

# UNIVERSIDADE ESTADUAL DE CAMPINAS FACULDADE DE ENGENHARIA MECÂNICA E INSTITUTO DE GEOCIÊNCIAS

JUAN NICOLAS TAUTIVA CALDERON

# Determination of Relative Permeability Curves of Equilibrated Carbonated Brine-Recombined Oil System Using a Compositional Simulator at Reservoir Conditions

Determinação das Curvas de Permeabilidade Relativa do Sistema Salmoura Carbonatada Equilibrada- Óleo Recombinado Usando um Simulador Composicional em Condições de Reservatório

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Orientador: Dra. Erika Tomie Koroishi Blini Coorientador: Dr. José Ricardo Pelaquim Mendes

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# UNIVERSIDADE ESTADUAL DE CAMPINAS FACULDADE DE ENGENHARIA MECÂNICA E INSTITUTO DE GEOCIÊNCIAS

DISSERTAÇÃO DE MESTRADO ACADÊMICO

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# Dedication

This work is dedicated to my mother and father, who have always been my inspiration and my guide. Their support and encouragement have been essential in helping me achieve my goals. I am grateful for their love and sacrifice, and I hope to make them proud with this accomplishment. I also dedicate this dissertation to my grandmothers whose love, encouragement, and solid faith in me have been a constant source of inspiration. I am grateful for their presence in my life. To my sister for her support and "friendship". I hope that this achievement inspires her to pursue her own dreams and aspirations.

Lastly, I would like to express my gratitude to my friends whose insights and support have been invaluable in forming this work. I would also like to extend my thanks to all the people who have been involved in this process, including my professors, colleagues, and mentors. Without their guidance, this work would not have been possible.

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# Resumo

Nos últimos anos, tem havido um crescente interesse no estudo do comportamento da permeabilidade relativa em meios porosos devido à sua importância fundamental na previsão do comportamento do fluxo de fluidos em reservatórios de petróleo. Portanto, a compreensão do comportamento da permeabilidade relativa em fluxos multifásicos é essencial para diversas aplicações, incluindo recuperação de petróleo, simulação de reservatórios e armazenamento geológico de CO2.

Os pesquisadores têm utilizado técnicas de coreflooding para medir as permeabilidades relativas em diferentes condições, a fim de entender o comportamento do escoamento multifásico. Este trabalho apresenta o desenvolvimento de um modelo em escala de laboratório para o processo de drenagem em estado transiente e descreve uma metodologia para ajustar as curvas de permeabilidade relativa com base em dados experimentais. Os dados experimentais foram usados para determinar as curvas iniciais de permeabilidade relativa para um sistema de água carbonatada equilibrada (ECB) e óleo recombinado em rochas carbonáticas pré-sal brasileiro em condições de reservatório. A validação do modelo foi realizada comparando os dados experimentais de coreflooding, incluindo pressão diferencial, produção de óleo e curvas de saturação, obtidos através de um balanço de massa. O modelo de simulação foi rodado utilizando o simulador composicional GEM/CMG e foi ajustado com a ferramenta CMOST/CMG. Os resultados do ajuste histórico forneceram valores ajustados dos exponentes de Corey para a curva de permeabilidade relativa para o teste de drenagem.

**Keywords**: Injeção de água carbonatada, Permeabilidade relativa, Rocha carbonática, Simulação composicional, Ajuste histórico, Escala de laboratório.

# Abstract

In recent years, there has been a growing interest in the study of relative permeability behavior in porous media due to its fundamental importance in predicting fluid flow behavior in oil reservoirs. Thus, an understanding of the relative permeability behavior of multiphase flow is essential for a range of applications, including enhanced oil recovery, reservoir simulation, forecasting and geologic CO<sub>2</sub> storage. Researchers have used coreflooding techniques to measure relative permeabilities under different conditions to understand multiphase flow behavior. This work presents the development of a laboratory-scale model for the unsteady-state drainage process and presents a methodology to adjust the relative permeability curves through history matching with experimental data. The experimental data was used to determine an initial relative permeability curves of equilibrated carbonated brine (ECB)-recombined oil system in Brazilian pre-salt carbonate rocks at reservoir conditions. The model validation was performed with coreflooding experimental data (differential pressure, oil production, and saturation curves) obtained using mass balance. The simulation model was run using the composition simulator GEM/CMG and adjusted with CMOST/CMG tool. The history matching results for the relative permeability curve provided Corey's exponents values for the drainage test.

**Keywords**: Carbonated water Injection, Relative permeability, Carbonate rock, Compositional Simulation, History matching, Laboratory scale.

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# **1 INTRODUCTION**

Oil is one of the world's most important energy sources for economic development and its high-energy demand. In recent years, the decline in oil production worldwide, the increase of mature oil fields, and the high costs of exploration and oil prices are encouraging the petroleum industry to invest in research and development of more efficient production methods (IEA, 2020).

Oil production is generally developed in three forms of recovery: primary, secondary, and tertiary or Enhanced Oil Recovery (EOR) methods. Primary oil recovery refers to oil production using the natural energy of the reservoir and its fluids and the difference in pressure between the reservoir and the production well pressure. Secondary oil recovery is generally used when primary oil production is not efficient, and a fluid is injected (gas or water) into the reservoir to increase the reservoir pressure. Enhanced oil recovery is applied to improve oil displacement efficiency and sweep efficiency to increase the total amount of oil recovered. The method usually targets the modification of interfacial tensions, wettability, and the mobility of the fluids through different techniques (thermal, chemical, solvent and others) (AHMED, 2006).

The exploration of pre-salt carbonate reservoirs in Brazil has unveiled substantial oil reserves under high-pressure conditions(FORMIGLI; CAPELEIRO PINTO; ALMEIDA, 2009). However, these reservoirs also pose a challenge due to the significant presence of  $CO_2$ , which cannot be released into the atmosphere due to environmental concerns. To address this issue, one promising solution is the reinjection of  $CO_2$  back into the reservoir. This approach not only enhances oil production beyond traditional recovery methods but also facilitates  $CO_2$  storage, thus contributing to the reduction of  $CO_2$  emissions. (PIZARRO; BRANCO, 2012).

As highlighted by Perera et al. (2016), CO<sub>2</sub> flooding for enhanced oil recovery (EOR) has proven to be a highly cost-effective technique for extracting additional oil from various types of reservoirs, including light, medium, and heavy oil. This approach has been widely implemented worldwide for over five decades, showcasing its enduring effectiveness and economic. The experimental investigations demonstrated a substantial enhancement in oil recovery, with an increase of up to 40% of the original oil in place, using CO<sub>2</sub> injection (HADLOW, 1999). The improved oil recovery can be attributed to several key factors, primarily associated with the reduction in interfacial tension, expansion of oil droplet

volumes, viscosity reduction, and mobilization of lighter components within the oil (BISWESWAR; AL-HAMAIRI; JIN, 2020).

The implementation of  $CO_2$  in oil displacement processes can be carried out through miscible and immiscible operations. However, achieving  $CO_2$  miscibility in certain reservoirs can be challenging due to various factors such as fluid composition properties, in-situ pressure, and temperature conditions. The miscibility between  $CO_2$  and reservoir oil is crucial for the success of  $CO_2$  injection-based miscible flooding enhanced oil recovery (EOR) and simultaneous  $CO_2$ -EOR and storage. Therefore, a comprehensive understanding of the fundamentals, including the theory, scientific principles, and engineering applications, of  $CO_2$ -reservoir oil miscibility is essential for the effective design, implementation, and operation of a miscible  $CO_2$ -EOR project (SAINI, 2019).

The drawback of using  $CO_2$  flooding is its high mobility, which can lead to finger-like patterns and reduce the sweep efficiency. In order to mitigate premature gas breakthrough, one of the techniques proposed is carbonated water injection. This technique exhibits favorable characteristics such as reduced fluid mobility and enhanced sweeping efficiency. By lowering the overall viscosity of the oil, carbonated water injection improves the overall sweep efficiency, thereby allowing for greater dissolution of oil compared to  $CO_2$  injection (SOHRABI et al., 2012).

Extensive experimental and numerical modeling investigations conducted in recent decades have focused on examining the behavior of biphasic systems in various rock samples (BURNSIDE; NAYLOR, 2014). These studies have utilized a combination of unsteady-state and steady-state core-flooding techniques to measure crucial parameters, including initial water and residual CO<sub>2</sub> saturations, as well as drainage and imbibition relative permeabilities, among other system properties. By conducting studies under diverse flow, temperature, and pressure conditions, researchers aim to enhance their understanding of multiphase flow in porous media and effectively replicate the recovery mechanisms observed in real reservoirs (HANARPOUR; MAHMOOD, 1988). The accurate estimation of relative permeability curves holds immense importance in various aspects of oil reservoir management. It plays a critical role in optimizing oil production, assessing the economic viability of a reservoir (GUO et al., 2017), improving reservoir modeling to ensure reliable and accurate results (AL-OTAIBI; AL-MAJED, 1998), and facilitating the design of an effective enhanced oil recovery process (LIAN; CHENG; MA, 2012).

## 1.1 Motivation

Relative permeability data obtained through laboratory measurements on cores extracted from the reservoir of interest are widely acknowledged as the most reliable source for reservoir evaluations. However, due to economic and time constraints, it is not always feasible or practical to acquire relative permeability data for every rock type of interest. In such cases, alternative approaches have been proposed to estimate relative permeability curves and enhance the accuracy of reservoir models using reservoir simulation tools.

Carbonated water injection (CWI) has been proposed as an efficient alternative to  $CO_2$  injection technique for enhanced oil recovery (EOR) in carbonate reservoirs. However, the physical-chemical phenomena involved in CWI are very complex and have been ignored in reservoir production (BISWESWAR; AL-HAMAIRI; JIN, 2020). The  $CO_2$  injection into the reservoir changes the relative permeabilities due to the interaction between the fluids and the porous medium resulting in a change in the fluids production (MAHZARI et al., 2018) . Due to the complexity of these processes, there have been some concerns raised regarding the modeling of  $CO_2$  mass transfer and its effect in the relative permeability curve.

To address these concerns, this research proposes to develop a model to reproduce a coreflooding experiment, thereby improving the capability of commercial simulators to replicate the processes involved in lab scale experiments. The simulated model approach and parameters will be modified by using history matching with the experimental data in order to capture the observed behavior and as a main focus estimate the relative permeability curves of the carbonated water-oil system. This will help to improve the accuracy of reservoir models and optimize oil production in carbonate reservoirs using CWI as an EOR technique.

Research works considering reservoir conditions for this system are limited in the literature, so the present work is a significant advance in simulating reservoir behavior from experimental data and building the relative permeability curves on a simulated fitting model. In addition, the research provides a methodology using the commercial simulator GEM from Computer Modelling Group (CMG) to reproduce the results of core flooding experiments and show more realistic and reliable results.

## **1.2 Objectives**

The research work aims to adequately reproduce a laboratory-scale model for the unsteady-state drainage process to determine the relative permeability curves of the equilibrated carbonated brine-recombined oil system in Brazilian pre-salt carbonate rocks under reservoir conditions using the commercial simulator GEM/CMG and the history matching tool CMOST/CMG.

In relation to the simulation of the carbonated water injection process, the following specific objectives have been identified:

- Understand the various physical mechanisms involved in Carbonated water injection (CWI).
- Model the multiphase flow and compositional alterations in the fluids during CWI.
- Apply an equation of state tuning method to simulate the interaction between the fluids in the porous media during CWI.
- Provide a reference to identify the parameters that contribute to the enhancement of simulations of CWI.
- Perform a history matching process using an actual coreflooding experiment carried out at the Laboratory of miscible methods of recovery (LMMR) to validate the simulation model.

# **2 LITERATURE REVIEW**

This chapter presents an overview of the fundamental concepts related to the fluid flow in porous media, the processes involving fluids and rock interaction, PVT tests, recombined oil, relative permeability, EOR-CO<sub>2</sub> methods, carbonate reservoirs, and a background review involving the relative permeabilities related to the carbonated water-oil systems and simulation.

## 2.1 Oil properties

Crude oil is a combination of hydrocarbons and minor components such as nitrogen, sulfur, oxygen, and helium (AHMED, 2006). The principal properties in petroleum engineering studies are gas-oil ratio, oil formation volume factor, viscosity, and compressibility.

# 2.1.1 Solution Gas-Oil Ratio (GOR)

The quantity of gas that can dissolve in a single stock-tank barrel of crude oil at a specific temperature and pressure is referred to as gas oil ratio (GOR). The gas solubility in crude oil is highly dependent on various factors such as the pressure, temperature, API gravity, and gas gravity (AHMED, 2006).

Under constant temperature conditions, the gas-oil ratio exhibits a progressive increase as pressure rises until it reaches saturation pressure. Once the bubble point pressure is reached, all gases become fully dissolved in the oil, resulting in maximum gas solubility.



Figure 2-1 Gas solubility pressure diagram. Source: AHMED (2006).

When laboratory analyses of the reservoir fluids are unavailable, it is possible to estimate the gas-oil ratio using empirical correlations. In 1947, Standing proposed a correlation method to estimate the gas-oil ratio from the following properties reservoir pressure, the reservoir temperature, the gravity of the oil tank, and the specific gravity of the produced gas as shown in Equation 2.1.

$$R_s = \gamma_g \left[ \left( \frac{p}{18.2} + 1.4 \right) 10^a \right]^{1.204}$$
 Eq. 2.1

Where,

 $\gamma_g = Specific \ gravity$   $a = 0.00091(T - 460) - 0.0125 \ API$   $T = temperature, ^F$ p = pressure, psia

## 2.1.2 Oil formation volume factor

The oil formation volume factor  $(B_0)$  is a dimensionless quantity that represents the ratio of the volume of oil in the reservoir at its original pressure and temperature conditions to

the volume of oil that the same mass of oil would occupy at standard surface conditions. It should be noted that the value of  $B_0$  is always greater than or equal to 1, as the volume of oil in the reservoir is always greater than or equal to the volume of oil at standard surface conditions. The factor can be expressed as:

$$B_o = \frac{(V_o)_{p,T}}{(V_o)_{sc}}$$
Eq. 2.2

Where,

 $B_o = oil formation volume factor, bbl/STB$  $(V_o)_{p,T} = volume of oil under reservoir pressure p and temperature T, bbl$  $(V_o)_{sc} = volume of oil under standard conditions, STB$ 

The curve of the oil formation volume factor ( $B_o$ ) as a function of subsaturated crude pressure is shown in Figure 2-2. The  $B_o$  increases at pressure values below the initial reservoir pressure ( $P_i$ ) due to the oil expansion, which will continue up to bubble point pressure ( $P_b$ ). At the bubble point pressure ( $P_b$ ), the oil undergoes maximum expansion, leading to the highest value of oil formation volume factor ( $B_{ob}$ ). When the pressure falls below  $P_b$ , the oil volume and  $B_o$  start decreasing because the liberated gas in the solution reduces the oil's volume. (AHMED, 2006).



Figure 2-2 Bo vs Pressure. Source: AHMED (2006).

The following methods are available for estimating the oil formation volume factor:

Standing's correlation

$$B_o = 0.9759 + 0.000120 \left[ R_s \left( \frac{\gamma_g}{\gamma_o} \right)^{0.5} + 1.25(T - 460) \right]^{1.2}$$
 Eq. 2.3

Where,

T = temperature, °R  $\gamma_o = specific \; gravity \; of \; the \; stock - tank \; oil$  $\gamma_g = specific \ gravity \ of \ the \ solution \ gas$ 

The Vasquez-Beggs correlation

$$B_o = 1.0 + C_1 R_s + (T - 520) \left(\frac{API}{\gamma_{gs}}\right) [C_2 + C_3 R_s]$$
 Eq. 2.4

,

Where,

$$\begin{split} R_s &= gas \ solubility \ , scf \ / STB \\ T &= temperature \ , ^R \\ \gamma_{gs} &= gas \ specific \ gravity \\ C_1 &= API \le 30; 4.677 x 10^{-4} \quad API > 30; 4.670 x 10^{-4} \\ C_2 &= API \le 30; 1.751 x 10^{-5} \quad API > 30; 1.100 x 10^{-5} \\ C_3 &= API \le 30; -1.811 x 10^{-8} \quad API > 30; 1.337 x 10^{-9} \end{split}$$

The Petrosky-Farshad Correlation

$$B_o = 1.0113 + 7.2046(10^{-5}) \left[ R_s^{0.3738} \left( \frac{\gamma_g^{0.2914}}{\gamma_o^{0.6265}} \right)^{0.5} + 0.24626(T - 460) \right]^{3.0936}$$
Eq.2.5

Where,

T = temperature, °R

 $\gamma_o = specific \; gravity \; of \; the \; stock - tank \; oil$ 

## 2.1.3 Oil viscosity

Crude oil viscosity is a crucial parameter that characterizes the fluid's resistance to flow, which plays a significant role in controlling and influencing the oil flow behavior in porous media and pipelines. The viscosity of crude oil can be measured under reservoir conditions in the laboratory; however, it is often necessary to estimate the oil viscosity in the reservoir. To this end, empirical correlations have been developed for estimating the oil viscosity below and at the bubble point pressure (CRAFT; HAWKINS; TERRY, 1991).

Crude oils can be categorized into three groups based on their viscosity levels corresponding to varying pressures. (AHMED, 2006):

• Dead-Oil Viscosity

It is the viscosity of oil at atmospheric pressure with no gas in solution and system temperature.

• Saturated-Oil Viscosity

It is the viscosity of the oil at the bubble-point pressure and reservoir temperature.

• Undersaturated-Oil Viscosity

It is the viscosity of the crude oil at a pressure above the bubble-point and reservoir temperature.

Some empirical methods have been developed to estimate the viscosity of oil, including:

#### • Dead oil

Beal's Correlation

$$\mu_{od} = \left(0.32 + \frac{1.8(10^7)}{API^{4.53}}\right) \left(\frac{360}{T - 260}\right)^a$$
 Eq. 2.6

Where,

 $\mu_{od} = viscosity of the dead oil as measured at 14.7 psi and reservoir temperature, cp$ 

T = temperature, °R

$$a = 10^{(\frac{0.433 + 8.33}{API})}$$

The Beggs-Robinson Correlation

$$\mu_{od} = (10)^x - 1$$
 Eq. 2.7

Where,

 $x = Y(T - 460)^{-1.163}$   $Y = 10^{Z}$  $Z = 3.0324 - 0.02023^{\circ} API$ 

Glaso's Correlation

$$\mu_{od} = [3.141(10^{10})](T - 460)^{-3.44}[\log{(API)}]^a$$
 Eq. 2.8

Where,

 $a = 10.313[\log(T - 460)] - 36.447$ 

• Saturated-Oil Viscosity

Standing

$$\mu_{ob} = (10)^a (\mu_{od})^b$$
 Eq. 2.9

With

$$a = R_{s}[2.2(10^{-7})R_{s} - 7.4(10^{-4})]$$

$$b = \frac{0.68}{10^{c}} + \frac{0.25}{10^{d}} + \frac{0.062}{10^{e}}$$

$$c = 8.62(10^{-5})R_{s}$$

$$d = 1.1(10^{-3})R_{s}$$

$$e = 3.74(10^{-3})R_{s}$$

Where,

 $\mu_{ob}$  = viscosity of the oil at the bubble – point pressure, cp  $\mu_{ob}$  = viscosity of the dead oil at 14.7 psia and reservoir temperature, cp

The Beggs-Robinson Correlation

$$\mu_{ob} = a(\mu_{od})^b \qquad \qquad \text{Eq. 2.10}$$

.

Where,

$$a = 10.715(R_s + 100)^{-0.515}$$
  
 $b = 5.44(R_s + 150)^{-0.338}$ 

#### • Undersaturated-Oil Viscosity

The Vasquez-Beggs Correlation

f  $\mu_o = a \left(\frac{p}{p_b}\right)^m$  Eq. 2.11

Where,

$$m = 2.6p^{1.187}10^a$$

With

$$a = -3.9(10^{-5})p - 5$$

## 2.1.4 Isothermal Compressibility Coefficient of Crude Oil

The isothermal compressibility is a measure of its volumetric response to a change in pressure at constant temperature. Mathematically, it is defined as the negative ratio of the relative change in volume to the change in pressure, holding temperature constant as it is shown in the following equation :

$$c = -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T$$
 Eq. 2.12

For pressures above the bubble-point, the isothermal compressibility coefficient (C<sub>o</sub>) of the oil can be determined using the following mathematical expressions.:

$$c_o = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$$
 Eq. 2.13

$$c_o = -\frac{1}{B_o} \left( \frac{\partial B_o}{\partial p} \right)_T$$
 Eq. 2.14

$$c_o = -\frac{1}{\rho_o} \left( \frac{\partial \rho_o}{\partial p} \right)_T$$
 Eq. 2.15

Where,

 $c_o = isothermal \ compressibility, psi^{-1}$   $ho_o = oil \ density, lb/ft^3$  $B_o = oil \ formation \ volume \ factor, bbl/STB$  For pressures that are lower than the bubble point pressure, the compressibility of the oil is characterized by the following expression:

$$c_o = -\frac{1}{B_o} \left( \frac{\partial B_o}{\partial p} \right) + \frac{B_g}{B_o} \frac{\partial R_s}{\partial p}$$
 Eq. 2.16

Where,

 $B_g = gas formation volume factor, bbls/scf$   $c_o = isothermal compressibility, psi^{-1}$   $\rho_o = oil density, lb/ft^3$   $B_o = oil formation volume factor, bbl/STB$  $R_s = solution gas oil ration scf/STB$ 

## 2.2 PVT tests

Laboratory experiments are performed in reservoir preserved samples or surface fluids and are applied equations of state, empirical correlations, and computational techniques to represent reservoir fluid properties and reproduce what takes place during oil and gas production. The common measurements of pressure-volume-temperature (PVT) properties are density ( $\rho$ ), formation volume factor ( $\beta$ ), viscosity ( $\mu$ ), interfacial tension (IFT), gas-oil ratio (GOR), gas solubility (Rs) and compressibility (c).The main PVT experiments include Differential liberations (DF), Flash liberation (FL), Constant composition expansion and compression (CCE), and separator test. They are required to determine the basic parameters ( $\beta$ , Rs,  $\mu$ ).

### 2.2.1 Differential liberation

This experimental procedure is designed to reproduce the depletion process of an oil reservoir and provide PVT data to calculate reservoir performance (DAKE, 1983).

During a differential liberation test, an oil sample from the reservoir is exposed to decreasing pressure below the bubble point (P<sub>sat</sub>), while being agitated until equilibrium is achieved. As the pressure is reduced, gas in the oil solution is liberated, and changes in the volume ( $\Delta V_g$ ), moles ( $\Delta n_g$ ), and specific gravity ( $\gamma_g$ ) of the released gas are recorded. This process results in a fluctuating hydrocarbon system composition, and other properties are determined from the measured data at a specific pressure and temperature.

Reservoir oil samples are used to conduct the differential liberation test, which is performed in a visual PVT cell with a liquid sample at reservoir temperature and bubble-point pressure. Figure 2-3 shows the scheme for Differential liberation test. The differential liberation test involves reducing the pressure in steps, typically at 10 to 15 pressure levels, and measuring the liberated gas volume at standard conditions while removing all gas from the system. Meanwhile, the remaining oil volume (VL) is also measured at each pressure level until atmospheric pressure is reached, where the residual volume of oil is measured and converted to a volume at a standard temperature of  $60^{\circ}$ F (V<sub>sc</sub>). By dividing the recorded oil volumes VL by the residual oil volume V<sub>sc</sub>, the differential oil formation volume factors B<sub>od</sub> (also known as relative oil volume factors) are calculated at various pressure levels. Additionally, the differential solution gas-oil ratio R<sub>sd</sub> is computed by dividing the volume of gas in solution by the residual oil volume (AHMED, 2006).



Figure 2-3 Differential liberation test. Source: Fluid modelling Group (2016).

### 2.2.2 Flash liberation

Figure 2-4 shows the scheme for flash liberation. The gas gets out of the solution while pressure decreases and keeps in contact with the liquid phase. The flash liberation presents the following characteristics: The total composition of the system keeps constant (the gas is not removed from the cell where the liberation is performed), and thermodynamic equilibrium between the phases is achieved. The process is finished when the maximum capacity of the cell is reached. The liberation flash test usually provides the bubble pressure and the liquid isothermal compressibility coefficient above bubble pressure. The formation volumetric factor under the bubble pressure and the initial solubility ratio can be obtained eventually if the cell capacity allows it to reach the standard conditions (pressure and temperature).



P3<P2<P1<Pb

Figure 2-4 Flash Liberation. Source: Produced by the author.

#### **2.2.3 Constant Composition Expansion (CCE)**

The CCE experiment, also called the Constant Mass Expansion (CME) experiment, is performed using gas condensate or oil to replicate the Pressure-Volume relationship within the system. In order to observe and record the saturation pressure and corresponding volume, a visual PVT cell is employed for maintaining the fluid under reservoir conditions. This PVT cell is depicted in Figure 2-5. The pressure within the cell is systematically reduced in incremental steps while keeping the temperature constant. This reduction in pressure is achieved by gradually removing mercury from the cell. At each pressure level, the total volume of hydrocarbons present in the cell is measured. It is important to note that no gas or liquid is extracted from the PVT cell during the entire experiment, ensuring the integrity and consistency of the measurements.



Figure 2-5 Constant composition expansion test. Source: produced by the author.

#### 2.2.4 Separator Test

The objective of the separator test is to estimate how the volumetric properties of reservoir fluid change as it flows through the separator and stock tank. This test is performed on oil and gas condensate using one or more separators, with the final stage being conducted at surface pressure and temperature.

In the laboratory, the reservoir fluid sample is brought to the bubble point pressure and reservoir temperature, and it is placed in a cell. The oil phase is then displaced from the cell to the subsequent separator stage, while the gas phase is released and transferred to standard conditions, where its volume and specific gravity are measured. This procedure is repeated until the stock tank conditions are attained.



Figure 2-6 Separator test. Source: Fluid modeling group (2016).

## 2.3 Permeability

Permeability is the ability of a porous medium to allow the flow of fluids through it. It is a fundamental property of rocks that controls the flow rate and direction of reservoir fluids in the formation. Henry Darcy was the first to define this property mathematically in 1856. The mathematical expression that relates permeability to measurable properties is known as Darcy's Law and is defined with the following expression. (TIAB, 2004).

$$q = \frac{kA\Delta p}{uL}$$
 Eq. 2.17

Where,

- q = flow rate through the porous medium, cm3/sec
- A = cross sectional area across which flow occurs, cm2
- u = Fluid viscosity, centipoise (cp)
- $\Delta p = Differential pressure, atm$
- L = the length of the sample, cm
- k = permeability of the sample, Darcy

The previous equation can only be applied under the following conditions:

- Newtonian fluid.
- Isothermal, laminar, and permanent flow regime.
- Incompressible, homogeneous, and constant viscosity flow under pressure variations.

- Homogeneous porous media with no chemical reactions between rock and fluids.

- Porous media saturated 100% with one fluid.

#### 2.3.1 Relative Permeability

Relative permeability is the proportion of effective permeability of a particular fluid at a specific saturation level, stated as a fraction of the permeability at full saturation (AHMED, 2006). The relative permeability varies from a value of zero at some fluid saturation to a value of 1.0 at 100% saturation of that fluid and can be expressed as:

$$k_{ro} = \frac{k_o}{k}$$
 Eq. 2.18

$$k_{rg} = \frac{k_g}{k}$$
 Eq. 2.19

$$k_{rw} = \frac{k_w}{k}$$
 Eq. 2.20

$$0 \le k_{rw}, k_{ro}, k_{rg} \le 1.0$$

Where,

kro = relative permeability to oil
krg = relative permeability to gas
krw = relative permeability to water
k = absolute permeability
ko = effective permeability to oil for a given oil saturation
kg = effective permeability to gas for a given gas saturation
kw = effective permeability to water at some given water saturation

Figure 2-7 presents a set of relative permeability curves for a water-oil system with the water being considered the wetting phase.



Figure 2-7 Relative permeability curve for a two-phase flow behavior. Source: AHMED (2006).

# 2.3.2 Drainage process

Drainage is the process in which the saturation of the wetting phase decreases while the non-wetting fluid flows through a media. Usually, the pore spaces of reservoir rocks were initially filled with water, and then the oil enters the reservoir and displaces the water until reaches residual saturation (AHMED, 2006).

## 2.3.3 Imbibition process

Imbibition is a process in which the wetting phase displaces the non-wetting phase until it reaches its irreducible saturation. The purpose of this process is to generate relative permeability data that can be used for water flooding or water drive calculations as shown in Figure 2-8 (AHMED, 2006).



Figure 2-8 Hysteresis effects in relative permeability. Source: AHMED (2006).

## 2.3.4 Laboratory Measurements of Relative Permeability

Relative permeability information is not directly measurable and is often determined by analyzing the production and pressure drop data from core samples. There are five primary methods for acquiring relative permeability data, including:

- Steady-state laboratory method.
- unsteady state laboratory method
- Calculation from capillary pressure data
- Estimation from field data
- Theoretical/empirical correlations

## 2.3.4.1 Steady-State Techniques

Steady-state techniques are widely recognized as the most accurate method for estimating relative permeability data for conventional formations. (KANTZAS; BRYAN; TAHERI, 2012). The steady-state condition is established when the pressure differential

across the core sample remains constant, allowing Darcy's law to be applied in determining the effective permeability for each phase at a specific saturation. To achieve this, two fluid phases are simultaneously injected into the core sample at constant rates and pressures, in known relative amounts as shown in Figure 2-9. The pressure differential across the core during flow and the outlet flow rate is measured and used in Darcy's law to estimate the effective permeability of the fluid at that saturation (SHEN; BREA, 1987).



Figure 2-9 Fluid saturation during steady-state test. Source: HONARPOUR ET AL (1982).

The primary drawback of steady-state testing is the significant amount of time required to complete a single saturation level, which can take several hours or even days. Consequently, these tests can be uneconomical. Despite this limitation, steady-state techniques remain the most precise and dependable approach for estimating core permeability (KANTZAS; BRYAN; TAHERI, 2012). There are several steady-state methods to carry out these tests. They include the Penn state or multi-core method, (HONARPOUR;

KOEDERITZ; HARVEY, 2018), Single sample or high-rate method, (HONARPOUR; KOEDERITZ; HARVEY, 2018), Hassler or uniform-capillary-pressure method, (HASSLER; BRUNNER, 1945) Stationary fluid method, (OBIORA EBUKA, 2010) and Hafford method, (HONARPOUR; KOEDERITZ; HARVEY, 2018).

## 2.3.4.2 Unsteady State Techniques

The unsteady state method involves saturating the core sample with one phase and then displacing it with another phase at a constant rate, unlike the steady-state method where both phases are injected simultaneously. The flow rate and composition of the outlet fluid are measured, and these values are used to determine the relative permeability. This technique is illustrated in Figure 2-10.



Figure 2-10 Unsteady state water flood procedure and typical relative permeability curve. Source: AHMED (2006).
Although unsteady-state relative permeability measurements can be conducted faster than steady-state measurements, the mathematical analysis of the unsteady-state procedure can be complicated. Therefore, the theory proposed by Buckley and Leverett, which has been expanded by Welge, is usually applied as a foundation for measuring relative permeability under unsteady-state conditions (HONARPOUR ET AL., 2018).

# Buckley – Leverett displacement theory

All unsteady state techniques for measuring relative permeability are based on Buckley-Leverett's theory. This theory has the following assumptions (BUCKLEY; LEVERETT, 1942):

- Fluids are immiscible and incompressible.
- Fluid viscosity values are constant (independent of pressure).
- Rock is homogeneous.
- Porosity is constant.
- Flow in one direction and perfectly dispersed flow.
- No capillary pressure or capillary end effects.
- No gravitational effects.
- The calculation is only applicable after the gas breakthrough in a drainage experiment.

# JBN Method

Given that the Johnson-Bossler-Naumann (JBN) technique originates from the Buckley-Leverett flow theory, it inherits all the assumptions (LIU et al., 2010). The primary objective of this approach is to provide the necessary quantities at the exit boundary of the core, which essentially corresponds to the location where volumetric flow measurements are conducted.

The average water saturation  $(S_{wav})$  is plotted against the quantity of displacing phase injected.



Figure 2-11 Average water saturation vs water injection. Source: GLOVER (2010).

The fractional flow of oil at the outlet face of the core sample is:

$$f_o = \frac{dS_{wav}}{dQ_i}$$
 Eq. 2.22

Also, we have:

$$f_o = \frac{Q_o}{Q_t} = \frac{\frac{k_{rokA\Delta P}}{\mu_o L}}{\frac{k_{rw}kA\Delta P}{\mu_w L}} = \frac{1}{1 + \frac{k_{rw}\mu_o}{k_{ro}\mu_w}}$$
Eq. 2.23

A plot of  $\frac{\Delta P}{\Delta P_i}$  against Qi is used to obtain the injectivity ratio.



Figure 2-12 Injectivity ratio. Source: GLOVER (2010).

k<sub>ro</sub> is obtained by plotting  $\frac{1}{Q_i IR}$  versus  $\frac{1}{Q_i}$  :



Figure 2-13  $\frac{1}{Q_i IR}$  versus  $\frac{1}{Q_i}$ . Source :GLOVER (2010).

In addition, using the relationship:

$$k_{ro} = f_o \frac{1}{\frac{d(1/Q_i l_R)}{d(1/Q_i)}}$$
 Eq. 2.24

 $k_{\mbox{\scriptsize rw}}$  can be calculated with the following equation:

$$k_{rw} = \frac{1 - f_o}{f_o} \frac{\mu_w}{\mu_o} k_{ro}$$
 Eq. 2.25

Unsteady-state tests have been widely used applying the JBN method for calculating relative permeabilities since they are very much more time-efficient and less costly than the steady-state displacement tests while keeping many advantages of the steady-state test (LAU, 2010). Table 2-1 shows the comparison between steady state and unsteady state techniques.

Table 2-1 Comparison between steady state and unsteady-state techniques. Adapted from TRAKI (2016).

Steady-state technique	Unsteady state technique
The maintenance of capillary equilibrium is	By applying a high injection rate, the effect of capillary
crucial as it ensures that the capillary	pressure can be ignored in coreflooding. However, this
characteristics of the reservoir rock are	approach does not consider the impact of capillary pressure and
preserved. Therefore, this method is considered	wettability on the measurement of relative permeability. To
more representative of actual reservoir	obtain the most accurate representation of water-oil
conditions.	displacement, it is essential to take these factors into account.

Steady-state technique	Unsteady state technique
This method is appropriate for rocks that present a strong preference for one phase. However, for rocks with intermediate or mixed wettability, the results obtained using this technique are not precise. This method is commonly used for both sandstone and carbonate reservoirs.	This technique is suitable for both strong and intermediate wettability and can yield highly reliable results.
This method is suitable for both viscous and non- viscous oil, as there is no occurrence of viscous fingering.	When dealing with high viscous oil, the issue of viscous fingering can arise, which can invalidate the assumption of uniform saturation during dynamic displacement. This can make the measurement of relative permeability more difficult.
To determine the core saturation, the sample must be removed from the set up and weighed. However, this process involves dismantling the sample, which exposes it to atmospheric pressure and may result in gas expansion and fluid loss.	Indirect measurement of saturations from production data offers greater flexibility with negligible inaccuracies.
It covers a wider extent of saturation.	It covers a limited range of saturation.
The calculation of relative permeability using Darcy's law equation is a simple mathematical process.	The accuracy of results is weakened by many simplifying assumptions (known as the seven assumptions). Although Buckley-Leverett theory can be applied when capillary pressure is neglected by using high injection rate, it cannot be ignored in practice. The interpretation must be corrected using simulations or correlations, as gravity and capillary pressure effects need to be incorporated. Relative permeability calculations should only be performed after water breakthrough.
Low permeability rocks make this technique impractical due to the extended period required to reach a steady-state or equilibrium case.	A steady-state (equilibrium) condition is not necessary, making this technique much faster and practical for both high and low permeability rocks.

### 2.3.5 Calculation from Field Data

Determining relative permeability using production history and fluid properties is a feasible method that provides average values based on complete production history data. The results are influenced by factors such as pressure and saturation gradients, varying depletion stages, and saturation fluctuations in stratified reservoirs (HANARPOUR; MAHMOOD, 1988b).

## 2.3.6 Empirical Correlations of Relative Permeability

Empirical correlations can be utilized to estimate relative permeability when either laboratory permeability testing is not feasible, or no core data is available. The Corey relations and the Honarpour correlations are two common methods used to calculate relative permeability.

#### **Corey Correlations**

Corey (1954) introduced a straightforward mathematical formula to generate relative permeability data for water-oil systems. This approximation is particularly effective for drainage processes.

$$k_{rw} = k'_{rw} \left(\frac{s_w - s_{wi}}{1 - s_{wi} - s_{or}}\right)^{nw}$$
 Eq. 2.26

$$k_{ro} = k'_{ro} \left(\frac{1 - s_w - s_{or}}{1 - s_{wi} - s_{or}}\right)^{no}$$
 Eq. 2.27

Where,

 $k_{rw}$  = Relative permeability to water  $k_{ro}$  = Relative permeability to oil k'<sub>rw</sub> = End point relative permeability to water k'<sub>ro</sub> = End point relative permeability to oil s<sub>w</sub> = Water Saturation s<sub>wi</sub> = Irreducible Water Saturation s<sub>or</sub> = Residual oil saturation nw = Corey Exponent for Water no = Corey Exponent for oil

Bennion and Bachu (2010) provides a summary of the average drainage and imbibition relative permeability characteristics for the three groups of rock types used in their study as shown in Table 2-2 and Table 2-3. As a generalization, these groups may represent a guide for approximating values of a Corey Exponent for carbonates rocks.

Table 2-2 Relative permeability and displacement characteristics for the drainage of carbonate rock samples in  $CO_2$ /brine Systems. Adapted from BACHU; BENNION (2008).

Rock	K brine @ 100% saturation (mD)	Kr CO <sub>2</sub> Q irreducible brine saturation	Sb-irr	Corey Model parameter for brine	Corey Model parameter for CO <sub>2</sub>
Low Permeability	2.05	0.4346	0.487	1.8	4.18
Mid Permeability	54.65	0.1238	0.519	2.22	3.69
High Permeability	293.13	0.0774	0.572	1.71	4.55

 Table 2-3 Relative permeability and displacement characteristics for the imbibition cycle of carbonate rock samples in CO<sub>2</sub>/brine Systems. Adapted from Bachu & Bennion (2008).

Rock	Kr brine @ Irreducible Gas saturation	Sco <sub>2</sub> - irreducible	Corey Model parameter for brine	Corey Model parameter for CO <sub>2</sub>
Low Permeability	0.1074	0.335	3.67	2.92
Mid Permeability	0.6162	0.157	3.12	2.89
High Permeability	0.3621	0.232	1.98	2.41

### Honarpour Correlations

In a notable contribution by Honarpour et al. (2018), a novel approach was introduced to establish correlations for the estimation of relative permeability. Diverging from conventional methods that primarily relied on theoretical solutions, Honarpour's methodology drew upon empirical data. Through an extensive collection of data from diverse oilfields worldwide, the study employed stepwise linear regression analysis to construct mathematical models that align with real-world observations. To ensure comprehensive coverage, the data sets were meticulously categorized according to the nature of the formations, distinguishing between carbonate and non-carbonate reservoirs, as well as further subdivided based on wettability and property ranges. By employing this innovative approach, a series of equations were derived, enabling accurate estimation of relative permeability under various reservoir conditions.

## 2.3.7 Factors affecting the Relative Permeability Measurement

It is very important to identify the factors that would affect the application in laboratory conditions to avoid errors during relative permeability measurement (ELHAJ; HASHAN; HOSSAIN, 2018). The main factors influencing the measurement of relative permeability are boundary effect, rate effect and hysteresis effect.

#### Boundary Effect.

When estimating relative permeability in a laboratory by flowing two immiscible fluids through a core sample, there is a capillary property discontinuity at the outflow end of the core (OSOBA *et al.*, 1951). This happens when the fluids move abruptly from the rock, which has a finite capillary pressure, into an open receiving vessel where capillary pressure is absent. As a result, the wetting phase saturation remains high at the outflow end while being low in the remaining part of the core (LEVERETT, 1941).

# Rate effect

The sensitivity of oil and gas relative permeabilities to flow rate in the absence of boundary effects is a subject of interest in laboratory measurements. It is unclear whether variations in flow rates through the core sample, which cause deviations in measured relative permeabilities, are due to boundary effects or rate sensitivity of the fluids (OSOBA *et al.*, 1951).

#### Hysteresis effect

Relative permeability is not solely determined by saturation in a core but is also influenced by hysteresis. It has been demonstrated in various research that hysteresis can significantly impact the accuracy of relative permeability measurements (BRAUN; HOLLAND, 1995; SKAUGE; LARSEN, 1995; SPITERI *et al.*, 2005).

## 2.3.8 Relative Permeability of a two-phase system (Oil-Water)

In a system with two phases, the flow of the wetting and non-wetting phases is separate and dependent on the saturation and wettability, resulting in varying permeability values. As the non-wetting phase saturation increases, the relative permeability curve of the wetting phase experiences a sharp decrease, while the relative permeability of the non-wetting phase decreases less rapidly as the saturation of the wetting phase increases. This is because the non-wetting phase flows through the center of the pore space, away from the rock walls, and disturbs the flow of the wetting phase, making the flow of water more challenging and less impactful on the flow of the non-wetting phase, resulting in a lesser reduction in the relative permeability of the non-wetting phase. (AHMED, 2006).

#### 2.3.9 Relative Permeability of a two-phase system (Oil-Gas)

This system assumes that the water saturation in the reservoir rock is fixed at the irreducible water saturation value, meaning that water is present in the pore space but is

immobile and reduces the available pore space for oil and gas. (DIMRI; SRIVASTAVA; VEDANTI, 2012).

The relative permeability curve of the wetting phase (oil) in an oil-wetted gas system differs significantly from that in a water-wetted oil system, where water is the wetting phase. In the case of a water-wetted system, the relative permeability curve of oil takes an S-shape. In contrast, in an oil-wetted gas system, where oil is the wetting phase, the curve takes a concave upward shape, as depicted in Figure 2-14 (AHMED, 2006).



Figure 2-14 Relative permeability curves for oil-gas system. Source: AHMED (2006).

#### 2.3.10 Factors affecting two-phase relative permeability.

The behavior and properties of rock and fluid have a significant impact on immiscible displacement, specifically wetting and non-wetting relative permeabilities. Several factors influence this impact, including:

# Wettability

The distribution and dynamics of fluid flow within a reservoir rock are intricately governed by its wettability characteristics (HONARPOUR, KOEDERITZ, & HARVEY,

2018). Wettability can assume various forms, ranging from strongly water-wet to intermediate-wet to strongly oil-wet. In strongly water-wet reservoir rocks, water preferentially occupies the fine pores and forms a film across the rock surfaces, while the oil tends to accumulate within the larger pores' central regions. Conversely, in oil-wet reservoirs, the oil phase dominates the pore surfaces, with water occupying the central regions of the pores (DONALDSON & THOMAS, 1971). Mixed-wet systems exhibit a more nuanced behavior, with oil coating the surfaces of larger pores and water coating the surfaces of smaller pores, or vice versa.

The spontaneous imbibition of the wetting phase into the core and displacement of the non-wetting phase are influenced by several factors, including wettability, viscosity, interfacial tension, pore structure, and initial saturation (ANDERSON, 1987). In strongly water-wet systems, the relative permeability of water at residual oil saturation is diminished due to the presence of oil within the central regions of the pores, which restricts water flow. Conversely, the relative permeability of oil at irreducible water saturation often approaches the absolute permeability, as water primarily occupies the smaller pores and coats the surfaces of larger pores, having minimal impact on oil flow (GEFFEN ET AL., 1951). In oil-wet systems, the relative permeability of water at residual oil saturation tends to be higher, as the residual oil accumulates on the pore surfaces, enabling the flow of water within the central regions of the pores.

#### Interfacial Tension (IFT)

In 1969, Taber JJ conducted experiments on reservoir rock samples and found that the displacement of residual oil by water in a porous medium is influenced by the ratio  $\frac{\Delta P}{L\sigma}$ , where  $\Delta P$  is the pressure drop across the distance L and  $\sigma$  is interfacial tension between the wetting and non-wetting phases. (TABER JJ, 1969).

Interfacial tension (IFT) occurs due to the repulsion forces between molecules at the interface of two immiscible phases. The resistance to the displacement of the wetting phase by the non-wetting phase is directly related to the magnitude of the IFT. This phenomenon affects the relative permeability of the non-wetting phase by limiting the number of capillary channels available for it to flow through, thus influencing its relative permeability. (TRAKI, 2016).

# Effect of IFT on the gas-oil relative permeability

As IFT decreases, the oil relative permeability curve remains unaffected, while gas relative permeability increases significantly. The viscous/capillary forces balance can explain this behavior and the viscosity ratio operating during each displacement (MCDOUGALL; SALINO; SORBIE, 1997).

#### Effect of IFT on the oil-water relative permeability

At low interfacial tensions (IFTs) in an oil-water system, the water relative permeability is dependent solely on the water saturation. When the IFT decreases, the pore size distribution index in the equations for relative permeability approaches unity. At extremely low IFTs, the relative permeability curves become almost linear with saturation, and hysteresis is greatly reduced. Under such conditions, the shape of the relative permeability curve may change without any alteration to the actual relative permeability values. (JAMALOEI, 2015).

#### **Pore Geometry**

Amyx and Whiting (1988) observed that the relative permeability of a rock is dependent on its pore geometry. Rocks with larger pores have lower irreducible water saturations, which leads to a greater amount of pore space available for fluid flow. This condition results in higher saturation and endpoints during two-phase flow. In contrast, rocks with smaller pores have larger surface areas and higher irreducible water saturations, which limit the available pore space for fluid flow. As a result, these rocks exhibit lower initial oil relative permeability and final water relative permeability values, with little change in saturation during two-phase flow (MORGAN; GORDON, 1970).

## Viscosity

The investigation performed by Odeh (1959) concluded that relative permeability to the non-wetting phase is directly proportional to the viscosity ratio, while the relative permeability to the wetting phase is not affected by the viscosity ratio.

Different studies concerning the influence of viscosity on relative permeability have shown diverse researchers' opinions about this topic. Therefore, it seems best to conduct laboratory relative permeability experiments with fluids that do not differ significantly in viscosity from the reservoir fluids (HONARPOUR; KOEDERITZ; HARVEY, 2018).

#### *Temperature*

The impact of temperature on relative permeability varies across different rock-fluid systems, and it is influenced by alterations in wettability, interfacial tension, and at times, pore geometry caused by changes in temperature. (ESMAEILI *et al.*, 2020).

# 2.3.11 Literature Review of Relative Permeability Curves for CO<sub>2</sub> /oil Systems

The characterization of relative permeability curves is essential for understanding the multiphase flow properties in porous media. Obtaining water-oil or oil-gas relative permeability data is typically accomplished through steady-state or unsteady-state displacement experiments utilizing core samples (WANG, Dai Gang et al., 2016a). Recent studies have explored various water/gas/oil systems, shedding light on their behavior. Ghoodjani and Bolouri (2011) focused on the influence of CO<sub>2</sub> on relative permeability and proposed a method based on the Corey model to calculate the CO<sub>2</sub>-oil relative permeability curve. Parvazdavani et al. (2013) investigated the relative permeability of CO<sub>2</sub>-light oil systems using dolomite and sandstone cores under different conditions. They employed empirical correlations and slim tube simulations to determine the minimum miscibility pressure. Duchenne et al. (2014) conducted experiments on intermediate wet carbonate cores saturated with light oil from a Middle East field. Their analysis involved gas chromatography for compositional analysis and differential pressure measurements for estimating relative permeability. LI et al. (2015) utilized slim tubes and long composite cores to acquire reliable experimental data on CO<sub>2</sub> flooding under near miscible or miscible conditions. They developed an improved empirical Corey model that considered shape defining factors in the displacement pressure function, along with a history-matching approach to calculate relative permeability curves. Wang et al. (2016) introduced a numerical inversion method for estimating the water-oil-gas relative permeability curve during immiscible water-alternatinggas (WAG) processes. They conducted laboratory tests, including phase behavior studies and immiscible WAG coreflood experiments, to generate accurate fluid properties under reservoir conditions. Parvazdavani et al. (2017) conducted experiments on reservoir core samples from sandstone formations in Iranian oil reservoirs. They used the inverse modeling method to

calculate relative permeability curves, finding that core length was a critical parameter for simulating miscible flooding. Modaresghazani et al. (2019) performed isothermal coreflood experiments to investigate two-phase and three-phase relative permeability behavior in multiphase flow, specifically with Canadian bitumen. They applied a history matching technique to determine relative permeabilities, observing drainage and imbibition processes. Finally, Alhammadi et al. (2020) examined carbonate samples saturated with crude oil and formation brine using X-ray microtomography and in-situ contact angle distribution measurements to characterize mixed wettability. They measured pressure drops and utilized high-resolution images to calculate brine and oil saturation and obtain relative permeability data.

## 2.4 Carbonated Water injection

Carbonated water injection (CWI) presents a highly promising approach that surpasses traditional CO<sub>2</sub> injection methods in terms of efficiency (Heinrich, Herzog, & Reiner, 2003). It holds the potential for achieving significantly higher incremental oil recovery compared to conventional water injection techniques. The key advantage of CWI lies in the CO<sub>2</sub> content within the carbonated water (CW), which interacts with the oil phase, resulting in enhanced oil mobility. This interaction induces oil swelling, reduces oil viscosity, and decreases interfacial tension (IFT), ultimately leading to a lower residual oil saturation. CWI is especially attractive for offshore oil reservoirs and other reservoirs with limited CO<sub>2</sub> access.

Notably, CWI holds an edge over other CO<sub>2</sub>-enhanced oil recovery (EOR) methods due to its superior sweep efficiency and capacity for reducing the channeling effect. Unlike bulk phase injection, CWI eliminates the risk of buoyancy-driven leakage since CO<sub>2</sub> is in solution rather than in a free phase. Furthermore, carbonated water, being denser than native brine, presents the potential for a safer storage method to mitigate greenhouse gas emissions (HEINRICH; HERZOG; REINER, 2003). In addition to its environmental benefits, CWI offers a more effective means of oil recovery compared to conventional water injection.

While various experimental and numerical studies have examined CWI to understand its production mechanisms, there remains a lack of systematic investigation into the effects of different factors on CWI performance. These factors include fluid-rock characteristics, mass

transfer coefficient, pore structure, and well configuration. Although mathematical approaches and simulation tools have been developed to simulate CWI at field and laboratory scales, there exists a discrepancy between the results obtained from these models and experimental data. This discrepancy may arise from uncertainties in the models and assumptions made, as well as the assumption of thermodynamic equilibrium in the simulations and the use of incorrect models for relative permeability and capillary pressure. Nonetheless, both experimental and modeling studies have confirmed that CWI results in wettability alterations, reduced oil viscosity, oil swelling, and an overall reduction in residual oil saturation, all contributing to increased total oil recovery (BROWN, 2014; DE NEVERS, 1964a; FOROOZESH; JAMIOLAHMADY, 2016; SOHRABI et al., 2012; YANG et al., 2019).

The process of injecting carbonated water entails a multitude of intricate physical and chemical phenomena. The transfer of  $CO_2$  between the injected carbonated water and the oil phase dynamically initiates interactions between the fluids, which can induce alterations in the composition of the oil and the emergence of a distinct third phase, thereby establishing a three-phase flow regime. It is worth noting that most commercial compositional simulators assume instantaneous equilibrium during the transfer of mass between the phases, assuming swift  $CO_2$  transfer into the oil upon contact with carbonated water. However, empirical studies have provided evidence that mass transfer occurs gradually and in a non-equilibrium way (ALMESMARI, 2019).

# 2.5 Brazilian pre-salt oil

The offshore Pre-salt in Brazil comprises a group of fields with promising oil reserves in the Coquinas formation in ultra-deeper waters. The rock matrix in pre-salt reservoirs is mainly composed of microbial carbonates and coquinas. Pepin *et al.*, (2014) studied coquinas formations and performed laboratory tests. They conclude that the rock matrix in Pre-Salt reservoirs is a very heterogeneous carbonate. In general, the pre-salt cluster oil has a 28- 30° API and a high solution gas ratio (200-300 m<sup>3</sup>/ m<sup>3</sup>), temperatures between 60 and 70°C, high salinity (23%) and low viscosity (DE ALMEIDA *et al.*, 2010). The CO<sub>2</sub> amount in these fields significantly varies, Jupiter with 79% CO<sub>2</sub>, Carioca with 16% of CO<sub>2</sub> and Lula with 8-12% (HAUVILLE; TERRAZAS; HENRIQUE, 2014a). Using CO<sub>2</sub> for EOR in Brazilian presalts fields was not used until the Lula field where venting was not an option for environmental reasons, nor transporting to land. So, it was decided to implement from the early stages of production, the usage as an EOR method through miscible WAG injection, showing a specially well response in petrophysical term due the dissolution in carbonate reservoirs. As the CO<sub>2</sub> concentration is low, an option is to select a specific region of the reservoir to be developed with WAG-CO<sub>2</sub> or to re inject all the produced gas, which could be done in the whole reservoir extent.(PIZARRO; BRANCO, 2012).

## 2.6 Carbonates

According to Kargarpour (2020), approximately 60% of the world's oil reserves are located in carbonate reservoirs, which are typically more heterogeneous than sandstone reservoirs due to their dual or multiple porosity and permeability features. These additional porous media are a result of basic diagenetic processes and fracturing. Intense dissolution of carbonate rocks leads to the formation of high permeability vugs, molds, natural fractures, and caverns. This process occurs prior to burial and is attributed to non-reservoir or seal units, as well as meteoric diagenesis. The resulting variation in the distribution of porosity and permeability within the reservoirs plays a significant role in defining the overall reservoir quality (TIAB, 2004).

Secondary or EOR projects in carbonate reservoirs must consider their specific characteristics. Carbonates are reactive and suffer more intense chemical diagenesis which creates a heterogeneous reservoir system. Carbonates have significant permeability contrast and the presence of fractures and faults that may develop pathways for the premature eruption of injected fluids. On the microscopic scale, heterogeneities in carbonates manifest as flow barriers caused by cementation and the presence of stylolite. Beside all these reservoirs characteristics, carbonates tend to be neutral to oil wet, which may impact the porous system's multiphase displacement and capillary behavior (PIZARRO; BRANCO, 2012).

## 2.7 Numerical Simulation of CWI

Due to their applicability and efficiency the oil industry extensively uses reservoir simulators to analyze and predict the relative permeability data. One of the most important parameters to get an accurate simulation is the input of quality data and properties of the fluids in the porous media.

The compositional simulation models accurately reproduce the fluid flow behavior in Enhanced Oil Recovery processes but are still based on PVT data. An Equation of State (EOS) model is usually employed to describe the phase behavior of a multi-component system (LAKE, 1989). The parameters of the EOS often need adjusting (tuning) to the experimental data; these parameters are a function of the heavy oil fraction's critical properties that usually present considerable uncertainty for the reproduction of the reservoir properties. Due to this, several researchers have developed different methods to reduce the uncertainties associated with experimental errors. These methods require the modification of critical parameters with high experimental uncertainties, such as the properties of the heavy plus fractions and binary interactions coefficient, and even non-linear regressions are used to modify EOS parameters. To improve simulation accuracy and computational efficiency, component lumping is a useful technique. This involves grouping fluid components with similar properties into pseudo components.

In reservoir modeling, history matching is crucial to ensure reliable future forecasts. It is an iterative process of adjusting parameters to obtain a satisfactory fit with historical data of pressure, flow rate, and saturation. There are two types of parameters to consider: reliable parameters (such as pressure, hydrocarbon PVT analysis, and fluid flow rates) and uncertain parameters (like reservoir permeability, porosity, relative permeability, capillary pressure, and reservoir fluid and rock properties). The main stages of history matching include defining the reservoir model and fluid system, selecting parameters, describing the model, and optimizing/minimizing the objective function. To validate laboratory results and gain a better understanding of injection fluid's oil production capability, compositional simulators are necessary. During history matching, a new set of matching parameters is obtained to fit the production data of coreflood tests and minimize the global error.

## 2.8 Equation of State (EOS)

An equation of state (EOS) is a mathematical formula that describes the relationship between the pressure, volume, and temperature of a substance. The equation is used to model the behavior of pure substances and mixtures and predict vapor-liquid equilibria (VLE) and thermal properties. Over time, numerous equations of state have been developed, starting with Van der Waals' equation in 1873. In reservoir engineering, various EOS are currently employed to accurately estimate the properties of reservoir fluids.

Certain EOS can be better suited for specific reservoir fluid types and properties, as evidenced by certain PVT experiments being better fit by a particular EOS. At present, the Soave-Redlich-Kwong (1972) and Peng Robinson EOS are the most utilized equations of state within the oil industry.

#### 2.8.1 Soave-Redlich-Kwong (SRK) EOS

The proposed equation known as SRK-EOS is as follows:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)}$$
 Eq. 2.28

Where,

$$a = 0.42747 \cdot \frac{R^2 T c^2}{P_c} \alpha(T)$$
 Eq. 2.29

$$b = 0.0867 \frac{RTc}{P_c}$$
 Eq. 2.30

 $R = 10.730 \text{ psia} \frac{\text{ft3}}{\text{lb} - \text{mol} - ^{\circ}\text{R}}$  P = system pressure, psia Tc = critical temperature  $Pc = critical \text{ pressure, psia} ^{\circ}\text{R}$ 

Soave used the concept of the Pitzer acentric factor to extend his modification of the Redlich-Kwong equation of state to all pure substances. He conducted a comparison of predicted vapor pressures using his modified equation and the original RK EOS, which demonstrated a significant improvement in vapor pressure predictions. In his modification,  $\alpha(T)$  is extrapolated for supercritical temperatures. Soave evaluated the saturation pressures of several binary systems by comparing measured and computed values, which yielded good agreement. (ASHOUR *et al.*, 2011).

#### 2.8.2 Peng Robinson (PR) EOS

The Peng-Robinson equation of state (PR-EOS) is recognized as the most widely used EOS. Peng and Robinson developed this cubic equation of state using two constants to define the molar volume (Vm) of a substance.:

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m (V_m + b) + b(V_m - b)}$$
 Eq. 2.31

Where,

$$a(Tc) = 0.45724 \left(\frac{(RTc)^2}{Pc}\right)$$
 Eq. 2.32

$$b = 0,007780 \frac{(RTc)}{Pc}$$
 Eq. 2.33

The generalized expression for the temperature-dependent parameter is given by:

$$a(T) = a(Tc)\alpha(T)$$
 Eq. 2.34

Where,

$$\alpha(T) = \left\{ 1 + m \left[ 1 - \sqrt{\frac{T}{Tc}} \right] \right\}^2$$
 Eq. 2.35

With

$$m = 0.3746 + 1.5423\omega - 0.26911\omega^2$$
 Eq. 2.36

Where,

 $\omega = accentric \ factor$   $R = 10.730 \ psia \frac{ft^3}{lb - mol - °R}$   $P = system \ pressure, psia$   $T = system \ temperature$   $Tc = critical \ temperature$   $Pc = critical \ pressure, psia °R$   $V_m = molar \ volume$ 

According to the literature, it has been found that PR-EOS provides more reliability than several other equations. Nevertheless, both PR and SRK equations face issues with C10 – C11 and heavier compounds. Peneloux and Rauzy (1982) proposed a modification to the SRK equation where they introduced a constant to be subtracted from the volume calculated by the SRK equation for each substance. This modification enhances the accuracy of liquid density predictions. However, the modification demands an additional fourth parameter, which includes critical temperature, critical pressure, and acentric factor, necessary for the SRK equation. (ASHOUR *et al.*, 2011).

#### 2.9 Compositional Reservoir simulation

Compositional reservoir simulation plays a vital role in modeling hydrocarbon recovery processes when the conventional black-oil two-component model falls short. Situations such as volatile oil or gas condensate reservoir depletion, non-equilibrium gas injection (dry or enriched) into a black-oil reservoir, and CO<sub>2</sub> injection into an oil reservoir require the use of compositional modeling. The significance of enhanced recovery through CO<sub>2</sub> injection has grown in recent years due to environmental concerns and the demand for comprehensive

reservoir analysis. Compositional simulation outcomes for CO<sub>2</sub> projects encompass critical operational parameters like breakthrough time and rate, produced fluid composition, and the optimization of production facilities and CO<sub>2</sub> recycling strategies. Moreover, modeling aids in pattern size optimization and determining optimal CO<sub>2</sub>/water injection rates to overcome the challenges posed by reservoir heterogeneity.

Numerous methodologies for compositional simulation have been discussed in the literature. Coats (1980) presents a comparative analysis of their approach with other techniques, including Fussell's (1979) iterative process. Nghiem, Fong, and Aziz (1981) introduce a simplified flash calculation method tailored for compositional simulation. Young and Stephenson (1983) outline a solution procedure for compositional model equations employing the Newton Raphson iteration method and simplified correlations such as the Redlich-Kwong and Peng-Robinson equations of state. Watts (1986) proposes a method that involves solving a pressure equation followed by velocity, implicit saturation, and relative permeability calculations. Wong, Firoozabadi, and Aziz (1990) analytically establish the relationship between two fully compositional, isothermal, three-phase numerical simulator types found in literature. Coats (2000) compares different compositional formulations and observes their similarities. Wang and Pope (2001) present the state-of-the-art in compositional simulation using equation of state models as of 2001. Voskov and Tchelepi (2008) conduct compositional simulations utilizing compositional space parameterization, while Pan and Tchelepi (2011) introduce an alternative set of variables and techniques to bypass stability analysis in compositional systems (BROWN, 2014).

# 2.10 Binary interaction coefficient

During the carbonated water injection (CWI) process, the transfer of  $CO_2$  involves complex mechanisms influenced by the varying solubility of  $CO_2$  in two immiscible fluids. However, the transportation of  $CO_2$  into the oil phase is predominantly regulated by the partition coefficient of  $CO_2$  between the oil and aqueous phases. The manipulation of this partition coefficient can be achieved by adjusting the binary interaction coefficients (BIC) between  $CO_2$  and other hydrocarbon constituents. Such adjustments have the potential to induce the formation of a third phase during carbonated water injection. It is important to note that the conventional BIC values derived from  $CO_2$  and oil interactions may not accurately predict the occurrence of a third phase when  $CO_2$  is transferred from carbonated water to the reservoir oil phase.(ALMESMARI, 2019).

The significance of interaction coefficients in phase behavior calculations, particularly in estimating saturation pressures, has been established in prior research by various authors including Peng and Robinson (1976), Conrad and Gravier (1980), and Whitson (1982). These coefficients are used to account for the molecular interaction between dissimilar molecules, and their values are often determined by fitting predicted saturation pressure curves to experimental data.

To facilitate the determination of interaction coefficients, the Institute of Thermodynamics at the Technical University of Berlin has compiled a vast collection of vapor-liquid equilibrium data. This database includes over 55,000 experimental data points for more than 120 binary systems, and has been evaluated by Oellrich, Plocker, Prausnitz, and Knapp (1981) to determine interaction coefficients for both hydrocarbon and non-hydrocarbon systems, for commonly used equations-of-state such as the PR and SRK equations.

This highlights the significance of interaction coefficients in phase behavior modeling and the availability of reliable data sources for their determination.(LI, 1983) used the following relations for hydrocarbon-hydrocarbon systems:

$$delij = 1 - \left| \frac{2*\sqrt{vc3(i)*vc3(j)}}{vc3(i)+vc3(j)} \right|^{PVC3}$$
Eq. 2.37

.....

Where,

delij = Binary interaction coefficient vc3 = (critical volume of component i) PVC3 = Real number used to generate binary coefficients.

Several research studies have reported values of interaction coefficients for hydrocarbon-nonhydrocarbon systems. The reported interaction coefficient values between  $CO_2$  and hydrocarbons generally ranges from 0.1 to 0.13 for PR EOS (OELLRICH *et al.*,

1981; HUGHES, MATTHEWS, AND MOTT, 1981; KATZ AND FIROOZABADI, 1978; MEHRA, 1981). In addition, CO<sub>2</sub>-HC correlations have been proposed by Kato, Nagahama and Hirata (1981); Mulliken and Sandler(1980) and Turek, Metcalfe, Yarborough and Robinson (1980). These correlations are generally temperature dependent and complicated.

# 2.11 Relative permeability curves fitting using history matching

In the realm of reservoir simulation, obtaining accurate relative permeability data from coreflooding experiments and incorporating them into simulation models is crucial. To enhance the precision of these models and address the limitations of estimated results, the technique of history matching has been adopted and implemented in reservoir simulator tools. This enables the representation of reservoir behavior that aligns with experimental performance.

Pioneering the estimation of relative permeability curves using reservoir simulators to match laboratory core flood data were Archer and Wong (1973). They iteratively adjusted the shapes of relative permeability curves until the calculated oil recovery and relative injectivity curves aligned with the laboratory displacement tests. Sigmund and McCaffery (1979) took a different approach, utilizing a power-law expression to model relative permeability curves based on pressure and recovery from laboratory displacement tests. Watson et al. (1980) employed automatic history matching of production data to estimate porosity, absolute permeability, and relative permeability. However, their application was limited to two-dimensional oil-water systems with homogeneous permeability and porosity.

Kerig et al. (1987) proposed an enhanced approach for estimating relative permeability curves based on two-phase displacement experiments. They employed cubic spline functional representations with adjustable coefficients and incorporated inequality constraints to maintain physically realistic relative permeability curves throughout the iterative minimization process. Ruth et al. (1988) presented an approach for determining relative permeability curves from unsteady-state displacement experiments. They introduced a new version of the Welge technique, which included explicit functional forms for relative permeability and analyzed the sensitivity of production and pressure history to the shape of these curves.

Yang and Watson (1991) introduced a Bayesian-type index into an automatic historymatching algorithm to estimate relative permeability curves. Mejia et al. (1994) proposed a parameter estimation approach that simultaneously predicted relative permeability and capillary pressure functions using data from production, pressure drop, and in situ saturation measurements during unsteady-state displacements. Their model considered heterogeneities in porosity, permeability, residual oil saturation, and initial saturation.

Hamon et al. (2000) investigated the influence of small-scale heterogeneity on determining relative permeability curves in laboratory experiments, combining experimental characterization and numerical interpretation of corefloods. Li et al. (2001) implemented a procedure for implicitly calculating absolute and relative permeability through Bayesian history matching of three-phase flow production data estimation. Reynolds and Oliver (2004) presented a methodology for simultaneously estimating relative permeability curves and absolute permeability through history matching three-phase production data.

Basbug et al. (2008) developed a numerical model for multiphase flow in fractured core samples, employing a physical framework to describe capillary pressure-relative permeability characteristics. They proposed an automated history matching approach to determine relative permeability and capillary pressure curves that align with the performance of the coreflood reservoir model. Eydinov et al. (2009) devised a procedure to estimate relative permeability curves with grid block porosities and permeabilities through automatic history matching of three-phase flow production data. Chen and Oliver (2010) introduced an optimization technique to implicitly estimate relative permeability through history matching production data from a larger scale synthetic case (Brugge field) using the ensemble Kalman filter method. Lastly, Zhang et al. (2021) presented a method to calculate the relative permeability curve of oil-CO<sub>2</sub>-water using a laboratory-scale compositional model in GEM-CMG simulation and employed a history matching process based on the particle swarm optimization (PSO) method.

#### 2.12 History Matching

The process of calibrating a reservoir simulation model to field or experimental data, known as history matching, poses a challenge due to its non-unique nature. This inverse procedure aims to optimize the model's uncertain parameters by finding combinations that best match the measured data. Traditionally, this has relied on time-consuming trial and error methods, which are hindered by insufficient constraints and data, leading to imprecise results. As a result, history matching is widely recognized as the most demanding phase of reservoir simulation. To address these limitations, a novel approach called automatic history matching has emerged, treating it as an optimization process. This methodology defines an objective function that quantifies the disparity between simulated and observed data and employs an appropriate optimization algorithm to minimize this function. However, the selection of the most suitable algorithm from the extensive literature is crucial, considering the complexity introduced by the numerous independent variables in reservoir simulation. Consequently, the history matching process must be tailored to the characteristics of each reservoir under analysis. (CANCELLIERE; VIBERTI; VERGA, 2013).

## 2.12.1 History Match Error

The History Match Error quantifies the relative disparity between the outcomes of reservoir simulation and the observed production data, with separate objective functions recommended for each well when dealing with multiple wells in a field. Each well's objective function encompasses multiple terms, each aligned with a specific production data type. Furthermore, it's common for the precision and significance of measured data to vary across these production data types. In manual history matching, these variations are typically addressed by reservoir engineers through intuition and qualitative assessments.

In contrast, computer-assisted history matching necessitates a quantitative approach to account for data quality and significance differences. Consequently, distinct absolute measurement errors and weighting factors must be assigned to various production data types originating from different wells when calculating objective functions.

In CMOST, the following equation is used to calculate the history match error for well i:

$$Q_{i} = \frac{1}{\sum_{j=1}^{N(i)} tw_{i,j}} x \sum_{j=1}^{N(i)} \frac{\sqrt{\frac{\sum_{t=1}^{T(i,j)} (mw_{i,j,t}^{m})^{2} (Y_{i,j,t}^{s} - Y_{i,j,t}^{m})^{2}}{\sum_{t=1}^{T(i,j)} (mw_{i,j,t}^{m})^{2}}}{Scale_{i,j}} x 100\% x tw_{i,j}$$
Eq. 2.38

Where,

*i*, *j*, *t* = Subscripts representing well, production data type, and time

N(i) = Total number of production data types for well NT(i,j) = Total number of measured data points  $Y_{i,j,t}^{s} = Simulated results$   $Y_{i,j,t}^{m} = Measured results$   $tw_{i,j} = Term weight$   $Scale_{i,j} = Normalization scale$  $mw_{i,j,t}^{m} = Weighting factor for each measured data point (the default is 1)$ 

The global history match error is calculated using the weighted average method:

$$Q_{global=\frac{1}{\sum_{i=1}^{NW} w_i} \sum_{i=1}^{NW} w_i Q_i}$$
 Eq. 2.39

Where,

 $Q_{global} = Global \ objective \ function$  $Q_i = Objective \ function \ for \ well \ i$  $NW = Total \ numbser \ of \ wells$  $w_i = Weight \ of \ Q_i \ in \ the \ calculation \ of \ Q_{global}$ 

# 2.12.2 History Matching Optimizers

# **CMG Bayesian Engine**

The CMG Bayesian Engine generates simulation models that capture forecast uncertainties, while honoring observed production data.

The CMG Bayesian Engine uses Bayes theorem to define a posterior probability density function (PDF) that represents model forecast uncertainty by incorporating the misfit between simulation results and measured production data. The engine supports two sampling methods:

• Markov Chain Monte Carlo (MCMC) sampling method requires a large number of iterations for the Markov chain to converge on the posterior PDF.

• CMG Proxy-based Acceptance-Rejection (PAR) sampling method requires far fewer simulation runs than MCMC.



Figure 2-15 CMG Bayesian Engine workflow for probabilistic forecasting using the PAR sampling method. Source: CMG Manual (2020).

#### **CMG DECE**

CMG's optimization technique, known as CMOST DECE (Designed Exploration and Controlled Evolution), is an iterative approach commonly employed by reservoir engineers to solve history matching and optimization problems. The DECE optimization encompasses two distinct stages: designed exploration and controlled evolution.

During the designed exploration stage, the primary objective is to explore the search space systematically and randomly, aiming to gather maximum information about potential solutions. To achieve this, experimental design techniques and Tabu search methods are utilized to select parameter values and generate simulation datasets that represent the search space comprehensively.

Subsequently, in the controlled evolution stage, statistical analyses are conducted on the simulation results obtained during the designed exploration phase. Based on these analyses, the DECE algorithm assesses every candidate value for each parameter, determining whether specific values should be discarded to enhance the quality of the solution. Rejected candidate values are stored and excluded from future exploration stages. To prevent getting trapped in local minima, the DECE algorithm periodically reevaluates the previously rejected candidate

values to ensure the validity of the rejection decisions. If any decisions are found to be invalid, the algorithm reinstates them, allowing the corresponding candidate values to be reconsidered.

The DECE optimization method has proven its effectiveness in practical reservoir simulation studies, delivering reliable and efficient results. It has been successfully applied in various real-world scenarios, further establishing its credibility as a valuable optimization approach.

## **Particle Swarm Optimization (PSO)**

The Particle Swarm Optimization (PSO) technique was developed in 1995 by James Kennedy and Russell C. Eberhart. Inspired by the social behavior of bird flocking and fish schooling, PSO mimics the optimization process by social influence and social learning. Social influence and learning enable individuals to maintain cognitive consistency and to change their beliefs, attitudes, and behaviors as they interact with each other. PSO initializes with a random population of solutions and searches for optimal solutions by updating generations. The individuals evaluate their candidate solutions iteratively and remember the location of their best success so far, making this information available to their neighbors. They also see where their neighbors have had success. Guided by these successes, movements through the search space converge the population towards reasonable solutions. PSO is a population-based stochastic optimization technique that is efficient and easy to implement, and it can be applied to a wide range of optimization problems (CMOST Manual , 2020).

# 2.13 Experimental study

This section presents the data of a coreflooding experiment in which equilibrated carbonated water is injected into a fully saturated oil system reservoir core. In this experiment, the reservoir oil was a recombination of stock tank reservoir crude oil with two gas components (C1, CO<sub>2</sub>) at a gas-oil ratio of 847.8 SCF/STB. The experiment used a composite core constituted of Brazilian pre-salt carbonate rocks and it was performed under reservoir conditions. All the experimental data and results were obtained and measured by the LMMR research group, using the methodologies implemented and validated in the research works of the COIN3 (carbon dioxide injection) project and presented in the internal report of the research sponsor company. In order to carry out the elaboration of the recombined oil, the methodology proposed in the research work of BERNA (2020) was utilized. The procedure for the experimental determination of the unsteady-state drainage relative permeability curves in a two-phase system presented by TOVAR, (2020) was used for the ECW-recombined oil system. In addition, the simulation methodology implemented for the determination of the relative permeability curves was validated in the technical paper of VIDAL VARGAS et al., (2022) and the preliminary results of this work were presented at the Rio Oil & Gas 2022 congress as a technical paper (TAUTIVA et al., 2022). Finally, the experimental coreflooding data produced by this research group were used to apply and validate the methodology to build the laboratory-scale simulation model of this research work.

# 2.13.1 Recombined Oil

The representation of a reservoir begins with the properly characterizing of the reservoir fluids. Accurate fluid sampling is necessary to determine reservoir fluid's PVT behavior and properties. The main objective of fluid reservoir sampling is to gather a fluid sample representing the original reservoir fluid when collected the sample (GUNDERSEN, 2013). The sampling methods used in the petroleum industry are the bottom hole samples collected at reservoir conditions and brought to surface conditions, where the fluid is pressurized, returned to a single phase, and then analyzed. The other sampling method is surface sampling.

where oil and gas samples are collected from separators, and eventually, the fluids are recombined at the producing gas-oil ratio (GOR).

The separator oil composition is obtained by flashing the separator oil to standard conditions, measuring the properties and compositions of the resulting surface oil and gas, and recombining these compositions to give the separator oil composition.

In order to simulate reservoir conditions accurately, it is crucial to ascertain the composition of the associated gas and the properties of the crude oil, including RGO, °API density, and viscosity. However, when conducting experimental studies in the LMMR, the composition of the recombined oil is a simplified representation of the actual fluid composition found in the reservoir. The preparation methodology for the recombined oil in the experimental studies is outlined as follows:

- Determine the required volumes of gas and oil to accurately mimic the crude composition.
- Transfer the fluids into a mixing vessel and utilize a positive displacement pump to elevate the mixture pressure above the bubble point pressure.
- Employ a DBR pump in constant pressure mode once the desired reservoir pressure is attained.
- Proceed to mechanically stir the mixture while applying heat until it reaches the reservoir temperature.

The oil company provided the associated gas composition and the crude oil PVT properties such as GOR, API, and viscosity. The simplified gas and dead oil compositions presented in Table 2-4 and Table 2-5 were used to perform the laboratory oil recombination sample and simulate the recombined oil in WinProp software.

Table 2-4 Gas composition of recombined oil. Source: Produced by the author.

Gas	Composition %
CO2	38.24
C1	61.76

Oil PVT (Flash Liberation 40°C)				
	Stock tank	Flashed	Reservoi	
Component	oil	Gas	Fluid	
CO2	0	38.24	27.6	
N2	0	0.71	0.51	
C1	0	43.14	31.13	
C2	0	6.13	4.43	
C3	0.41	5.07	3.77	
iC4	0.22	0.87	0.69	
nC4	0.7	2.11	1.72	
iC5	0.56	0.75	0.7	
nC5	0.89	0.92	0.92	
C6	2.08	0.94	1.25	
C7	4.22	0.72	1.7	
C8	5.75	0.35	1.86	
C9	5.18	0.03	1.47	
C10	4.6	0	1.28	
C11	4	0	1.12	
C12	3.57	0	1	
C13	3.97	0	1.11	
C14	3.28	0	0.91	
C15	3.3	0	0.92	
C16	2.74	0	0.76	
C17	2.53	0	0.7	
C18	2.62	0	0.73	
C19	2.51	0	0.7	
C20+	46.85	0	13.03	
	99.98	99.98	100.01	
Gas gravity		1		
Molar mass	376.01	32.89	128.44	
Molar mass C20+		626.45		
Density C20+		0.9645		
Oil API		21.85		
Flash Bo (Psat & Tres) (m <sup>3</sup> sat/m <sup>3</sup> std)		14.070		
Total GOR (scf/STB)		847.792		

Table 2-5 Oil Composition data on flash liberation test. Source: Produced by the author.

The properties of the recombined oil and gas dissolved used in the experiment are defined in Table 2-6 and Table 2-7 respectively. Finally, the molar fraction of the recombined oil sample including the dopant (Iododecane) is presented in Table 2-8.

Property	Value	Unit
Dead oil volume	480	ml
API density	21.85	
Oil density	0.9218	
Dead oil mass	442.46	g
Oil molar mass	376.0126	gr/mol
Dead oil moles	1.1767	mol
GOR	151	m <sup>3</sup> std/m <sup>3</sup> std
Gas Volume	0.07248	m <sup>3</sup> std
Laboratory temperature	25.6	°C
Atmospheric pressure	13.6048	psi
Standard temperature	15.56	°C
Gas volume Lab	24301.3105	$cm^3/mol@$ Lab T°C and 1 atm
Gas Moles	3.0594	Moles

Table 2-6 Recombined oil properties. Source: Produced by the author.

Table 2-7 Properties of the gas dissolved in the recombined oil. Source: Produced by the author.

Property	CO <sub>2</sub>	CH4	Unit
Composition	38.24	61.76	%
Moles	1.1699	1.8895	
Mole weight	44.01	16.04	g/mol
Mass	51.4872	30.3071	g
Cylinder Pressure	850	550	psi
Cylinder Temperature	23	23	°C
Cylinder Density	0.18891	0.026431	g/ml
Volume	272.55	1146.65	ml

	Original (%molar)	New (%molar)
Components	Dead oil	Dead oil + Iododecane
CO2	0	0
N2	0	0
C1	0	0
C2	0	0
C3	0.41	0.3279
iC4	0.22	0.1760
nC4	0.7	0.5598
iC5	0.56	0.4479
nC5	0.89	0.7118
C6	2.08	1.6636
C7	4.22	3.3752
C8	5.75	4.5990
С9	5.18	4.1431
C10	4.6	3.6792
Iododecane	25.0463	20.0328
C11	4	3.1993
C12	3.57	2.8553
C13	3.97	3.1753
C14	3.28	2.6234
C15	3.3	2.6394
C16	2.74	2.1915
C17	2.53	2.0235
C18	2.62	2.0955
C19	2.51	2.0075
C20+	46.85	37.4721
Total	125.0263479	100

Table 2-8 Dead oil and dead oil + iododecane molar composition. Source: Produced by the author.

# 2.13.2 Equilibrated carbonated brine.

Equilibrating the carbonated brine is a procedure established in the LMMR in order to reduce the reactions (precipitation and dissolution) with rock minerals. The geochemical

simulator PHREEQC is used to obtain the equilibrated fluid composition and it is shown in Table 2-9.

Compound	Molecular mass (g/mol)	ECW(g/L)
KCl	74.5513	0.9490
$Na_2SO_4$	142.04	0.0587
MgCl <sub>2</sub> :6H <sub>2</sub> O	203.3027	16.9717
SrCl <sub>2</sub> :6H <sub>2</sub> O	266.6177	0.0272
CaCl <sub>2</sub> :2H <sub>2</sub> O	147.0146	7.3213
NaI	149.89	47.46
NaHCO <sub>3</sub>	84.0066	9.0083
Na <sub>2</sub> CO <sub>3</sub>	105.9888	0.0029

Table 2-9 Equilibrated brine composition. Source: Produced by the author.

# 2.13.3 Core characterization

The coreflood experiments involved the utilization of a composite carbonate core consisting of four core plugs. To restore its wettability to an oil-wet state, the composite core underwent an ageing process with recombined oil. Subsequently, the composite core was subjected to a cleaning and drying procedure to achieve its irreducible water saturation ( $S_{wi}$ ). The cores properties were characterized in the laboratory, and it is presented in Table 2-10 and Table 2-11.

Table 2-10 Core properties. Source: Produced by the author.

				Laboratory	
Sample ID	D (cm)	L (cm)	Dry Mass(g)	Permeability(md)	Porosity (%)
S001	3.781	5.003	134.090	50.90	11.98
S002	3.819	6.763	174.810	43.90	17.97
S003	3.777	3.787	96.060	41.70	16.70
S004	3.821	6.952	173.050	27.35	20.81
Average	3.800			40.9625	16.8653

Length(cm)	Diameter (cm)	Porosity (%)	Permeability(md)	PV (cc)
22.5	3.8	0.1576	24.78	37.42

Table 2-11 Properties of the composite core used in the experiment. Source: Produced by the author.

#### 2.13.4 Coreflooding experiment

The coreflooding test for ECB-recombined oil was carried out at 8,500 psi and 70°C using a composite core constituted by Brazilian pre-salt carbonate rocks. The volume of the non-wetting phase (ECB) and the volume of fluid produced (oil) were monitored and recorded along the coreflooding test to estimate the end points saturation using mass balance method. The pressure differential and injection rate were recorded and, together with the fluid and rock properties were used for the estimation of the permeability in the end points by using Darcy's equation. Finally, relative permeability curves were constructed using the modified model of Brooks and Corey (1966) and the Corey's exponents for equilibrate carbonated brine ( $N_w$ ) and recombined oil ( $N_o$ ) found in the literature.

 Table 2-12 Irreducible water and residual oil saturations values experimentally determined. Source:

 Produced by the author.

Sor	0.4458
S <sub>wi</sub>	0.2047

 Table 2-13 Absolute and effective permeability calculated at irreducible saturations from drainage test.

 Source: Produced by the author.

K <sub>abs</sub> (md)	24.79874
ko@Swi(md)	0.191
kw@Sor(md)	0.435909

The coreflooding experiment was conducted by our laboratory team, and it employed the methodology established during the  $CO_2$  injection project conducted by the LMMR. It was used the experimental setup depicted in Figure 2-16 to replicate the drainage procedure.

Subsequently, the data obtained from these experiments was employed by the author of this study to construct a simulation model at the laboratory scale.



Figure 2-16 Experimental Set-up layout. Source: Adapted from Caicedo, 2020.

# **3** Methodology

This chapter presents the methodology to build the laboratory scale simulation for a coreflooding drainage test (ECB-recombined oil) on a carbonate rock under reservoir conditions using CMG software. Finally, it will describe the methodology to fit the experimental data to optimize the model's permeability curves.

#### 3.1 Simulation model

The construction of the simulation model was divided into two stages. The first stage was the characterization of the ECB-recombined oil system in the WinProp program. The second one consisted of laboratory-scale model elaboration in the BUILDER program to be later run in the GEM compositional simulator.

# 3.1.1 Reservoir fluids model

The modeling process in the WinProp program starts with selecting the equation of State (EOS), specification of unit, and feed (mole). The EOS selected is the Peng-Robinson 1978 (PR 1978) because it is the most used EOSs in the petroleum industry due to its applicability to multicomponent systems. The next step in the simulation process involves selecting the reservoir fluid components and estimating their respective physical and critical properties. The eicosane plus fraction (C20+) was defined using its molecular weight and specific gravity. The recombined oil was doped with iododecane to increase the phase contrast and allow the measurement by CT. So, it was necessary to add and define this component in the model using molecular weight, specific gravity, and boiling temperature. After that, the composition of each fluid component, either in mole fraction or percentage is specified in the model.


Figure 3-1 describes the flowchart of fluid model construction for the simulation.

Figure 3-1 Flowchart to build the EOS fluid model. Source: Produced by the author.

The oil recombination process was experimentally prepared in the laboratory to obtain a representative reservoir fluid sample. It was necessary to carry out the laboratory recombination process at WinProp considering the GOR and the molar composition from two-phase (oil and gas) separator. The calculated recombined fluid composition is sensitive to the values assigned to the oil and gas densities, and these fluids' properties are calculated in WinProp from the EOS. Table 3-1 describes the components and molar percentages of gas and dead oil inputted into WinProp.

Component	Dead Oil (%)	Gas (%)
CO2	0	38.24
N2	0	0
C1	0	61.76
C2	0	0
C3	0.41	0
iC4	0.22	0
nC4	0.7	0
iC5	0.56	0
nC5	0.89	0
C6	2.08	0
C7	4.22	0
C8	5.75	0
С9	5.18	0
C10	4.6	0
Iododecane	0.05	0
C11	4	0
C12	3.57	0
C13	3.97	0
C14	3.28	0
C15	3.3	0
C16	2.74	0
C17	2.53	0
C18	2.62	0
C19	2.51	0
C20+	46.85	0
	99.98	100

Table 3-1 WinProp oil recombination. Source: Produced by the author.

The EOS adjustment process began after the preparation of recombined oil at reservoir conditions (8,500 psi and 70°C). The following step was adjusting the saturation pressure ( $P_{sat}$ ) to the model, defined experimentally. The simulated value does not match the input value, so the regression process should be added to make a better match between the values. The experimental PVT tests should be added to the model to make it more accurate. Table 3-2 presents the differential liberation data from the reservoir oil, which was used to fit the EOS

of the recombined oil since the main objective of the adjustment process is to represent these properties.

		Oil PVT		
P(psi)	Bo	$R_s(scf/STB)$	$\mu_o(cP)$	$\rho_o(g/cm3)$
9257.70	1.3126	847.7920	6.0556	0.8437
8546.70	1.3180	847.7920	5.7787	0.8402
7835.70	1.3238	847.7920	5.5103	0.8365
7124.70	1.3301	847.7920	5.2334	0.8326
6759.00	1.3366	847.7920	5.0918	0.8303
6413.70	1.3370	795.5913	4.9580	0.8282
3547.80	1.3260	699.8411	4.4443	0.8189
2836.80	1.2800	577.1968	5.1465	0.8274
2125.80	1.2354	453.9985	6.3142	0.8356
1414.80	1.1861	324.6932	8.4702	0.8464
714.75	1.1355	191.2996	12.8869	0.8569
14.70	1.0386	0	29.2551	0.8794
API Residual Oil		22.40	0474	
Standard				
conditions		1 atm and	d 15.6 °C	
T Reservoir(°C)		6	9	
Pres(psi)		8272	2.14	

Table 3-2 Differential liberation test data. Source: Provided by the LMMR (2020).

For instance, the fluid properties have been estimated experimentally to obtain a better model fitting, and some parameters of EOS were altered (critical pressure, critical temperature, and interaction coefficients) for the component with the most uncertainty ( $C_{20}$ +). WinProp uses the regression by Agarwal et al. (1990) developed to tune the EOSs. The WinProp estimates how close the current EOS is to modeling the real behavior and fits it by adding some parameters to the regression (tuning). Regression aims to minimize the square error between EOS predicted results and the experimental values, ensuring that the sensitive parameters are fitted. The methodology of Coats & Smart (1986) was adopted in order to fit the parameters.

# 3.1.1.1 EOS Tuning Methodology

The Coats and Smart method (1986) defines that regression can be done based on the EOS for each "n" component of the mixture. The parameters represent a correction ratio between the critical variables of an uncertain component that were applied to the heavy fraction (higher degree of uncertainty in the characterization) and to the methane (high molar fraction). In addition to the matching parameters, the volume shift and molar mass was selected based on the methodology performed by Péneloux-Rauzy-Fréze (1982). The Omega "A" and "B" of methane are parameters of tuning the Coats and Smart method and can be explained by the difference in methane interaction coefficient with the other hydrocarbons. The volume shift is the critical volume correction. It is a way to correct the uncertainty of the Peng Robinson EOS on the liquid region without changing the EOS formulation of the simulator (Péneloux, 1982). The EOS (PR1978) used in the model was tuned using a set of parameters defined according to the method used by the industry and based on the Coats & Smart (1986) and Péneloux-Rauzy-Fréze (1982) methods. The first part of the tuning was performed by matching the volumetric properties by modifying EOS parameters using the WinProp program's regression tool. The regression parameters (16 parameters) include the molar mass of iododecane and C20+, volume shift of C11 to C20+, and Omega "A" and "B" for C1 and C20+. The weights applied to the properties of the fluids in the differential liberation experimental data were added to the model representing the contribution of the variable in the objective function were 1 for OIL FVF, 40 for GOR, 10 for OIL SG, and 1 for the other parameters. Figure 3-2 presents the parameters used to model tuning and, Figure 3-3 shows the flowchart of the adopted methodology.

Component	Pc (atm)	Vc (l/mol)	Tc (K)	Ace. factor	Mol. W	Vol. shift	V Shift Coef1 (1/deg F)	Omega A	Omega B
CO2									
N2									
CH4								X	X
C2H6									
C3H8									
IC4									
NC4									
IC5									
NC5									
FC6									
FC7									
FC8									
FC9									
FC10									
IODODECA					x				
FC11						x			
FC12						x			
FC13						x			
FC14						x			
FC15						x			
FC16						X			
FC17						X			
FC18						X			
FC19						X			
C20+					X	X		×	X

Figure 3-2 WinProp image with the parameters selected for the EOS tuning. Source: Produced by the

author.



Figure 3-3 Flowchart of tuning method of Coats and Smart (1986) adapted to the model. Source: Produced by the author.

The second part of the EOS tuning was performed by viscosity matching. For this stage, all the weights established for the volumetric properties were zero, because the viscosity is

independent of the volumetric parameters. It was established with a weight of 1 for the viscosity and used the coefficients of the Pedersen viscosity correlations parameter for regression to match the property.

# 3.1.1.2 Lumping of Components

The accuracy of an EOS model in predicting the phase and volumetric behavior of a modeled system is crucial. To achieve this, the model utilizes properties such as density, viscosity, phase volume split, and phase compositions in its calculations. The required number of components in the EOS model may vary based on the range of p-T-z space being modeled. (ALAVIAN; WHITSON; MARTINSEN, 2014).

To reduce the simulation run time and complexity, lumping was used to minimize the number of components. The process of lumping involves grouping together components with similar properties, based on their composition and critical properties.

The following constraints were considered to determine the number of possible lumping schemes:

- Component lumping of non-hydrocarbons was restricted to group to methane.
- Tracers (Iododecane) should not lump.
- CO<sub>2</sub> was set as a single lumped component due to its molar fraction.

• Components with similar composition and properties defined the pseudo components.

• Hydrocarbons are lumped only by contiguous carbon numbers.

• It is recommended contiguous ordering of the original components for isomers with the same carbon number.

### **3.1.1.3 Exporting the Model to GEM Simulator**

After finishing the fluid model construction, the next step is to export it to the simulator to be used. In this work the simulator chosen was GEM and before running it, it is necessary to include the injected fluid composition and the mineral's reaction with the porous media. The equilibrated carbonated brine was modeled by analyzing the interactions between rock and the brine and it is represented by the aqueous and mineral reactions presented in Table 3-3.

 Table 3-3 Mineral and aqueous reactions considered in the simulation model. .Source: Produced by the author.

Aqueous Reactions
$CO_2 (aq) + 'H_2O = (H^+) + (HCO_3)$
$NaCl = (Na^{+}) + (Cl^{-})$
$KCl = (K^{+}) + (Cl^{-})$
$(NaSO_{4}) = (Na^{+}) + (SO4)$
$(MgCl^{+}) = (Mg^{++}) + (Cl^{-})$
$(CaCl^{+}) = (Ca^{++}) + (Cl^{-})$
$NaHCO_3 = (Na^+) + (HCO_3^-)$
$(NaCO_{3}^{-}) + (H^{+}) = (Na^{+}) + (HCO_{3}^{-})$
Mineral Reactions

Calcite + $(H^+) = (Ca^{++}) + (HCO_3^{-})$	
Dolomite + 2 (H <sup>+</sup> ) = (Ca <sup>++</sup> ) + (Mg <sup>++</sup> ) + 2 (HCO <sub>3</sub> <sup>-</sup> )	

Additionally, the equilibrated carbonated brine (ECB) was defined as an aqueous phase that has 1.324 gmol per kg water of  $CO_2$  molality soluble in the previously defined brine. The solubility model of the GEM simulator was utilized to model the solubility of  $CO_2$  in the aqueous phases (brine) during the injection process. GEM's internal model was used and activated with the keyword HENRY-MOD1-CO2 to estimate Henry's Law constant which uses Harvey's correlation for  $CO_2$  as a basis for estimation of the physical properties of carbonated brine. The reaction of mineral dissolution and precipitation is modelled with an equilibrium constant and an activity product (BETHKE, 1996): The sequential steps involved the construction of the compositional reservoir model for the coreflooding simulation in this study are illustrated in the flowchart depicted in Figure 3-4.



Figure 3-4 Flowchart of the reservoir model construction used in this work. Source: Produced by the author.

The first step in creating a simulation model was constructing the reservoir grid system, representing the experimental study performed at the LMMR laboratory. Cores are radial in dimension, but the linear simulation models are often built in cartesian grids. In order to

simplify the calculation process, the cartesian grid system was created without local grid refinement. It is necessary to preserve the experimental core volume to model the coreflooding experiment. The composite was represented by a three dimensional cylindrical, Cartesian, horizontal and homogeneous model. The model is composed of 25\*11\*11 grid blocks previously estimated from a sensitivity analysis considering simulation time and the accuracy of simulation results with the experimental data. The model was constructed with dimensions of each block of 0.88 cm (I-direction) and 0.34 cm (J-K direction) to constitute a total of 3025 blocks with dimensions of 22.5 cm (length) and 3.8 cm (diameter) as is illustrated in Figure 3-5, to construct the approached circular cross section, some blocks were removed using the NULL blocks option. The definitive grid block model comprised a total of 2.725 active grid blocks.



Figure 3-5 Views of the core simulation model. Source: Produced by the author.

This reservoir model was adapted from a previous experimental study and coreflooding tests. The experimental core sample has an average permeability of 24.80 md and average porosity of 15.76%. The model was assumed to have a homogenous porous in all spatial directions. Therefore, a constant absolute permeability was assigned for all the directions (I,J, K). Furthermore, the compressibility of the rock was presumed to be the default value of 5x10 <sup>-8</sup> 1/kPa. The modeled composite was initially set with the irreducible saturation (S<sub>wi</sub>=0.2047) at reservoir conditions, 8,500 psi, and 70°C.

# 3.1.3 Rock-fluid properties

The simulation model incorporated the ECB-recombined oil relative permeability curves by utilizing established correlations in GEM. The two-phase relative permeability was determined using Corey's model, considering the saturation endpoints. The experimental coreflooding test provided the values for the end-point oil relative permeability ( $k_{ro}$ ) at connate water saturation ( $S_{wi}$ ) and the end-point water relative permeability( $k_{rw}$ ) at residual oil saturation ( $S_{or}$ ).

In the Corey model, there are two exponents ( $n_w$  and  $n_o$ ) used to calculate relative permeabilities for a biphasic system, in this case were used exponents from the literature for this system and specifically for carbonate rock. The CMG-Builder Module initially set these exponents at 3.42 for oil and 1.58 for water. However, in this research work, the exponents were adjusted to achieve better agreement between the simulation results and experimental data, which is the main focus of this study. The values inputted in the simulation model are shown in Table 3-4.

Value
3.42
1.58
0.2047
0.4459
0.19
0.43

 Table 3-4 Corey exponents and Critical saturations to estimate the ECB/oil relative permeability values.

 Source: Produced by the author.

# 3.1.4 Wells configuration and operational conditions

There are two active wells, where one injector (Injector) is located in the cell (1,6,6) and one producer (Producer) in (25,6,6). The injection and production rates and pressure are controlled with the wells by operations constraints (injection rate and pressure) to reproduce the experimental conditions. The model was constructed using Builder, from CMG, and running in the GEM simulator. The well restrictions for the simulation model are presented in Table 3-5.

Limits	Well
Reservoir Pressure (Kpa)	58605.44
Water injection rate (m <sup>3</sup> /day)	0.000288-0.036
MAX BHP Water injection pressure (Kpa)	80000
Water rate producer (m <sup>3</sup> /day)	0.000288-0.036
MIN Bottom Hole pressure producer (Kpa)	58605.44

Table 3-5 Well restrictions for the simulation model. Source: Produced by the author.

The ECB injection rate was incorporated in the model by considering the solubility of  $CO_2$  and its composition in brine under the specific operating conditions. Table 3-6 shows the experimental rates through the core flooding experiment.

	Time (Day)	q(m3/day)
0	0.1117	0.000576
0.1118	0.1398	0.001152
0.1399	0.161	0.001728
0.1611	0.1676	0.000432
0.1677	0.7738	0.000288
0.7739	0.7853	0.00072
0.7854	0.8016	0.00144
0.8017	0.8082	0.00288
0.8083	0.8186	0.0036
0.8187	0.8328	0.00288
0.8329	0.8371	0.00028

Table 3-6 Injection rates in the core flooding experimental test. Source: Produced by the author.

# 3.1.5 Model initialization

To initialize the simulation model, the initial conditions of the reservoir prior to water flooding were utilized. As the carbonated brine process does not generate free gas, the CMG GEM simulator selected a two-phase water-oil fluid system that was consistent with the equilibrated state. Furthermore, the compositions of the aqueous and oil phases were assigned during initialization, incorporating the tuned EOS characteristics imported from CMG WinProp.

For the selection of the best model option prior to performing the history matching, variables such as simulation time and initial global error with the experimental data were considered, three models were tested , the first was a model that does not consider the core cylindrical shape (volume adjustment was made), the oil components are lumped, and the mesh is composed of 625 grid blocks; this model shows a global error of 48.25% and a simulation time of 0.07 hours. The second one considers the cylindrical shape to test the boundary conditions influence, the oil components are lumped as well, and the mesh is composed of 3025 grid blocks; the model shows a global error of 38.79% and a simulation time of 2.25 hours. Finally, the last model considers the cylindrical shape. The oil components are not lumped, and the mesh comprises 3025 grid blocks. This model was created to test the influence of the lumping process. It shows a global error of 35.2%. However, the simulation time increases to 6.4 hours; for this reason and considering that the global error did not present a significant improvement, the model selected to perform the history matching was the second one. Figure 3-6 to Figure 3-9 show the plots for the curves of the three models and the experimental data.



Figure 3-6 Differential pressure curve for the sensitivity analysis. Source: Produced by the author.



Figure 3-7 Cumulative oil curve for the sensitivity analysis. Source: Produced by the author.

Cumulative Oil RC - Producer



Figure 3-8 Oil average saturation curve for the sensitivity analysis. Source: Produced by the author.



Figure 3-9 Water average saturation curve for the sensitivity analysis. Source: Produced by the author.

Water Ave Sat SCTR - FIELD

# 3.1.6 Model History matching

CMOST was used to minimize the global objective function in the history matching process to assemble the assisted procedure in this study. CMOST uses different optimization engines to generate several simulation experiments from the uncertain input parameters to converge on a solution to match the model and see the influence of input parameters on simulation results.

The objective functions must be defined based on the data with the least uncertainty, specifically the experimental data obtained during CWI. These objective functions are used to operate the optimizer and select appropriate parameter values, with the aim of minimizing the global objective function. This process helps to improve the accuracy and reliability of the history-matching.

The objective functions used in this study for assisted history matching consisted of a set of experimental data including cumulative oil volume, differential pressure across the core, and average oil and water saturation recorded during the coreflooding experiment. The uncertain parameters affecting the simulation were mainly related to assumptions about modeling and measurement errors and were classified into four key groups: those affecting the equation of state (EOS) modeling, such as the interaction between  $CO_2$ -CW-oil, parameters related to injectivity, parameters related to porous media-fluids flow (i.e., relative permeability parameters), and properties measured in the experiments (i.e., permeability and porosity). Therefore, a sensitivity analysis (SA) was conducted to assess the contribution of each input parameter to minimize the objective function error and identify the interactions influence among them.

To adjust the model to the experimental data were used two engines methodologies, the CMG Bayesian Engine and Particle Swarm Optimization (CMOST/CMG simulator). Table 3-7 describes the seven parameters and the selected ranges that were defined based on the properties measured experimentally (sample and composite core), and values based on typically ranges on the literature for each optimization process. The model fitting results are consistent with the experimental results (differential pressure, oil production curve, and saturation profiles). The history matching results on the relative permeability curve provided the Corey's exponents values for the drainage test.

Parameter	Range
No (Corey's exponent)	1-5
N <sub>w</sub> (Corey's exponent)	1-5
Perm (Permeability)	24-40
Poro (Porosity)	0.09-0.20
PVC (Interaction coefficients)	0.1-1.60
W <sub>inj</sub> (Well index injector)	0.5-2
W <sub>prod</sub> (Well index producer)	0.5-2

Table 3-7 Model parameters and their range value. Source: Produced by the author.

#### 3.1.6.1 Relative Permeability Curves

Accurate estimation of relative permeability curves is essential for reliable prediction of fluid flow in porous media. However, the presence of significant uncertainties attributed to the Corey exponents sets a challenge to this estimation. In the Corey model, these exponents ( $n_w$  and  $n_o$ ) are assigned to each fluid of the system. In our research, these exponents were initially set based on literature values for a carbonate rock and fluids (ECB-oil), and residual saturations derived from coreflooding experiments were employed to construct the relative permeability curves in the CMG-Builder Module. However, these exponents can be adjusted to improve the agreement between the simulation results and experimental data.

To overcome the challenge of uncertain estimation of relative permeability curves due to the uncertainty in the Corey exponents, it was employed an adjustable parameter approach during the history matching process. This approach involved conducting numerous simulations using different combinations of the exponents and selecting the optimal parameters that reproduce the experimental data behavior. Through this iterative process, a new set of Corey's exponents was obtained, resulting in a more accurate relative permeability curve for the ECB-oil system.

# **4 RESULTS AND DISCUSSIONS**

This chapter presents the drainage results of the core-flooding experiment, the simulation model results for a coreflooding experiment using equilibrated carbonated brine and recombined oil at reservoir conditions, and the history matching process.

### 4.1 Experimental Results

One of the main results of the drainage test are the ECB and recombined oil saturation curves, obtained by the mass balance. It can be observed in Figure 4-1 the gradual increase of ECB saturation ( $S_w$ ) and the decrease of recombined oil saturation ( $S_o$ ) until reaching a residual saturation ( $S_{or}$ ) of 0.4458. The saturation curves will be used in the simulation model optimization process.

The composite core in the drainage test showed an absolute permeability to the ECB of 24.80 mD. The permeability is considered low to perform a displacement test with recombined oil with a viscosity of approximately 6.25 cp. During the process the recombined oil is injected until reaching the irreducible saturation of 0.2047, the effective permeability of the recombined oil was measured equivalent to 0.191 mD. Considering this unfavorable scenario, the drainage test presented very high differential pressure that can be observed in Figure 4-2. The secondary axis of Figure 4-2 shows the changes in flow throughout the test that are correlated with the differences in the behavior of the differential pressure after the breakthrough. Finally, the differential pressure curve was used in the history matching of the simulation model.

Figure 4-3 shows the cumulative production of recombined oil during the drainage test. The data from this production curve are the result from the mass balance performed based on two-phase separator with images captured. Some images have not been recorded due to operational limitations. Due to this issue the production and saturation curves present a discontinuity in the curvature trend. However, it is still possible to use these data in the calculation of the relative permeability curves and the process of simulation model history matching.

Table 4-1 presents the properties and their respective values for two-phase relative permeability system recombined oil and ECB during the drainage. The values for relative permeability in the endpoints, the Corey's exponents, and the values calculated from mass balance during drainage are shown in Table 4-1. Based on the saturation data in Figure 4-1 and the parameters shown in Table 4-1, the relative permeability curve values for each saturation point were calculated using the equation of Brooks and Corey (1966). Figure 4-4 presents the relative permeability curve for the ECB-recombined oil system, where the intersection point of the curves is located in water saturation lower than 0.5 indicating that the rock wettability is preferential to oil and confirming that the experimental aging process was performed successfully.



Figure 4-1 Recombined oil (s<sub>o</sub>) and equilibrated carbonated brine (s<sub>w</sub>) saturation curve. Source: Produced by the author.



Figure 4-2 Differential pressure and flow rate curve. Source: Produced by the author.



Figure 4-3 Production of recombined oil. Source: Produced by the author.

Parameter	Value
K <sub>abs</sub> (mD)	24.80
$k_o@S_{wi}(mD)$	0.191
$k_w @S_{or}(mD)$	0.436
$k_{ro}$ (2) $S_{wi}$	0.00682
$k_{rw}$ ( $a$ ) $S_{or}$	0.01557
$N_{w}$	1.58
No	3.42
$\mathbf{S}_{\mathrm{wi}}$	0.2047
S <sub>or</sub>	0.4458

Table 4-1 Parameters values used in the experimental test. .Source: Produced by the author.



Figure 4-4 Relative permeability curve for the ECB-recombined oil system.Source: Produced by the author.

### 4.2 Simulation results

### 4.2.1 Fluids model

The hydrocarbon fluid and gas compositional data have been inserted into the model as a primary and secondary composition in mole fraction. The reservoir fluid model was recombined into a single composition at separator conditions. Separator pressure, temperature, and GOR were needed for this. Once recombined, the oil properties were estimated using a cubic equation of state, while CO<sub>2</sub> solubility in water was calculated using correlations in function of the reservoir properties. Experimental results of saturation pressure and differential liberation were used to alter the equation of state (EOS) to imitate the fluid behavior.

In order to accurately model the transfer of  $CO_2$  in CWI, it is necessary to consider the dynamic process influenced by the difference in solubility between  $CO_2$  and two immiscible fluids. The  $CO_2$  partition coefficient between the aqueous phase and oil controls the dissolution of  $CO_2$  into the oil, which can be modified by adjusting the binary interaction coefficient (BIC) values of  $CO_2$  and hydrocarbon components. Default BIC values may not accurately capture the  $CO_2$  transfer from carbonated water to reservoir oil, making it necessary to fine-tune these values by history matching experimental data (ALMESMARI, 2019).

In our compositional simulation model, we recombined the oil and gas components into one composition using CMG WinProp. Table 4-2 presents the final compositions after the recombination.

	Primary		
Component	(Dead Oil)	Secondary (Gas)	<b>Recombined fluid</b>
CO2	0	38.24	0.2815
N2	0	0	0
C1	0	61.76	0.4548
C2	0	0	0
C3	0.41	0	0.0008
iC4	0.22	0	0.0004
nC4	0.7	0	0.0014
iC5	0.56		0.0011
nC5	0.89	0	0.0018
C6	2.08	0	0.0043
C7	4.22	0	0.0088
C8	5.75	0	0.01212
C9	5.18	0	0.01092
C10	4.6	0	0.0096
Iododecane	0.05	0	0.05280
C11	4	0	0.0084
C12	3.57	0	0.0075
C13	3.97	0	0.0083
C14	3.28	0	0.0069
C15	3.3	0	0.0069
C16	2.74	0	0.0057
C17	2.53	0	0.0053
C18	2.62	0	0.0055
C19	2.51	0	0.0052
C20+	46.85	0	0.0987
	99.98	100	1

Table 4-2 Oil composition from recombined process on WinProp. Source: Produced by the author.

Through the simulation of various pseudo components, it was evident that the most suitable grouping scheme, in accordance with the PVT data, was the 7-component model. The composition of the crude oil utilized for constructing the fluid model in WinProp and developing an EOS model with the Peng-Robinson equation is presented in Table 4-3. Due to the substantial number of fractions obtained from the crude oil, a lumping process was employed to combine them into seven distinct components for the oil phase.

Lumped	Composition	
Components	(Molar fraction)	
CO2	0.28159901	
N2- CH4	0.45480007	
C2-NC5	0.00586125	
C6-C10	0.04602556	
IODODECANE	0.05280679	
C11-C19	0.06013051	
C20+	0.0987768	

 Table 4-3 Lumped Components and their respective composition for the simulated model. Source:

 Produced by the author.

The preliminary findings revealed that the simulated fluid's behavior did not align with the primary equation of state (EOS), and the calculations deviated from the laboratory data. Consequently, it became necessary to refine the EOS parameters to achieve a more accurate representation of the reservoir fluid's behavior. To accomplish this, a regression analysis was employed, utilizing the experimental PVT data presented in Table 3-2, in order to calibrate the EOS model. Several properties were matched during this calibration process, including the saturation pressure ( $P_{sat}$ ), API degree, gas-oil ratio (GOR), oil formation volume factor ( $B_o$ ), and oil viscosity. Table 4-4 compares the experimental data, model before and after the EOS tuning, and a summary of the global error of the recombined fluid properties. Reducing error is an essential part of the methodology at the time to reproduce the reservoir fluid properties in this research work accurately.

 Table 4-4 Oil properties comparison between experimental and simulated data. Source: Produced by the author.

Properties	Experimental	Model EOS tunning	Error %
Sat Pressure (psi)	6759	6759	0
API	22.4	22.4	0
GOR (scf/stb)	795.68	972.34	22.2
Bo (Rb/stb)	1.33	1.43	7.51
Oil Visc (cp)	5.06	4.24	16.36

Upon completion of the EOS tuning process, the experimental results were compared to the simulation outcomes, revealing a satisfactory agreement between the two. This comparison demonstrated that the simulation model was able of accurately replicating the experimental data with an acceptable level of agreement, which was obtained in the plots shown in Figure 4-5 and Figure 4-6.



Figure 4-5. Adjusted curve for GOR and FVF (Differential liberation test). Source: Produced by the author.



Figure 4-6. Adjusted curve for oil viscosity (Differential liberation test). Source: Produced by the author.

Figure 4-5 shows the GOR and FVF curves of the simulated model (lines) and the experimental data (points). The oil formation volume factor (red curve) behaves as an ascending curve till the bubble point, this is due to the gas dissolution in the oil that generates an increase in its volume. After the bubble point, the curve decreases gradually due to the compression of the fluid. The gas oil ratio (green curve) increases until it reaches the bubble point, representing the maximum gas volume dissolved in the dead oil at a specific temperature and pressure. An essential improvement in the model curves matching the experimental data was achieved by the tuning process with the regression method. In addition, the saturation pressure corresponds with the experimental value in the differential liberation test. Figure 4-6 shows a comparison between the fluid's experimental and final viscosity for the recombined oil, it can be observed that the lower value of viscosity is in the bubble point because all the gas is dissolved in the oil at the lower pressure. Based on the model comparison to the experimental data (showing a relative minimum difference), it can be concluded that the modelled fluid represents the behavior of the reservoir fluid, and this fluid model was exported to the compositional simulator GEM to continue with the simulation process.

## 4.2.2 Model Results

The water and oil saturation data obtained from the coreflooding experiment were utilized as input data for the simulation model. The model employed Corey's correlation to generate representative data for the initial relative permeability curves. Figures 4-7 to 4-11 present the simulation results of the coreflooding model and experimental data in terms of cumulative oil production, differential pressure, and oil and water saturation profiles. The experimental data are depicted by red points, while the simulation data are represented by green and blue lines. Overall, the model demonstrated good agreement with the experimental data, given the underlying assumptions of the model. However, to accurately capture the CO<sub>2</sub>-fluid interactions, the model requires further improvement through the history matching process. The subsequent section of this work presents the results of this process.

The drainage model was built using the tool Builder/CMG and run in GEM/CMG simulator according to the procedure described in section 3.1 and considering the

experimental data presented in section 2.13. The simulation time was 135 min. ECB flooding results (water average saturation, oil average saturation, cumulative oil production, and differential pressure) were used to build water-oil-relative permeability curves.

The waterflooding experiment was carried out at different injection rates at reservoir conditions, as is shown in Table 3-6, and it was reproduced in the model, setting operational constraints in the injector well (Table 3-5). Figure 4-7 shows the water rate injection in blue from the simulated model.



Figure 4-7 ECB injection rates in the simulation model. Source: Produced by the author.

Figure 4-8 shows the differential pressure curve. One of the discrepancies concerning water injection and carbonated water injection is the impact of the GOR on the differential pressure across the core as a consequence of the formation of the new gaseous phase and its trapping mechanism in porous medium. The pressure changes in Figure 4-8 represent the variation in injection rate through time, showing that the differential pressure is directly proportional to the injection rate. By comparing the experimental data (red circles) with the simulated model data (blue curve), we observe that the curve's trend is the same, but with a significantly greater magnitude at the beginning of injection (nearly four times) due to the instantaneous implementation of the injection rate, as well as during injection rate changes. Furthermore, we observe that the differential pressure stabilizes after 0.17 days, which coincides with a steady injection rate, indicating that the breakthrough has occurred by this

point. From then on, the curves match accurately until the end of injection. In conclusion, concerning the curve fitting error, the base model shows an error of 24.3% using the equation 2.38.



Figure 4-8 Differential pressure curve for the ECB- oil system. Source: produced by the author.

The oil cumulative production data obtained from the simulation shown in the Figure 4-9 was compared with the oil production profile obtained from the core flooding experiment. The comparison revealed that the simulated model predicted oil production reasonably well during the early stage of the injection process. However, after 0.12 days of injection, the simulated model showed a significant deviation from the experimental data, indicating an inaccurate prediction of the oil production profile. This deviation is likely attributed to the simplified assumption of homogeneous properties of the rock in the model, which does not capture the heterogeneity of the core sample. Additionally, the model's assumption of high CO<sub>2</sub> solubility in oil may have resulted in an overestimation of oil viscosity reduction, which can impact the oil recovery process. It should be noted that the increase in water injection rate does not always result in increased oil production, as this can be limited by the oil's relative saturation to CW. Finally, the simulated model showed an error of 56.9%, which indicates the need for further refinement and calibration of the model to better reflect the actual reservoir conditions.



Figure 4-9 Cumulative oil production curve for the ECB-oil system. Source: Produced by the author.

Figure 4-10 and Figure 4-11 present the model curves of the average water saturation and average oil saturation for the ECB-Recombined oil system during a drainage coreflooding test. The experimental drainage curves show an initial trend that is well captured by the model. However, after 0.17 days of carbonated water injection, the model data deviates from the experimental data.

To decrease the oil saturation, the core sample was CW-flooded at different injection rates in the coreflooding test and reproduced in the simulated model. However, not all saturation points of fluids can be completely reliable in this experiment (mass balance estimation) due to the lack of information about in-situ saturation measurements.

At the end of the simulation, the residual simulated water saturation was found to be higher than the experimental value. This discrepancy could explain the additional oil production observed in Figure 4-9.



Figure 4-10 Water Average Saturation curve for the ECB-Recombined oil system. Source: Produced by the author.



Figure 4-11 Oil Average Saturation curve for the ECB-Recombined oil system. Source: Produced by the author.

### **4.2.3 History Matching Results**

The history matching process was conducted using the CMOST/CMG module program and was divided into two stages. In the first stage, a sensitivity analysis of the uncertain input parameters was carried out to determine their impact on the model. In this study, 16 parameters were considered, as illustrated in Figure 4-12. To achieve this, 770 experiments were performed using the CMG Bayesian Engine method. The main advantage of this procedure was to identify the parameters that significantly influenced the objective functions.

Parameter	Default value	
Injector rad	0.076	
Producer rad	0.076	
$N_{g}$	3	
No	3.48	
$N_{ m w}$	1.58	
Permeability I	24.8	
Permeability J	24.8	
Permeability K	24.8	
Porosity	0.15	
PVC	1.27	
$\mathbf{S}_{\mathrm{oirg}}$	0.37	
$\mathbf{S}_{\mathrm{org}}$	0.37	
$S_{wc}$	0.24	
WI injector	1	
WI Producer	1	
Y <sub>aq</sub> Rate	0.02	

Figure 4-12 Parameters used to perform the sensitive analyses on CMOST. Source: Produced by the author.

To determine the degree of influence of each parameter on the variance of the model output, the Sobol' method technique was used through the CMOST/CMG tool. The total sensitivity index of a parameter is the sum of its main effects and interaction effects, which are reported in Figure 4-13 for all uncertain parameters considered in the simulations. The

results indicated that PVC3, which corresponds to the parameter used to calculate binary interaction coefficients, was the most influential parameter with a 22% main effect and 12% interaction effect. This parameter plays a crucial role in accurately reproducing  $CO_2$  mass transfer and interaction with the oil. The porosity (8.4% main effect) was also found to be an important parameter, particularly in its interaction with other parameters (21%). This is due to its influence on fluid storage capacity in the porous media and the overestimation of the simulated results, such as produced oil and fluid saturations, which can occur due to the assumption of homogenous properties.



Figure 4-13 The relative influences of the parameter change on the objective function, (GlobalHMError) .Source: Produced by the author.

A Sobol' method analysis was carried out for each objective function to determine the factors and their respective influence on the history matching process as well. For instance, Figure 4-14 presents the relative influences of the parameters for the cumulative oil production, which has the greatest error and is considered overestimated. The porosity and PVC were identified as the most influential parameters for this objection function. The most influential parameters for the differential pressure are the porous medium properties (permeability and porosity) and well injectivity (Well index) as shown in Figure 4-15. Finally, Figure 4-16 illustrates the influences of the parameters for oil and water saturation. The porosity was found to be the most significant parameter, as it is linked to the available pore space in the rock, while the PVC's influence was related to the possible formation of a gas

phase. Although not considered in this experimental research, this phenomenon has been observed in other several research studies. (ALMESMARI, 2019; DE NEVERS, 1964b; KECHUT et al., 2010; KECHUT; JAMIOLAHMADY; SOHRABI, 2011; RAMESH; DIXON, 1973; SOHRABI et al., 2012).



Figure 4-14 The relative influences of the parameter change on the objective function (Cumulative Oil).Source: Produced by the author.



Figure 4-15 The relative influences of the parameter change on the objective function (Differential Pressure). Source: Produced by the author.



saturation). Source : Produced by the author.

The second stage of the history matching process involved selecting a set of 7 influential parameters for adjustment. To achieve this, 1000 new simulations were run using the Particle Swarm Optimization (PSO) method, and 1000 simulations using the CMG Bayesian Engine Method. After running 486 PSO simulations, the method produced the best result on a model designed as optimal solution, with a global error of 8.51%. The variation of the global error of the historical matching with the experimental data is illustrated in Figure 4-17. Figure 4-17 to Figure 4-21 present the history matching trials performed for 2000 iterations to obtain the minimal error for the cumulative oil production, differential pressure, and oil and water saturations. The figures also display the base case (black curve) and the optimal model (red curve) of the coreflooding experiment simulation. Figure 4-22 to Figure 4-27 present the variation of the parameters value through the history matching trials performed. During our analysis, it was observed that certain parameters, including permeability, porosity and well index reached the upper or lower boundaries of their predefined ranges during the adjustment process. This behavior suggests the potential need for a reconsideration of the parameterization approach. It is possible that the adjustment, which assumed homogeneity in the reservoir, attempted to compensate for the effects of heterogeneity by reaching these parameter limits.



Figure 4-17 Convergence of algorithm for the history matching process. Source: Produced by the author.



Figure 4-18 History matching results for cumulative oil. Source: Produced by the author.



Figure 4-19 History matching results for differential pressure. Source: Produced by the author.



Figure 4-20 History matching results for water average saturation. Source: Produced by the author.



Figure 4-21 History matching results for oil average saturation. Source: Produced by the author.



Figure 4-22 Convergence of the No for the history matching process. Source: Produced by the author.


Figure 4-23 Convergence of the Nw for the history matching process. Source: Produced by the author.



Figure 4-24 Convergence of the permeability for the history matching process. Source: Produced by the author.



Figure 4-25 Convergence of the porosity for the history matching process. Source: Produced by the author.



Figure 4-26 Convergence of the injector well index for the history matching process. Source: Produced by the author.



Figure 4-27 Convergence of the producer well index for the history matching process. Source: Produced by the author.



Figure 4-28 Convergence of the binary coefficient interaction for the history matching process. Source: Produced by the author.

The history matching process generated the best result, which is shown as the black curve in Figure 4-29, Figure 4-30, Figure 4-31, and Figure 4-32, with the legend "history matched model." Figure 4-29 demonstrates that the pressure differential adjustment had an overestimate increase during the early stage of CWI until oil production began, followed by a

decline in the trend of differential pressure. The model's order of magnitude in the peaks was reduced, and almost a perfect fit was achieved in the stable part of the curve (constant injection rate) compared to the experimental value, resulting in a reduced error of 6.09%, as shown in Table 4 5. The binary interaction coefficient's influence suggests that the compositional behavior of the  $CO_2$  mass transfer from CW to oil had a significant impact on differential pressure.

The history matched model shows a significant improvement in predicting the oil production curve, with a close fitting to the experimental data. The model successfully predicts the trend of increasing oil production, expected in the drainage coreflooding process. However, the produced oil presented relatively greater values after water breakthrough than the experimental data, which can be attributed to the complexity of  $CO_2$  mass transfer into the oil during the CWI process. This phenomenon is particularly relevant in reservoirs, where  $CO_2$  can dissolve and diffuse into the oil phase. This process can significantly affect the behavior of the system and alter the predicted values of oil production.

It is important to note that the heterogeneities of the porous medium were not considered in the model because the limitations of the experimental study data and the new gas phase formation, which may also contribute to the observed differences between the predicted and experimental data. However, despite these limitations, the final cumulative oil recovery of the history matched model agrees with the experimental values, as shown in Figure 4-30, with an error of 8.51%. These results suggest that the model can effectively capture the main features of the experimental carbonated water flooding process, highlighting the importance of considering mass transfer phenomena in enhanced oil recovery processes.

Finally, the oil average and water average saturation curves presented an error reduction to 9.34%, as can be seen in Table 4-5 and Figure 4-31, and Figure 4-32. Even in the simulation model is not directly include the new gas formation that is vastly recommend in the literature for simulated models to better reproduce the  $CO_2$  behave, the final residual saturation after the history matching shows a good match to the experimental data.

In conclusion, the simulation model achieved a significant reduction in the global error of up to 80%, using only seven parameters, as presented in Table 4-5. The presence of heterogeneities in the porous medium, such as differences in porosity and permeability, was identified as a major source of discrepancy between the model and experimental data. The lack of consideration of these heterogeneities in the simulation model can significantly affect the behavior of the system. However, despite this limitation, the final global error of the history matched model is considered satisfactory, with a value of less than 10%. This is attributed to the assumptions, complexity of the process, and uncertainties involved. Therefore, the simulation model can effectively capture the main features of the experimental carbonated water flooding process and can be useful in estimating the relative permeability curves for this system.

Parameters results of the model Parameters Value (Experimental)						
3.4	1.58	24.8	0.1576	1.2	1	1
			Parameters Error			
Global Error (%)		Error_DP(%)	Error_CumOil(%)	Error_S <sub>o</sub> (%)	Error_S <sub>w</sub> (%)	
38.79		24.38	56.94	38.06	35.78	
		Parameters	results of the History m	atching		
			Parameters Value			
Now	Nw	Perm (mD)	Por	PVC	$\mathbf{W}_{inj}$	Wpro
5	1.65	40	0.09	1.3751	1.99	2
			Parameters Error			
Global Error(%)		Error_DP(%)	Error_CumOil(%)	Error_S <sub>o</sub> (%)	Error_S <sub>w</sub> (%)	
8.51		6.09	9.25	9.34	9.34	

Table 4-5 Model and history matching results. Source: Produced by the author.



Figure 4-29 Differential pressure curve for the ECB-recombined oil system. Source: Produced by the author.



Cumulative Oil RC



Figure 4-30 Cumulative Oil production curve for the ECB-recombined oil system. Source: Produced by the author.

Figure 4-31 Oil average saturation curve for the ECB-recombined oil system. Source: Produced by the author.



Figure 4-32 Water average saturation curve for the ECB-recombined oil system. Source: Produced by the author.

Another important output that is compared between the base case model and the history matched model is the oil saturation map captured in different states of displacement (1 PV, 2 PV, 3 PV and in the end of the injection) and in three different positions of the core (inlet

cross section, middle and outlet cross section) as shown in the Figure 4-33, Figure 4-34, Figure 4-35, and Figure 4-36. During the carbonated water flooding, several simulated saturation profiles along the flow direction were utilized to have an insight of the front and fluid movements due to the absence of computer tomography data in the coreflooding experiment. It should be emphasized that the numerical model is homogeneous, however it is a good starting point to analyze the carbonated water flow through the porous media and a way to evaluate the impact of the history matching process in the model.



Figure 4-33 Oil saturation map at 1 pore volume ECB injection. Source: Produced by the author.



Figure 4-34 Oil saturation map at 2 pore volume ECB injection. Source: Produced by the author.



Figure 4-35 Oil saturation map at 3 pore volume ECB injection. Source: Produced by the author.



Figure 4-36 Oil saturation map at the end of the simulation. Source: Produced by the author.

In complement to the saturation maps, it was generated oil saturation profiles along the core's length and the flow direction. These profiles depict the evolution of oil saturation at various time intervals during the experiment, specifically at 1 PV, 2 PV, 3 PV, and at the end of injection. This graphical representation offers a visual means to illustrate the displacement of oil along the core's length at distinct time points. Consequently, it provides a basis for a

comparative analysis between the initial simulated model and the history-matched model that is shown in the Figure 4-37.



Figure 4-37 Oil saturation profile along the core length at different injection times.

The Brooks and Corey (1966) model is widely used in the petroleum industry to estimate relative permeability curves in reservoir simulation. Accurate derivation of these curves holds paramount importance, as it directly supports the reliability of predictions relating to fluid flow in porous media. Within this research context, the study conducted a comprehensive history matching methodology, assisted by the utilization of CMOST software. This history matching was employed with the primary objective of estimating and adjusted Corey's exponents and subsequently generating the relative permeability curves, as illustrated in Figure 4-38. The saturation endpoints, estimated from experimental data, were maintained as fixed parameters throughout the process. Furthermore, the initial experimental characterization of relative permeability was used as an input data, and it was performed a subsequent fine-tuning of water and oil relative permeability curves being realized through the variation of fluid parameters within Corey's model. This adjustment process aimed to achieve congruence between measured production data, differential pressure, and saturation, and the outcomes yielded by the simulation.

Figure 4-38 summarizes the relative permeability curves in function of water saturation, comparing Corey's exponents extracted from existing literature with the exponents resulting from the history matching process. Showing, as the parameter  $N_w$  ascends, the water relative permeability curve shifts towards the right of the plot. Consequently, for equivalent water saturation levels, the relative permeability of water presents a diminishment, indicative of a concurrent reduction in fluid flow rates. An increase in the exponent  $N_{ow}$  prompts the oil relative permeability curve to shift in the opposite direction This alteration consequently yields a reduced relative permeability of oil for identical water saturation levels, thereby decreasing the flow of oil and consequently diminishing oil production rates. A salient observation from our analysis is the determination of the water saturation corresponding to the crossover point within the oil-water relative permeability curve, which was quantified at 30%. This observation substantiates the oil-wet nature of the reservoir, a characteristic commonly encountered in Brazilian pre-salt carbonates, which can impact the oil recovery from the reservoir.

The comparative examination of relative permeability curves, as discerned from the simulation model (gray and yellow curves) and those extracted from existing literature (blue and red curves), revealed a notable degree of congruence. Crucially, the study succeeded in determining the Brooks-Corey correlations' exponents for oil and water relative permeability curves. These exponents were accurately fine-tuned via the history matching process to

achieve a matching agreement with experimental data. Consequently, this process holds the potential to present greater accuracy of the simulated model in estimating the Corey exponents when compared with values from the literature. This enhanced accuracy is primarily attributed to the detailed consideration of diverse factors, including specific fluid properties, rock characteristics, and experimental data. Finally, the relative permeability curves obtained through history matching on this work serve as a valuable starting point for reservoir studies, particularly when transitioning from laboratory-scale adjustments to field-scale investigations.



Figure 4-38 Relative permeability curves comparison for the ECB-recombined oil system. Source: Produced by the author.

## **5** CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

This chapter presents the conclusions obtained by this work and the main recommendations for future works.

- The methodology implemented allowed to simulate the two-phase system (ECB-Recombined oil) displacement experiment (relative permeability experimental study) under reservoir conditions in carbonate rocks.
- Combining laboratory measurements with modeling resulted in great outcomes, overcoming the uncertainties and complications of both methods.
- The WinProp model reproduces the PVT properties of the fluids accurately, showing very close values of the experimentally determined data.
- The adapted Coats & Smart methodology showed a successful way to perform the EOS tuning for compositional modeling.
- The CO<sub>2</sub>-hydrocarbon binary interaction coefficients adjust is an effective way to simulate the CO<sub>2</sub> partitioning in water and oil of the experimental process.
- The coreflooding experiment for carbonated water injection (CWI) was successfully history matched, resulting in accurate determination of the oil-water relative permeabilities. The simulation demonstrated its capability to model the underlying mechanisms effectively, indicating that once the fundamental physics of the process are comprehended and applied in the simulation, the results fit well with the observed behavior.
- The analysis of the experimental data is an important step prior to its implementation in the reservoir simulation. Reliable experimental data helps to reproduce the reservoir behavior and provides information to fill the remaining gaps in the simulation process.
- sensitivity analysis during the history matching is an indispensable tool for reservoir model calibration and for the evaluation of the parameters impact. it can assist and improve the history matching process while allow a better understanding of the CWI phenomena.

• The history matching process using the CMOST/CMG program resulted in a new relative permeability curve for the ECB-Recombined oil system considering the exponents of Brooks and Corey (1966) obtained from the optimization process. Even though no sample heterogeneity was considered, the results showed that the error was minimized to match the model and the experimental data.

### 5.2 Recommendations

- Performed more experimental studies to validate the simulation methodology and improve the accuracy of the models. These studies could involve performing additional laboratory measurements for different rock types and fluid compositions to obtain more reliable data for the simulation models and to analyze the sensitivity of the simulation parameters.
- Investigate the impact of sample heterogeneity and carry out upscale from laboratory to reservoir scale to test the accuracy of the simulation results.
- Investigate the impact of different binary interaction coefficients on the fluid phase behavior during simulation scenarios. This can help improve the accuracy of the simulation results, especially in cases where CO<sub>2</sub>- recombined oil are involved.
- Investigate alternative simulation tools or software that can support the simultaneous transfer of CO<sub>2</sub> from carbonated water into the oil. This could involve the use of specialized software or the development of new simulation models that can better represent these complex phenomena.
- To a better modelling of carbonated water injection (CWI) for enhanced oil recovery, future works should focus on estimating the formation of new gas phases during CWI experiments in live oil systems. This could involve using advanced imaging techniques such as X-ray CT scanning to visualize the fluid distribution and estimate the amount of trapped gas within the oil phase. Additionally, the estimation of the new gas phase could assist in understanding the impact of gas trapping on oil swelling during the coreflooding process.

• To accurately simulate the coreflooding experiments it is necessary to identify the measurement errors and other anomalies that generate uncertainties in obtained data, future works should include a thorough uncertainty analysis in the study design. This can involve conducting sensitivity analyses and performing error analysis to identify the impact of these uncertainties on the study results. Additionally, conducting repeat experiments and ensuring the reliability of the data collected can improve the accuracy of the analysis and reduce uncertainties in the results.

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# **APPENDIX A- WINPROP FLUID MODEL (PARAMETERS)**

\*\*\*\*\*\*\*\*\*\*\*\*\*\* \* \* WINPROP 2020.10 \* \* EOS Phase Property Program \* General Release for Win x64 2020-Aug-14 18:40:15 \* \* (c) Copyright 1977 - 2020 Computer Modelling Group Ltd., Calgary, Canada All Rights Reserved \* \* \*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\* Command-line Arguments: -dd -f PVT\_GEM.dat Maximum Dimensions: = 200Component SCN Group in + Fractions = 200; Lab. Calculation points = 300Streams in Process = 300; Units in Process = 20Regression variables = 150; Regression data points = 10000\*\*FILE NAME: PVT GEM.dat \*FILENAMES \*OUTPUT \*SRFOUT \*REGLUMPSPLIT \*NONE \*GEMOUT \*STARSKV \*NONE \*GEMZDEPTH \*NONE \*IMEXPVT \*NONE \*WINPROP 2020.10 \*\*=-=-Titles/EOS/Units \*\*REM 2D Recombined + Iodecane \*TITLE1 '' \*TITLE2 ' ' \*TITLE3 '' \*UNIT \*FIELD \*INFEED \*MOLE \*MODEL \*PR \*1978 \*\*=-=-Component Selection/Properties \*\*REM \*NC 7 7 \*TRANSLATION 1 \*EXCESSPROP \*EOS \*COMPNAME 'CO2' 'N2 toCH4' 'C2HtoNC5' 'C6 toC10' 'IODECANE' 'C11toC19' 'C20+' \*HCFLAG 3 1 1 1 1 1 1 \*PCRIT 72.8 45.4 35.75989 28.289439 56.640791 13.44 7.9743198 \*TCRIT 304.2 190.6 438.63699 606.83229 665.48273 685.4 937.08049 \*AC 0.225 0.008 0.21102518 0.36458313 0.18735748 0.62457727 1.3159386

\*MW 44.01 16.043 63.371511 111.8841 268.18 239.24 672.29889 \*VSHIFT  $0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0$  $0.0 \ 0.0$ \*VSHIF1  $0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0$  $0.0 \ 0.0$ \*TREFVS  $60.0\ \ 60.0\ \ 60.0\ \ 60.0$ 60.0 60.0 \*ZRA  $0.2736 \ \ 0.2876 \ \ 0.27187194 \ \ 0.25938608 \ \ 0.44273529$ 0.23633105 0.25104709 **\*VCRIT** 0.094 0.099 0.27305479 0.43762133 0.24800884 0.75174156 1.8941842 \*VISVC 0.094 0.099 0.27392446 0.43886716 0.24800884 0.75544846 1.8941842 \*OMEGA  $0.45723553 \ 0.58804 \ 0.45723553 \ 0.45723553 \ 0.45723553$ 0.45723553 0.45723553 \*OMEGB 0.077796074 0.10028459 0.077796074 0.077796074 0.077796074 0.077796074 0.077796074 \*BETA\_LFU 1.0 1.0 1.0 1.0 1.0 1.0 1.0 \*SG 0.818 0.3 0.59830006 0.75330655 1.257 0.83160453 0.9645 \*TB -109.21 -258.61 63.369114 261.60459 269.6 500.48648 1124.0053 \*PCHOR 78.0 77.0 203.78345 321.91425 696.59627 541.95494 1148.6664 \*IGHCOEF 0.09688 0.158843 -3.3712e-05 1.48105e-07 -9.66203e-11 2.073832e-14 0.151147 -2.83857 0.538285 -0.000211409 3.39276e-07 -1.164322e-10 1.389612e-14 -0.602869 8.4959353 0.095596587 0.00025480207 6.9708825e-08 -4.9380246e-11 7.6198418e-15 0.33783338  $0.0 \ -0.041900903 \ 0.00042617557 \ -6.3558242e{-}08 \ 0.0 \ 0.0 \ 0.0$ 0.0 -0.13469409 0.00026705238 -5.131e-08 0.0 0.0 0.0 0.0 -0.036303362 0.00041686683 -6.1755607e-08 0.0 0.0 0.0 0.0 -0.0099352671 0.00039408739 -5.5033784e-08 0.0 0.0 0.0 \*HEATING\_VALUES 0.0 844.29001 2957.0286 5396.2452 0.0

9327.4349 0.0

141

18.751507 8.302691 \*TCRITS 304.2 190.6 438.63699 578.4799 658.56185 709.81612 1012.6752 \*VSHIFTS  $0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0$  $-0.0015766311 \ \ 0.0076912965$ \*VSHIF1S  $0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0$  $0.0 \ 0.0$ \*OMEGAS  $0.45723553 \ 0.45723553 \ 0.45723553 \ 0.45723553 \ 0.45723553$ 0.45723553 0.45723553 \*OMEGBS  $0.077796074 \ \ 0.077796074 \ \ 0.077796074 \ \ 0.077796074 \ \ 0.077796074$ 0.077796074 0.077796074 \*IDCOMP  $0 \ 0 \ 0 \ 0 \ 0$ 0 0

72.8 45.4 35.75989 28.289439 56.640791

\*VISCOR \*MODPEDERSEN

\*VISCOEFF 0.00010432 2.6812773 0.0088536 1.4776 0.41384 \*HREFCOR \*HARVEY

\*PVC3 1.2771307

\*BIN 0.105 0.1168705 0.115 0.0 0.115 0.0 \*PVC3S 1.2 \*BINS 0.0 0.0 0.0 0.0

\*PCRITS

0.0 0.0 0.0 0.0

\*\*=-=-=Composition \*\*REM \*COMPOSITION \*PRIMARY 0.28159901 0.45480007 0.0058612493 0.046025563 0.052806792 0.060130512 0.098776805

\*\*=\_=-=Saturation Pressure \*PRESSAT \*LABEL " \*FEED \*MIXED 1.0 \*KVALUE \*INTERNAL \*LEVEL 1 \*OUTPUT 1 \*PRES 5000.0 \*TEMP 158.0 \*SATFLAG 2 \*EXPERIMENTAL \*PSAT \*DATA 6759.0 \*WEIGHT 800.0 \*\*=-=-=Differential Liberation \*DIFLIB \*LABEL " \*FEED \*MIXED 1.0 \*KVALUE \*INTERNAL \*LEVEL 1 \*OUTPUT 1 \*PRES 6759.0 \*TEMP 158.0 \*SATFLAG 2 \*STP 14.69595 \*STT 60.0008 \*CONSISTENCYCHECKS \*YES \*NPSTEPS 10 \*PRES-DIFL 9245.145 8533.98 7822.815 7111.65 3533.9211 2822.7561 2111.5911 1400.4261 700.213 14.7 \*GORM 795.5864583 795.5864583 795.5864583 795.5864583 795.5864583 699.8578125 577.1791667 453.9952083 324.6913542 191.2888542 0.0 \*FVFO 1.334958765 \*DENO 0.83 \*SGRO 0.919399 \*\*NC 7 7 \*\*NUMBER\_OF\_COLUMNS 10 \*VAPCOMP  $0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0$  $0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0$  $0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0$  $0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0$  $0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0$  $0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0$  $0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0 \ 0.0$ \*EXPERIMENTAL \*ROV \*DATA 1.4372 1.4414 1.4153 1.4219 1.4292 1.31 1.27 1.23 1.19 1.14 1.05 \*WEIGHT 1.0 \*GOR \*DATA 972.34 972.34 972.34 972.34 972.34 585.33 483.41 379.05 271.47 158.53 0.0 \*WEIGHT 1.0 \*DL \*DATA  $0.81411 \ \ 0.82916 \ \ 0.82527 \ \ 0.82107 \ \ 0.81651$ 0.83277 0.84147 0.85181 0.86351 0.87553 0.876 \*WEIGHT 1.0

\*MUL \*DATA  $4.2469 \ 4.1487 \ 4.8331 \ 4.6394 \ 4.4439$ 5.2886 6.0159 7.2068 9.3431 13.553 24.663 \*WEIGHT 1.0 \*DR \*DATA 0.919399 \*WEIGHT 1.0 \*\*=-=-=CMG GEM EOS Model \*\*REM \*\*NC 7 7 \*PRINT \*INTCOEFTABLE \*LOWER \*SOLUBILITY \*TEMP 158.0 \*PRES 8500.0 \*PRNGEM \*TRES 158.0 \*AQUEOUS-DENSITY \*LINEAR \*EOSSET 1 \*DER-CHEM-EQUIL \*ANALYTICAL \*DER-REACT-RATE \*ANALYTICAL \*RFCALC \*OFF \*ACTIVITY-MODEL \*DEBYE-HUCKEL \*SALINITY-CALC \*ON \*AQFILL \*OFF \*YAQU-RATE-CUTOFF  $0.023 \ 0.0 \ 0.0 \ 0.0 \ 0.0$ 0.0 0.0 \*GEOCHEM V2 \*GEOCHEM\_DATABASE \*WOLERY \*NC-AQUEOUS 15 \*COMPNAME-AQUEOUS 'H+' 'Na+' 'Cl-' 'K+' 'SO4--' 'Mg++' 'Ca++' 'HCO3-' 'NaCl' 'KCl' 'NaSO4-' 'MgCl+' 'CaCl+' 'NaHCO3' 'NaCO3-' \*MW-AQUEOUS 1.0079 22.9898 35.453 39.0983 96.0576 24.305 40.08 61.0171 58.4428 74.5513 119.0474 59.758 75.533 84.0069 82.999 \*ION-SIZE-AQUEOUS 9.0 4.0 3.0 3.0 4.0  $8.0\ 6.0\ 4.5\ 4.0\ 4.0$ 4.0 4.0 4.0 4.0 4.0 \*CHARGE-AQUEOUS 1.0 1.0 -1.0 1.0 -2.0 2.0 2.0 -1.0 0.0 0.0 -1.0 1.0 1.0 0.0 -1.0 \*NC-MINERAL 2 \*COMPNAME-MINERAL 'Calcite' 'Dolomite'

\*NC-MINERAL 2 \*COMPNAME-MINERAL 'Calcite' 'Dolomite' \*MW-MINERAL 100.0892 184.4034 \*MASSDENSITY-MINERAL 2709.94747387 2864.96387788
\*NUMAQRXNS 8

```
***** original full reactions strings *****
** CO2(aq) + H2O = H + HCO3-
** NaCl = Na++ Cl-
** KCl = K + Cl-
** NaSO4- = Na+ + SO4--
** MgCl+=Mg+++Cl-
** CaCl+ = Ca++ Cl-
** NaHCO3 = Na++ HCO3-
** NaCO3- + H+ = Na+ + HCO3-
*****
*AQURXNS V2
"'CO2' + 'H2O' = 'H+' + 'HCO3-'"
" 'NaCl' = 'Na+' + 'Cl-'"
" 'KCl' = 'K+' + 'Cl-'"
" 'NaSO4-' = 'Na+' + 'SO4--'"
" 'MgCl+' = 'Mg++' + 'Cl-'"
" 'CaCl+' = 'Ca++' + 'Cl-'"
" 'NaHCO3' = 'Na+' + 'HCO3-'"
"'NaCO3-' + 'H+' = 'Na+' + 'HCO3-'"
```

## \*NUMMINRXNS 2

```
***** original full reactions strings *****
** Calcite + H+ = Ca++ + HCO3-
** Dolomite + 2.0 H+ = Ca++ + Mg++ + 2.0 HCO3-
*****
*REACTION-RATE-TST
"'Calcite' + 'H+' = 'Ca++' + 'HCO3-'''
"'Dolomite' + 2.0 'H+' = 'Ca++' + 'Mg++' + 2.0 'HCO3-'''
```

\*MINRXNAREA 75.006 139.61 \*MINRXNRATE -5.81 -10.0 \*MINRXNENERGY 24430.0 41030.0

```
*NUM-CHEM-EQUIL-TEMPS 8

*CHEM-EQUIL-TEMPS

0.0 25.0 60.0 100.0 150.0 200.0 250.0 300.0

*LOG-CHEM-EQUIL-KVALS

-6.557 -6.366 -6.3325 -6.433 -6.742 -7.188 -7.763 -8.465

1.855 1.5994 1.2945 0.9856 0.635 0.2935 500.0 500.0

1.757 1.5876 1.388 1.1997 1.0036 0.8339 500.0 500.0

-0.6409 -0.6938 -0.7905 -0.8826 -1.0065 -1.1805 -1.4969 -2.2298

-0.354 -0.1503 -0.0528 -0.1077 -0.3556 -0.7869 -1.4524 -2.5537

-0.9687 -0.7 -0.5157 -0.4688 -0.5789 -0.8602 -1.356 -2.2451

-0.353 -0.129 0.1269 0.4263 0.8067 1.226 500.0 500.0

9.842 9.8396 10.093 10.6556 11.5593 12.6046 13.7334 14.7613

2.0683 1.713 1.2133 0.6871 0.0762 -0.5349 -1.2301 -2.2107

3.3936 2.5207 1.3391 0.1312 -1.2393 -2.582 -4.0861 -6.1856
```

\*\*=-=-= END

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Equilibrium Properties at 6758.281 psia and 158.000 deg F Phase Split: Liquid-Vapour

-----

Peng-Robinson Equations of State

## mole percent

component Feed Phase01 Phase02
CO228.1599028.1599025.11121N2 toCH445.4800145.4800166.31020C2HtoNC50.586120.586120.53601C6 toC104.602564.602562.34836IODECANE5.280685.280683.48655C11toC196.013056.013052.06849C20+9.877689.877680.13918
component ln (fug, atm) K-values w.r.t. phase 1
Phase01/02 Phase02
CO23.92668E+001.12141E+008.91737E-01N2 toCH45.63224E+006.85867E-011.45801E+00C2HtoNC5-1.52404E+001.09349E+009.14500E-01C6 toC10-2.41507E+001.95990E+005.10229E-01IODECANE-2.08408E+001.51459E+006.60246E-01C11toC19-3.64442E+002.90698E+003.44000E-01C20+-1.55291E+017.09712E+011.40902E-02
liquid         vapour           Z-factor         2.4476         1.1986           Molar vol, m3/kmol         0.14987         0.14987         0.07339           MW, g/mol         120.165         120.17         39.89           Ideal H,BTU/lbmol         14881.437         14881.44         5694.14           Enthalpy,BTU/lbmol         5515.023         5515.02         2706.11           Ideal Cp, BTU/lbmol-R         44.3160         13.2650           Cp, BTU/lbmol-R         53.1605         18.3327           Ideal S, BTU/lbmol-R         57.9879         39.7641           Entropy, BTU/lbmol-R         48.7992         36.3231           Density, lb/ft3         50.0542         33.9307           Viscosity, cp         3.9723         0.1217           IFT (Ref: Liquid), dyne/cm         0.0002           Phase volume %         100.0000         0.0000           Phase mole %         100.0000         0.0000
Enthalpy is zero for ideal gas at absolute zero Interfacial tension, IFT, is referenced to phase 1
Convergence status : Total iterations in phase equilibrium calculation 21 Total iterations in phase stability test 90 Residual sum of squares error 9.90774E-25
1 *************************************
* *
* WINPROP 2020.10 *
* 2020-Aug-14 18:40:15 *
* Computer Modelling Group Ltd., Calgary, Canada * * 1 *
**********

Differential liberation calculation

Summary of Differential Vaporization at 158.0 deg F

## Initial feed is 1.000E+00 lbmol of fluid

 component
 feed,%

 CO2
 28.160

 N2 toCH4
 45.480

 C2HtoNC5
 0.586

 C6 toC10
 4.603

 IODECANE
 5.281

 C11toC19
 6.013

 C20+
 9.878

	pressure, psia	gas,mole	oil,litre o F	oil S.G. o VF(1) C	oil solu GOR (2) :	ition devia factor Z I	tion gas FVF(3) (A	gas S.G Air=1) tot	). relativ .vol(4) d	e IFT yne/cm	oil vis,cp	gas vis, cp
0.1217	6758.28	0.0000	67.9804	0.80179	1.45100	982.33	1.1986	0.00310	1.3770	1.451	0.0002	3.9723
0 1/18	9245.15	0.0000	66.5979	0.81844	1.42149	982.33	1.5004	0.00283	1.3770	1.421	0.0000	4.6406
0.1410	8533.98	0.0000	66.9476	0.81416	1.42895	982.33	1.4148	0.00290	1.3770	1.429	0.0000	4.4513
0.1364	7822.82	0.0000	67.3309	0.80953	1.43713	982.33	1.3286	0.00297	1.3770	1.437	0.0000	4.2605
0.1307												
0 1249	7111.65	0.0000	67.7535	0.80448	1.44616	982.33	1.2419	0.00305	1.3770	1.446	0.0001	4.0683
0.1248	3533.92	141.8659	61.15	78 0.824	495 1.3	0537 5	79.55 (	).8463 0	.00418	0.9864	1.605	0.3865
5.3215	0.0357 2822.76	34.8789	59.3187	0.83444	1.26612	2 480.52	0.8143	0.00504	0.9445	5 1.716	0.9071	6.1031
0.0277	2111.59	35.9886	57.3682	0.84593	1.22449	9 378.35	0.8056	0.00666	0.9289	0 1.941	1.8977	7.3844
0.0224												,
	1400.43	37.7698	55.2568	0.85940	1.17942	2 271.11	0.8283	0.01033	0.9521	2.488	3.5863	9.7095
0.0191	700.21	40.5947	52.9272	0.87385	1.12970	155.86	0.8889	0.02217	1.0519	4.394	6.0274	14.3591
0.0176	14 70	54 8970	49 3783	0 87236	1 05395	0.00	0 9947	1 18192	1 9963	207 842	8 1023	23 9024
0.0222	1	2	.,	0.07200	1.00070	5.00	0.2217		1.,,,00	201.012	0.1020	20.9021

vol of residual oil / vol of saturated oil = 0.6892S.G. of residual oil at 60.0 deg F= 0.9194API gravity of residual oil at 60.0 deg F= 22.4

(1) FVF: oil formation vol. factor, vol of oil + dissolved gas at indicated P & T / vol residual oil at 60.0 deg F (2) cu. ft. of gas at 14.70 psia 60.0 deg F / bbl of residual oil at 60.0 deg F (3) FVF: formation volume factor, vol of gas at indicated P & T per vol at 14.70 psia 60.0 deg F (4) vol of oil and gas at indicated P & T / vol of residual oil at 60.0 deg F 1 \*\*\*\*\*\* \* \* \* WINPROP 2020.10 \* \* \* 2020-Aug-14 18:40:15 \* Computer Modelling Group Ltd., Calgary, Canada \* \* 2 \*

\*\*\*\*\*\*

Print component properties

Peng-Robinson Equations of State (Zc = 0.30740131)

CO<sub>2</sub> N2 toCH4 C2HtoNC5 C6 toC10 IODECANE C11toC19 C20+Identifier CO2 16 HC 16 HC 16 HC 16 HC 16 HC 16 HC 16 0.8180000E+00 0.3000000E+00 0.5983001E+00 0.7533066E+00 0.1257000E+01 0.8316045E+00 Sg0.9645000E+00 -0.1092100E+03 -0.2586100E+03 0.6336911E+02 0.2616046E+03 Tb, deg F 0.2696000E+03 0.5004865E+03 0.1124005E+04 Pc, atm 0.7280000E+02 0.4540000E+02 0.3575989E+02 0.2828944E+02 0.5664079E+02 0.1344000E+02 0.7974320E+01 Pcs, atm 0.7280000E+02 0.4540000E+02 0.3575989E+02 0.2828944E+02 0.5664079E+02 0.1875151E+02 0.8302691E+01 0.940000E-01 0.990000E-01 0.2730548E+00 0.4376213E+00 0.2480088E+00 vc, m3/kmol 0.7517416E+00 0.1894184E+01 Tc, deg K 0.3042000E+03 0.1906000E+03 0.4386370E+03 0.6068323E+03 0.6654827E+03 0.6854000E+03 0.9370805E+03 0.4386370E+03 0.5784799E+03 0.3042000E+03 0.1906000E+03 0.6585618E+03 Tcs, deg K 0.7098161E+03 0.1012675E+04 0.2741385E+00 0.2873679E+00 0.2712756E+00 0.2486132E+00 0.2572348E+00 0.1796362E+00 Zc 0.1964306E+00 0.2250000E+00 0.800000E-02 0.2110252E+00 0.3645831E+00 0.1873575E+00 Acentric Factor 0.6245773E+00 0.1315939E+01 Molecular Weight 0.4401000E+02 0.1604300E+02 0.6337151E+02 0.1118841E+03 0.2681800E+03 0.2392400E+03 0.6722989E+03 Beta-Factor 0.100000E+01 0.100000E+01 0.100000E+01 0.100000E+01 0.100000E+01 0.1000000E+01 0.1000000E+01 Omega A 0.4572355E+00 0.5880400E+00 0.4572355E+00 Omega S 0.4572355E+00 0.4572355E+00 0.7779607E-01 0.1002846E+00 0.7779607E-01 0.7779607E-01 0.7779607E-01 0.7779607E-Omega B 01 0.7779607E-01 Omegb S 0.7779607E-01 0.7779607E-01 0.7779607E-01 0.7779607E-01 0.7779607E-01 0.7779607E-01 0.7779607E-01 vc for viscosity 0.940000E-01 0.990000E-01 0.2739245E+00 0.4388672E+00 0.2480088E+00 0.7554485E+00 0.1894184E+01 0.7800000E+02 0.7700000E+02 Parachor 0.2037834E+03 0.3219142E+03 0.6965963E+03 0.5419549E+03 0.1148666E+04 0.2736000E+00 0.2876000E+00 0.2718719E+00 0.2593861E+00 0.4427353E+00 Rackett Const, Zra 0.2363311E+00 0.2510471E+00 Vol Shift/b 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00 0.0000000E+00 0.000000E+00 Vol Shift, m3/kmol 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00 Vol Shifts/b 0.000000E+00 0.000000E+00 0.000000E+00 -0.0000000E+00 0.0000000E+00 0.1576631E-02 0.7691296E-02 Vol Shifts, m3/kmol 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00 -0.3810021E-03 0.5988781E-02 Vol Shif1/b, 1/F 0.0000000E+00 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00 Vol Shif1,m3/kmol-F 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00 Vol Shif1s/b, 1/F 0.000000E+00 0.0000000E+00 0.000000E+00 0.0000000E+00 0.0000000E+00 0.000000E+00 0.000000E+00 Vol Shif1s,m3/kmol- 0.000000E+00 0.000000E+00 0.000000E+000.000000E+000.000000E+00 0.000000E+00 0.000000E+00 VSHIFT Tref, deg F 0.6000000E+02 0.6000000E+02 0.6000000E+02 0.6000000E+02 0.600000E+02 0.600000E+02 0.600000E+02

EOS bc, m3/kmol	0.2667568E-0	1 0.3454866E-01	0.7830630E-01	0.1369405E+00	0.7500584E-01					
EOS bcs, m3/kmol	0.2667568E-0	0.2680123E-01	0.7830630E-01	0.1305424E+00	0.7422580E-01					
EOS Cappa Term 0.1247078E+01 0.2087098E+01	0.7079838E+0	0 0.3869608E+00	0.6880757E+00	0.9010440E+00	0.6541190E+00					
H-ideal parameter A 0.0000000E+00 0.0000000E+00	9.6880000E-02	-2.8385700E+00	8.4959353E+00	0.0000000E+00	0.0000000E+00					
H-ideal parameter B 3 6303362E-02 -9 9352671E-03	1.5884300E-01	5.3828500E-01	9.5596587E-02	-4.1900903E-02 -1	.3469409E-01 -					
H-ideal parameter C -	-3.3712000E-05	-2.1140900E-04	2.5480207E-04	4.2617557E-04	2.6705238E-04					
H-ideal parameter D 6 1755607E-08 -5 5033784E-08	1.4810500E-07	3.3927600E-07	6.9708825E-08	-6.3558242E-08 -5	5.1310000E-08 -					
H-ideal parameter E -	9.6620300E-11	-1.1643220E-10	-4.9380246E-11	0.0000000E+00	0.0000000E+00					
H-ideal parameter F	2.0738320E-14	1.3896120E-14	7.6198418E-15	0.0000000E+00	0.000000E+00					
H-ideal parameter G 0.0000000E+00 0.0000000E+00	1.5114700E-01	-6.0286900E-01	3.3783338E-01	0.0000000E+00	0.0000000E+00					
Primary Composition 6.0130512E-02 9.8776805E-02	2.8159901E-01	4.5480007E-01	5.8612493E-03	4.6025563E-02	5.2806792E-02					
The following values are	calculated at 15	8.00 deg F								
Ideal H, cal/mol 0.1622382E+05 0.4902002E+05	0.2641818E+04	0.2791846E+04	0.6149807E+04	0.7566746E+04	0.9828885E+03					
Low p viscosity, cp 0.0000000E+00 0.000000E+00	0.0000000E+00	0.0000000E+00	0.0000000E+00	0.0000000E+00	0.0000000E+00					
Henry Con., psia 7.9462822E+07 3.3554200E+12	1.0538684E+05	4.4228026E+04	1.6097385E+05	7.0060418E+05	1.4818446E+05					
Henry Pref, psia 0.8500000E+04 0.8500000E+04	0.8500000E+04	0.8500000E+04	0.8500000E+04	0.8500000E+04	0.8500000E+04					
V infinity, l/mol 0.4002354E+00 0.9187665E+00	0.3491009E-01	0.3540743E-01	0.9830240E-01	0.1699031E+00	0.9427208E-01					
Moles of Primary fluid, kmol: 4.5359237E-01										
Ideal Enthalpy, H-ideal = A + B*T + C*T**2 + D*T**3 + E*T**4 + F*T**5 with T in deg R and H-ideal in BTU/lb H-ideal is zero for ideal gas at absolute zero.										
Viscosity correlation parameters: COEMU(1:5), EMIXVC 1.0432000E-04 2.6812773E+00 8.8536000E-03 1.4776000E+00 4.1384000E-01 1.0000000E+00										
Listing of pairs selected for group $\# = 1$ , exponent	for 1st set: t value = 1.2771	3070								

3,24,24,35,25,35,46,26,36,46,57,27,37,47,57,6

Interaction Coefficient Table For hydrocarbon-hydrocarbon pairs - 1st set dij = 1 - (2\*sqrt(vc3i\*vc3j)/(vc3i+vc3j)) \*\* hc exp. vc3i= vci\*\*(1/3)

 CO2
 0.000000

 N2 toCH4
 0.105000
 0.000000

 C2HtoNC5
 0.116871
 0.018007
 0.000000

 C6 toC10
 0.115000
 0.038044
 0.003935
 0.000000

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IODECANE 0.000000 0.014791 0.000164 0.005696 0.000000  $C11 to C19 \quad 0.115000 \quad 0.069054 \quad 0.017943 \quad 0.005172 \quad 0.021456 \quad 0.000000$  $0.000000 \quad 0.138135 \quad 0.063325 \quad 0.037005 \quad 0.069429 \quad 0.014976 \quad 0.000000$ C20+ Listing of pairs selected for 2nd set: group #=1, exponent value = 1.20000000 3,2 4,2 4,3 5,2 5,3 5,4 6,2 6,3 6,4 6,5 7.2 7,3 7,4 7,5 7.6 Interaction Coefficient Table For hydrocarbon-hydrocarbon pairs - 2nd set dij = 1 - (2\*sqrt(vc3i\*vc3j)/(vc3i+vc3j)) \*\*hc exp $vc3i = vci^{**}(1/3)$ CO2 0.000000 N2 toCH4 0.000000 0.000000 C2HtoNC5 0.000000 0.016929 0.000000 C6 toC10 0.000000 0.035788 0.003697 0.000000 IODECANE 0.000000 0.013904 0.000154 0.005353 0.000000 C11toC19 0.000000 0.065022 0.016869 0.004860 0.020173 0.000000  $0.000000 \quad 0.130363 \quad 0.059617 \quad 0.034809 \quad 0.065376 \quad 0.014078 \quad 0.000000$ C20+ WinProp 2020.10 Total EOS calls without derivatives = 475 Total EOS calls with derivatives = 384 Total calculations performed 8 = CPU seconds used : 0.03

Date and Time of End of Run: Feb 22, 2022 10:00:01