The Impact of the Double Cross-Phase Diffusion Mechanism on Oil Recovery during CO2 Injection into Fractured Rocks: A Simulation Study

Morteza Sistan, Mohammad Hossein Ghazanfari,* and Saeid Jamshidi

ABSTRACT: In this research, a new diffusion mechanism called “double cross-phase diffusion” is introduced and applied to simulate the non-equilibrium gas injection process into fractured rocks. This new mechanism represents additional multicomponent gas diffusion into the crude oil through the water phase, existing in porous media as initial water saturation. Therefore, a lab-scale simulator, by implementing the generalized Fick’s law of multicomponent diffusion, is developed and used for predicting the experimental data of oil recovery during CO2 injection in chalk fractured rocks in the presence of initial water saturation. The results revealed a significant difference in the oil recovery predicted by the model when the double cross-phase diffusion mechanism is considered. The transient behavior of produced oil composition, predicted by the simulation model, is matched well with the experimental data. The portion of active oil recovery mechanisms in the system has been evaluated for the first time and it was observed that the molecular diffusion mechanism induced 75.4% of the total oil transfer rate in the initial time oil recovery, in which 23.1% of this value was supplied by the double cross-phase diffusion mechanism. The results of sensitivity analysis showed that by increasing the initial water saturation, the impact of the double cross-phase diffusion mechanism on oil recovery increases. In contrast, the transferred rate by the diffusion mechanism decreases from 85.4% to 60.8% when matrix permeability increases from 0.1 to 10 mD. The results of this work illustrate that the double cross-phase diffusion mechanism introduced in this study plays a significant role in the simulation results since the water is responsible for accelerating the diffusivity of CO2 into the crude oil and, in consequence, increasing the oil recovery.

INTRODUCTION

For decades, gas injection methods have successfully been applied to enhance oil recovery in fractured oil reservoirs. Among different injection gas scenarios, CO2 has been much attended since it not only helps to reduce environmental issues but also may provide further oil recovery efficiency due to its higher value of molecular diffusion. Despite several experimental and simulation studies, a fundamental understanding of how initial water saturation existing in porous media may enhance the diffusion of CO2 into crude oil is not explored in the available literature. This paper discussed this aspect by introducing a new diffusion mechanism called “double-cross phase diffusion”. The new mechanism represents additional diffusion of CO2 into the crude oil through the water phase, existing in porous media as initial water saturation.

In intensely fractured reservoirs with a low matrix permeability, a small matrix-block height, under certain pressure and temperature conditions, and specific fluids properties, the mass transport from the matrix blocks to the fracture system is majorly controlled by the diffusion mechanism. The purpose of this work is to analyze the oil recovery from fracture rocks during the CO2 injection when the molecular diffusion is the main force acting mass transport through porous media. The diffusion of gas into oil in naturally fractured reservoirs has been simulated by several researchers. For example, da Silva and Belery proposed an analytical model to study the effect of molecular diffusion in fractured reservoirs. They demonstrated the importance of molecular diffusion in the model of the oil recovery from fractured reservoirs. They used a dual-porosity, fully implicit, and fully compositional model, in which the implemented molecular diffusion coefficients were obtained.

Received: March 13, 2022
Accepted: May 30, 2022
Published: June 16, 2022
with the aid of Sigmund correlations. Coats presented a numerical simulation of fluid flow in a dual-porosity model, which considered only molecular diffusion between the matrix and fracture, and intraphase diffusions for both oil and gas phases in the matrix were ignored. Hoteit and Firoozabadi presented a numerical simulation based on the generalized Fick’s law to investigate the effect of molecular diffusion during gas injection into fractured oil reservoirs. They showed that molecular diffusion plays a significant role in the oil recovery, but in their model, only mass transfer in a two-phase system of gas and oil was investigated. Jamili et al. applied a mathematical model that described the mass transfer between the fracture and matrix. He used a dual-continuum approach and discretized the matrix into fine grids and set the fractures as boundaries. The limitation of his model was applying classical Fick’s law to describe molecular diffusion.

The available experimental data on non-equilibrium CO₂ injection into matrix-fracture media for enhancing oil recovery in live oil systems are limited in the literature. Three examples are as follows: (1) Darvish designed experiments to investigate the oil recovery from a long vertical core plug surrounded by a fracture during CO₂ injection in a live crude oil in the presence and absence of initial water saturation. He addressed that oil recovery is majorly influenced by molecular diffusion mechanisms instead of gravity drainage. Also, he attempted to predict the experimental data with a compositional simulator, which was not sufficiently successful. (2) Karimia et al. conducted some experiments on a matrix-fracture system to investigate the effect of CO₂ and N₂ injection on oil recovery from a fractured rock that was saturated with synthetic binary mixtures of n-heptane and methane as the live oil. He reported that several mechanisms such as swelling, gravity drainage, and molecular diffusion contributed to the oil recovery. However, in his experiments, the core sample was fully saturated with the live oil, and the initial water saturation did not exist. (3) Ghasemi et al. reported the experimental results of CO₂ injection in a matrix-fracture system in which a single fracture is represented by a centralized hole along the core in chosen reservoir conditions using stock tank oil/experimental oil. Also, he presented the results of a compositional simulation model for predicting the experimental data of oil recovery. However, he did not attempt to evaluate the portions of oil recovery induced by different active mechanisms, and also he did not discuss the role of initial water saturation on the oil recovery efficiency. Therefore, in this study, we will use the result of Darvish’s experiments because not only the initial water saturation is present in his tests but also the compositions of recovered oil versus time are reported, which both are advantages to verifying our model. Moortgat and Firoozabadi presented a comprehensive simulation study to regenerate the experimental results reported by Darvish. In their studies, only the case of the core saturated with live oil containing no initial water saturation was simulated. In another study, Alavian and Whitson attempted to model the case of a core saturated with oil containing initial water saturation with a compositional reservoir simulator and extended Sigmund correlation for estimating diffusion coefficients. It was mentioned in their paper that CO₂ solubility in the initial water saturation is not considered. Therefore, the initial water saturation could not play a mechanistic role in the oil recovery. Since the impact of initial water saturation on oil recovery efficiency caused by molecular diffusion during CO₂ injection is still an open question, this research focused on discussing this gap by introducing a new diffusion mechanism called double cross-phase diffusion because the water accelerates the diffusivity of multicomponent injected gas into the crude oil and, in consequence, increases the oil recovery.

In this article, a lab-scale simulation model has been developed, verified by the available experimental data, and used for the analysis of the impact of the double cross-phase diffusion mechanism, as a new concept, on oil recovery from fractured rocks during the CO₂ injection when initial water saturation is present.

This paper is organized as follows: First, the methodology used for developing our model has been introduced. Thus, the generalized Fick’s law and mass transfer formulation have been represented, inclusively. Then, based on the geometry and experimental data available in the literature, a lab-scale simulator was developed, and its validity was checked. Next, the concept of double cross-phase diffusion as a new mechanism has been introduced. In the Results and Discussion section, the oil recovery in the presence and absence of the double cross-phase diffusion mechanism has been evaluated and compared. Also, the transient behavior of recovered oil compositions and the CO₂ composition along the core sample are determined. The portions of oil recovered by different mechanisms are evaluated, and the impact of the double cross-phase diffusion mechanism on the oil recovery is quantified. In the last part, some sensitivity analyses are performed, and the effect of initial water saturation and matrix permeability on the oil recovery when the double cross-phase diffusion mechanism is considered in the simulation model is discussed.

**METHODOLOGY**

The purpose of this study is to develop a lab-scale model for simulating the CO₂ injection experiments reported by Darvish and to explore the effect of the double cross-phase diffusion mechanism. Such a lab-scale simulation model could also provide the opportunity to compare the performance of different diffusion models that exist in the literature.

First, the formulation used for modeling molecular diffusion is introduced. It has been proven that Stefan–Maxwell (SM) and the generalized Fick’s law are the most accurate models to describe mass transfer in multicomponent systems. To express the SM model, the matrix form of the formulation can be used as

\[
J = -\rho B^{-1} \Gamma \nabla x
\]

\[
B = [B_{ij}]_{i,j=1,2,\ldots,n_l-1}, B_{ij} = \left\{ \begin{array}{ll}
\frac{x_i}{D_{m_i}} + \sum_{k=1}^{n_l} \frac{x_k}{D_{m_k}} & i = j \\
-x_i \left( \frac{1}{D_{ij}} - \frac{1}{D_{m_i}} \right) & i \neq j
\end{array} \right.
\]

\[
\Gamma_{ij} = \delta_{ij} + x_i \frac{\partial \log \rho}{\partial x_j}, \delta_{ij} = \left\{ \begin{array}{ll}
1 & i = j \\
0 & i \neq j
\end{array} \right.
\]

In the above equations, \(J\) represents the diffusion flux, \(\rho\) is the molar density, \(D\) is the SM diffusion coefficient, the matrix \(B\) is a function of the inverse of the SM coefficients, \(x\) denotes the mole fraction in the mixture, \(\varphi\) is the fugacity coefficient, and \(\Gamma\) represents the thermodynamic non-ideality effect, which for ideal mixtures is the identity matrix. The generalized relation to computing diffusion coefficients for multicomponent mixtures is given by
\[
D_j = (D_j^\infty)^{n_i} \left( \prod_{k=1}^{n_i} (D_k^\infty)^{n_j} \right)^{1/2}, \quad i, j = 1, \ldots, n_c
\]

\[i \neq j\]

In Appendix A, all the parameters used in eq 4 are introduced, and the method applied for the calculation of \(D_j\) has been presented. It has been proven that the generalization of Fick’s law is more convenient than the SM model because of numerical implementation.\(^{18}\) Therefore, the correlations developed by Leahy-Dios and Firoozabadi\(^ {17}\) are applied for calculating the SM diffusion coefficients, which are then implemented in the generalized Fick’s law.\(^ {19}\) In other words, the SM diffusion coefficients have been calculated by eq 4. Then, matrix B has been found via eq 2. Matrix B has been substituted in eq 6 to calculate the diffusion coefficients of the generalized Fick’s law. Thus, the SM diffusion coefficients are implemented indirectly to calculate diffusion coefficients of the generalized Fick’s law.\(^ {17-19}\)

In multicomponent mixtures, the diffusion flux based on the generalized Fick’s law is written as\(^ {6}\)

\[
\begin{align*}
J_i &= -\rho \sum_{j=1}^{n_c} \frac{\partial}{\partial x_j} D_{ji} \nabla x_j, \quad i = 1, \ldots, n_c - 1 \\
\sum_{j=1}^{n_c} J_j &= 0, \quad i = n_c
\end{align*}
\]

\[D = B^{-1} \Gamma\]

Based on the previous studies for gas injection modeling in fractured reservoirs, the dual-porosity approach is efficient.\(^ {24}\) Dual-porosity models consider a flowing domain (fracture) and a stagnant domain (matrix) in which mass balance equations are solved for both domains, independently. Source and sink terms consider the transfer of fluids between these two domains.\(^ {5,26}\) The mass balance equation for a component \(i\) in the fracture, which contains \(n_p\) phases and \(n_c\) components, where the participating mechanisms are advection, diffusion, and gravity, can be written as\(^ {27}\)

\[
\frac{\partial C_i}{\partial t} + \nabla \cdot F_i + \nabla \cdot H_i - \Gamma_i = q_i, \quad i = 1, \ldots, n_c
\]

(7)

The mass balance equation for a component \(i\) in the matrix can be written as

\[
\frac{\partial C_i}{\partial t} + \Gamma_i = 0, \quad i = 1, \ldots, n_c
\]

(8)

where the overall molar density, \(C_o\) the overall molar advective flux, \(F_i\), and the overall molar diffusive flux, \(H_i\), are given by eqs 9–11 as

\[
C_i = \sum_{j=1}^{n_c} x_{ij} \rho_j S_{ij}, \quad i = 1, \ldots, n_c
\]

(9)

\[
F_i = \sum_{j=1}^{n_c} x_{ij} \rho_j v_j, \quad i = 1, \ldots, n_c
\]

(10)

\[
H_i = \sum_{j=1}^{n_c} \left( H_{ij} + \sum_{k=j+1}^{n_c} H_{ik,jk} \right), \quad i = 1, \ldots, n_c
\]

(11)

\(H_{ij}\) is the molar diffusive flux of component \(i\) in phase \(j\) (intraphase diffusion), and \(H_{ik,jk}\) is the molar diffusive flux of component \(i\) between phases \(j\) and \(k\) (cross-phase diffusion). In eqs 8–11, \(\varphi\) is the porosity; \(C_i\) is the mole fraction; \(t\) is the time; \(x_i\) is the mole fraction; \(\rho_i\) is the molar density; \(S_{ij}\) is the saturation; \(v_j\) is the velocity; \(q_i\) is the source/sink term; and \(\Gamma_i\) represents the transfer of components from the matrix to the fracture. The formulation and notations used in this article are mainly based on the study reported by Shojaei and Jessen.\(^ {24}\) The transfer rate of component \(i\) from the matrix to the fracture is given by

\[
\Gamma_i = \Gamma_{i,ed} + \Gamma_{i,gl} = \Gamma_{i,gl} \quad i = 1, \ldots, n_c
\]

(12)

where \(\Gamma_{i,ed}\) is the transfer rate due to expansion, \(\Gamma_{i,gl}\) is the transfer rate due to diffusion, and \(\Gamma_{i,gl}\) is the transfer rate due to gravity drainage. The transfer rate due to expansion can be written as

\[
\Gamma_{i,ed} = \sigma_{i,ed} B_{i,ed} K_m \sum_{j=1}^{n_c} \lambda_{j,m} x_{j,m} \rho_{i,m} (p_m - p_j), \quad i = 1, \ldots, n_c
\]

(13)

where \(\sigma_{i,ed}\), \(B_{i,ed}\), \(K_m\), \(\lambda_{j,m}\), \(x_{j,m}\), \(\rho_{i,m}\), \(p_m\) and \(p_j\) are the shape factor, the correction factor for the expansion term, matrix permeability, mobility of phases in the matrix, the mole fraction of component \(i\) in phase \(j\) in the matrix, the molar density of phases in the matrix, and pressure in matrix and pressure in the fracture, respectively. The shape factor used in this study is suggested by Lim and Aziz.\(^ {28}\)

\[
\sigma_i = \frac{\pi^2}{K_m} \left( \frac{K_{m,x}}{L_x} + \frac{K_{m,y}}{L_y} + \frac{K_{m,z}}{L_z} \right)
\]

(14)

The irreversible thermodynamic model can be applied for calculating the mass transfer between the phases. In fact, the chemical potential gradient is responsible for the diffusion of \(\text{CO}_2\) into the water. Also, the \(\text{CO}_2\) dissolution rate depends on the diffusion coefficient of \(\text{CO}_2\) in water.

\textbf{Figure 1.} Illustration for the computation of the chemical potential gradient between grid cells A and B.
where $\pi$ is the mathematical constant, $L_x$, $L_y$, and $L_z$ are the block lengths, and $K_{m,xx}$, $K_{m,yy}$, and $K_{m,zz}$ are the matrix permeabilities along the $x$, $y$, and $z$ directions, respectively.

The transfer rate of each component due to the molecular diffusion mechanism is the summation of intraphase diffusion rates, and cross-phase diffusion rates represent the molecular diffusion rate of each component. Thus, for a three-phase system including gas, oil, and water, the transfer rate of component $i$ is as follows

$$\Gamma_{i,\text{diff}} = \Gamma_{i,\text{gas}} + \Gamma_{i,\text{oil}} + \Gamma_{i,\text{water}}$$

where $\Gamma_{i,\text{gas}}$, $\Gamma_{i,\text{oil}}$, and $\Gamma_{i,\text{water}}$ are the transfer rates due to gas−gas (intra-phase), oil−oil (intra-phase), water−water (intra-phase), gas−oil (cross-phase), gas−water (cross-phase), and oil−water (cross-phase) molecular diffusion, respectively. The transfer rate of component $i$ due to gas−gas diffusion is calculated from

$$\Gamma_{i,\text{gas}} = \alpha_i B_{i,k} \rho_{m,i} \rho_{g,k} S_k \sum_{k=1}^{n-1} D_{k,g} \left( y_{km} - y_{gf} \right),$$

$$i = 1, ..., n_i - 1$$

(16)

where $\alpha_i$ is the shape factor; $B_{i,k}$ is the boost or correction factor for the diffusion term; $\rho_{m,i}$ is the matrix porosity; $\rho_{g,k}$ is the gas molar density; $S_k$ is the gas saturation; $D_{k,g}$ is the diffusion coefficient of component $i$ due to the gradient of component $k$ in the gas phase; $y_{km}$ and $y_{gf}$ are the mole fractions of component $k$ in the matrix and fracture, respectively. The transfer rates of components due to oil−oil and water−water diffusions are calculated in the same manner as the gas−gas diffusion.

$$\Gamma_{i,\text{oil}} = \alpha_i B_{i,k} \rho_{m,i} \rho_{o,k} S_o \sum_{k=1}^{n-1} D_{k,o} \left( y_{km} - y_{gf} \right),$$

$$i = 1, ..., n_i - 1$$

(17)

$$\Gamma_{i,\text{water}} = \alpha_i B_{i,k} \rho_{m,i} \rho_{w,k} S_w \sum_{k=1}^{n-1} D_{k,w} \left( y_{km} - y_{gf} \right),$$

$$i = 1, ..., n_i - 1$$

(18)

where $o$ and $w$ denote the oil and water phase, respectively. Film theory can be used to calculate the transfer rate of each component from the matrix to the fracture due to cross-phase diffusion. This theory emphasizes the continuity of the diffusive flux across the interface. Therefore, for the matrix−fracture system

$$\sigma_i \rho_m \rho_i^m S \sum_{k=1}^{n-1} D_{k,i} \left( \psi_{k,i} - \psi_{k,j} \right) = \sigma_2 \rho_i^f S \sum_{k=1}^{n-1} D_{k,i} \left( \psi_{k,i} - \psi_{k,j} \right),$$

$$i = 1, ..., n_i - 1$$

(19)

where $D_{k,i}$ and $D_{k,j}$ are the diffusion coefficients of component $i$ due to the gradient of component $k$ in the matrix and fracture; $\psi_{k,i}$ and $\psi_{k,j}$ are the chemical potentials of component $k$ in the interface and bulk phase, respectively. Also, $\sigma_2$ is given by

$$\sigma_2 = n^2 \left( \frac{1}{L_x b_j} + \frac{1}{L_y b_j} + \frac{1}{L_z b_j} \right)$$

(20)

where $b_j$ and $b_j$ are the fracture openings in the $x$, $y$, and $z$ directions, respectively. Ultimately, the transfer rate of component $i$ from the matrix to the fracture due to gravity drainage is estimated by

$$\Gamma_{i,\text{gd}} = \sum_{j=1}^{n} \rho_m x_{j,m} \rho_m \sum_{k=1, k \neq j}^{n} T_{jk} \delta_{i,j},$$

$$i = 1, ..., n_i$$

(21)

where $T_{jk}$ is the displacement of phase $j$ by phase $k$ due to gravity drainage in the vertical direction. The readers interested in more details of the governing equations could refer to the paper by Shojaei and Jessen. To remind, the purpose of this study is to involve the water phase in the molecular diffusion mechanism. We extended the governing equations of the gas injection system for the first time, to the condition that the initial water saturation accelerates the diffusion of multicomponent gas into oil, called a double cross-phase diffusion mechanism.

**MODEL DESCRIPTION**

The geometry selected for the simulation model in this study is based on the experimental data reported by Darvish. The reported experimental data was collected during CO2 injection into an artificially fractured chalk core saturated with a crude live oil in the presence and absence of water saturation. Figure 2 shows a schematic of the porous media as a 59.7 cm long and 46 mm diameter cylindrical chalk core placed in the center of a steel tube, as a core holder, having an inside diameter of 50 mm. The 2 mm annular space between the outer boundary of the core and the wall of the steel tube, the 1.5 mm space for the top, and the 1.5 mm space for the bottom are considered as artificially fractured chalk core saturated with a crude live oil.

**Figure 2.** Geometry used for simulation of CO2 injection into core samples for oil recovery.

The results of two experiments are available, the first with zero initial water saturation (run #1)
and the second with 26% initial water saturation (run #2). The core samples’ properties, the operation conditions of the tests, and also the compositions of the live oil used in the experiment are given in Tables 1 and 2, respectively.

**Table 1. Testing Conditions of Runs #1 and #2**

| property         | run #1 | run #2 |
|------------------|--------|--------|
| permeability     | 4 mD   | 4 mD   |
| T                | 130 °C | 130 °C |
| P                | 300 bar| 300 bar|
| S_w              | 0%     | 26.3%  |
| porosity         | 44.4%  | 44.4%  |
| CO_2 injection rate | 0.3 cm³/min | 0.3 cm³/min |

**Table 2. Oil Composition Used in the Experiments for Runs #1 and #2**

| component | (mol %) |
|-----------|---------|
| nitrogen  | 0.12    |
| carbon dioxide | 0.83  |
| methane   | 44.15   |
| ethane    | 7.56    |
| propane   | 4.21    |
| i-butane  | 0.91    |
| n-butane  | 2.24    |
| i-pentane | 0.87    |
| n-pentane | 1.31    |
| hexanes   | 2.07    |
| heptanes  | 2.31    |
| octanes   | 3.33    |
| nonanes   | 2.58    |
| C_{10+}   | 27.51   |

In this lab-scale simulation, a single core sample surrounded by artificial fractures is used to investigate the matrix–fracture interaction. Thus, two different regions can be defined. First, the core sample with 10 grid blocks is in a radial direction, and second, the five radial grids represent the fracture area. Also, in the vertical direction, the core sample is divided into 46 grid cells, and 4 other grid cells represent the fracture on the top and bottom. The finite difference method was applied for discretizing the governing equations. The boundary conditions are (1) a constant CO_2 injection rate of 0.3 cm³/min from the top of the core sample and (2) a constant bottom hole pressure of 300 bar in the bottom of the core sample.

**Figure 3** shows a schematic of the double cross-phase diffusion mechanism in 4 neighboring grid cells between the gas in the fracture and water and oil phases in the matrix. It is mentioned that the initial water is distributed along the core sample in all grid cells with its saturation. The gas injected from the top of the core diffuses through the surrounded fracture into the matrix. Once the CO_2 injection begins in the system, the area that represents fracture is filled with CO_2. Based on the properties of the components in the system, CO_2 can diffuse through oil and water. In this circumstance, CO_2 in the fracture has two different paths to diffuse into the matrix. The first path is through the oil phase, and the second is through the water phase. The major part is cross-phase diffusion through the oil phase, shown by the blue color in **Figure 3**, because the contact area between the CO_2–oil phase is more than the CO_2-water phase. Also, the intraphase diffusion would occur in the oil phase, indicated by the green color. It is noticeable that in the water phase, two cross-phase diffusions would occur, which are shown by the red color in **Figure 3**. The first one is between the CO_2 and water and the second is between the water and oil phases. This aspect is an innovative approach in molecular diffusion as the water phase accelerates gas diffusion through the oil. This mechanism is introduced as a new concept called “double cross-phase diffusion”.

**RESULTS AND DISCUSSION**

Based on the presented model, explained in the last section of this work, a lab-scale simulator is developed and applied for predicting the experimental data of oil recovery during CO_2 injection in fractured rocks. The result of produced oil versus time for run #1 is shown in **Figure 4**. This figure shows the oil recovery from the core sample for 25 days of CO_2 injection. For comparison, the results of oil recovery for the generalized and classical Fick’s law are compared in this figure. It is evident that classical Fick’s law fails to predict the experimental data accurately. A close match observed between experimental and the generalized Fick’s law results confirms that the model could be successfully applied in the compositional simulation of the gas injection process.

Therefore, in this study, the generalized Fick’s law was chosen to simulate the double cross-phase molecular diffusion mechanism in the next section. It should be mentioned that a similar result to **Figure 4** is also reported by Moortgat and Firoozabadi.

Thus, we could claim that the simulation model developed in this study is sufficiently accurate and reliable for investigating the gas injection process in a more complex diffusion system considered double cross-phase diffusion.

Our lab-scale simulator can predict the composition of produced oil as a function of time. These results are shown in **Figures 5–7**, which show that the model prediction accurately matches experimental data. For comparison, the estimation of classical Fick’s law has been shown in these figures. Results of classical Fick’s law represent the intention of heavier components to be produced during the gas injection, which are far from the experimental results. The experimental results helped to verify the capability of the lab-scale simulator in modeling of the diffusion mechanism. Also, the regeneration of these experimental results has been done for the first time in this study, which is valuable. Therefore, the lab-scale simulator can be used as an efficient tool for investigating diffusion mechanisms.

For run #2, which has 26% water saturation, the simulator can predict the oil recovery during CO_2 injection. In this case, two methods for simulation have been selected. The first one just considers the molecular diffusion between oil and gas. Therefore, the transfer function just has three elements and includes oil–oil, gas–gas, and gas–oil parameters. The second one is the comprehensive one and includes gas–water, water–oil, and water–water elements. Thus, the diffusivity effect of the existing water in the matrix can be included in the simulation. Therefore, we can investigate the effect of the double cross-phase diffusion mechanism on oil recovery prediction. This result is shown in **Figure 8**. It is evident that there is a difference in oil recovery prediction when the double cross-phase diffusion mechanism is considered in the simulation. It brings to attention the idea that using the generalized Fick’s law with considering the double cross-phase diffusion mechanism contributes to accurate prediction and can have a noticeable effect on the results and remarkably match with the experimental data. Consequently, the double cross-phase diffusion mechanism has

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ACS Omega 2022, 7, 21630−21642

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ACS Omega 2022, 7, 21630−21642

21634

https://doi.org/10.1021/acsomega.2c01503

ACS Omega 2022, 7, 21630−21642

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a significant impact on the simulation results. It is noticeable that this investigation has been done for the first time, and the double cross-phase diffusion mechanism has not been considered in other studies.

In Figure 9, the overall CO$_2$ composition along the core sample after 5 days of CO$_2$ injection in the absence and presence of the double cross-phase diffusion mechanism for run #2 has been shown. It is evident from the figures that the diffusion mechanism has been accelerated by considering a double cross-phase diffusion mechanism. Therefore, the mole fraction of CO$_2$ along the core sample increases when the double cross-phase diffusion mechanism contributes to the oil recovery process. The results of CO$_2$ composition along the core sample after 15
days of CO2 injection in the absence and presence of the double cross-phase diffusion mechanism for run #2 are shown in Figure 10. Thus, similar consequences have been proven. As a result, eliminating the double cross-phase diffusion mechanism in simulation can generate inaccurate outcomes.

Figures 11 and 12 represent the mass fraction of produced oil components for run #2. It is plainly visible that considering the double cross-phase diffusion mechanism consequences the accurate prediction of produced oil composition. On the other end, eliminating the double cross-phase diffusion mechanism leads to inaccurate results.

It is important to note that when the water diffusivity terms are included in the simulation of molecular diffusion, the injected gas can diffuse into the water and, after that, into the oil. Thus, the injected gas has two ways of diffusing into the oil. One of them is directly into the oil, and another one is from the water to the oil. Therefore, the presence of water diffusivity terms in simulation can have a significant impact on the results of oil recovery because the water can accelerate the diffusivity of gas into the oil and increase the recovered oil.
Based on Figures 11 and 12, the presence of water diffusivity terms in simulation can contribute to accelerating the production of lighter components of the oil. Therefore, lighter components begin to produce more rapidly, and the final oil present in the matrix would be heavier. This is evidence that ultimate oil recovery when the water diffusion terms have been considered would be increased.

The approach of considering a double cross-phase diffusion mechanism, in the case of CO₂ injection, can be clarified as follows: When the water phase exists in the matrix, the CO₂ quickly diffuses into the water because of the high solubility of CO₂. This is the first cross-phase diffusion. Then, due to the high concentration gradient of CO₂ between the water and the oil phases, the CO₂ is transported to the oil phase through another cross-phase diffusion mechanism. Therefore, a double cross-phase diffusion mechanism would happen. As a result, the oil phase would swell and recover from the matrix.

In this part, the portion of transfer rates due to each mechanism in the initial time of oil recovery has been investigated to analyze the effect of each mechanism in oil recovery from the matrix to the fracture. It is noticeable that expansion, molecular diffusion, and gravity drainage are the mechanisms that have been considered in the simulation. The transfer rate of each mechanism has been divided by the overall transfer rate. For run #2 with Sw = 26% and K = 4 mD, the portion of each mechanism in the initial time of oil recovery would be described in Figure 13. It is important to note that molecular diffusion has a significant impact on oil recovery from run #2. The transfer rate due to the molecular diffusion mechanism is 75.4% of the total transfer rate. In this sense, the controlling mechanism in oil recovery from the matrix to the fracture is molecular diffusion. In comparison, it is estimated that 19.15% of the transfer rate is due to the gravity drainage mechanism. Also, the active participation of the expansion mechanism in components transferring is 5.45%.

75.4% is the portion of the transfer rate due to the molecular diffusion mechanism at the initial time of oil recovery. To provide a detailed analysis of the transition for the contribution of different active oil recovery mechanisms, Figure 14 shows the portions of transfer rate due to molecular diffusion, gravity drainage, and expansion mechanisms for run #2 as a function of time. It is concluded that the molecular diffusion mechanism controls the oil recovery, although it decreases over time. However, mass transfer via the gravity drainage mechanism would increase over time. Also, mass transfer from the expansion mechanism slightly increases with time. Thus, molecular

**Figure 10.** Overall CO₂ composition along the core after 15 days of injection (a) in the absence and (b) in the presence of the double cross-phase diffusion mechanism from run #2.

**Figure 11.** Ethane, propane, and butane mass fraction in oil recovered from run #2.

**Figure 12.** Heptane, octane, and nonane mass fraction in oil recovered from run #2.
diffusion would stay a controlling mechanism over time, although some of its effect shifts to gravity drainage. The portions of transfer rates of intraphase and cross-phase diffusion mechanisms, shown in Figure 15, have been calculated using eqs 16–19, respectively. The transfer rates of intraphase diffusion depend on the diffusion coefficients and gradient components; however, film theory and the irreversible thermodynamic model can be applied to calculating the transfer rates of cross-phase diffusion. It is obvious that the transfer rate due to gas–oil diffusion is significantly higher than the other intraphase and cross-phase diffusions. It is partly because the contact area of gas and oil is higher than the other cross-phases. It is important to note that gas–water and water–oil transfer rates are %23.1 of the total transfer rate. In this regard, the elimination of the double cross-phase diffusion mechanism in fracture reservoir simulations causes an underestimation of the molecular diffusion effect.

To provide more detailed data, Figure 16 illustrates the portion of transfer rates due to cross-phase, double-cross-phase, and intraphase molecular diffusion for run #2 as a function of time. It is evident that mass transfer via cross-phase diffusion...
slightly decreased during the oil recovery, although mass transfer via double-cross-phase diffusion would increase. Also, intra-phase diffusion mass transfer is increasing over time. By producing the lighter components of oil, the role of double-cross-phase diffusion is more efficient because CO₂ would diffuse through the water phase more conveniently than in the heavy oil phase.

**SENSITIVITY ANALYSIS**

To investigate the effect of water saturation on ultimate oil recovery, three different simulations have been arranged. Run #2 has been considered, but its water saturation has been changed to 20%, 30%, and 40%. For analyzing the effect of water diffusion terms on the oil recovery, the difference between the simulation without water diffusion terms and the simulation with water diffusion terms has been considered. The results of these cases are shown in Figure 17. It brings to attention the idea that considering the water phase in components transferring causes accelerating molecular diffusion mechanisms. Therefore, a significant difference has been shown after 8 to 10 days of oil recovery.

To compare and clarify the effect of considering water diffusivity terms in simulation, the difference in oil recovery for each case is shown in Figure 18. Based on Figure 18, it has been proven that when the water saturation in a core sample increases, the oil recovery will deviate sharply. Although the differences rise until 10 days of oil recovery, the falling part will begin because the oil phase is compensating for the water phase effect. However, oil recovery timing in the simulation would be different if the water effect was ignored. The oil recovery difference of about 8% for $S_Wi = 40\%$ has been reported to emphasize the importance of considering water diffusivity terms.

In another sensitivity analysis, the effect of matrix permeability on transfer rate due to active oil recovery mechanisms in fractured reservoirs under gas injection has been investigated. Therefore, run #2 has been considered, but its matrix permeability has been changed to 0.1, 1, and 10 mD. These matrix permeabilities would be logical because molecular diffusion is an active mechanism when matrix permeability is low. In Figure 19, the transfer rates due to different mechanisms have been shown for run #2 with permeabilities of 0.1, 1, and 10 mD in the initial time of oil recovery. Due to changing permeability, molecular diffusion would be an active and controlling mechanism in oil recovery during the gas injection process for low permeability matrices in fractured reservoirs. It is evident that increasing the matrix permeability makes a real difference in controlling oil recovery mechanisms. The gravity drainage mechanism has a significant rise when the matrix permeability increases. The transfer rate of this mechanism has risen from 13.4% to 30.3% when permeability has increased from 1 to 10 mD. In contrast, the transfer rate of molecular diffusion mechanisms has fallen from 78.3% to 60.8%. However, molecular diffusion is still the controlling mechanism for oil recovery.

**CONCLUSIONS**

In this article, a new double cross-phase diffusion mechanism was introduced and applied for developing a comprehensive simulation model to predict oil recovery during CO₂ injection in fractured rocks when initial water saturation is present. The developed simulator, implementing the generalized Fick’s law of multicomponent diffusion, was validated by the experimental results.
data available in the literature. Well-matched observations between model predictions and experimental data confirm the reliability of the double cross-phase diffusion mechanism considered in the model. Also, it may be concluded that the generalized Fick’s law is sufficient for simulating gas injection in fractured rocks when double cross-phase diffusion is considered.

Based on the results of this study, it has been revealed that the effect of the double cross-phase diffusion mechanism on oil recovery from fractured reservoirs during the CO₂ injection process is remarkable. In other words, there is a significant difference in oil recovery prediction when the effect of initial water saturation has been considered in the simulation model. In fact, water is responsible for accelerating the diffusivity of CO₂ into the oil and increasing the recovered oil. In other words, due to the high solubility of CO₂ in water and the high concentration gradient of CO₂ between the water and the oil phase, more CO₂ is transferred to oil through the liquid–liquid diffusion mechanism.

The developed simulation model predicts the experimentally measured mass fraction of produced oil components during the gas injection process with close agreement, which is an interesting result. Also, the portions of active oil recovery mechanisms are evaluated. For the core samples tested by CO₂ injection analyzed in this study, the molecular diffusion mechanism is 75.4% of the total transfer rate in the initial time of oil recovery, which is a significant value, and a more interesting result is that 23.1% of that is induced by the double cross-phase diffusion mechanism, which is also a remarkable value. Based on the results of sensitivity analysis, it has been observed that by increasing the initial water saturation, the impact of the double cross-phase diffusion mechanism on oil recovery increases, while the transferred rate by diffusion mechanism decreases from 85.4% to 60.8% when matrix permeability increases from 0.1 to 10 mD.

This work demonstrates for the first time the role of initial water saturation in enhancing the diffusion of multicomponent gas into crude oil through the water phase, called a double cross-phase diffusion mechanism, and in consequence enhancing oil recovery during non-equilibrium gas injection in fractured oil reservoirs.

### APPENDIX A

All the parameters needed for the estimation of the SM diffusion coefficients have been presented in this appendix. Therefore, Leahy-Dios and Firoozabadi’s approach has been selected to estimate \( D_{ij} \). \( D_{ij} \) can be defined by the following equation

\[
\rho_j D_{ij}^\infty = A \left( \frac{\rho_j D_{ij}^\infty}{(\rho D)_j} \right) = A_0 \left( \frac{P_{r,i} T_{r,i}}{T_{r,j} P_{r,j}} \right)^{A_1} \left( \frac{h_j}{\mu_j} \right) \left[ A_2 (\omega_i \omega_j) + A_3 (\rho, T) \right]
\]  

(A1)

The parameters that appear in eq A1 can be found by

\[
A_0 = e^{a_1}
\]  

(A2)

\[
A_1 = 10 a_2
\]  

(A3)

\[
A_2 = a_3 \left( 1 + 10 \omega_1 - \omega_1 + 10 \omega_1 \omega_j \right)
\]  

(A4)

\[
A_3 = a_4 \left( P_{r,i}^{a_1} - 6 P_{r,j}^{a_1} + 6 T_{r,j}^{10 a_4} \right) + a_7 T_{r,i}^{a_6} + a_2 \left( \frac{T_{r,i} P_{r,i}}{T_{r,j} P_{r,j}} \right)
\]  

(A5)

\[
a_1 = -0.0472
\]  

(A6)

\[
a_2 = 0.0103
\]  

(A7)

\[
a_3 = -0.0147
\]  

(A8)

\[
a_4 = -0.0053
\]  

(A9)

\[
a_5 = -0.3370
\]  

(A10)

---

**Figure 18.** Difference between the oil recovery predicted by the model in the presence and absence of the double cross-phase diffusion mechanism for different values of initial water saturation, 20%, 30%, and 40%.

**Figure 19.** Portion of transfer rate due to the active oil recovery mechanism for run #2 with different matrix permeabilities in the initial time of oil recovery.
\[ a_6 = -0.1852 \]  
\[ a_7 = -0.1914 \]  
(A11)  
(A12)

where \( a \) is the acentric factor, \( P \) is the reduced pressure, \( T \) is the reduced temperature, and \( \mu^0 \) is the dilute-gas viscosity. Poling et al.\(^{30}\) recommended an expression to estimate the dilute gas density diffusion coefficient product

\[
(\rho D)_i^0 = 1.01 \times 10^{-2} T^{0.75} \left[ \frac{1}{M_i} + \frac{1}{M_j} \right]^{0.5} \left[ \left( \sum \nu_i \right)^{1/3} + \left( \sum \nu_j \right)^{1/3} \right] 
\]

where \((\rho D)_i^0\) is the dilute gas density-diffusion coefficient product given in \((\text{mol/m s})\); \(M\) is the molecular mass \((\text{g/mol})\); \( T \) is the temperature \((\text{K})\), and \( \nu \) is the diffusion volume increment, which is calculated by summing the atomic diffusion volumes given in Table A1. The low-pressure viscosity for each component is given by

\[
\mu_i^0 = \begin{cases} 
34 \times 10^{-8} (T_{r,i})^{0.94}, & (T_{r,i} < 1.5) \\
17.78 \times 10^{-8} (4.58 T_{r,i} - 1.67)^{5/8}, & (T_{r,i} > 1.5)
\end{cases}
\]

(A14)

Where

\[
\xi_i = \frac{T_{r,i}^{1/6}}{M_i^{1/2} (0.987 \times 10^{-5} P_c)^{1/3}}
\]

(A15)

and the dilute gas viscosity of the mixture can be written as

\[
\mu^0_y = \frac{\mu_i^0 M_i^{1/2} + \mu_j^0 M_j^{1/2}}{M_i^{1/2} + M_j^{1/2}}
\]

(A16)

### Table A1. Atomic Diffusion Volumes\(^{30}\)

| Component | Atomic and structural diffusion increments | Diffusion volumes of simple molecules |
|-----------|-------------------------------------------|-------------------------------------|
| C         | 15.9                                      | He                                  |
| H         | 2.31                                      | Ne                                  |
| O         | 6.11                                      | Ar                                  |
| N         | 4.54                                      | Kr                                  |
| aromatic ring | −18.3                                   | H₂                                 |
| heterocyclic ring | −18.3                                   | D₂                                 |
| S         | 7.27                                      | N₂                                 |
| O₂        | 16.3                                      | air                                 |
|            |                                           |                                     |
|            |                                           |                                     |
|            |                                           |                                     |

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