2.158(10^6)(C_1)^{5.632}}{M_{C_{7+}} T^{0.25}}$$

where

T = temperature, °F

C_1 = mole fraction of methane

$x_{C_2-C_5}$ = sum of the mole fraction of C_2–C_5 in the oil phase

<u>*Glaso*</u>

Function of temperature, heptane plus molecular weight, methane molar fraction and intermediate components molar fraction.

For API < 40:

$$\text{MMP} = 80.14 + 35.35H + 0.76H^2$$

where

$$H = \frac{M_{C_{7+}}^{0.88}(T-460)^{0.11}}{(x_{C_2-C_6})^{0.64}(x_{C_1})^{0.33}}$$

For API > 40:

$$\text{MMP} = -648.5 + 2619.5H - 1347.6H^2$$

where

$$H = \frac{M_{C_{7+}}^{0.48}(T-460)^{0.25}}{(x_{C_2-C_6})^{0.12}(x_{C_1})^{0.42}}$$

CHAPTER 3

Method

3.1 Project Overall Method

The objective of this study is to analyze the effect of oil composition on minimum miscibility pressure using mixtures of gas containing CO2, nitrogen and lean gas. Minimum miscibility pressures that make the data for our assessment are estimated using a numerical simulator. The first step is to validate the numerical simulation by comparing its results to other experiment results published in the literature and other trusted correlations. After validation, the effect of each grouped component is examined by running multiple MMP simulations using oil compositions that are different only in the molar fraction of the correspondent component. The injection gas is also changed to see the effect of oil components on mixtures. The components are grouped into 3 groups: the light component, which is methane, the intermediate components, from C2 to C6, and the heavy components, C7+. The fluid models are generated using the Schlumberger simulator package PVTi, before being included into the data file of each run. The observed changes in the estimated MMPs are analyzed through graphs and conclusions are drawn.

3.2 Fluid compositional model specification

The fluid model is characterized using the PVTi module of the Schlumberger simulation package. The input parameters are the molar composition, the plus fraction molecular weight, and the plus fraction specific gravity. All other fluid characteristics or component characteristics are taken from the PVTi library. The fluid phase behavior is generated and then exported into a PVO file at a specific temperature.

The injection fluids are pure carbon dioxide, pure nitrogen, lean gas, mixtures of CO2 and N2, and mixtures of CO2 and lean gas. The lean gas used in this study is 98% methane and 2% ethane (Table 1).

Table 1: Injection fluids compositions

	CO2	LG	N2
	100%	**0%**	**0%**
LG Analysis	75%	25%	0%
	50%	50%	0%
	25%	75%	0%
	0%	100%	0%
N2 Analysis	75%	0%	25%
	50%	0%	50%
	25%	0%	75%
	0%	0%	100%

3.3 Slim-tube model

The slim-tube model created in ECLIPSE 300 is one-dimensional model that is 33 ft long with an ID of approximatively 0.5 inches. It has 200 cells , each 2 inches long, with a uniform and homogeneous porosity and permeability of 10% and 2000 mD respectively. The input relative permeability curves are shown in Figure 3-1. The fluid model is exported from PVTi and incorporated using the INCLUDE keyword. An injector and a producer are places at each end of the tube and act as the pumping system and the collection system respectively.

For each run, the reservoir pressure is set to the desired one. The pore volume is saturated with the oil with gas saturation explicitly set at 0%. Injection gas is injected at a constant rate of 10 rcc/hour, which is 10% of the total pore volume per hour. The injection is ended when 1.2 pore volume of injection gas in injected, which correspond to 12 hours. The producer is controlled by bottom hole pressure and is set at the reservoir pressure. That way, the pressure in the reservoir is maintained during the displacement process.

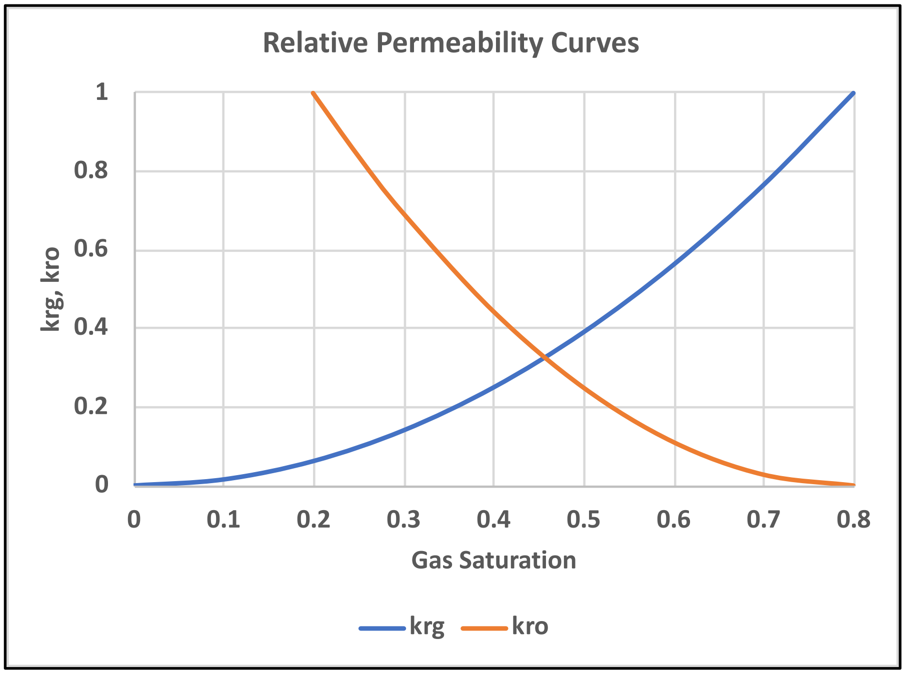

Figure 3-1: ECLIPSE Relative permeability curves

CHAPTER 4

Numerical Simulation Validation

The entirety of results in this study is supported by MMPs estimated using a numerical method. From the slim-tube model, to the oil compositional model, to the simulation tool itself, this method can be validated by comparing simulation results to actual experimental results and correlation results. Five published MMP experiments are selected from the literature where the oil composition, the plus fraction molecular weight and specific gravity and the experiment temperature are provided. Our method is validated if the estimated MMP falls inside a reasonable range of other methods.

4.1 Oil sample Selection

In order to simulate a slim-tube experiment using our simulator, the following parameters must be provided: the oil molar composition, the plus fraction molecular weight, the plus fraction specific gravity, and the temperature. Other parameters regarding the slim-tube apparatus itself such as relative permeability curves or porosity are not considered. An effort is made to select experiments that use recombined oil instead of dead oil because we are ultimately concerned about MMP at reservoir conditions.

The five MMP experiments are selected such that the oil compositions are different in terms of molar fraction and heptane plus molecular weight (Table 2). This ensures that the method is valid for a large range of composition. For the selected oil, the molar fraction varies between 16% and 35%, the heavy molar fraction between 32% and 70%, the molecular weight between 136 g/mol and 203 g/mol, and the temperature between 158 F and 237 F.

Table 2 shows the composition for oil samples used in each experiment:

- **Experiment 1**: Rising bubble experiment performed on Bakken recombined oil provided by Marathon Oil Company. The MMP was found to be 2963 psia at a temperature of 215 F.
- **Experiment 2**: Bakken reservoir oil provided by Marathon Oil Company. The MMP was found to be 3350 psia at a temperature of 237 F.

- **Experiment 3**: Slim-tube experiment from Perdersen and Christensen. The experimental MMP was 1986 psia at a temperature of 158 F.
- **Experiment 4**: CT experiments of Bakken oil by Ke Zhang. The experimental MMP was 2838 psia and at a temperature of 237 F
- **Experiment 5**: Dr. Talal Gamadi given experimental results. The MMP was 2500 psia at a temperature of 178 F.

Table 2: Oil compositions from experiemnts

Experiment 1		Experiment 2		Experiment 3		Experiment 4		Experiment 5	
Comp.	Mol%	Comp.	Mol%	Comp.	Mol%	Comp.	Mol%	Comp.	Mol%
N2	0.00	N2	3.22	N2	0.39	N2	0.00	N2	0.00
CO2	0.00	CO2	0.32	CO2	0.06	CO2	0.26	CO2	0.00
C1	38.84	C1	26.87	C1	13.88	C1	25.06	C1	41.44
C2	0.00	C2	10.8	C2	1.75	C2	11.87	C2	0.00
C3	25.92	C3	7.72	C3	4.05	C3	9.76	C2-C3	18.34
IC4	0.05	IC4	1.04	IC4	1.65	C4	6.40	IC4-NC5	8.18
NC4	0.42	NC4	4.33	NC4	3.06	C5	4.03	C6-C9	14.61
IC5	0.44	IC5	1.31	IC5	1.67	C6	3.38	C10-C19	12.48
NC5	1.04	NC5	2.53	NC5	1.57	C7-C10	18.35	C20-C29	3.11
C6	2.16	C6	3.67	C6	2.7	C11-C13	7.87	C30+	1.84
C7+	31.12	C7+	38.19	C7+	69.22	C14-C17	6.09		
						C18-C21	3.24		
						C22+	3.70		
M7+	**180**	**M7+**	**199**	**M7+**	**135.9**	**M7+**	**203**	**M7+**	**181**
C1 + N2	**39**	**C1 + N2**	**30**	**C1 + N2**	**14**	**C1 + N2**	**25**	**C1 + N2**	**41**
C2 - C6	**30**	**C2 - C6**	**32**	**C2 - C6**	**17**	**C2 - C6**	**36**	**C2 - C6**	**27**
C7+	**31**	**C7+**	**38**	**C7+**	**69**	**C7+**	**39**	**C7+**	**32**
T [F]	215	T [F]	237	T [F]	158	T [F]	237	T [F]	178
MMP [psi]	**2963**	MMP [psi]	**3350**	MMP [psi]	**1986**	MMP [psi]	**2848**	MMP [psi]	**2500**

4.2 Results comparison for validation

Table 3 shows the MMP values estimated from actual experiments, numerical simulation, and correlations. Two MMP values are recorded for the numerical simulation: the reading at the slope change and the reading at 95% oil recovery after 1.2 PV injected. The four correlations shown, Alston's, Cronquist's, Yellig's and Glaso's correlations, are the ones that estimated MMP values close to the experimental results. Figure 4-1 shows how these results compare to each other and Figure 4-2 shows how the simulation results and the correlations compare to the experimental data. Close analysis of these figures should help validate the numerical simulation method, and which of the two numerical simulation records (slope change reading or 95% recovery at 1.2 PV injected) is the best.

Experiments are considered the best way to estimated MMP, but they are not immune to errors. Major mistakes during an experiment can lead to completely wrong results. The correlations are used to confirm these MMP values or to check if they are reasonable. Table 3 shows that the correlation results fall within 8% to 15% from the experimental results on average, which is enough to confirm that the experimental results are reasonable. Figure 4-1 and Figure 4-2 show the deviation for each experiment. For experiments 3, the correlation does not accurately estimate the MMP and this can be explained by the different nature of the oil used in terms of composition. The oil used in experiment 3 is relatively heavy, with a high heptane plus fraction (69%) and a relatively low intermediate (C2 to C6) fraction (16.45%). Because some correlations do not take into consideration these factors (Yellig is only a function of temperature) while others do, the results can vary considerably.

With experimental MMP that can be trusted, let's compare them to the numerical simulation results. Figure 4-1 and Figure 4-2 show that the numerical simulation results reasonably match the experimental results for all five experiments. Table 3 shows that the average deviation from the experimental results is 11% for the line intercept method and only 7% for the 95% recovery at 1.2 PV method. This close match validates the capability of the numerical simulation method to accurately estimate the MMP. Furthermore, the second method, which is the pressure at 95% recovery at 1.2 PV injected is the best method for MMP estimation. For that reason, MMP will be estimated with only this method for the remaining of this study.

Table 3: MMP results from experiments, ECLIPSE, and correlations

Experiment	Paper MMP	ECLIPSE Reading	Eclipse 95%	Alston	Cronquist	Yellig	Glaso
Experiment 1	2963	3200	3173	2569	2391	2667	2595
Experiment 2	3350	3900	3646	3129	2764	2940	2905
Experiment 3	1986	2200	2076	1210	1443	1981	2240
Experiment 4	2848	3200	2900	3035	2830	2940	2931
Experiment 5	2500	2350	2177	2675	2281	2161	2126
	Avg Dev.:	11%	7%	15%	15%	8%	11%

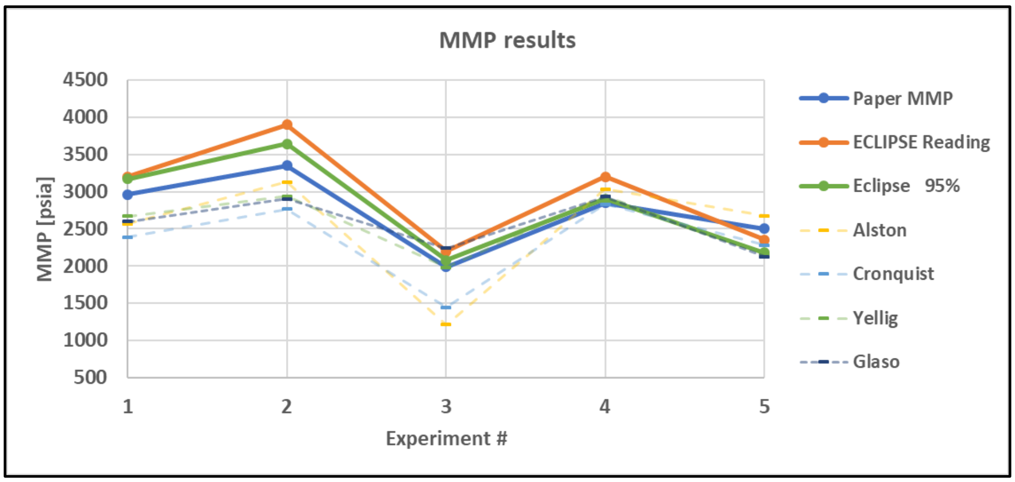

Figure 4-1: Plot of MMP results for validation

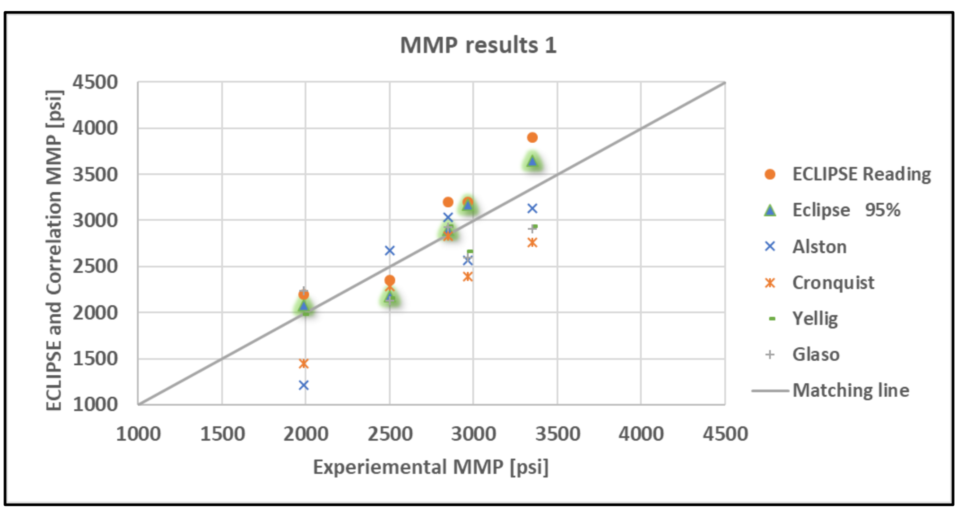

Figure 4-2: Plot Experimental MMP vs Simulation et Correlations MMP

CHAPTER 5

Parameters of interest

From the literature, the MMP is a function of the oil content of light components, intermediate components, heavy components, the molecular weight of heptane plus fraction, and the temperature. For the purpose of this study, the temperature is kept constant throughout, and the other four parameters treated as variables.

Because oil composition is often given in terms of percentage, tracking the effect of one component on the MMP can be tricky. In fact, because the sum of all component percentage should add up to 100%, varying the percentage of one component also varies the percentage of all other components, thus making it impossible to relate the observations to a specific component. The solution to this problem is to change the molar fraction of the component of interest while keeping the ratio between all other component fractions constant. To understand this method, let us take a different approach.

A sample composed of three components X1, X2 and X3, is subject to an experiment "A" that outputs an observation (see Figure 5-1).

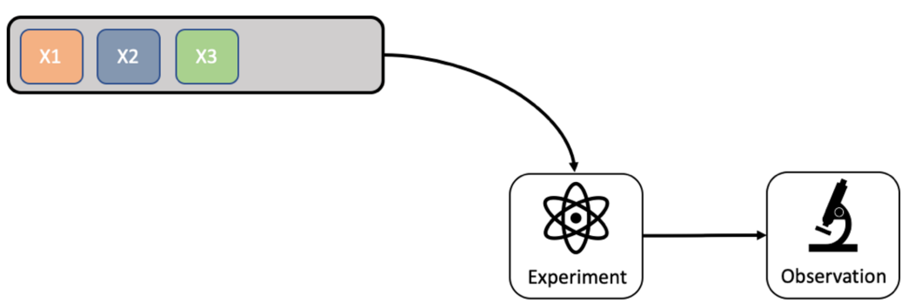

Figure 5-1: Composition sensitivity method example- part 1

An additional volume of X3 is added to an oil sample with the original composition and subjected to the same experiment "A" (Figure 5-2). Because the only difference between the samples is the volume of X3, the change in the observations can be considered as the effect of X3 volume.

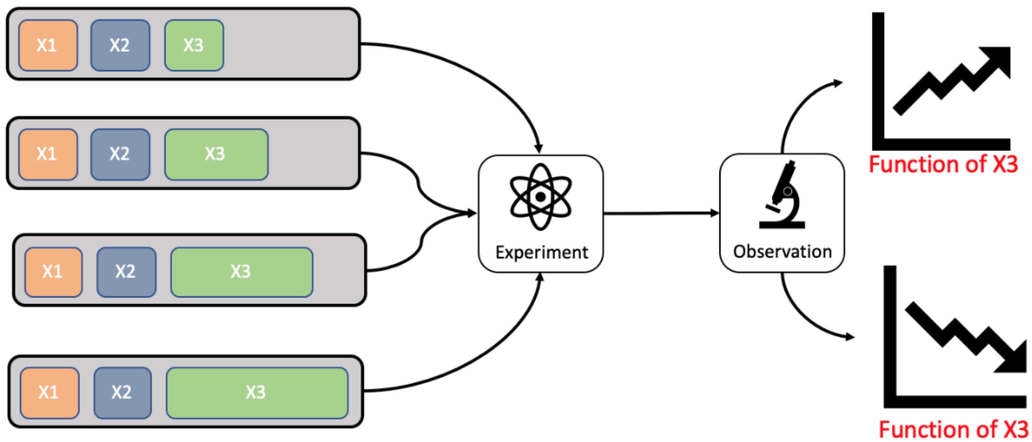

Figure 5-2: Composition sensitivity method example- part 2

Looking at it in terms of molar fraction, it would have been difficult to attribute the change in the observations to one component because the molar fraction of each component is different in all the samples. One thing that did not change however is the ratio between X1 and X2 (Figure 5-3).

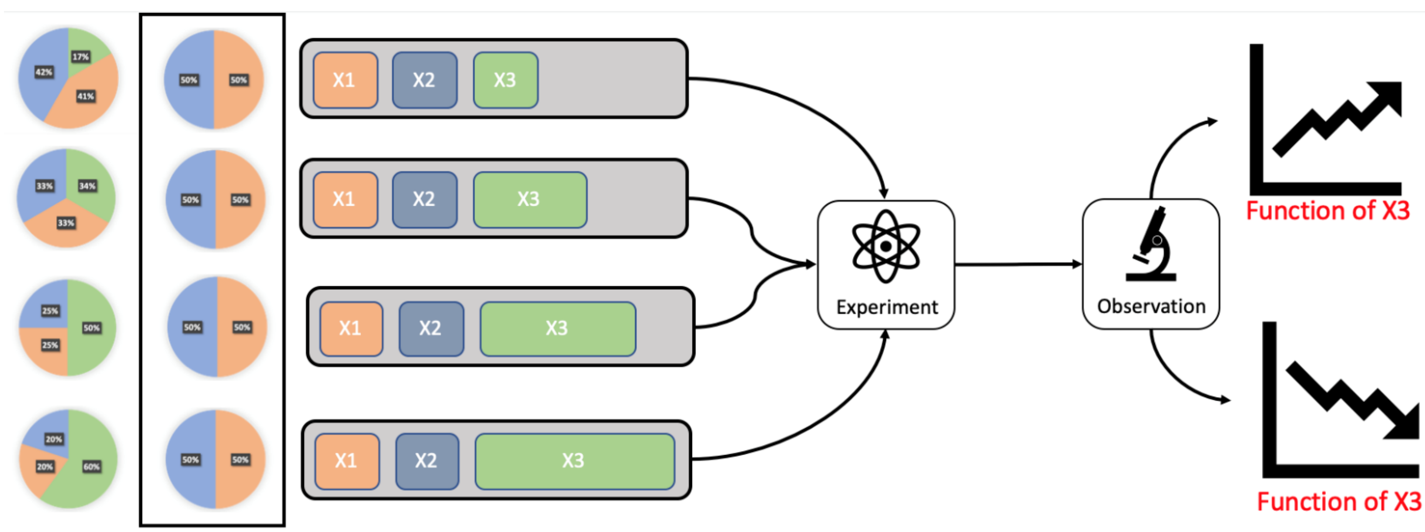

Figure 5-3: Composition sensitivity method example- part 3

In conclusion, we can study the individual effect of one component by changing its molar fraction while keeping the ratio between all the other components constant. When studying the effect of one of the grouped components on the MMP, its molar fraction is varied while the ratio between the other two grouped components is kept constant.

As shown later in this paper, for a specific oil composition, the MMP increases linearly with the percentage of added solvent (N2 or LG) in the injection gas. This observation allows us to summarize our results in the form of lines, with only two parameters to describe them, a point and a slope. An illustration is shown in Figure 5-4.

- The point of interest is the 100% CO2 MMP. This point represents the initial MMP from which MMP for gas mixtures depart. It is the reference pressure from which the effectiveness of an added solvent is evaluated.
- The slope here represents the ineffectiveness of the added solvent (N2 or LG). It is the increase in MMP that would result from increasing the molar fraction of an added solvent in the injection gas. The lower the rate of change, the more efficient the solvent.

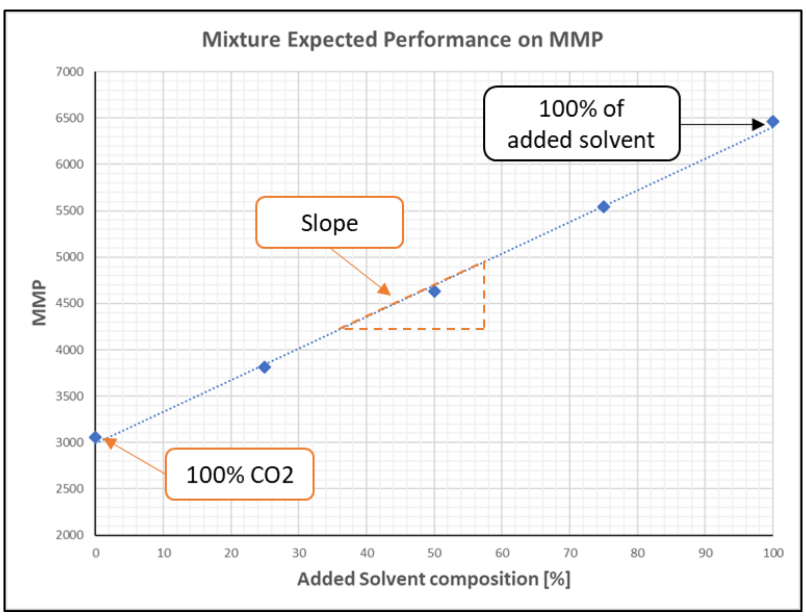

Figure 5-4: Example of composition effect analysis 1

In this presentation it makes more sense to talk about effectiveness instead of ineffectiveness. For comparison purposes, we'd like to quantify it. For that, we define the effectiveness as the additional percentage of solvent needed to increase the MMP by 1000 psi. This value can be calculated by taking the inverse of the slope and multiply it by 1000 as show in following equation:

$$Effectiveness = \left(\frac{1}{slope}\right) * 1000$$

Evaluating the effect of oil composition on injection gas mixture MMP comes down to evaluating the effect of oil composition on these two parameters. Before deciding to add N2 or LG to CO2 for injection purposes, the CO2 MMP should first be reasonable and possible to reach, then the increment not too high. Let us look at Figure 5-5. If a change in oil composition causes changes the line from oil 1 to oil 2, we observe an increase in CO2 MMP and a decrease in the solvent effectiveness. If instead it changes from oil 1 to oil 3, we observe a decrease in CO2, which is good, but no change in the solvent effectiveness. For oil 4, we observe both a decrease in CO2 MMP and an increase in solvent effectiveness.

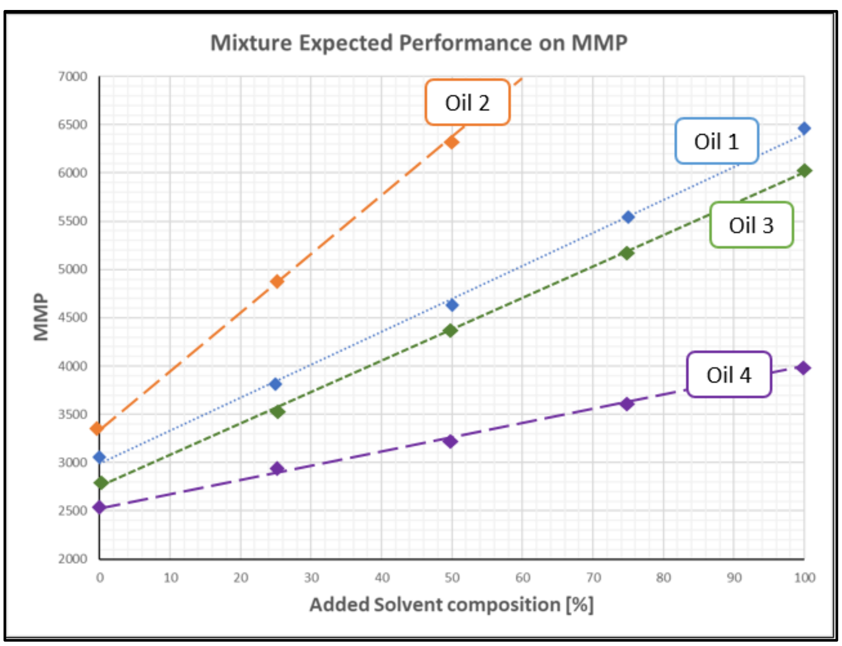

Figure 5-5: Example of composition effect analysis 2

Table 4: Interpretation of Figure 5-5

Line Observed	Change in slope	Conclusion
Oil 2	Increase	Decrease in solvent effectiveness
Oil 3	No change	No change in solvent effectiveness
Oil 4	Decrease	Increase in solvent effectiveness

5.1 Cases

The base case oil is composed of 30% light components, 30% intermediate components, and 40% heavy components. The heptane plus molecular weight is 200 g/mol and the temperature is set at 200F.

The light component molar fraction and the intermediate component molar fraction are both varied from 10% to 40%, while the heavy component molar fraction is varied from 30% to 70%. For each case, the ratio between the other two grouped components is equal to the one of the base case. Finally, the heptane plus molecular weight is changed from 120 g/mol to 300 g/mol.

The percentage of solvent in the injection gas for both N2 and LG is changed from 0% (pure CO2) to 100% (pure solvent) with an increment of 25%.

Table 5: All cases of oil composition

		Base Oil	Oil 2	Oil 3	Oil 4
Composition	**Xvol**	**30**	**10**	**20**	**40**
	Xint	30	39	34	26
	Xheavy	40	51	46	34
	M7+	200	200	200	200

		Base Oil	Oil 5	Oil 6	Oil 7
Composition	Xvol	30	39	34	26
	Xint	**30**	**10**	**20**	**40**
	Xheavy	40	51	46	34
	M7+	200	200	200	200

		Base Oil	Oil 8	Oil 9	Oil 10
Composition	Xvol	30	35	25	15
	Xint	30	35	25	15
	Xheavy	**40**	**30**	**50**	**70**
	M7+	200	200	200	200

		Base Oil	Oil 11	Oil 12	Oil 13
Composition	Xvol	30	30	30	30
	Xint	30	30	30	30
	Xheavy	40	40	40	40
	M7+	**200**	**120**	**150**	**250**

	CO2	**LG**	**N2**
	100%	**0%**	**0%**
LG Analysis	75%	25%	0%
	50%	50%	0%
	25%	75%	0%
	0%	100%	0%
N2 Analysis	75%	0%	25%
	50%	0%	50%
	25%	0%	75%
	0%	0%	100%

CHAPTER 6

Effect of Oil Composition

6.1 Effect of light component fraction

To study the effect of the light components on MMP, four different oil compositions with different C1 fraction, the same intermediate to heavy fraction ratio and the same heptane plus molecular weight were tested (Table 6). Each of the four oils were tested with the 9 injection gases shown in Table 5. This section is divided into 3 sub-sections each focusing on the effect of light component on respectively: pure CO2 MMP, CO2 and lean gas mixtures MMP, and CO2 and nitrogen gas mixtures MMP.

Table 6: Light component fraction sensitivity cases

		Oil1	Oil 2	Oil 3	Oil 4
Composition	**Xvol**	**30**	**10**	**20**	**40**
	Xint	30	39	34	26
	Xheavy	40	51	46	34
	M7+	200	200	200	200

6.1.1 Effect of light component fraction on CO2 MMP

Figure 6-1 shows how the CO2 MMP changes with the light component molar fraction in the displaced oil. What we observe is a positive and linear relationship. Increasing the light component fraction in the displaced oil increases the CO2 MMP. In this particular case where the temperature is at 200 F and the heptane plus molecular weight is 200 g/mol, each percent of light component in the oil increases the MMP by about 13 psi.

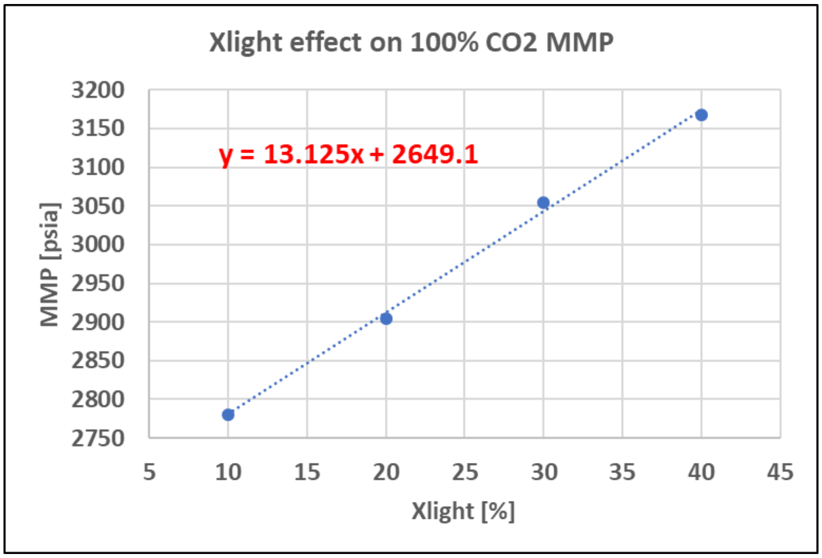

Figure 6-1: Effect of light component fraction on 100% CO2

6.1.2 Effect of light component fraction on CO2 + lean gas mixtures MMP

In this section, the oil samples in Table 6 were used for different injection gas mixtures of CO2 and lean gas. Figure 6-2 shows the change in MMP as a function of lean gas fraction for each of the four oil samples. Each line represents different oil compositions. Figure 6-3 shows the change in lean gas effectiveness as a function of light component fraction.

- Similarly to the pure CO2 case, increasing the light component fraction in the oil increases the MMP of all mixtures of CO2 and lean gas.
- The MMP increases linearly with the lean gas fraction for each oil composition.
- Each percent of lean gas in the injection gas increases the MMP by 34 to 35 psi.
- When plotted against the light component mole fraction in the oil, the effectiveness of lean gas is almost constant.
- **The effectiveness of lean gas is not affected by the light components mole fraction in the displaced oil.**

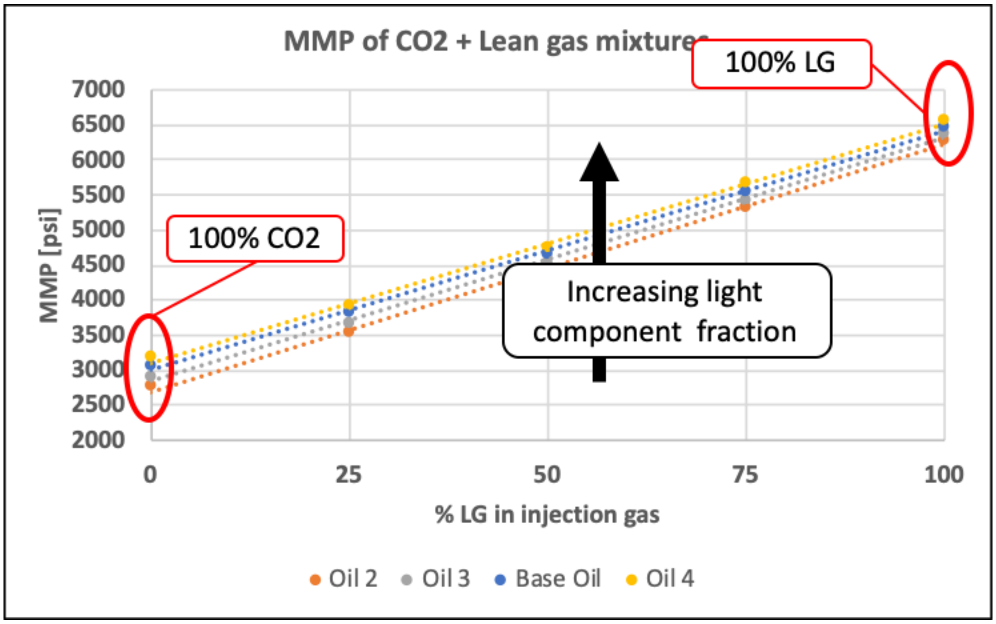

Figure 6-2: Effect of Xlight %: MMP as a function of LG%

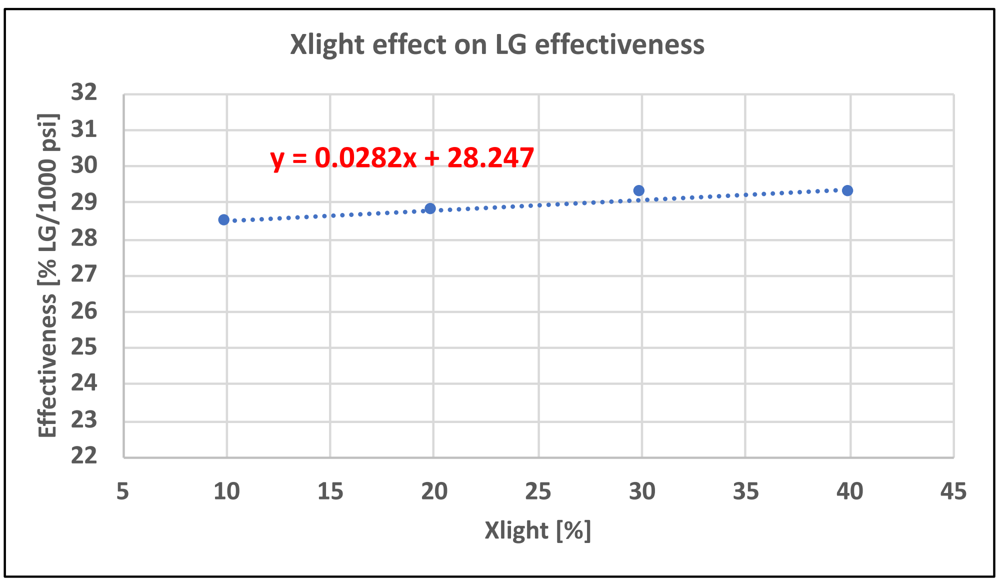

Figure 6-3: Effect of Xlight %: LG Effectiveness as a function of Xlight

6.1.3 Effect of light component fraction on CO2 + nitrogen mixtures MMP

Figure 6-4 shows the MMP results using mixtures of CO_2 and nitrogen as injection gas for the 4 oil samples shown in Table 6. The MMP's higher than 8000 psi were not considered here because they are not reasonable. Each line here represents different oil compositions. Figure 6-5 shows the change in nitrogen effectiveness as a function of light component fraction. Here are what can be taken from the graphs:

- Similarly to the pure CO2 case, increasing the light component fraction in the oil increases the MMP of all mixtures of CO2 and nitrogen.
- In this particular case of temperature and heptane plus molecular weight, nitrogen increases the MMP at a much greater rate that lean gas. Each percent of nitrogen added to CO2 increases the MMP by 90 psi, compared to 35 psi for lean gas. For the four oil used in this section, reasonable MMPs were reachable only for nitrogen percentage less than 40%.
- When plotted against the light component mole fraction in the oil, the effectiveness of nitrogen is almost constant.
- **The effectiveness of nitrogen is not affected by the light component mole fraction in the displaced oil.**

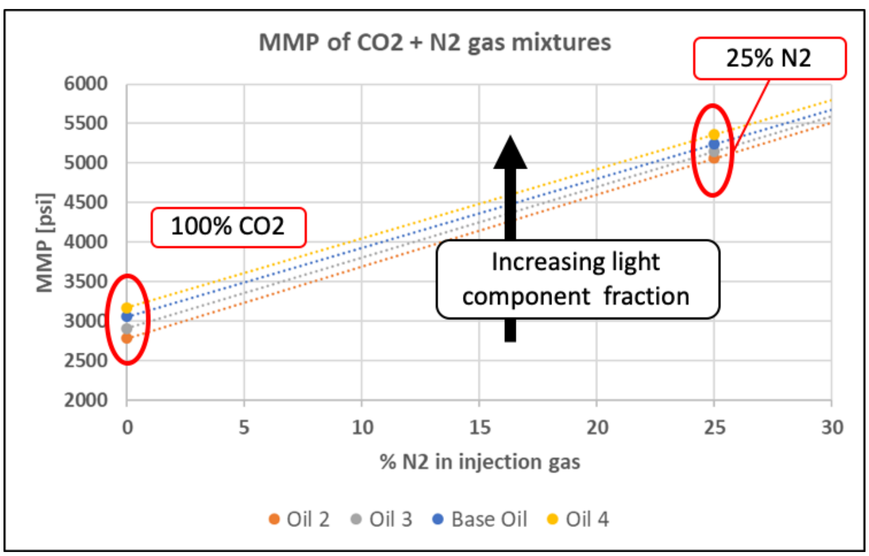

Figure 6-4: Effect of Xlight %: MMP as a function of N2%

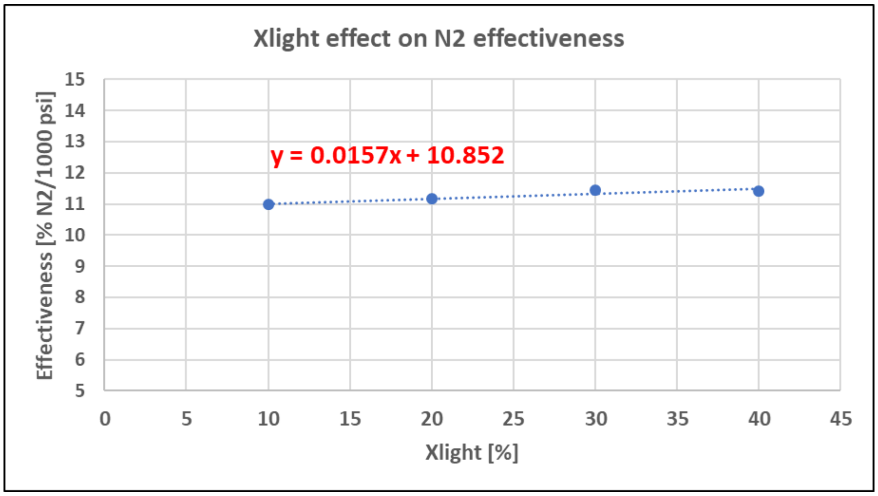

Figure 6-5: Effect of Xlight %: N2 Effectiveness as a function of Xlight%

6.2 Effect of intermediate component fraction

To study the effect of the intermediate components on MMP, four different oil compositions with different C2-C6 fraction, with the same light to heavy fraction and with the same heptane plus molecular weight were tested (Table 7). Each of the four oils were tested with the 9 injection gases shown in Table 5. This section is divided into 3 sub-sections each focusing on the effect of intermediate component on respectively: pure CO2 MMP, CO2 and lean gas mixtures MMP, and CO2 and nitrogen gas mixtures MMP.

Table 7: Intermediate component fraction sensitivity cases

		Oil1	Oil 5	Oil 6	Oil 7
Composition	Xvol	30	39	34	26
	Xint	**30**	**10**	**20**	**40**
	Xheavy	40	51	46	34
	M7+	200	200	200	200

6.2.1 Effect of intermediate component fraction on pure CO2 MMP

Figure 6-6 shows how the CO2 MMP changes with the intermediate component fraction in the displaced oil. What we observe is a decreasing and linear relationship. Increasing the intermediate component fraction in the displaced oil decreases the MMP. In this particular case where the temperature is at 200 F and the heptane plus molecular weight is 200 g/mol, each percent of intermediate component in the oil decreases the CO2 MMP by about 26 psi.

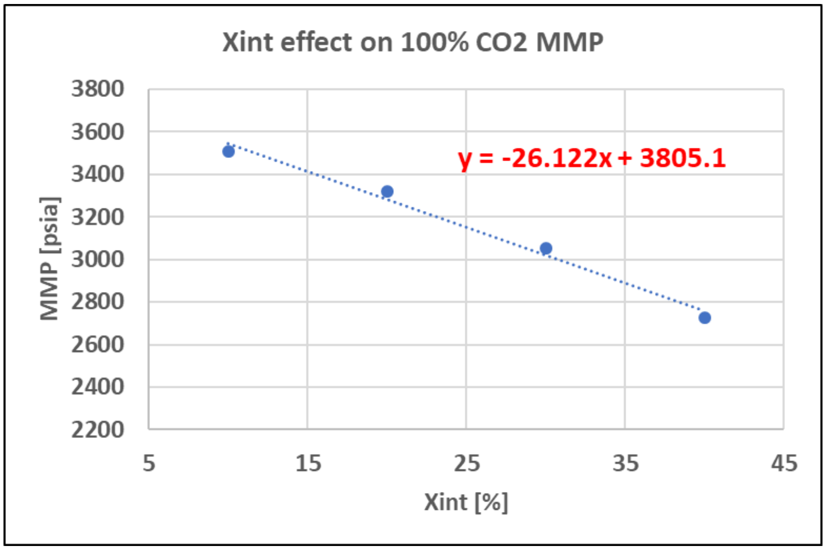

Figure 6-6: Effect of intermediate component fraction on 100% CO2

6.2.2 Effect of intermediate component fraction on CO2 + lean gas mixtures

In this section, the oil samples in Table 7 were used for different injection gas mixtures of CO2 and lean gas. Figure 6-7 shows the change in MMP as a function of lean gas fraction for each of the four oil samples. Each line represents different oil compositions. Figure 6-8 shows the change in lean gas effectiveness as a function of intermediate component fraction.

- Similarly to the pure CO2 case, increasing the intermediate component fraction in the oil decreases the MMP of all mixtures of CO2 and lean gas.
- For each oil composition, the MMP increases linearly with the lean gas fraction in the injection gas.
- The slope of each line clearly decreases as the intermediate component fraction increases. Particularly to the cases in this section, the slope drops from 42 MMP/%LG at an intermediate fraction of 10% to 38 MMP/%LG at an intermediate fraction of 40%. A high intermediate fraction in the displaced oil is then desirable when injecting mixtures for CO2 and lean gas.
- When plotted against the light component mole fraction in the oil, **the effectiveness of lean gas increases**.

- **The effectiveness of LG is improved by the intermediate components molar fraction in the displaced oil.**

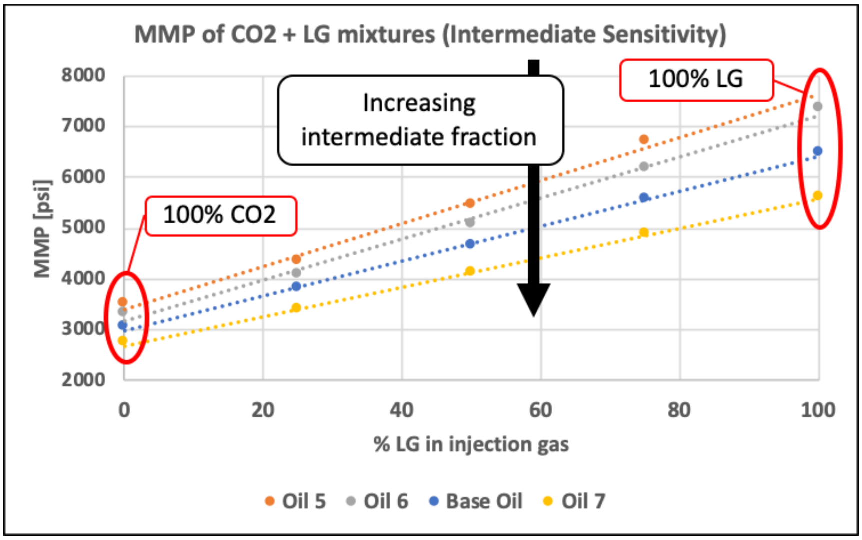

Figure 6-7: Effect of Xint %: MMP as a function of LG%

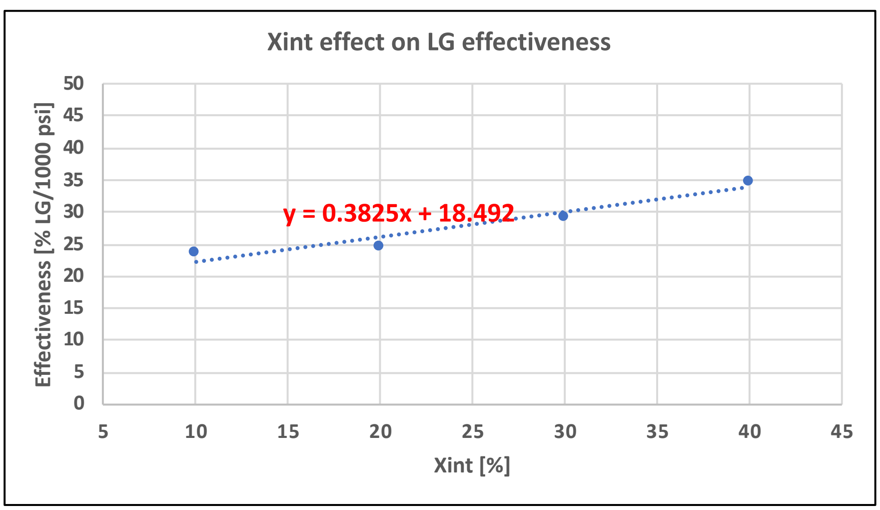

Figure 6-8: Effect of Xint %: LG effectiveness as a function of Xint %

6.2.3 Effect of intermediate component fraction on CO2 + nitrogen mixtures

Figure 6-9 shows the MMP results using mixtures of CO2 and nitrogen gases. The MMP's higher than 8000 psi were not considered here because they are not reasonable. Each line here represents different oil compositions. Figure 6-10 shows the change in nitrogen effectiveness as a function of intermediate component fraction. Here are what can be taken from the graphs:

- Similarly to the pure CO2 case, increasing the intermediate component fraction in the oil decreases the MMP of all mixtures of CO2 and nitrogen.
- In this particular case of temperature and heptane plus molecular weight, nitrogen increases the MMP at a much greater rate that lean gas. Each percent of nitrogen added to CO2 increases the MMP by at least 76 psi, compared to 28 psi for lean gas. For the four oil used in this section, reasonable MMPs were reachable for nitrogen percentage less than 25%.
- The slope of the lines decreases as the intermediate fraction increases. Looking at the oil samples considered in this section, the slope dropped from 116 MMP/%N2 at an intermediate fraction of 10%, to 76 MMP/%N2 at an intermediate component fraction of 40%. A high intermediate component fraction is then desirable when injecting mixtures of CO2 and nitrogen.
- **The effectiveness of LG is improved by the intermediate components molar fraction in the displaced oil.**

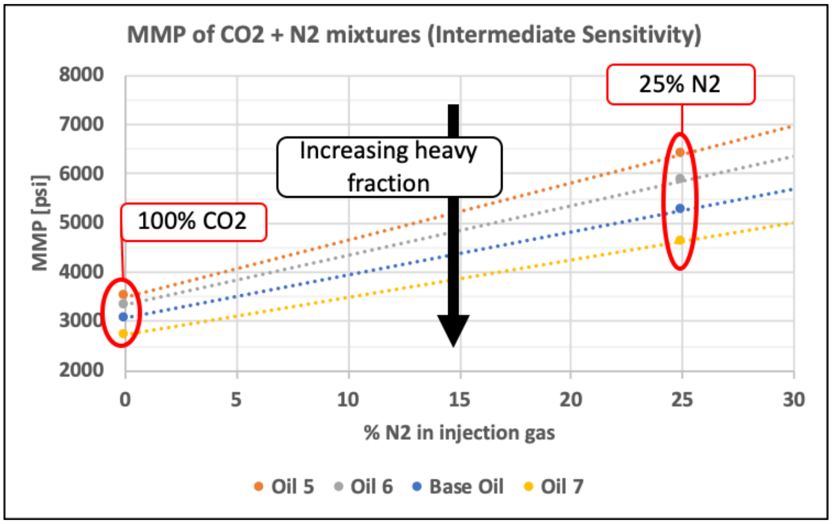

Figure 6-9: Effect of Xint %: MMP as a function of N2%

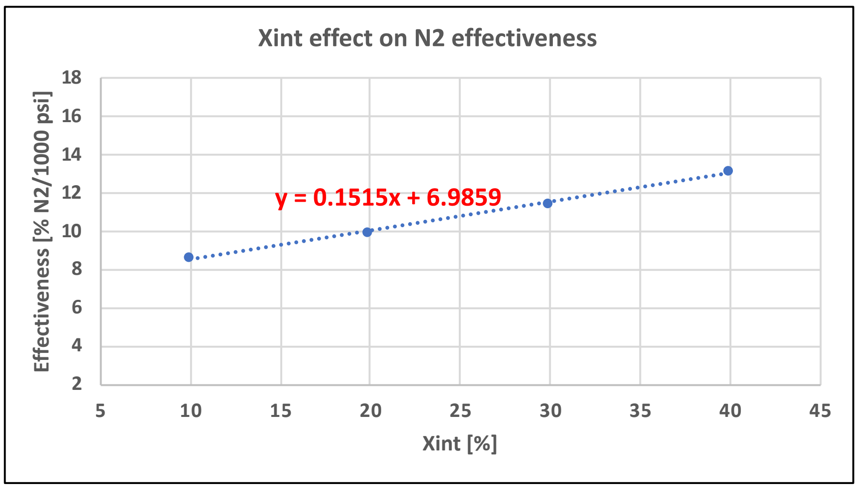

Figure 6-10: Effect of Xint %: N2 effectiveness as a function of Xint %

6.3 Effect of heavy component fraction

To study the effect of the heavy components on MMP, four different oil compositions with different C7+ fraction, with the same light to intermediate fraction ratio and with the same heptane plus molecular weight were tested (Table 8). Each of the four oils were tested with the 9 injection gases shown in Table 4. This section is divided into 3 sub-sections each focusing on the effect of heavy component fraction on respectively: pure CO2 MMP, CO2 and lean gas mixtures MMP, and CO2 and nitrogen gas mixtures MMP.

Table 8: Heavy component fraction sensitivity cases

		Oil1	Oil 8	Oil 9	Oil 10
Composition	Xvol	30	35	25	15
	Xint	30	35	25	15
	Xheavy	**40**	**30**	**50**	**70**
	M7+	200	200	200	200

6.3.1 Effect of heavy components fraction on pure CO2 MMP

Figure 6-11 shows how the CO2 MMP changes with the heavy component fraction in the displaced oil. What we observe is an increasing and linear relationship. Increasing the heavy component fraction in the displaced oil increases the CO2 MMP. In this particular case where the temperature is at 200 F and the heptane plus molecular weight is 200 g/mol, each percent of heavy component in the oil increases the MMP by about 13 psi.

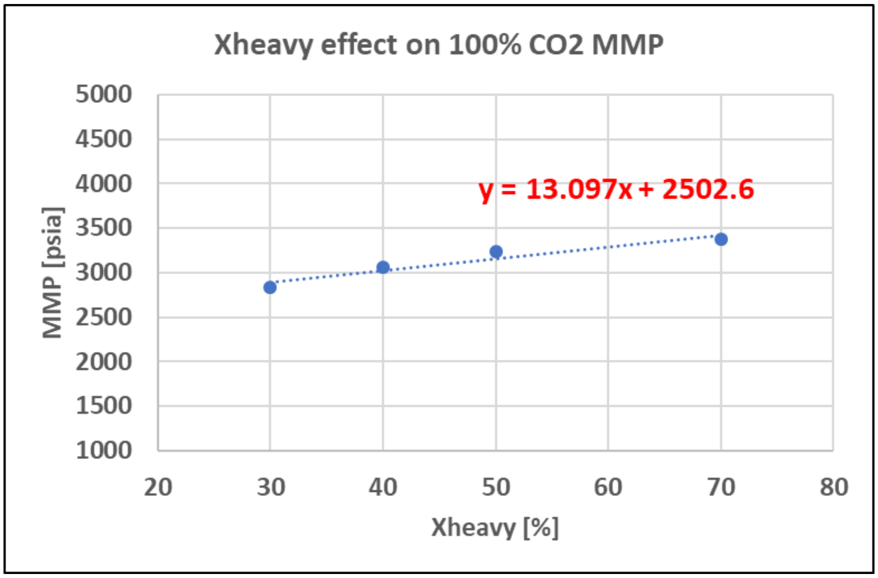

Figure 6-11: Effect of heavy component fraction on 100% CO2

6.3.2 Effect of heavy component fraction on CO2 + lean gas mixtures MMP

In this section, the oil samples in Table 8 were used for different injection gas mixtures of CO2 and lean gas. Figure 6-12 shows the change in MMP as a function of lean gas fraction for each of the four oil samples. Each line here represents different oil compositions. Figure 6-13 shows the change in lean gas effectiveness as a function of heavy component fraction.

- Similarly to the pure CO2 case, increasing the heavy component fraction in the oil increases the MMP of all mixtures of CO2 and lean gas.
- For each oil composition, the MMP increases linearly with the lean gas fraction in the injection gas.
- The slope of each line clearly increases as the heavy component fraction increases. Particularly to the cases in this section, the slope jumps from 28 MMP/ %LG at a heavy fraction of 30% to 48 MMP/%LG at a heavy fraction of 70%. A low heavy fraction in the displaced oil is then desirable when injecting mixtures for CO2 and lean gas.

- When plotted against the heavy component molar fraction in the oil, **the effectiveness of lean gas decreases considerably**.
- **The effectiveness of LG is deteriorated by the heavy components molar fraction in the displaced oil.**

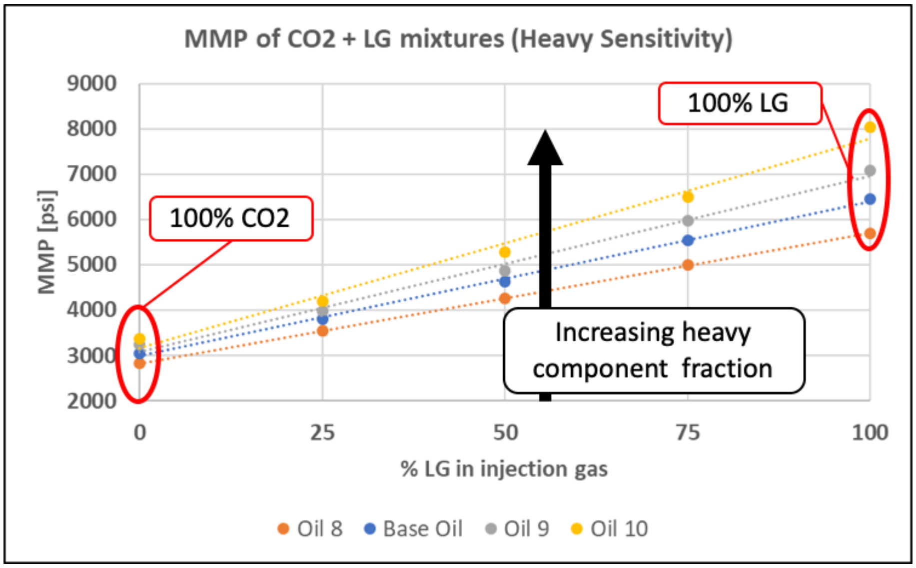

Figure 6-12: Effect of Xheavy %: MMP as a function of LG%

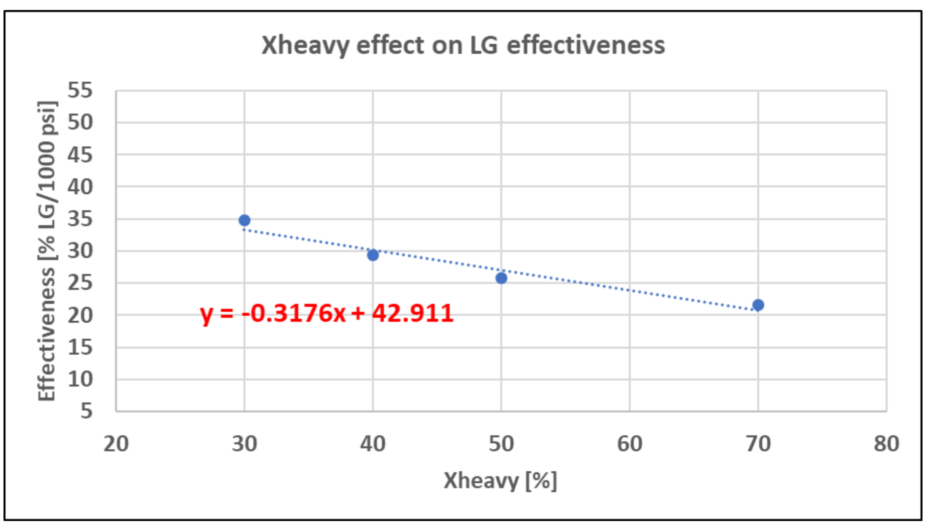

Figure 6-13: Effect of Xheavy %: LG effectiveness as a function of Xheavy %

6.3.3 Effect of heavy component fraction on CO2 + nitrogen mixtures MMP

Figure 6-14 shows the MMP results using mixtures of CO2 and nitrogen gases. The MMP's higher than 8000 psi were not considered here because they are not reasonable. Each line here represents different oil compositions. Figure 6-15 shows the change in nitrogen effectiveness as a function of intermediate component fraction. Here are what can be taken from the graphs:

- Increasing the heavy component fraction in the oil increases the MMP of all mixtures of CO2 and nitrogen.
- In this particular case of temperature and heptane plus molecular weight, nitrogen increases the MMP at a much greater rate that lean gas. Each percentage of nitrogen added to CO2 increases the MMP by at least 78 psi, compared to 28 psi for lean gas. For the four oil samples used in this section, reasonable MMPs were reachable for nitrogen percentage less than 25%.
- The slope of the lines increases considerably as the heavy component molar fraction increases. The slope jumped from 78 MMP/%N2 at an heavy fraction of 30%, to 116 MMP/%N2 at an heavy component fraction of 70%. A low heavy component fraction is then desirable when injecting mixtures of CO2 and nitrogen.
- When plotted against the heavy component fraction in the oil, the effectiveness of nitrogen decreases considerably.
- **The effectiveness of N2 is deteriorated by the heavy component molar fraction in the displaced oil.**

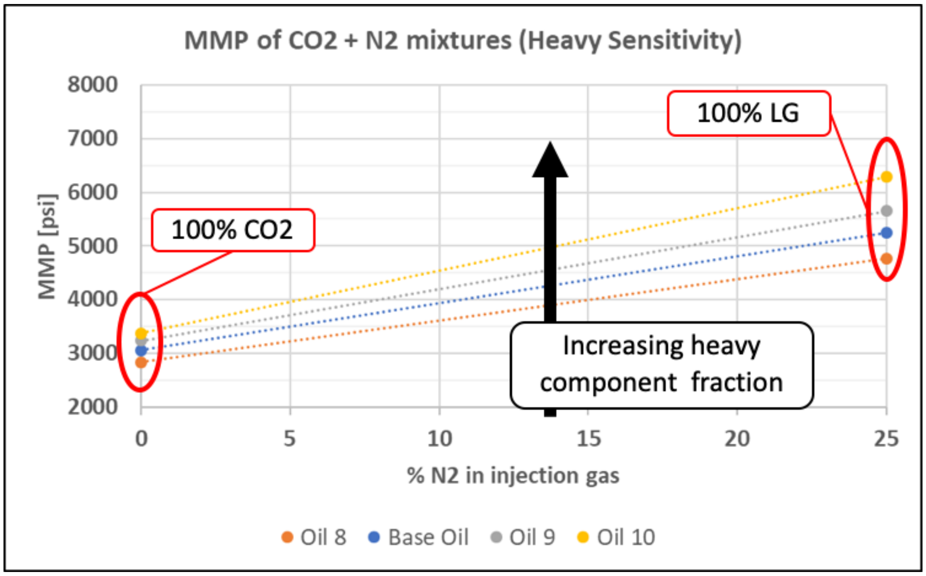

Figure 6-14: Effect of Xheavy %: MMP as a function of LG%

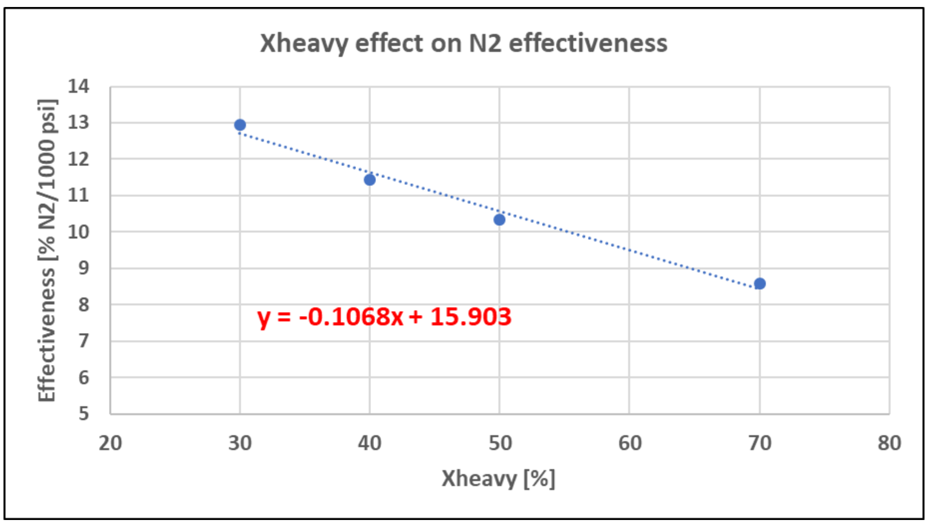

Figure 6-15: Effect of Xheavy %: N2 effectiveness as a function of Xheavy %

6.4 Effect of MC7+

To study the effect of the MC7+ on MMP, four different oil compositions with different MC7+, and the same C1 to C7+ fraction were tested (Table 9). Each of the four oils were tested with the 9 injection gases shown in **Table 5**. This section is divided into 3 sub-sections each focusing on the effect of MC7+ on respectively: pure CO2 MMP, CO2 and lean gas mixtures MMP, and CO2 and nitrogen gas mixtures MMP.

Table 9: MC7+ sensitivity cases

		Oil1	Oil 11	Oil 12	Oil 13
Composition	Xvol	30	30	30	30
	Xint	30	30	30	30
	Xheavy	40	40	40	40
	M7+	**200**	**120**	**150**	**250**

6.4.1 Effect of MC7+ on CO2 + lean gas mixtures MMP

Figure 6-16 shows how the CO2 MMP changes with the MC7+ in the displaced oil. What we observe is an increasing and linear relationship. Increasing the MC7+ in the displaced oil increases the CO2 MMP. In this particular case where the temperature is at 200 F and the C1 to C7+ fraction is set as in Table 9, each g/mol of heptane plus molecular weight in the oil increases the MMP by about 16 psi.

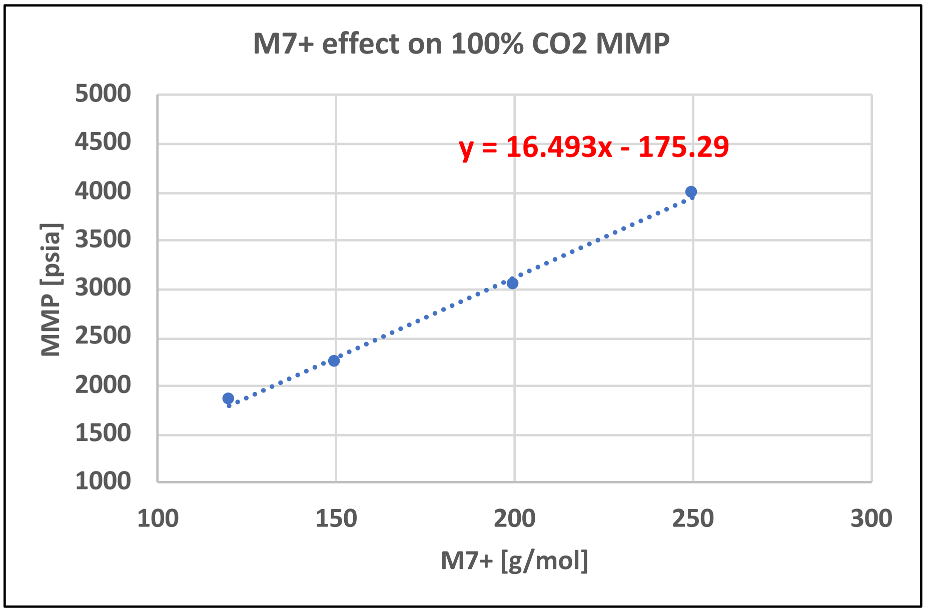

Figure 6-16: Effect of MC7+ on 100% CO2

6.4.2 Effect of MC7+ on CO2 + lean gas mixtures MMP

In this section, the oil samples in **Table 9** were used for different injection gas mixtures of CO2 and lean gas. Figure 6-17 shows how the MMP for each oil sample changes as the fraction of lean gas in the injection gas is increased. Each line here represents different oil compositions. Figure 6-18 shows how the slope for each line changes for each oil composition.

- Increasing the MC7+ in the oil increases the MMP of all mixtures of CO2 and lean gas.
- For each oil composition, the MMP increases linearly with the lean gas fraction in the injection gas.
- The slope of each line clearly increases as the MC7+ increases. The slope jumps from 16MMP/%LG at an MC7+ of 120 g/mol to 40 MMP/%LG at a MC7+ of 250 g/mol. A low heptane plus molecular weight in the displaced oil is then desirable when injecting mixtures for CO2 and lean gas.
- When plotted against the heptane plus molecular weight in the oil, the effectiveness of lean gas decreases considerably.

- **The effectiveness of LG is deteriorated by the C7+ molecular weight of the displaced oil.**

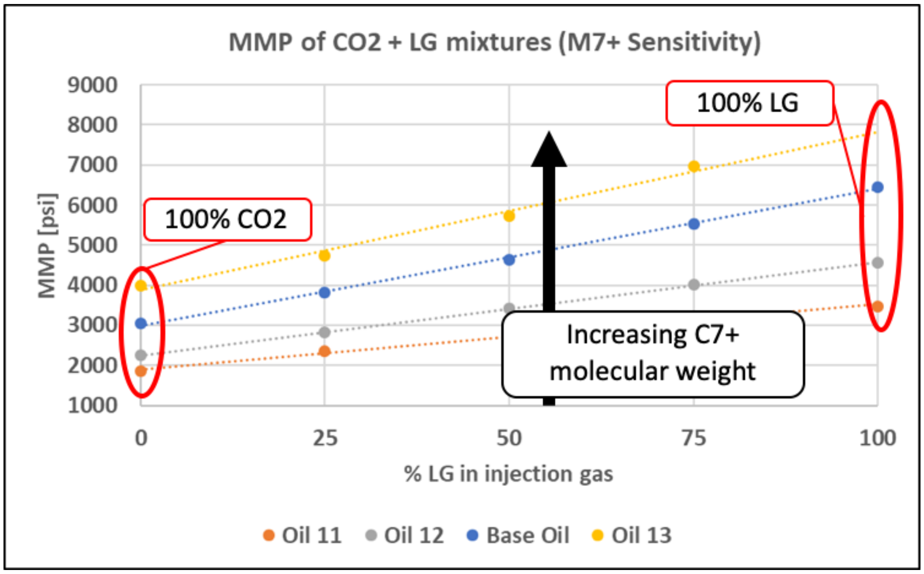

Figure 6-17: Effect of MC7+: MMP as a function of LG%

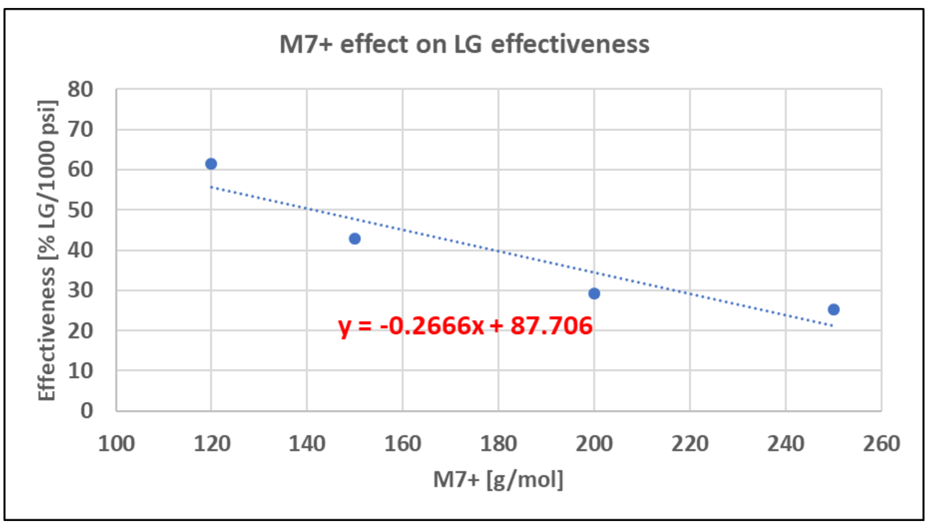

Figure 6-18: Effect of MC7+: LG effectiveness as a function of MC7+

6.4.3 Effect of MC7+ on CO2 + nitrogen mixtures MMP

Figure 6-19 shows the MMP results using mixtures of CO2 and nitrogen gases. The MMP's higher than 8000 psi were not considered here because they are not reasonable.

Each line here represents different oil compositions. Figure 6-20 shows the change in nitrogen effectiveness as a function of intermediate component fraction. Here are what can be taken from the graphs:

- Increasing the MC7+ in the oil increases the MMP of all mixtures of CO2 and nitrogen.
- In this particular case of temperature and C1 to C7+ molar fraction, nitrogen increases the MMP at a much greater rate that lean gas. Each percentage of nitrogen added to CO2 increases the MMP by at least 62 psi, compared to 16 psi for lean gas.
- At a low MC7+ of 120 g/mol (Oil 11, orange line in Figure 6-19), reasonable MMPs are reachable at higher nitrogen concentration, up to 90%. At higher molecular weight, the allowable nitrogen concentration to reach reasonable pressure drops considerably.
- The slope of each line increases considerably as the MC7+ increases. The slope jumped from 62 MMP/%N2 at an MC7+ of 120 g/mol, to 122 MMP/%N2 at an MC7+ of 250 g/mol. A low MC7+ is then desirable when injecting mixtures of CO2 and nitrogen.
- When plotted against the C7+ molecular weight, the effectiveness of nitrogen decreases considerably.
- **The effectiveness of N2 is deteriorated by the C7+ molecular weight of the displaced oil.**

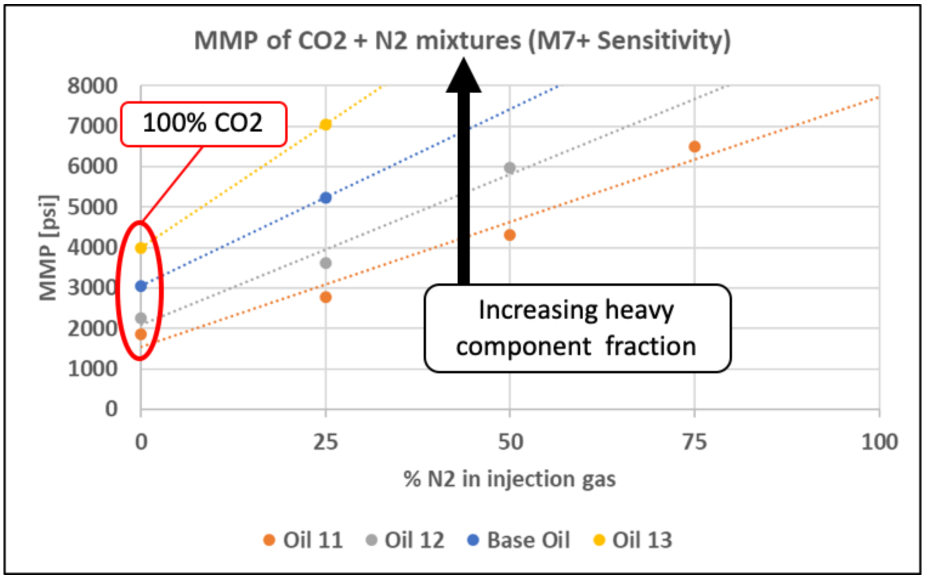

Figure 6-19: Effect of MC7+: MMP as a function of N2%

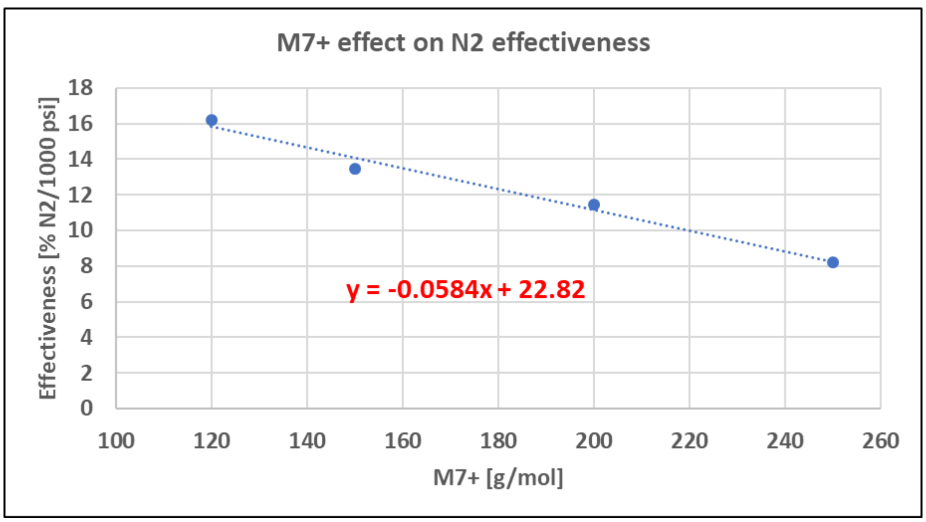

Figure 6-20: Effect of MC7+: N2 effectiveness as a function of MC7+

6.5 Combined Analysis

When given an oil composition, it is sometimes difficult to combine the effect of each of the three grouped components on MMP. A better way to analyze and compare different oil compositions is to combine the effect of the light and heavy molar fractions into the effect of the ratio between them. That way, the number of factors is reduced and better assessment can be made. Figure 6-21 and Figure 6-22 presents another way to look at all the results in one graph. The x-axis is the intermediate molar fraction and the y-axis is the MMP. Each shaded area enlightens results using the same injection gas. A total of 13 MMP values for different oil compositions are plotted.

For any injection gas, the MMP changes linearly with the intermediate molar fraction as long as the ratio between the light and heavy component stays constant. When this ratio changes, the corresponding MMP values fall away from the straight line. When using pure CO_2 injection gas, the ratio between light and heavy component has a negligible effect on the MMP. (Blue shade). However, as the percentage of lean gas is increased in the injection gas, this ratio has a stronger effect. In this particular case where T= 200F and MW(C7+)= 200 g/mol, varying the ratio between light and heavy fraction can change the MMP by a maximum of 200psi when using 100% CO_2, and up to 1200 psi when using 100% LG. Let's define the ratio between light and heavy molar fractions as:

$$Ratio = \frac{x_{heavy}}{x_{light} + x_{heavy}}$$

We observe that for the same intermediate fraction, higher ratio means higher MMP. **In general, it is desirable to have more volatile component than heavy.**

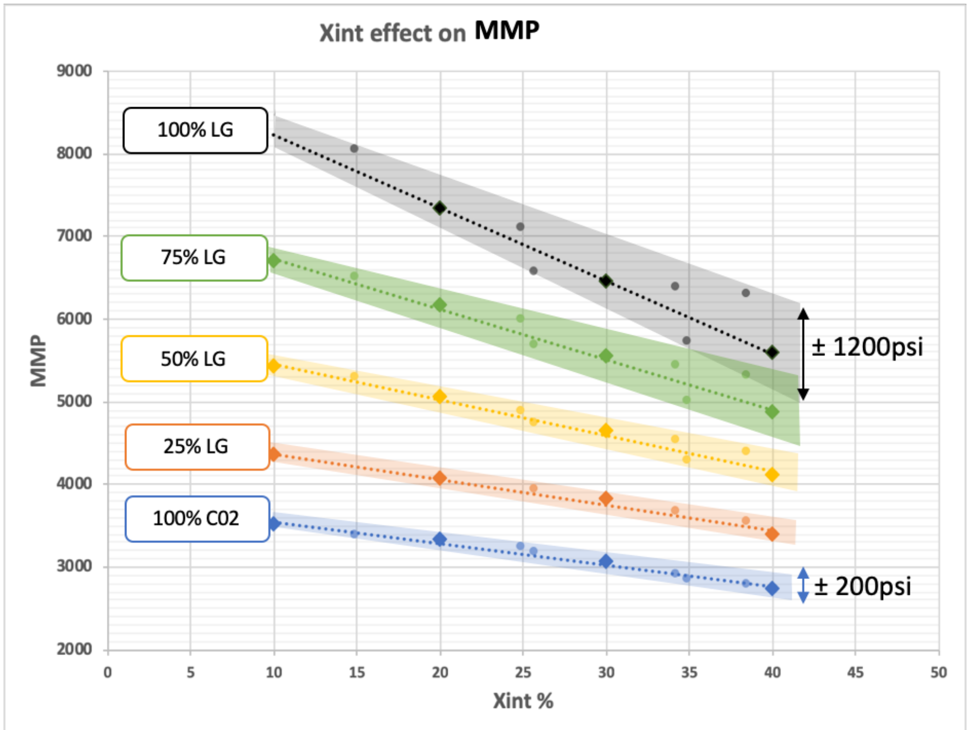

Figure 6-21: MMP as a function of Xint% for all cases using LG mixtures

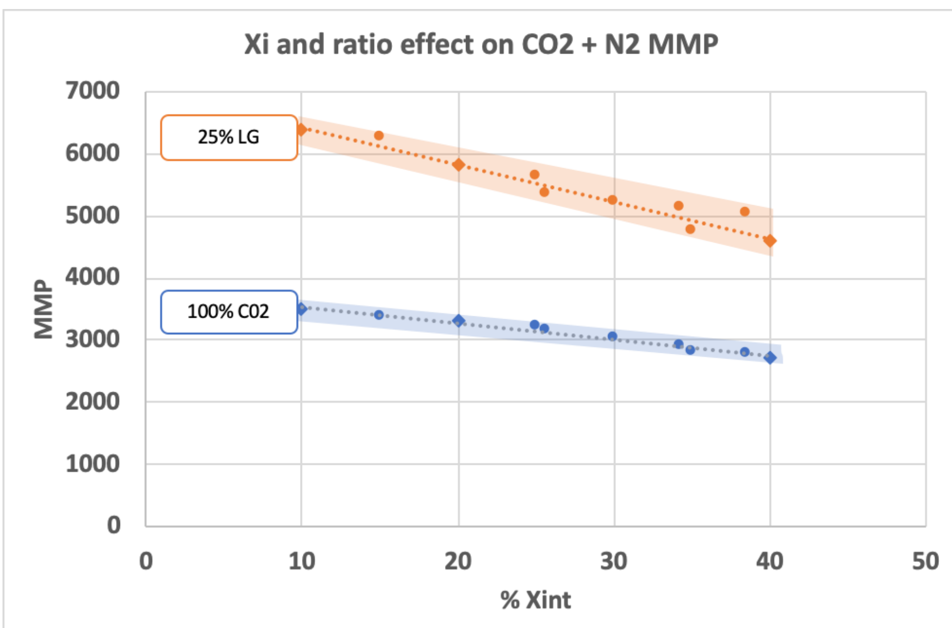

Figure 6-22: MMP as a function of Xint% for all cases using N2 mixtures

6.6 Summary of oil composition effect

6.6.1 Effect of oil composition on pure CO2 MMP

It is important to determine which of the MMP factors is the most influential when using 100% CO2. Figure 6-23 shows the MMP change per percent of molar fraction for the light component group, the intermediate group, and the heavy group side by side. The effect of MC7+ is also plotted but because the units are not the same, it should not be compared with the effect of oil composition. As mentioned before, the light and the heavy component fractions increase the MMP, while the intermediate component fraction decreases it. Furthermore, the light molar fraction is as influential as the heavy fraction. The intermediate molar fraction has a stronger effect on the CO2 MMP compared to the other components, almost double the effect of the other components. However, the MC7+ also has a very strong effect.

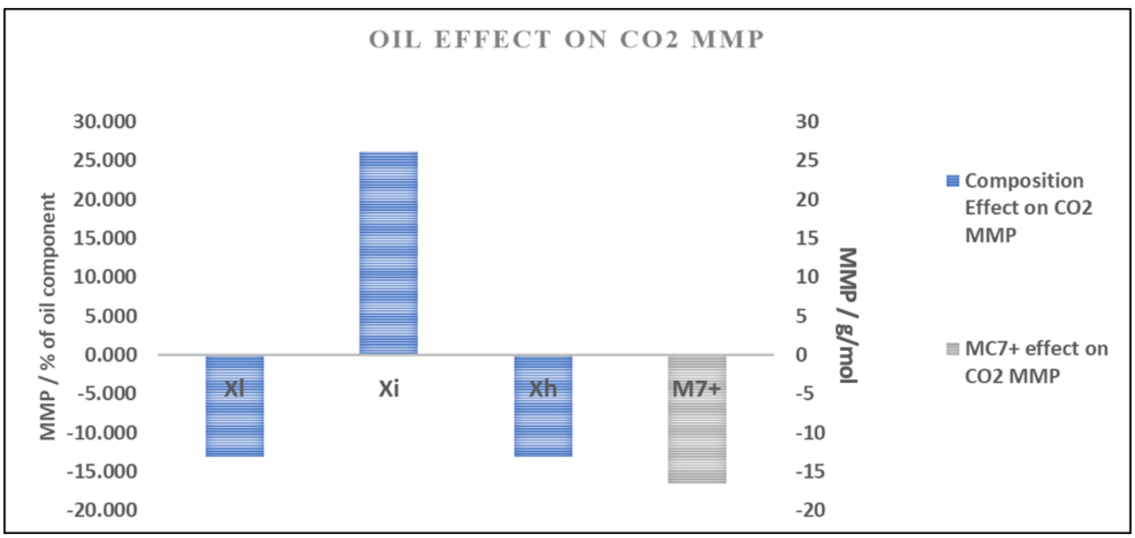

Figure 6-23: Summary of Effect of oil composition on CO2 MMP

6.6.2 Effect of oil composition on LG and N2 effectiveness

As a reminder, the lean gas effectiveness is measured as the change in MMP per percent of lean gas added to pure CO2. The lower that slope, the more effective it is. In this section, we are interested in the effect that the molar composition of the displaced oil has on this effectiveness. Figure 6-24 shows the change in lean gas effectiveness caused by the light, the intermediate and the heavy molar fractions, side by side. As discusses before, the light molar fraction does not influence the lean gas effectiveness, the intermediate improves it and the heavy molar fraction deteriorates it. Again, the intermediate molar fraction has the strongest influence, but the heavy molar fraction also has a strong influence.

The light component molar fraction does not affect the effectiveness of LG or N2. The intermediate component fraction increases both the N2 and the LG effectiveness. The effect on LG effectiveness is almost double the effect on N2 effectiveness. The heavy component fraction decreases the LG and N2 effectiveness. This effect is 3 times stronger on the LG effectiveness than on the N2 effectiveness. The C7+ molecular has the same effect than the C7+ fraction on the LG and N2 effectiveness.

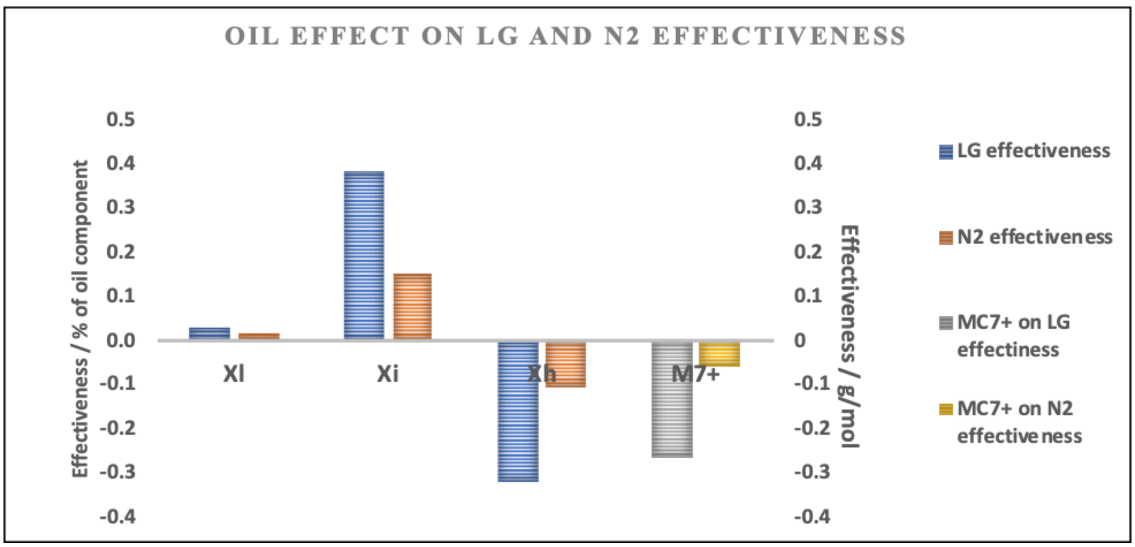

Figure 6-24: Summary of the effect of oil composition on LG and N2 mixtures

CHAPTER 7

Effect of Lean gas and Nitrogen

Now that the effect of the oil molar composition is understood, the focus can be turned to the injection gas composition. The goal here is to be able to predict when mixtures of nitrogen or lean gas with CO_2 can be used. It is considered that pressures above 7000 psi are not reasonable, thus setting our limits. Of course, the maximum allowable pressure is different for every reservoir.

Table 10 shows the effectiveness of lean gas and nitrogen in terms of MMP per percent of solvent added for the 13 oil compositions. Figure 7-1 shows the same results in form of a graph for better comparison, and Figure 7-2 shows the effectiveness in terms of percent of solvent per 1000 psi. The first observation is that the lean gas is at least twice as effective than nitrogen. On average, every percent of nitrogen added to the injection gas increases the MMP by 80 psi, when lean gas increases it by 40 psi. Lean gas is a better solvent to mix with CO_2 compare to nitrogen. For each solvent, the best case is highlighted in green and the worst case in yellow in Table 10. The best case for both lean gas and nitrogen is Oil 11. Oil 11 has the lowest heptane plus molecular weight, which explains why. The worst case for lean gas is Oil 10, which has a very low intermediate molar fraction. The worst case scenario for nitrogen is Oil 13, which has the highest heptane plus molecular weight. These effectiveness values are meaningless unless combined with the pure CO_2 MMP. With the pure CO_2 MMP known, the effectiveness can be used to calculate the maximum solvent fraction that can be used in the injection gas to stay within desired limits.

Table 10: LG and N2 effectiveness for all the cases

	Base Oil	Oil 2	Oil 3	Oil 4	Oil 5	Oil 6	Oil 7
LG	34	35	35	34	43	41	29
N2	87	91	90	88	116	101	76

	Oil 8	Oil 9	Oil 10	Oil 11	Oil 12	Oil 13
LG	29	39	46	16	23	40
N2	77	97	116	62	74	122

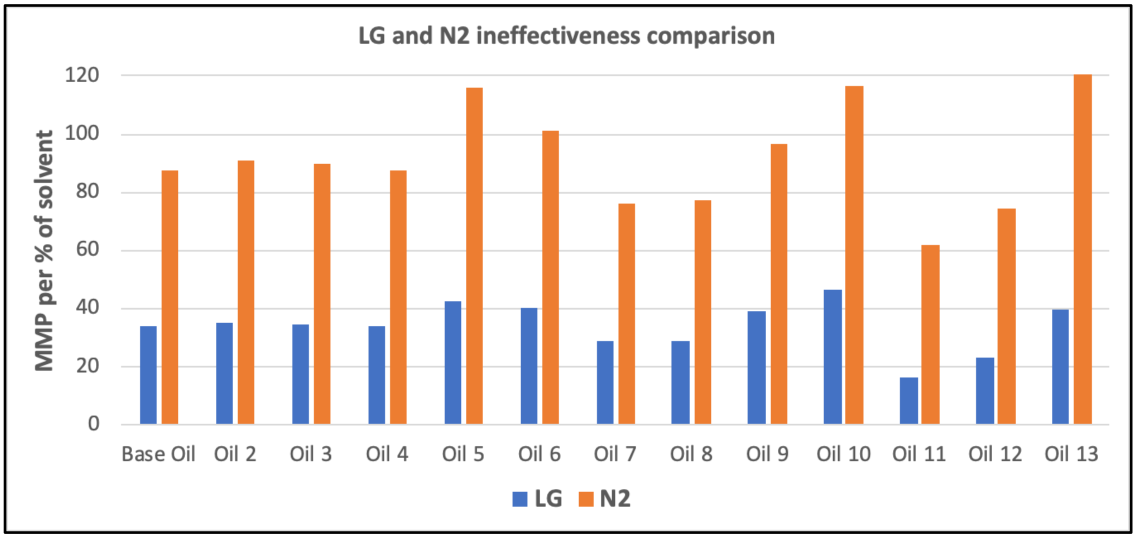

Figure 7-1: LG and N2 ineffectiveness comparison

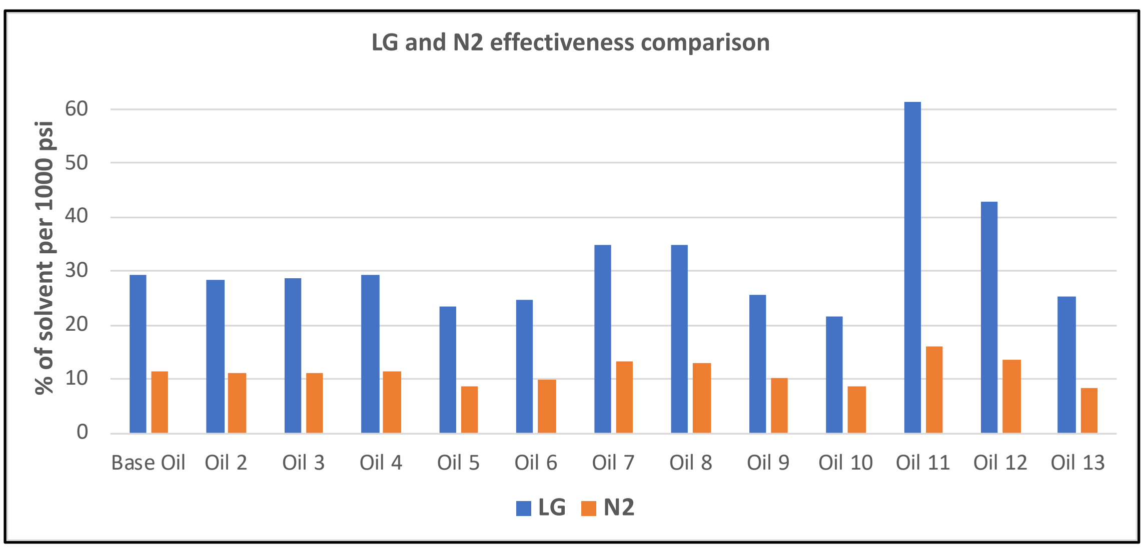

Figure 7-2: LG and N2 effectiveness comparison

The ultimate goal is to estimate the maximum amount of solvent that can be mixed with CO2 for gas injection purposes. To do this, the method is to combine the pure CO2 MMP and the added solvent effectiveness. For illustration purposes, let's assume that the maximum injection pressure for a field is 6000 psi. What would be the maximum allowable amount of solvent that can be added to CO2 in order to reach miscibility pressure below 6500 psi? Table 11 shows these results for the 13 oil compositions. Figure 7-3 shows a graph of these same results for comparison. Again, it can be seen on that graph, the lean gas is about twice as effective as the nitrogen. For each solvent, the best case is highlighted in green and the worst case in yellow in Table 11. For the lean gas, the worst case scenario was for Oil 13, which has the highest heptane plus molecular weight. Oil 13 is also the worst case scenario for the nitrogen. Oil 7, 8, 11 and 12, are miscible with 100% lean gas at pressures lower than 6000 psia. The best case scenario for nitrogen is Oil 11, with which the maximum fraction of nitrogen in the injection gas possible to reach miscibility at pressures lower than 6000 psi is 67%. Oil 11 has the lowest heptane plus molecular weight.

Table 11: Max % of solvent for a MMP leass than 6000 psia at 200 F

	Base Oil	Oil 2	Oil 3	Oil 4	Oil 5	Oil 6	Oil 7
LG	86%	92%	89%	83%	59%	66%	100%
N2	34%	35%	35%	32%	21%	27%	43%

	Oil 8	Oil 9	Oil 10	Oil 11	Oil 12	Oil 13
LG	100%	71%	57%	100%	100%	51%
N2	41%	29%	23%	67%	50%	16%

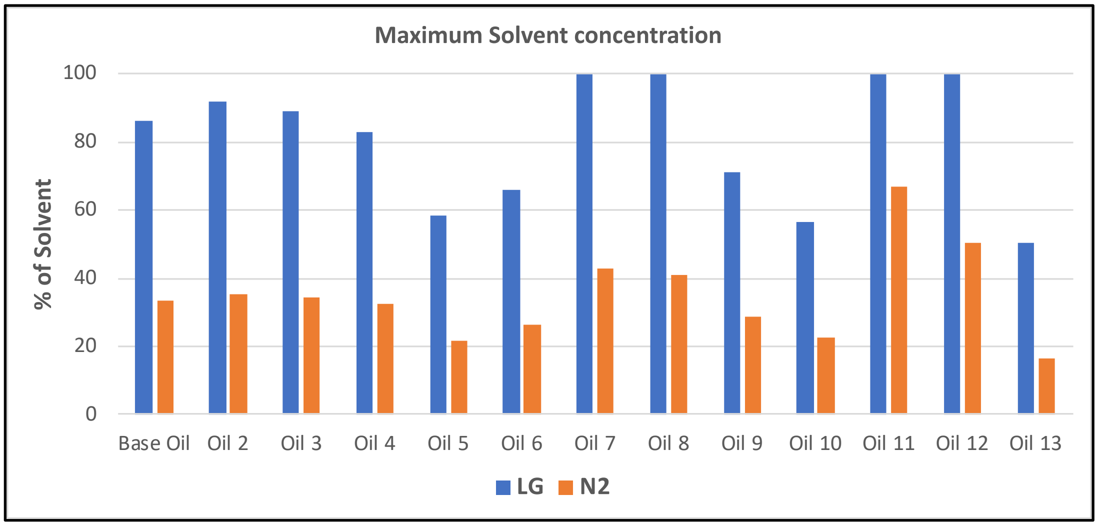

Figure 7-3: Max % of solvent for a MMP less than 6000 psia at 200 F

According to our previous analysis on the effect of oil composition, Figure 7-3 can be explained with the molar composition of the oil. Molecular weight has the strongest effect on MMP compared to the molar fractions. Oil 11 and 12 have the lowest heptane plus molecular weight, which explains why they are the best case scenarios. Oil 13 is the worst case scenario because it has the highest heptane plus molecular weight. All the other oil compositions have the same heptane plus molecular weight. The next most influential parameter is the intermediate molar fraction. Oil 7 is the fourth best scenario because it has the highest intermediate molar fraction. Oil 2 has a higher intermediate molecular weight than Oil 8, but because it also has a lower ratio of light to heavy molar fraction, it performs worse than Oil 8. Oil 5 and Oil 10 have the lowest intermediate molar fraction, which explains their relatively bad performance.

CHAPTER 8

Conclusion

The minimum miscibility pressure using mixtures of CO2, nitrogen and lean gas depend on the oil light molar fraction, the intermediate molar fraction, the heavy molar fraction, and the heptane plus molecular weight. The molecular weight molar fraction has the strongest effect, followed by the intermediate molar fraction. The effect of light and heavy molar fractions can be combined as the effect of the ratio of light to heavy molar fraction.

When analyzing mixtures of CO2 and nitrogen or lean gas, pure CO2 MMP and solvent effectiveness are the parameters of interest. The effect of oil composition on these two parameters are as follow:

Effect on CO2 MMP:

- Increasing the molecular weight of the heptane plus fraction increases the pure CO2 MMP.
- Increasing the intermediate molar fraction of the oil decreases the pure CO2 MMP.
- The ratio of light to heavy molar fraction has no effect on the CO2 MMP.

Effect on lean gas effectiveness:

- Increasing the molecular weight of the heptane plus fraction decreases the effectiveness of lean gas.
- Increasing the intermediate molar fraction of the oil increases the effectiveness of lean gas.
- Increasing the ratio of light to heavy molar fraction increases the effectiveness of lean gas.

Effect on nitrogen effectiveness:

- The effect of oil composition on nitrogen effectiveness is the similar in trends to the effect on lean gas effectiveness. The effects of each parameter are more pronounced on nitrogen than on lean gas.

Combining A total of 13 oil compositions were used in this study and here are the conclusions that can be drawn from them:

- MMP increases linearly with the fraction of lean gas or nitrogen added.
- Lean gas is twice as effective as nitrogen when it is mixed with CO2. Specifically to the 13 oil compositions in this study, on average each percent of nitrogen in the injection gas increases the MMP by 80 psi, while each percent of lean gas increases the MMP by 40 psi.
- For a maximum injection pressure of 6000 psi, the maximum lean gas fraction in the injection gas in order to reach miscibility ranges from 50% to 100%, depending on the oil composition. For a typical oil composition with 30% light component, 30% intermediate component, 40% heavy component fraction and 200 g/mol heptane plus molecular weight, up to 85% lean gas can be mixed with CO2 to reach miscibility pressure under 6000 psi.
- For a maximum injection pressure of 6000 psi, the maximum nitrogen fraction in the injection gas in order to reach miscibility ranges from 15% to 70%, depending on the oil composition. For a typical oil composition with 30% light component, 30% intermediate component, 40% heavy component fraction and 200 g/mol heptane plus molecular weight, up to 35% lean gas can be mixed with CO2 to reach miscibility pressure under 6000 psi.

CHAPTER 9

Recommendation

The numerical simulation estimation of miscibility pressure should be compared to more experiment results to validate this method for a larger range of oil composition. Experiments using nitrogen and lean gas are also needed to validate the numerical method using these different injection gases. Reaching miscibility using nitrogen may require very high pressures so the equipment should be able to handle such kinds of pressures. Slim-tube experiments are believed to provide better results compare to other experiments because it actually mimics the displacement of oil by gas injection. However, if multiple MMP values are required just like in this study, the RBA method may be considered because of its execution speed.

The work done in this study should be repeated at different heptane plus molecular weight and at different temperatures. The values and the trends may be different in different conditions. With enough data covering a large range of input parameters, a new correlation may be generated for mixtures of gases.

This study does not include any economic or operational analysis of injection of gas mixtures. Attaching an economic analysis to this study would reveal the gains and losses that come with these strategies.

Bibliography

Imad A. Adel, Francisco D. Tovar, and David S. Schechter, "Fast-Slim Tube: A Reliable and Rapid Technique for the Laboratory Determination of MMP in CO_2 - Light Crude Oil Systems", SPE-179673-MS, Improved Oil Recovery Conference, Tulsa, Oklahoma, USA, 11–13 April 2016.

Jamiu M. Ekundayo, "Minimum Miscibility Pressure Measurement with Slim Tube Apparatus - How Unique is the Value?", SPE 165966, SPE Reservoir Characterization and Simulation Conference and Exhibition, Abu Dhabi, UAE, 16–18 September 2013.

Ria Ayu Pramudita And Won S. Ryoo, "Minimum Miscibility Pressure Calculation For Co_2 Injection Flooding Based On Oil PVT Properties", Advances In Civil, Environmental, And Materials Research

Sheng, J. J. "Optimization of huff-n-puff gas injection in shale oil reservoirs", Advance Research Evolving Science, 2017.

Verma, M.K. 2015. Fundamentals of Carbon Dioxide-Enhanced Oil Recovery (CO2-EOR)—A Supporting Document of the Assessment Methodology for Hydrocarbon Recovery Using CO2-EOR Associated with Carbon Sequestration. *U.S. Geological Survey*.

Zhang, K.; Experimental And Numerical Investigation Of Oil Recovery From Bakken By Miscible Co_2 Injection, Ms. Department Of Energy Resources Engineering Of Stanford University, 2016

Zuo, Y.-X., Chu, J.-Z., Ke, S.-L. And Guo, T.-M., 1993. A Study On The Minimum Miscibility Pressure For Miscible Flooding Systems. Z Pet. Sci. Eng., 8: 315-328.

Appendix

MMP simulation results for 5 experiments

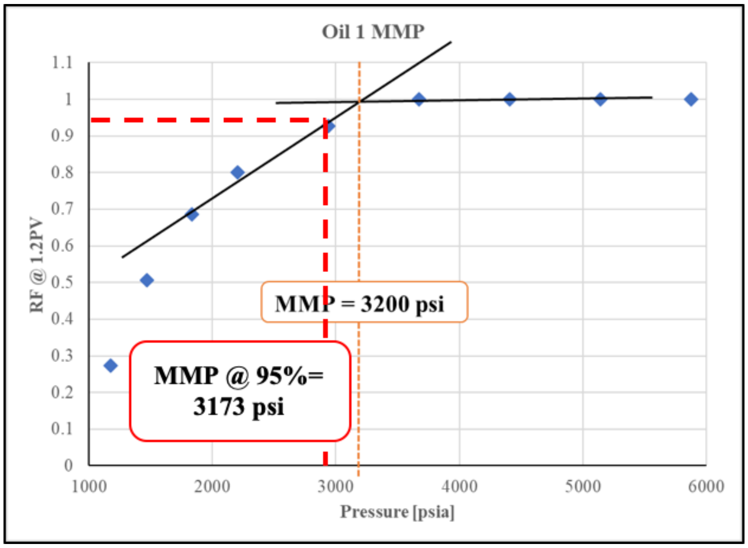

Figure 0-1: Experiment 1 numerical simulation MMP

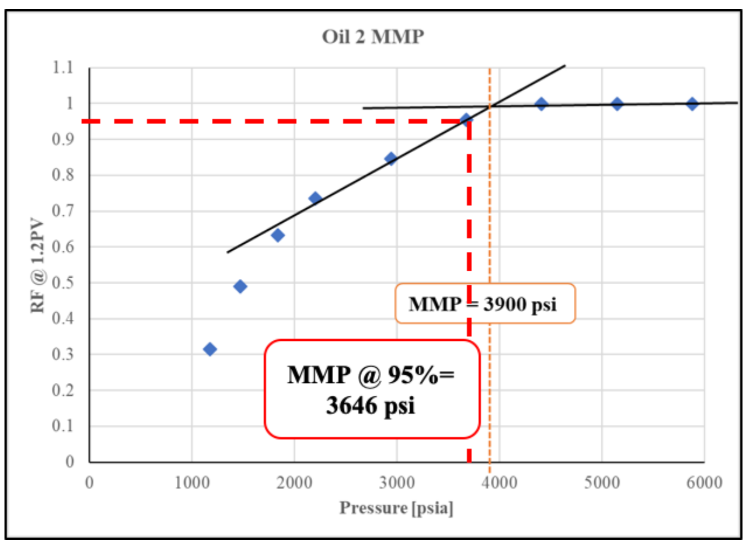

Figure 0-2: Experiment 2 numerical simulation MMP

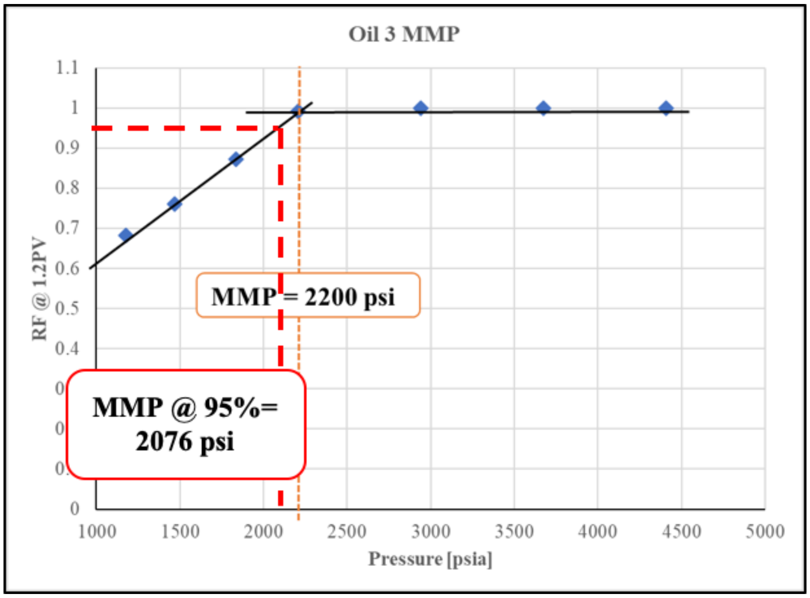

Figure 0-3: Experiment 3 numerical simulation MMP

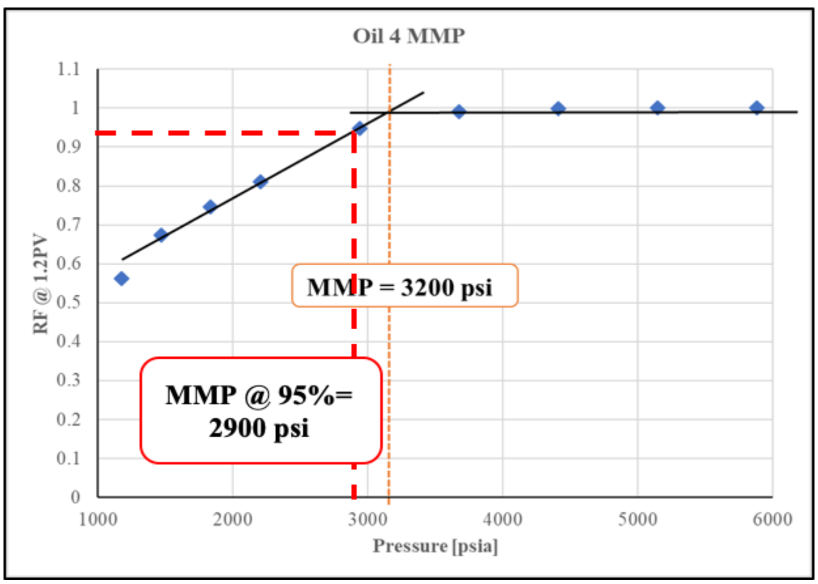

Figure 0-4: Experiment 4 numerical simulation MMP

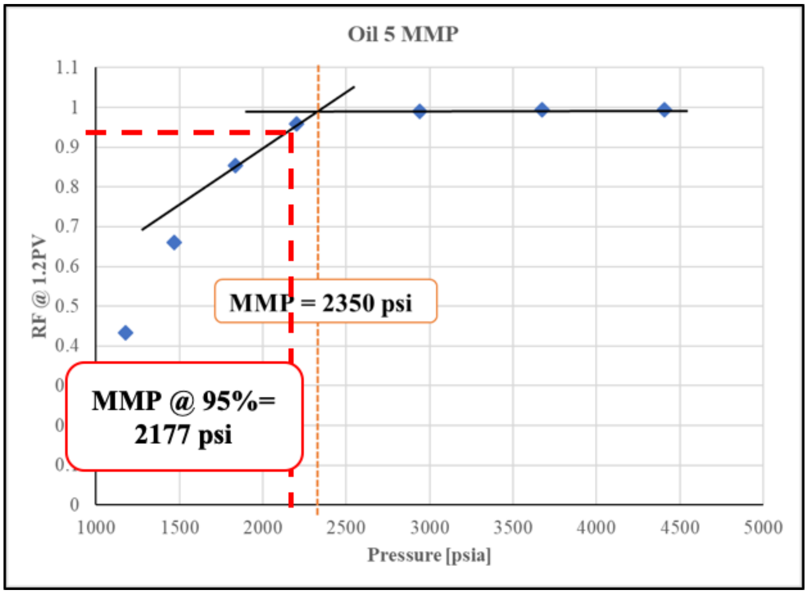

Figure 0-5: Experiment 5 numerical simulation MMP