A FLUID MODEL STUDY IN AN OIL/CO$_2$ SYSTEM

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Abstract. *A dependable project of solvent injection for enhanced oil recovery (EOR) process requires accurate representation of phase behavior between the injected and in-situ fluids in a wide range of pressure, temperature, and composition conditions. This article presents a fluid model study for carbon dioxide (CO$_2$) injection in an oil reservoir. The primary objectives of this study are to determine under what pressure and temperature conditions a vaporizing/condensing gas drive process occurs, and to identify the miscibility conditions by various special PVT experiments including swelling test and continuous multiple-contact experiments. These are reviewed along with their importance in building an accurate equation of state (EOS) model to be used in the compositional simulation. The procedure includes collecting samples from the literature based on field´s studies, the characterization of the oil, the determination of the number of pseudo-components, the tuning of the EOS parameters, the numerical EOS modeling of the fluids, the analysis of the phase regions and the development of dynamic miscibility, and the determination of the minimum miscibility pressure (MMP). The PVT simulator Winprop is used in the study. The results show that the implemented procedure provides a reliable and efficient tool for representing PVT properties and phase behavior of the reservoir fluids.*

Keywords: *Carbon Dioxide, Equation of State, Model Fluid, Enhanced Oil Recovery, Miscible.*

1. INTRODUCTION

The EOR of miscible CO$_2$ floods has been steadily increasing in the last few years, as has the number of projects have been developed as a successful oil recovery method in many reservoirs around the world. These projects has been furthered by the environmental motivation, the current high oil prices, the increasing worldwide oil demand, the maturation of oilfields worldwide, and few new-well discoveries (Aladasani and Bai, 2010; Alvarado and Manrique, 2010)

The phase behavior of the multicomponent fluid mixture study is necessary for better understanding the effects of different reservoir dynamic parameters for a successful CO$_2$ flooding and water alternating gas (WAG) projects. These projects are significantly affected by the match of experimental PVT data. Therefore, accurate characterization of the mixture composition and then tuning of the EOS model, used in a compositional simulator are crucial for the accuracy of the reservoir model. Reservoir fluids are classified in three categories of components: the well-defined components, single carbon number (SCN) fractions, and undefined petroleum fractions, which are those heavy compounds lumped together and identified as the plus-fraction (C$_{7+}$) (Pedersen, et al. 2007; Ahmed, 2007). The characterization of crude oil is an important step in the application of EOS for PVT predictions and phase behavior calculations. Various methods have been proposed for characterizing the C$_{7+}$ fraction. These methods are grouped into two main categories: splitting and lumping. The characterization of plus fraction usually consists of four parts: (1) splitting the fraction into a certain number of component groups called SCNs; (2) estimation of the physicochemical properties of the SCN; (3) lumping of the generated SCNs and (4) estimation of the physicochemical properties of the multiple carbon numbers (MCNs) (Pedersen, et al. 2007). The splitting to estimate the mole distribution of the compounds in the plus fraction and lumping to reduce the number of SCN groups into three to five MCN groups (pseudo-components) are used (Pedersen, et al. 1982; Ahmed et al. 1985; Whitson 1983; Whitson, 1980; Ahmed, 1989; Pedersen, et al. 1989; Danesh, 1998). EOS tuning techniques for accurate prediction have been studied (Coats, et al 1986; Pedersen, et al. 1989; Danesh, 1998; Ahmed, 2007).

In an Oil/CO$_2$ system the phase behavior have two main categories of miscible flooding mechanisms include: (1) First Contact Miscibility (FCM) and (2) Multiple Contact Miscibility (MCM). To achieve FCM, the flooding pressure should be higher than Minimum Miscibility Pressure (MMP). In MCM, miscibility between reservoir oil and the injected gas is after multiple contacts between the two fluids generated through condensing gas drive and vaporizing gas

drive (Stalkup, 1983; Danesh, 1998; Lake, 1998; Green and Willhite, 1998). In this study, the effects of CO_2 on oil physical properties are determined by commercial simulator and are verified by laboratory studies.

2. METHODOLOGY

The EOS characterization in this paper proceeds in five steps: 1) EOS characterization for CO_2 floods process 2) splitting the plus fraction (C_{7+}) to generate analytical PVT data using a detailed of C_7 up to C_{40+} pseudo-components characterization as original fluid; 3) lump the original fluid characterization to fewer pseudo-components and determine their properties; 4) tune the lumped EOS model to the PVT data using non-linear regression; and, 5) match the model with experimental PVT data.

2.1 EOS characterization

EOSs have been extensively used in industry to generate PVT and compositional phase behavior calculations of petroleum fluids. The Peng-Robinson (PR-EOS 1976, 1978) and Soave-Redlick-Kwong (SRK-EOS 1972) equations are most widely used in the petroleum industry. These EOSs were originally developed to predict PVT and phase behavior for pure substances with known critical properties and acentric factor. These EOSs together with the mixing rules are suitable for accurately predict the phase equilibria in multicomponent mixtures, such as hydrocarbon mixtures and hydrocarbon/CO_2 mixtures at wide range of pressures-temperature-composition conditions (Danesh 1998; Ahmed 2007; Okuno et al. 2010).

2.2 Splitting

Usually limited information on the composition of the reservoir fluid is available. This typically means a breakdown of non-hydrocarbon compounds (i.e., H_2S, CO_2, N_2), of hydrocarbon compounds into C_1-C_6 with the heavy end lumped as C_{7+} for which only the molecular weight and specific gravity information is available. The reservoir fluid composition expressed in mole percent is shown in Table A.1.

The splitting technique refer to the procedures of distribution the heptanes-plus fractions into hydrocarbon groups with a single carbon number (C_7, C_8, C_9… …C_{n+}), described by the same physical properties used for pure components. Three distribution functions are available in WinProp: exponential, two-stage exponential, and gamma distribution. The implementation of the distribution functions depends on the experimental data available.

The gamma distribution function was used to obtain distribution of carbon number of simple of C_7 up to C_{40+}. This extended analysis is shown in Figure 1. Only three mixture bulk properties such as molecular weight, specific gravity, and fraction of C_{7+} are needed for this technique. The gamma molar distribution is used to describe the molar distribution (mole fraction vs. molecular weight) for C_{7+} fractions.
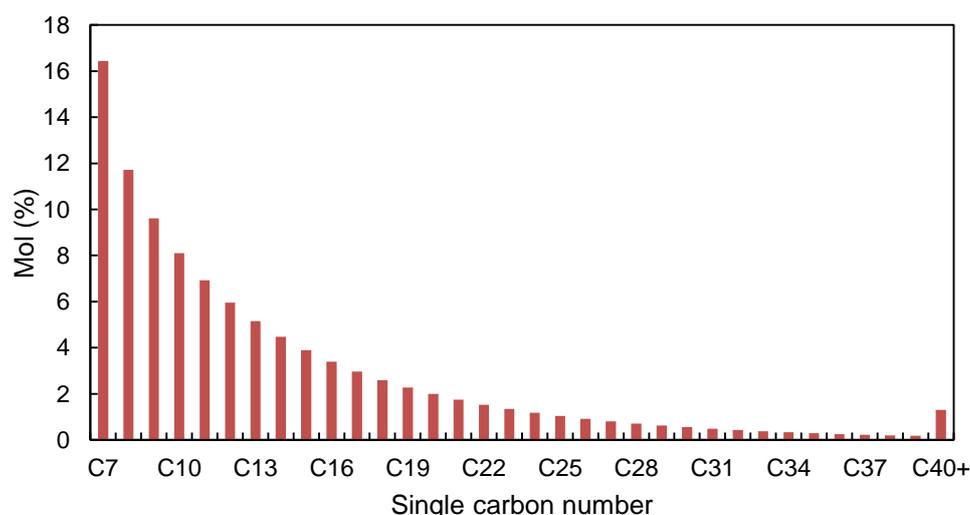
Figure 1. Saturation pressure with CO_2 concentration at 55°C.

2.3   Lumping

The use of a large number of components in compositional reservoir simulation is time consuming. Hence, the reduction the number of components used would ease the process of simulation. However, during the process of decreasing the number of hydrocarbon components, care should be taken so that the fluid properties do not change too much in comparison with the original fluid. Pedersen et al. (2007) state that lumping consists of two parts: (1) deciding what carbon number fractions are to be lumped into same pseudo-component and (2) deciding the mixing rules that will average T_c, P_c, ω of the individual carbon number fractions to one T_c, P_c, ω to represent the lumped pseudo-components.

The lumping scheme is shown in Table 1. This was used to group the 44 components system into 7 pseudo-components. The non-hydrocarbon component CO_2 was kept separate, light hydrocarbon components and non-hydrocarbon component (N_2) were grouped together (C_1-N_2), intermediate hydrocarbon components were grouped (C_2-C_3) and (IC_4-C_6), and heavier hydrocarbon components formed between C_7 and C_{40+} were also grouped together into three pseudo-components. After components are grouped into pseudo-components, it is necessary to determinate the pseudo-properties (T_c, P_c, ω) using the Lee-Kesler mixing rules, (Lee and Kesler 1975). The application of mixing rules implies that pseudo-properties such as (T_c, P_c, ω) should be known for all the components of the mixture, and then grouped together to perform calculations (Danesh 1998; Ahmed 2007). The compositions of characterized oil and solvent are shown in Table.A.2.

Table 1. Lumping and splitting components system.

Components Original System	Operation	Pseudo-Components Final System	Pseudo-Components for Ternary Diagram
CO_2		CO_2	CO_2
N_2	Lumping	N_2-C_1	N_2-C_6
C_1			
C_2	Lumping	C_2-C_3	
C_3			
iC_4	Lumping	iC_4-C_6	
nC_4			
iC_5			
nC_5			
C_6			
C_{7+}	Splitting and Lumping	HP01	C_{7+}
		HP02	
		HP03	

2.4   Tuning EOS parameters

The EOS is used to predict the phase behavior when crude oil and gas mix in the reservoir. This EOS fluid characterization must be tuned to minimize the difference between the predicted and experimental data. The tuning of the EOS follows the methodology: (1) selection of the pseudo-components; (2) determination of EOS properties for the pseudo-components; and (3) adjustment of pseudo-component EOS properties by regression to the PVT data.

The EOS parameters used to achieve a match between the two results, experimental and numerical are:

- Properties of the lumped pseudo-components that include T_c, P_c, and ω.
- Binary interaction coefficient, δ_{ij}, between the CO_2 and lumped pseudo-components.
- When an injection gas is a non-hydrocarbon components (CO_2 and N_2), the binary interaction, δ_{ij}, between these fractions and hydrocarbon also should be modified.

PVT laboratory sample data based on field's studies were used in the tuning of the EOS. PVT laboratory data included constant composition volumetric expansion (CCVE) and multiple contact tests. These data were used to tune an EOS capable of characterizing the CO_2/reservoir-oil system above the minimum miscibility pressure (MMP).

2.5 Match the model with experimental PVT data

After lumping 40 components into 7-pseudo-component fluid system, a regression adjustment was done to fit saturation pressure data and a swelling test. The main parameters used to match were the binary interaction coefficients between CO_2 and pseudo-components of the C_{7+} and CO_2 volume shift.

3. RESULTS

3.1 Physical properties of pseudo-compenents

The fluid properties of system into 7 pseudo-components are calculated using the EOS and mixing rules. This is the final step in the characterization procedure, and the resulting hydrocarbon mixture description is given in Table 2, below.

Table 2. Properties of the fluid characterized

Pseudo-Component	P_c (MPa)	T_c (K)	ω	Mw (g/mol)	SG	T_b (°C)
N_2 - C_1	4.5894	189.9641	0.0083	16.1557	0.3031	-160.1082
CO_2	7.3765	304.2000	0.2250	44.0100	0.8180	-78.4500
C_2 - C_3	4.5362	341.7704	0.1270	37.6115	0.4383	-46.9870
IC_4 - C_6	3.5398	458.1032	0.2271	69.0217	0.6259	31.9125
HYP01	2.7863	592.7747	0.3308	115.1488	0.7654	132.2769
HYP02	1.5661	759.2653	0.6749	230.2260	0.8406	306.5642
HYP03	0.8916	946.9789	1.1762	475.0000	0.9273	521.6830

3.2 Match Model

Results for the numerical simulations comparison of predicted pressure saturation whit corresponding experimental data by Chaback et al. (1988), was summarized in Figure 2. Figure 3 shows the swelling factor with CO_2 composition predict for EOS before and after of the tuned EOS parameters to achieve the match.
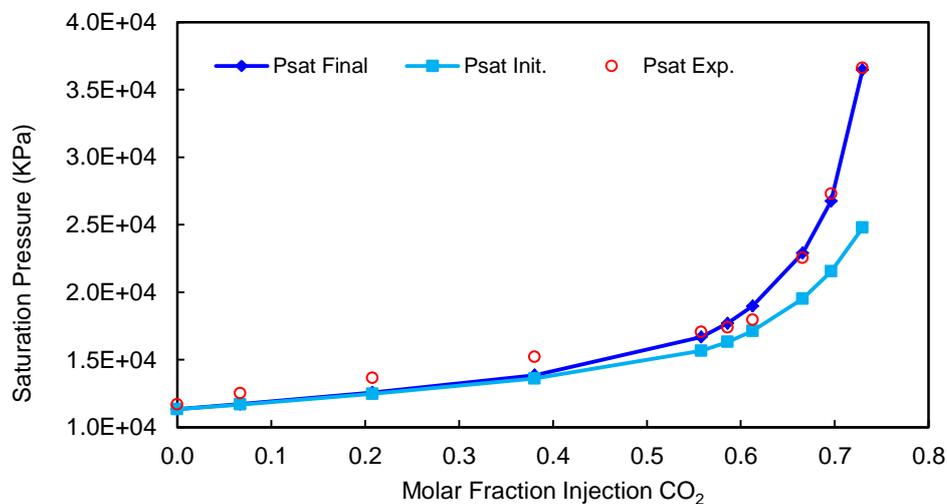
Figure 2. Comparison of saturation pressure experimental and simulated data with tuned EOS and non-tuned EOS at 55°C.
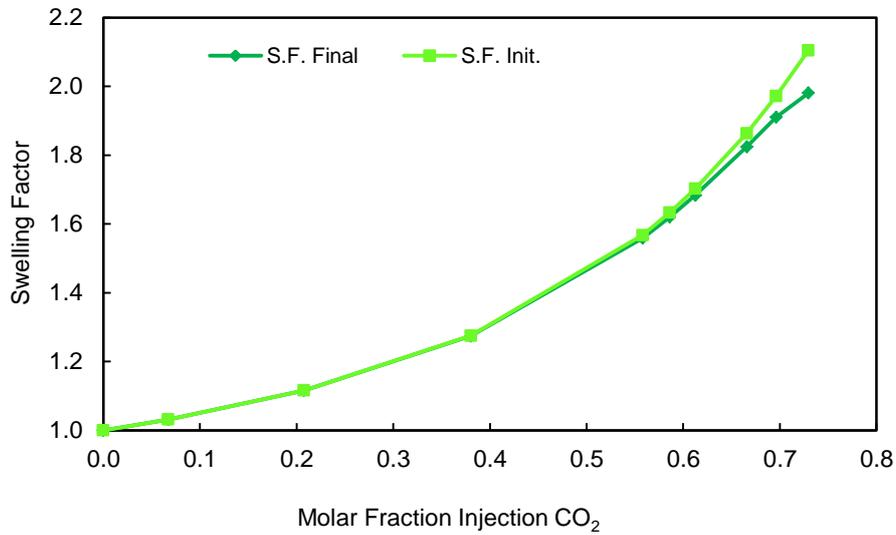
Figure 3. Comparison of swelling factor tuned EOS and non-tuned EOS at 55°C.

3.3 Numerical results

Results of behavior phase are shown using ternary diagrams at several pressures constructed using EOS model. These diagrams are used to predicting dynamic miscible displacement performance of CO_2/oil systems and evaluate various injection strategies.
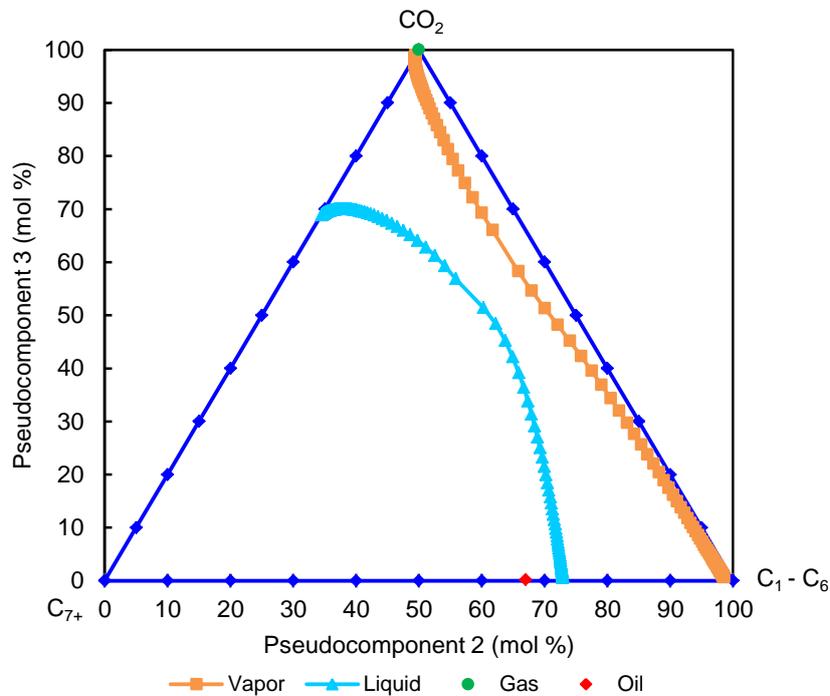
Figure 4. Ternary diagram for C_{7+}, C_1-C_6 and CO_2 at 16.000 MPa and 55°C.

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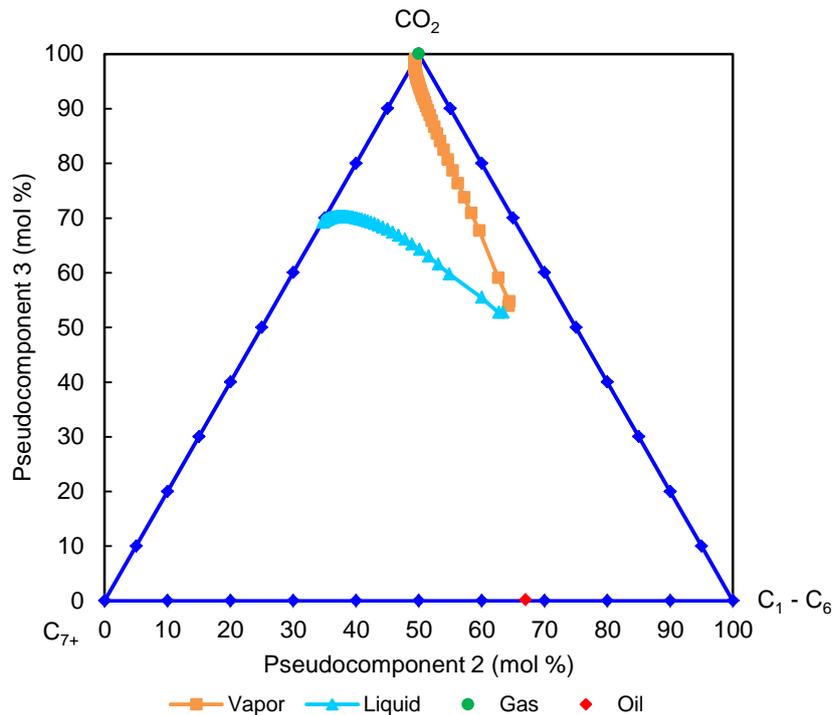
Figure 5. Ternary diagram for C_{7+}, C_1-C_6 and CO_2 at 17.053 MPa and 55°C.

Figure 4 shows that the ternary diagram CO_2 and oil reservoir are separated by a region of two phases being immiscible under these reservoir conditions. The extent of the two-phase region depends on the pressure. For a constant temperature, the size of the two-phase region decreases as the pressure increases.

Figure 5 presents the results at a given pressure, where two-phase region was broken, delimiting the region by dew-point curve and bubble-point curve, which are joined at the critical point. This condition represents the minimum miscibility pressure, at this condition, the CO_2 mixes with the reservoir fluid and a mixture composition, separates into a gas phase and liquid phase at equilibrium condition. The CO_2 mixes with oil developing miscibility for multiple contacts by the combination of vaporizing and condensing.

4. CONCLUSION

This work has presented a methodology for obtain a fluid model with pseudo-components for compositional simulation, and their conclusions are given below:

- Heavier components (C_{7+}) must be characterized accurately for EOS-component selection. Rigorous splitting and lumping methods, such as number of components minimization is necessary, since the fluid properties do not change too much in comparison with the original fluid and robust solution techniques are needed to model CO_2 flooding processes;
- The volume shift parameter should be included with the parameters δ_{ij}, T_c, P_c, and ω when tuning the EOS in the prediction of multiple contact experiment;
- The experimental study that comprises fundamental studies of phase equilibria in the crude oil/ CO_2 system are required for adjustment the EOS model;
- The MMP estimated by the EOS model is close to what determined from the multiple contact experiment;
- The procedures adopted in this work may be extended to simulate CO_2-EOR coupled carbon storage projects, provided that good quality of data is available.

5. ACKNOWLEDGEMENTS

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A. Appendix - PVT Oil Data

Table A.1. Composition oil and solvent, properties of heavier fraction

Component	Compositions (mol%)	
	Oil	Solvent
N_2	0.28	
C_1	29.45	
CO_2	0.20	100.00
C_2	10.44	
C_3	12.14	
IC_4	0.57	
NC_4	6.08	
IC_5	1.48	
NC_5	2.96	
FC_6	3.45	
C_{7+}	32.95	
Total	100.00	100.00
Molecular weight C_{7+}	190.00	
Specific gravity C_{7+}	0.83	
API gravity	37.50	
Bubblepoint temperature, °C	55.00	
Bubblepoint pressure, MPa	11.69	

Source: Fonte: Chaback et al. (1988)

Table A.2. Lumping and mole fraction of the 7 pseudo-components system.

N°	Pseudo-Component	Mole Fraction (%)	
		Oil	Solvent
1	N_2 - C_1	29.73	
2	CO_2	0.20	100.00
3	C_2 - C_3	22.58	
4	IC_4 - C_6	14.54	
5	HYP01	17.34	
6	HYP02	12.87	
7	HYP03	2.74	