Investigation of the Oil Recovery Mechanism during Laboratory CO\textsubscript{2} EOR Experiment with Unconventional Shale Cores through Compositional Simulation
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Abstract
After implications of hydraulic fracturing operations, the commercial production of tight formations and shale plays were successfully achieved in past decades. Due to the rapid decline rate after primary depletion of fractured reservoirs, extracting the remaining liquid hydrocarbon from the nano-Darcy permeability matrix becomes the next step.

Previously conducted laboratory experiments demonstrated promising results by successfully recovering liquid hydrocarbon from preserved and unfractured sidewall unconventional core plugs. However, what are the driving forces behind this observed result was not well understood. In other words, is the hydrocarbon recovery associated with commonly known recovery mechanisms during CO\textsubscript{2} EOR processes, such as viscous displacement, oil volume expansion, viscosity reduction and vaporization of lighter hydrocarbon components? Or, is it driven by other mechanisms that are frequently considered insignificant during conventional CO\textsubscript{2} EOR processes?

This study utilizes a commercial compositional simulator to investigate the oil production mechanisms from the matrix into the fractures. The process includes constructing a fine grid 3D model to simulate the previously conducted laboratory experiment, performing systematic sensitivity analysis, and evaluating the mechanisms that could potentially contribute to the oil recovery observed during the experiments. With laboratory scale modeling, the dominating mass transfer mechanism between the matrix and fractures, which in turn translates into oil recovery mechanism, is concluded to be diffusion. The work provided in this study can be used to enhance the accuracy for upscaled field simulations. However, whether CO\textsubscript{2} EOR will unlock the unconventional liquid reservoir potential and make significant economic impacts at field scale needs to be carefully evaluated on a case by case basis.

Introduction
For the past few decades, due to the increasing demand of energy and the advancements in horizontal drilling and hydraulic fracturing technologies, the industry reallocated its resources into exploring ways to produce oil from the previously unprofitable shale plays. The current technique to produce from the shale plays is through primary depletion. However, studies have shown that the recovery factor remains
low, and large sums of the reserves are left behind in the reservoirs (Liu et al. 2014). To look ahead into the future production of the remaining reserves because of the declination of primary recovery to an uneconomic level, operators are shifting their attentions into research that focuses on EOR methods in shale reservoirs.

Enhanced oil recovery (EOR), also known as tertiary recovery, serves the purpose of producing the remaining hydrocarbons after the depletion of the reservoir energy or after pressurizing the reservoir and displacing the hydrocarbon with gas or water. EOR processes are necessary when pressure maintenance becomes insufficient or in the cases where secondary recovery processes are not applicable due to the low recovery potential. When investigating methods to recover from unconventional reservoirs with low injectivity, EOR is considered as a suitable candidate. Because unlike primary and secondary recovery, EOR processes increase production mainly by altering the rock and fluid properties.

However, due to the many differences in properties between conventional and unconventional reservoirs, the EOR methods that are applicable in conventional reservoirs need to be re-evaluated when applied in unconventional reservoirs. For instance, during a conventional EOR scheme, the overall recovery is determined by both macroscopic and microscopic displacement efficiency. The macroscopic displacement efficiency is affected by the reservoir heterogeneities and anisotropy, characteristics of the matrix, fluid mobility, flood patterns, etc. The microscopic displacement efficiency is affected by interfacial tension, wettability, capillary pressure and relative permeability (Terry 2001). Because of the differences in mass transfer mechanisms, some of the above factors remain significant in unconventional cases, whereas some factors do not affect recovery. Laboratory experiments conducted by various researchers have shown success in oil recovery when applying CO₂ as the EOR agent to unconventional cores. In these studies, considering diffusion as a critical oil recovery mechanism was brought to attention (Hawthorne et al. 2013; Kovscek et al. 2008; Vega et al. 2010).

To continue on the journey of understanding the underlying oil recovery mechanism of oil recovery from unconventional rocks when CO₂ is applied as the EOR agent to aid in the future evaluation of the economic potential of this method, work shown in this paper is composed of simulation studies conducted using data collected from the first CO₂ experiment described in the paper by Tovar et al. (2014). During the experiment, oil was successfully extracted from shale cores that are in preserved and un-fractured condition. To Summarize, this study is designed to address the following two questions: During the CO₂ experiment described by Tovar et al. (2014),

1) Which microscopic characteristics of the rock have predominant effects on recovery (Sensitivity Analysis)?
2) What is the dominating oil recovery mechanisms?

Laboratory Experiment
The core scale simulation in this study is based on the experimental data obtained from the first set of the experiment described in the work by Tovar et al. (2014). During the experiment, two preserved sidewall cores from the same well in an unconventional play were used. The petrophysical properties and the saturations of the cores were not measured before the experiments to preserve its original conditions. However, since the cores are not stored in a pressurized environment, the fluids saturating the cores can be assumed as dead oil and water. The dimensions of the cores are summarized in Table 1.

<table>
<thead>
<tr>
<th>Core Number</th>
<th>1-1</th>
<th>1-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core Diameter, cm</td>
<td>2.53</td>
<td>2.53</td>
</tr>
<tr>
<td>Core Length, cm</td>
<td>3.97</td>
<td>3.48</td>
</tr>
<tr>
<td>Core Bulk Volume, cm³</td>
<td>19.94</td>
<td>17.50</td>
</tr>
</tbody>
</table>

Table 1 – The dimensions of the cores used in the experiment (Modified after Tovar et al. 2014).

Glass beads were packed outside the cores, to allow CO₂ to have direct contact with the cores and to simulate the presence of a highly permeable fracture around the cores. Two Berea sandstone
cores were placed on each end of the set up to block the glass beads from entering the production tube. The core holder was then placed in a water bath which circulates hot water to simulate the reservoir temperature. And, the assembly was mounted in a CT (computed tomography) scanner. The cores were kept horizontally during the experiment. The schematic of the experimental setup can be seen in Fig. 1.

![Laboratory Setup to Simulate Mass Transfer Between the Matrix and Fracture](image)

**Fig. 1 – Schematic of the experiment setup.**

The experiment was performed under constant pressure conditions (where viscous displacement was absent) at 3000 psi at 150 °F. Periodic scanning of the cores with the CT scanner was performed throughout the experiment. The experiment lasted approximately 100 hrs. Production was allowed twice a day on average by lowering the pressure at the outlet, which is controlled by a back pressure regulator. The CT images of the core revealed constant density/saturation/composition changes of the resident fluid during both experiments, which indicated CO₂ was constantly penetrating into the core throughout the process. A final oil production volume of 0.4 ml was recorded after the experiment.

### Build Core-Scale Simulation Models

The purpose of the numerical simulation is to provide a mathematical model that validates the observed physical phenomena during laboratory experiments or field production and to be used for forecasting and optimization. Since one of the objectives is to investigate the mass transfer mechanisms behind the observed oil recovery during experiments, the following section provides theoretic background on material transfer and the calculations behind the simulator used in this study.

#### Mass Transfer Theory

**Dispersion**

Dispersion is the mixing of fluids within a porous medium. Dispersion of the fluid is controlled by two main mechanisms: convection and molecular diffusion (Bird *et al.* 2002; Deen 1998). The convective transport is accompanied by bulk motion. It is the mechanism caused by the heterogeneities of the porous medium, which caused local fluid velocity variations (Lie 2013). On the other hand, molecular diffusion is caused by the compositional difference or chemical potential of the species. It results from the motion of the molecules, and it is related to small pore-scale molecular displacement (Deen 1998). Longitudinal dispersion in a porous medium is represented by **Eq. 1** (Jarrell *et al.* 2002).

\[
K_l = D_e + \alpha_1 v 
\]

**Eq. 1**

\[
K_l \text{ is the longitudinal dispersion coefficient, } D_e \text{ is the effective molecular diffusion coefficient, } \alpha_1 \text{ is the longitudinal dispersivity and } v \text{ is the superficial velocity which is the product of porosity and}
\]
interstitial velocity (Jarrell et al. 2002). Based on Eq. 1, the rate of dispersion is a sum of the convective and diffusive spreading.

To understand the dominant mechanism for dispersion, Lie (2013) used the characterization of the flow described by Sahimi (2011), which explains the five different regimes using the Péclet number. The Péclet number is defined as the ratio between convection and diffusion transport as shown in Eq. 2.

\[
P_{e} = \frac{d \cdot v}{D_{m}} = \frac{D_{L}}{D_{m}}
\]

(Eq. 2)

Where \(d\) is the average diameter of the particle in meter, \(v\) is the interstitial velocity in m/s, and \(D_{m}\) is the molecular diffusion coefficient in m\(^2\)/s. \(D_{L}\) is the longitudinal dispersion coefficient, which is proportional to the average fluid velocity (Perkins and Johnston, 1963), and describes the transport in the direction of the bulk flow. Fig. 2 below shows the characterization of the five dispersion regimes in terms of the Péclet number.

![Fig. 2 – Five dispersion regime characterization. (Adapted from Lie 2013).](image)

In Region I, where the Péclet number is smaller than 0.3, the dispersion is dominated by diffusion. In this region, the fluid velocity is too low, and it gives enough time for molecular diffusion to take place.

In Region II, where the Péclet number is greater than 0.3 but smaller than 5, diffusion is still dominating. However, convection will also aid in the process of dispersion.

In Region III, where the Péclet number is greater than 5 but smaller than 300, the velocity is large enough for convection to become the dominant mechanism. However, the effect of diffusion on dispersion cannot be neglected in this flow regime. In this region, the flux caused by diffusion is inversely proportional to the diffusion coefficient of the species. This is because when diffusion influx is coming from the transverse direction, the higher diffusion coefficient reduces the amount of time for the molecules to move forward along with the longitudinal convective flow.

In Region IV, where the Péclet number is greater than 300 but smaller than 10\(^5\) the dispersion is completely dominated by convection due to the considerably higher interstitial velocity. This is also referred to as mechanical dispersion.

Region V, which is also called the turbulent regime, is not of interest for the dispersion mechanism between shale matrix and the fractures.

During a CO\(_2\) injection in conventional reservoirs, either under miscible or immiscible conditions, CO\(_2\) is able to flow through the permeable rock matrix. The oil recovery mechanism is a combination of gravity drainage, light component stripping, oil swelling, viscosity reduction, and viscous displacement. Perkins and Johnston (1963) stated that if the fluid is able to flow through the porous media, the flow mechanism is dominated by convective dispersion, meaning the velocity of the bulk fluid is too high for diffusion to have any significant effect on dispersion. However, to consider the
scenario when CO\textsubscript{2} flows through the fractures in an unconventional reservoir, the flow will not significantly go through the rock matrix. Therefore, convection could be eliminated as the main mechanism responsible for the mass transfer between the matrix and fracture (Hawthorne et al. 2013).

In the scope of this study, which is to investigate the mechanism of oil recovery from the shale matrix into the fractures, the dispersion process is characterized into dispersion Region I because of the nano scale permeability values. Therefore, when modeling CO\textsubscript{2} EOR in unconventional reservoirs, molecular diffusion is an important factor to be included. Many studies have reached similar conclusions (Hawthorne et al. 2103; Wan and Sheng 2015; Lie 2013; Grogan and Pinczewski 1987; Darvish et al. 2006; Hoteit and Firoozabadi 2009).

Diffusion
Molecular diffusion describes the random movement of molecules inside a system. Diffusion differs from convection because it happens with or without external forces, such as a pressure gradient and gravity. In an isobaric system, when there is a temperature or concentration gradient, the gradient tends to disappear as a function of time due to diffusion. In an isothermal and isobaric system in a porous medium, the rate of mass influxes due to diffusion is a function of pressure, temperature, composition, particle sizes, and the characteristics of the porous medium. The modeling of mass transfer across a phase boundary has been extensively studied in the field of chemical engineering. The common approach is based on the film model, which assumes thermodynamic equilibrium at the gas-oil interface and the continuity of component fluxes across the interface (Hoteit 2013).

The rate and direction of the diffusion process are the diffusion flux. There are different models describing the calculation of the diffusion influx. The next two sections discuss the two models available in the simulator used in this study.

The Classical Fick’s Law
The classical Fick’s law is a very simple conceptual model to describe the movement of chemical components from one location to another. Analogous to Newton’s Law of motion, Ohm’s Law of electrical conduction and Fourier’s Law of heat conduction, the Fick’s Law describes the relationship between mass flux quantity and concentration gradient as shown in Eq. 3.

\[ J_i = -D_i \frac{\partial c_i}{\partial d} \]  
(Eq.3)

Where
\( J_i \) is the diffusion flux,
\( D_i \) is the diffusion coefficient,
\( \frac{\partial c_i}{\partial d} \) is the concentration gradient.

The classical Fick’s law is ideal for diffusion calculation of a binary ideal fluid system. It simply assumes the diffusion process of each component is based on its concentration gradient and is independent of other components, which does not hold true in a realistic case with multicomponent mixture. Even for a binary system, one cannot predict when and where it may fail. Hoteit (2013) provided examples of both binary and multi-component system diffusion studies. The examples showed the use of different diffusion coefficients for different components violated the molar flux balance and caused pressure variations in an isothermal and isobaric system. The solution to eliminating this pressure variance is to set the diffusion coefficients of all components to be equal or modify the diffusion coefficient of the last component so that the overall molar balance is honored. The variation in pressure is more significant when the system is under non-ideal conditions. Therefore, this study uses the irreversible thermal dynamic model, which uses the chemical potential to determine the diffusion flux instead of using the concentration gradient.
The Irreversible Thermodynamic Model

The irreversible thermodynamic model for diffusion flux calculation considers the chemical potential gradient to be the driving force for diffusion. The calculation takes the form as shown in Eq. 4.

\[
J_i = -cD_i^a x_i \frac{1}{RT} \left[ \mu_i - M_i g(h - h_a) + M_i D_i^f \ln(T) \right] \quad \text{(Eq. 4)}
\]

The above equation takes gravity and temperature gradients in addition to the chemical potential gradients into consideration. For an isothermal system that ignores gravity, Eq. 4 can be written as Eq. 5.

\[
J_i = -cD_i^a x_i \frac{\partial}{\partial d} \ln(f_i) \quad \text{(Eq. 5)}
\]

\[D_i^a\] is the activity-corrected diffusion coefficient. Combining Eq. 3 and Eq. 5, the activity-corrected diffusion coefficient can be expressed by Eq. 6.

\[
D_i^a = \frac{D_i}{\partial \ln(f_i) / \partial \ln(x_i)} \quad \text{(Eq. 6)}
\]

Chemical Potential and Fugacity

According to Eq. 5, the contributing parameters involved in the diffusion flux calculation in an oil and gas system are porosity, oil and gas saturation, molar density of the oil and gas, mole fractions of the components, diffusion coefficients, and fugacity. Out of the above parameters, the molar density, diffusion coefficient, and fugacity are functions of pressure and temperature. Therefore, although the initiation of the diffusion process is not governed by the system pressure, the rate of diffusion is controlled by the system pressure.

To understand the effect of physical conditions on diffusion flux, the term chemical potential needs to be briefly reviewed. This concept was introduced by Gibbs in 1957. This section will briefly explain the definition of chemical potential and fugacity. The detailed definition can be found in the work published by Firoozabadi (1999).

For an open system in which there is no restriction of material and energy transfer, the differential form of the fundamental equation is expressed in Eq. 7.

\[
dU = \left( \frac{\partial U}{\partial S} \right)_{V_2} dS + \left( \frac{\partial U}{\partial V} \right)_{S_2} dV + \sum_{i=1}^{\ell} \left( \frac{\partial U}{\partial n_i} \right)_{s,v,n_i} dn_i \quad \text{(Eq. 7)}
\]

Where

\[n \equiv (n_1, n_2, ..., n_\ell),\]

\[U\] is the internal energy of the system,
\[S\] is the entropy of the system,
\[V\] is the volume.

The first two partial derivatives on the right side of Eq. 7 are given as:

\[
\left( \frac{\partial U}{\partial S} \right)_{V_2} = T \quad \text{(Eq. 8)}
\]

\[
\left( \frac{\partial U}{\partial V} \right)_{S_2} = -P \quad \text{(Eq. 9)}
\]

Where

\[T\] is the thermodynamic temperature,
$P$ is the pressure.

And the coefficient of the last term is defined as the chemical potential, denoted by $\mu$:

$$\mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{s,v,n}$$ (Eq. 10)

The function of the chemical potential is similar to that of the pressure and temperature of a system. When a chemical potential gradient exists within a system, diffusion occurs from regions with high chemical potential to regions with low chemical potential despite gravity or other external forces.

Combining Eq. 7 to Eq. 10, the expression for internal energy change can be written as Eq. 11.

$$dU = TdS - PdV + \sum_{i=1}^{c} \mu_i dn_i$$ (Eq. 11)

In general, for two cells separated by a permeable wall, which permits free transport of all components, the direction of the flow is solely determined by the chemical potential difference between the two cells. It is a form of work done by an isothermal and isobaric system due to composition changes to achieve thermal equilibrium.

The entropy of the two systems are:

$$dS^1 = \frac{dU^1}{T^1} + \frac{P^1}{T^1} dV^1 - \sum_{i=1}^{c} \left( \frac{\mu_i^1}{T^1} \right) dn_i$$ (Eq. 12)

$$dS^2 = \frac{dU^2}{T^2} + \frac{P^2}{T^2} dV^2 - \sum_{i=1}^{c} \left( \frac{\mu_i^2}{T^2} \right) dn_i$$ (Eq. 13)

Use the maximum entropy principle and rearranging Eq. 11 to Eq. 13:

$$dS = d(S^1 + S^2) = (\frac{1}{T^1} - \frac{1}{T^2})dU^1 + (\frac{P^1}{T^1} - \frac{P^2}{T^2}) dV^1 - \sum_{i=1}^{c} \left( \frac{\mu_i^1}{T^1} - \frac{\mu_i^2}{T^2} \right) dn_i = 0$$ (Eq. 14)

The conditions for the two cells to achieve thermal equilibrium are $T^1 = T^2$, $P^1 = P^2$ and $\mu_i^1 = \mu_i^2$.

Therefore, for an isothermal and isobaric system, the two cells need to have equal chemical potential instead of having equal mole fraction as defined in the classical Fick’s law shown in Eq. 5.

Chemical potential is the partial molar Gibbs free energy, $G$. The Gibbs free energy is a function of temperature, pressure, and composition.

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n}$$ (Eq. 15)

Where

$$dG = VdP - SdT$$ (Eq. 16)

For an isothermal system,

$$dG = VdP$$ (Eq. 17)

For an ideal gas

$$V = \frac{RT}{P}$$, therefore combining Eq. 16 and Eq. 17
\[ dG_{\text{ideal}} = \frac{RT}{P} dP = RTd\ln P \]  \hspace{1cm} (Eq. 18)

Combining Eq. 15 and Eq. 18

\[ d\mu_i = RTd\ln(f)_{T,G} \lambda_i \text{ and } \lim_{P \to \infty} \left( \frac{f_i}{x_i P} \right) = 1 \]  \hspace{1cm} (Eq. 19)

Where

\[ x_i \] is the mole fraction,

\[ f_i \] is the fugacity.

The term \( \frac{f_i}{x_i P} \) is the fugacity coefficient. At low pressure, the fugacity coefficient equals one, which indicates the fluid behaves like an ideal fluid. In other words, fugacity is defined to represent the correct chemical potential for a real fluid with pressure \( P \). The unit for fugacity is the same as the unit for pressure.

In an isothermal system, with diffusion as the only driving mechanism for mass transfer, the rate of mass transferring depends on the chemical potential (fugacity) of each component existing in the different phases.

For ideal gases, the fugacity is simply the pressure. For non-ideal gases, the fugacity does not equal the true pressure and needs to be corrected in terms of the compressibility factor and the pressure because of the change in Gibbs free energy.

\[ \ln\left(\frac{f_i}{P}\right) = \int_{0}^{P} (z-1) \frac{dP}{P} \]  \hspace{1cm} (Eq. 20)

For liquid, the fugacity at low-pressure ideal conditions equals to the saturation pressure. At higher pressure, since the fluid properties do not change significantly, although there is a correction term for non-ideal liquid fugacity, the Gibbs free energy of a non-ideal liquid does not change much compared with ideal liquid.

**Diffusion Coefficient**

Numerous studies demonstrated or proposed methods to either physically measure the diffusion coefficient in the laboratory or estimate it using correlations.

Physically measuring the diffusion coefficient for a multi-component mixture can be challenging and sometimes inaccurate due to the fact that other factors such as gravity, capillary forces, convective mixing could interfere with the results. Correlations such as the ones proposed by Sigmund and Wilke-Chang are widely used in literature to predict the diffusion coefficient of mixtures. New models for diffusion coefficient estimation, such as the one developed by Leahy-Dios and Firoozabadi (2007), are not available in commercial software and could be considered for future studies. The correlation used in this study is the Sigmund correlation (Sigmund 1976a; Sigmund 1976b) shown in \textbf{Eq. 21} to \textbf{Eq. 30}.

\[ D_{ij} = \frac{\rho_{ik}^0 D_{jk}^0}{\rho_k} \left(0.99589 + 0.096016 \rho_{\nu_r} - 0.22035 \rho_{\nu_r}^2 + 0.032874 \rho_{\nu_r}^3\right) \]  \hspace{1cm} (Eq. 21)

\[ \rho_{kr} = \frac{\sum_{i=1}^{n} y_{ik} V_{ci}^{5/3}}{\sum_{i=1}^{n} y_{ik} V_{ci}^{2/3}} \]  \hspace{1cm} (Eq. 22)
\[
\rho_i^0 D_{ij}^0 = \frac{0.00185837^{1/2}}{\sigma_{ij}^2 \Omega_{ij} R} \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{1/2} \text{ (Eq. 23)}
\]

\[
\sigma_i = (2.3551 - 0.087 \omega_i) \left( \frac{T_e}{P_e} \right)^{1/3} \text{ (Eq. 24)}
\]

\[
\varepsilon_i = k_B (0.7915 + 0.1963 \omega_i) T_e \text{ (Eq. 25)}
\]

\[
\sigma_{ij} = 0.5(\sigma_i + \sigma_j) \text{ (Eq. 26)}
\]

\[
\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \text{ (Eq. 27)}
\]

\[
T_{ij}^* = \frac{k_B}{\varepsilon_{ij}} \text{ (Eq. 28)}
\]

\[
\Omega_{ij} = 1.06306(T_{ij}^*)^{-0.1561} + 0.193 \exp(-0.47635T_{ij}^*)
+ 1.03587 \exp(-1.52996T_{ij}^*) + 1.76474 \exp(-3.89411T_{ij}^*) \text{ (Eq. 29)}
\]

Lastly, the diffusion coefficient for component I in the mixture is calculated using an equation based on Wilke formula:

\[
D_{ik} = \frac{1 - y_{ik}}{\sum_{j \neq k} y_{ik} D_{ij}^0} \text{ (Eq. 30)}
\]

As mentioned in numerous studies, the diffusion coefficients for the components are parameters subjected to adjustment during history matching. Therefore, the estimated diffusion coefficients only serve as baseline values for future adjustments.

**Commercial Simulators**

Since one of the critical oil recovery mechanisms, diffusion, is being studied in this study, Commercial simulator A and Commercial simulator B were both investigated because the two simulators offer different capabilities when modeling diffusion.

**Commercial Simulator A**

Attempts to use Simulator A was made at first for the laboratory modeling. When using single porosity model, Simulator A has the capability of activating the diffusion coefficients calculated using either Sigmund or Wilke-Chang correlation or enabling the user to define the value of the diffusion coefficients explicitly. However, it was discovered that Simulator A is only capable of calculating the intra-phase diffusion for single porosity models, which means the cross phase diffusion is being neglected. When there is phase discontinuity at the boundary between the gas bearing fracture and the oil bearing matrix, small amounts of CO\(_2\) are mixed into the oil phase due to the initial pressure difference. However, as the pressures in the fracture and the matrix regions become equal, no more CO\(_2\) will enter the oil phase. The amount of CO\(_2\) that is already mixed with the oil phase will diffuse within the oil phase and evenly distributed inside the homogeneous core given enough time.

Lie (2013) mentioned in his work that Simulator A is unable to model the diffusion of supercritical CO\(_2\), which is treated as a gas-phase in the simulation, into the oil phase. Also, the simulation results do not agree with the observation from experimental work as shown in the simulation performed by Vega et al. (2010). With the above reason, the single porosity model with Simulator A
was not select for this study and is not recommended to use for simulations where diffusion between two phases is considered.

**Commercial Simulator B**

Simulator B has the capability of modeling both intra phase and cross phase diffusion fluxes with single porosity models. There are two models available for the calculation of diffusion fluxes. The model selected for this study is based on the irreversible thermodynamics model discussed earlier, in which the diffusion is driven by the chemical potential gradient. To model the cross phase diffusion process, the cross phase diffusion coefficient is calculated with Eq. 31.

\[ D_{ij}^a = \sqrt{D_{ij}^a \times D_{ij}^a} \] (Eq. 31)

**Fluid Model**

Workflow of modeling the dead oil used in the experiments is shown in the Fig. 3.

![Fluid Model Workflow](image)

After the regression, a dead oil model is obtained to be used in the simulation. **Table 2** summarizes the properties of the fluid mode.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction, %</th>
<th>Critical Pressure, atm</th>
<th>Critical Temperature, K</th>
<th>Acentric Factor</th>
<th>Molecular Weight, g/mol</th>
<th>Critical Volume, m³/kg-mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>1E-6</td>
<td>72.80</td>
<td>304.20</td>
<td>0.225</td>
<td>44.01</td>
<td>0.09</td>
</tr>
<tr>
<td>COMP1</td>
<td>33.18</td>
<td>34.30</td>
<td>559.74</td>
<td>0.254</td>
<td>95.33</td>
<td>0.36</td>
</tr>
<tr>
<td>COMP2</td>
<td>30.51</td>
<td>23.97</td>
<td>593.36</td>
<td>0.399</td>
<td>124.12</td>
<td>0.54</td>
</tr>
<tr>
<td>COMP3</td>
<td>22.90</td>
<td>17.17</td>
<td>673.34</td>
<td>0.617</td>
<td>181.06</td>
<td>0.77</td>
</tr>
<tr>
<td>COMP4</td>
<td>13.41</td>
<td>14.74</td>
<td>634.14</td>
<td>0.719</td>
<td>259.99</td>
<td>1.07</td>
</tr>
</tbody>
</table>

**Table 2** - Properties of the fluid model after regression.

The MMP and FCM were calculated with PVTsim. At 150 °F, the MMP was determined at 1727 psi, and the FCM was achieved at 1934 psi. The MMP value is further confirmed with a simulated slim-tube experiment. A 1D model with 200 cells was used.

**Slab Core Model**

Before building a 3D core model to simulate the actual experiment, a 2D model was used for property sensitivity study. The slab model is shown in Fig. 4. It is more discretized both in the matrix and the fracture regions compared with the actual 3D model.
The sensitivity analysis was conducted using the 2D slab model for the following properties: matrix porosity, matrix permeability, fracture porosity, fracture permeability, water saturation, capillary pressure, diffusion coefficient, and system pressure. Results will be shown in the discussion section.

**Heterogeneous 3D Core Model**

**Grid Sensitivity**

Both radial and Cartesian grids of different degrees of refinement were investigated during this study. It was considered more reasonable to use a radial grid model to represent the flow behavior during the experiment, however, the Cartesian grid was also considered for the purpose of capturing the heterogeneous properties of the cores. Grid sensitivity analysis was performed to ensure a Cartesian grid model yields the same results as a radial grid model. **Fig. 5** below shows the 5 models built for grid sensitivity analysis. **Table 3** shows the dimensions of each model.

As seen in **Fig. 6** below, although the models did not agree very well in the early times, the ultimate recovery yielded were fairly close. In addition, the Cartesian models gave fairly close results to the radial models. To accomplish the ultimate goal of this study, Cartesian 1 grid, which agrees well with the radial models in both early and late time, is selected for the 3D modeling.
Incorporating Heterogeneous Property Maps

To determine the porosity and permeability maps of the core model, the CT images from the experiment was carefully examined. As seen in Fig. 7 below, the core displayed very distinguished bedding plan features. Since CT number corresponds to density, the change in density can be clearly observed in the images. Fig. 7 also shows the changes in density occurred mostly along the bedding plane, and the rest of the core experienced very minimal to no change in density.

In this case, Changes in CT number could be regarded as the only indication for the presence of CO₂, because either CO₂ adoption or mixing with the oil phase would cause potential density changes. On the other hand, there are three reasons for no density change. One is there is no oil in the regions, which means the pores are filled with water, and the density change of water when CO₂ is dissolved in it is negligible. The second reason is the regions are isolated, which means CO₂ cannot reach those areas. And, the third reason is the porosity is zero. The first and second reasons are most likely to be the case in experiment I. However, since CO₂ solubility in water is not included in this study, and defining a saturation map purely based on the CT images is not practical and does not add any values, the voxels with zero delta CT values are defined with very small porosity values in the range of 0 to 0.01. In future studies where the process of CO₂ diffuses through the water phase and recovers the trapped oil is being modeled, defining a saturation map becomes necessary.

After processing the CT images, each image was constructed into a gridded structure. The grid of the image corresponds to the dimension of the Cartesian grid model described in the earlier section with a ∆CT value associated with each block. Co-kriging was used to aid in the process of defining the property maps. Various realizations were made. The goal of picking the appropriate porosity distribution is to match the ultimate 4 ml production with the least need of changing the diffusion coefficients. Fig. 8 shows a sample slice of the porosity map used in the simulation. The diffusion coefficients used to match the cumulative production volume are listed in Table 4.
After obtaining a porosity value for each grid block, the permeability value was determined based on porosity using the correlation proposed by Sigal (2002) shown in Eq. 32.

\[ k = 60r_{\text{eff}}^2 \phi^m \]  

(Eq. 32)

where

- \( r_{\text{eff}} \) is the effective pore throat size in micron,
- \( \phi \) is porosity,
- \( m \) is the cementation factor, which is chosen to be 2 in this study.

Based on Sigal (2013), the effective pore throat size for the particular type of rock that is similar to the one in this study measured with mercury injection was approximately 0.001 micron. Water saturation of the core was explicitly assigned at an immobile value 0.1.

After obtaining the above properties, a fine micro-scaled core model was built to mimic experiment I. Property maps were input for the matrix grid cells. The model contains two saturation regions with individually assigned relative permeability and capillary pressure data. Injectors and producers were placed at each end of the grid. The condition of the simulation is at 3000 psi and 150 °F.

**Results of Experiment Simulation**

The simulation with the heterogeneous core model described above follows the same CO\(_2\) injection and oil production schedule as performed during the experiment. A cumulative oil production of 0.4 mL was achieved at the end of the simulation as shown in Fig. 9.
Fig. 10 below shows the oil density change inside the core over time. The slice is the same slice as shown in Fig. 8.

![Image of oil density change over time](image)

Fig. 10 – Oil density change for the experiment I 3D heterogeneous model at time 0hr, 5hr, 10hr, 24hr, 48hr, and 72hr.

In addition, as shown in Fig. 10, the rate at which oil density changes differs from cell to cell because of the different porosity and diffusivity values. And regions that have larger changes in density correspond to the streaks with high porosity values defining the bedding plane existed in the core.

**Discussion on Property Sensitivity**

Table 5 shows the results of the sensitivity analysis using the 2D slab model. For each property, several cases were run and oil recovery results were compared with a baseline value (10.59%). Table 6 shows the baselined diffusion coefficient calculated using the Sigmund correlation.

<table>
<thead>
<tr>
<th>Property</th>
<th>Property Value</th>
<th>Recovery Factor (RF), %</th>
<th>ΔRF, %</th>
<th>Property Baseline Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix Porosity, %</td>
<td>12</td>
<td>9.76</td>
<td>-0.83</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>11.22</td>
<td>0.63</td>
<td></td>
</tr>
<tr>
<td>Matrix Permeability, mD</td>
<td>10</td>
<td>10.59</td>
<td>0</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>10.59</td>
<td>0</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td>0.00001</td>
<td>10.65</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Fracture Porosity, %</td>
<td>20</td>
<td>7.79</td>
<td>-2.82</td>
<td>0.45</td>
</tr>
<tr>
<td>Fracture Permeability, mD</td>
<td>10000</td>
<td>10.59</td>
<td>0</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>10.59</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Water Saturation, %</td>
<td>20</td>
<td>10.62</td>
<td>0.03</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>10.65</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Capillary Pressure @ 1600 psi</td>
<td>Low</td>
<td>8.79</td>
<td>-1.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mid</td>
<td>8.79</td>
<td>-1.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>8.22</td>
<td>-1.77</td>
<td></td>
</tr>
<tr>
<td>Diffusion Coefficient</td>
<td>Baseline X 10</td>
<td>21.81</td>
<td>11.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Baseline X 0.1</td>
<td>3.43</td>
<td>-7.15</td>
<td></td>
</tr>
<tr>
<td>System Pressure, psi</td>
<td>1600</td>
<td>3.79</td>
<td>-1.8</td>
<td>3000</td>
</tr>
</tbody>
</table>

Table 5 – Summary of property sensitivity analysis.

<table>
<thead>
<tr>
<th>Component</th>
<th>CO₂</th>
<th>COMP1</th>
<th>COMP2</th>
<th>COMP3</th>
<th>COMP4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas, cm³/hr</td>
<td>8.69E-04</td>
<td>4.28E-05</td>
<td>3.86E-05</td>
<td>2.72E-05</td>
<td>2.04E-05</td>
</tr>
<tr>
<td>Oil, cm³/hr</td>
<td>2.96E-04</td>
<td>3.52E-05</td>
<td>3.26E-05</td>
<td>2.62E-05</td>
<td>2.05E-05</td>
</tr>
</tbody>
</table>

Table 6 – Diffusion Coefficient calculated using the Sigmund correlation.

An interesting phenomenon was observed during the sensitivity study of matrix permeability. As seen in Table above, high permeability cases are associated with very slightly lower oil recovery. To look further into this phenomenon, few more cases were run.

Table 7 shows the permeabilities and corresponding recovery factors. Fig. 11 below shows the cumulative oil production for each case.
### Table 7 – Permeability values and the corresponding recovery factors for cases with different matrix permeability values.

<table>
<thead>
<tr>
<th>Case</th>
<th>Permeability, mD</th>
<th>Recovery Factor, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>10</td>
<td>10.59</td>
</tr>
<tr>
<td>Case 2</td>
<td>1.00E-03</td>
<td>10.59</td>
</tr>
<tr>
<td>Case 3</td>
<td>1.00E-04</td>
<td>10.59</td>
</tr>
<tr>
<td>Case 4</td>
<td>1.00E-05</td>
<td>10.65</td>
</tr>
<tr>
<td>Case 5</td>
<td>1.00E-06</td>
<td>11.12</td>
</tr>
</tbody>
</table>

The results still turned out to be counterintuitive. Case 5, which has the smallest permeability, yielded the highest recovery than the rest of the cases. Whereas the rest of the cases have similar production values. Pressure profiles of the core for each case were plotted and compared as shown in **Fig. 12**. It was discovered that in this case, the pressure inside the core played a role in determining recovery because it directly affects the chemical potential for each of the components. Since the permeability was different for each case, according to Darcy’s law, the rate at which pressure builds up inside the core is directly proportional to the permeability value. As one can observe from **Fig. 12**, Case 5 has significantly lower pressure than the rest of the cases for approximately 40 hours inside the core region. Although the fugacity of a non-ideal liquid does not change much with pressure, it still has some effect. For Case 5, the fugacity of the fluid inside the core is less than that of the rest of the cases, whereas the fugacity in the fracture is the same. This fugacity gradient resulted in the higher mass transfer rate for Case 5 compared with the other cases. Again, as mentioned in the earlier section, since the fugacity of fluid does not change significantly with pressure, the increase in production is only minor.
In addition, as mentioned in Eide et al. (2014), the concentration of a component is a linear function of the square root of time if the flow is dominated by diffusion. Fig. 13 shows the oil production versus the square root of time. The early time shows a nonlinear relationship between the two due to the initial convection caused by the pressure gradient between the fracture and matrix region. After that, a linear relationship can be observed, indicating diffusion is the dominant mechanism.

![Fig. 13 – Production versus square root of time. The linear relationship represents diffusion dominated flow.](image)

Overall, the permeability of the matrix has only minor effects on oil recovery when diffusion is the dominating recovery mechanism. The study conducted by Vega et al. (2010) reached a similar conclusion that heterogeneity has limited effects on cumulative recovery.

**Discussion on Recovery Mechanism**

The recovery mechanisms being investigated in this paper include:

1) Diffusion
2) Viscous displacement
3) Gravity effect
4) Oil viscosity reduction
5) Vaporization of light hydrocarbon components

**Diffusion**

The importance of diffusion was already highlighted in the sensitivity analysis section. To further study the effects of diffusion, diffusion coefficients were deactivated in this part of the study as shown in Table 8. And, the effective diffusion coefficient (served as the baseline) used in case 3 are shown in Table 6.

<table>
<thead>
<tr>
<th>Case</th>
<th>Diffusion Coefficient, cm$^2$/hr</th>
<th>Recovery Factor, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>No Diffusion Coefficient</td>
<td>0</td>
</tr>
<tr>
<td>Case 2</td>
<td>Diffusion Coefficient X 0.1</td>
<td>3.43</td>
</tr>
<tr>
<td>Case 3</td>
<td>Diffusion Coefficient</td>
<td>10.59</td>
</tr>
<tr>
<td>Case 4</td>
<td>Diffusion Coefficient X 10</td>
<td>21.81</td>
</tr>
</tbody>
</table>

*Table 8 – Diffusion coefficient values and the corresponding recovery factors.*

For all cases shown in Table 8, a porosity of 8%, permeability of 1E-4 mD and water saturation of 0.1 were used. In case 1, only shallow CO$_2$ penetration into the core was observed in early time, and no hydrocarbon was produced from the matrix. The observation from case 1 not only proves that the mass transfer mechanism is diffusion, it also shows that oil swelling has little contribution in the oil
recovery process, which agrees with the conclusion made by Hawthorn et al. (2013). The second case and fourth case used the baseline diffusion coefficients multiplied by a factor. As observed in the recovery factors listed in Table 8 and Fig. 14, increasing the diffusion coefficients significantly increases the recovery factor.

Viscous Displacement

In a scenario where CO₂ is injected into the system where the core matrix has high permeability, viscous displacement is considered as a main source of oil recovery. In the scope of this study, the simulation runs are designed to mimic the actual experimental processes and conditions mentioned in the previous section. During the experiment, CO₂ is slowly injected into the porous glass beads (simulating fractures) through the inlet, while the outlet of the system is being controlled by a back pressure regulator and remained shut until the pressure of the system reaches the desired targets. The process itself differs from a conventional core flood process in a sense that the displacement of material should happen mainly within the glass beads regions, not the core regions. To look further into the role of viscous displacement during the experiment, the possibility of viscous displacement taking place during the process was eliminated by eliminating the initial pressurizing process of the system using CO₂. The initial pressure was set at 3000psi for all the cases shown in Table 9. Different permeability scenarios were run for the purpose of comparison, and the resulting recovery factors are listed. The cumulative oil production and production rate from the matrix into the fracture was plotted versus time as shown in Fig. 15.

<table>
<thead>
<tr>
<th>Permeability, mD</th>
<th>Recovery Factor, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>10</td>
</tr>
<tr>
<td>Case 2</td>
<td>1.00E-03</td>
</tr>
<tr>
<td>Case 3</td>
<td>1.00E-04</td>
</tr>
<tr>
<td>Case 4</td>
<td>1.00E-05</td>
</tr>
</tbody>
</table>

Table 9 – Permeability values for different cases and the corresponding yielded recovery factors.
As seen in Fig. 15, the recovery factors for all cases are equal despite the large permeability contrast. The result further confirmed that the production is only controlled by molecular diffusion, which is independent of pressure or bulk fluid movement. The production rate in this case is only influenced by the chemical potential and the diffusion coefficient of each component, which are the same in all cases.

Gravity Effect
The model was built vertically instead of horizontally as in the experiment. Therefore, gravity effect was investigated. By inspecting the simulation result images from the 2D slab model, gravity only affected the oil distribution in the fracture region, the amount of CO₂ penetration and oil saturation were symmetrical in the top and bottom slices inside the matrix region. Fig. 16 below shows the mole fraction profile for COMP2 at 10 hours. Since the mole fraction inside the fracture region for COMP2 is very small in comparison to CO₂, the figure on the right shows the mole fraction of COMP2 at 10 hours in a log scale, which clearly shows the gravity effect in the fracture region. In addition, the slices closer to the two ends of the core observed lower COMP2 mole fraction than the slices in the middle section of the core because these slices were affected by both radial and axial flows. No gravity effect was observed from the results. It is only reasonable due to the high capillary pressure that exists inside the matrix region.
Oil Viscosity Reduction
As mentioned in many studies, CO$_2$ reduces the viscosity of the oil to enhance the oil mobility, which can also be observed from the simulation as shown in Fig. 17 below.

![Fig. 17 – Oil viscosity reduction for the experiment I 3D heterogeneous model at time 0hr, 5hr, 24hr, 48hr.](image)

However, since it has been discussed earlier that diffusion governs the mass transfer process, the reduced viscosity will not be observed if the diffusion of CO$_2$ into the oil phase is deactivated. In other words, oil viscosity reduction occurs after the initiation of dispersion processes and may have played a role in enhancing the magnitude of produced oil volume.

Vaporization of Light Hydrocarbon Component
Fig. 18 shows the molar fraction in the exported oil for each individual oil component, namely COMP1, COMP2, COMP3, and COMP4. Similar to a miscible CO$_2$ flooding scheme, the “lighter” components have the highest total production volume. This is the result of the lighter components having higher diffusion coefficients, and also easier to be vaporized into gas phase by CO$_2$. However, similar to oil viscosity reduction, light component stripping occurs after diffusion initiated dispersion and may have played a role in enhancing the magnitude of produced oil volume.

![Fig. 18 – Molar fraction of each hydrocarbon components in the exported oil.](image)

Conclusion
The following five conclusions can be drawn from this study
1. Cross-phase diffusion must be included to properly model the diffusion process.
2. During the experiment, diffusion was the dominant mass transfer mechanism. Deactivating diffusion resulted in zero oil production despite the fact that certain amounts of CO$_2$ were able to enter the core due to the initial pressure difference between the fracture and the matrix (convection).
3. Oil viscosity reduction and light component stripping served the purpose of enhancing the magnitude of oil recovery.
4. The oil recovery factor is sensitive to the following parameters: matrix porosity, saturation, region pressure, and diffusion coefficient.
5. The oil recovery factor is not sensitive to the following parameters: matrix permeability, relative permeability, and capillary pressure.
References


