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Molecular Simulation of Enhanced Oil Recovery in Shale

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Abstract

Enhanced oil recovery (EOR) techniques (miscible/near miscible gas injection, chemical flooding and thermal) aim at increasing oil recovery factor, over which that would be achieved from natural depletion and pressure maintenance methods. As we embark on more complex EOR processes (e.g. miscible hydrocarbon/non-hydrocarbon, surfactant/polymer, smart water and combination of the three), complex phase equilibria, complicated rock/fluid interaction, and sophisticated transport through porous media will create a number of key technical challenges that must be addressed. The issue is significantly increased in unconventional resources as the physics behind the process is not very well understood.

For these resources, effective enhanced oil recovery (EOR) techniques are required to displace oil from nanoscale shale matrix. Due to small permeability, it is difficult to conduct water and chemical flooding in these resources. Maintaining a stable flood front in immiscible gas flooding due to the severe fingering phenomenon in fractured shale formations. Gas huff-n-puff becomes the most suitable EOR method in shale reservoir development. For decades, CO₂ (EOR) techniques that have been successfully applied in conventional reservoirs to improve oil production. In this work, we will investigate the physics behind CO₂ injection into organic nanopores of shale using molecular dynamics simulations. A 3D kerogen structure is used with dodecane to study the huff-n-puff process at a molecular level. Results show that there is an optimal soaking time after which the recovery factor is not affected by soaking time anymore. Furthermore, carbon dioxide has high affinity to be adsorbed to kerogen walls and therefore desorbing the hydrocarbon molecules.

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1. Introduction

There is significant oil content in unconventional shale resources that cannot be recovered using primary depletion

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stage because of small pore sizes and extremely low permeability of shale matrix. For these resources, effective enhanced oil recovery (EOR) techniques are required to displace oil from nanoscale shale matrix. Due to small permeability, it is difficult to conduct water and chemical flooding in these resources. Maintaining a stable flood front in immiscible gas flooding due to the severe fingering phenomenon in fractured shale formations. Gas huff-n-puff becomes the most suitable EOR method in shale reservoir development [1]. For decades, CO₂ (EOR) techniques that have been successfully applied in conventional reservoirs to improve oil production. Recent studies have proved the effectiveness of these techniques for organic-rich shale gas reservoirs because of the CO₂ adsorption ability of organic matter [2]. CO₂ injection can be employed to recover more hydrocarbons by changing the fluid-fluid and rock fluid interactions.

There have been several core experiments on CO₂ injection studies in tight oil plays. Habibi et al. [3] presented comprehensive rock-fluid experiments to study the possibility of oil recovery improvement when CO₂ is injected as a fracturing fluid in the Montney tight-oil play. The results of cyclic CO₂ injection showed that oil swelling because of CO₂-oil interactions, solution CO₂ drive, and oil viscosity reduction lead to a high oil recovery factor from the oil-saturated core plugs. Song and Yang [7] experimentally evaluated the performance of four recovery schemes (i.e., waterflooding, immiscible CO₂ huff-n-puff, near-miscible CO₂ huff-n-puff, and miscible CO₂ huff-n-puff processes) on Eagle Ford core samples and Wolf camp dead oil. The results showed that both near-miscible and miscible CO₂ huff-n-puff processes achieve superior recovery performance compared to the immiscible CO₂ huff-n-puff process. Allawzi et al. [4] investigated the possibility of extracting oil from Jordanian oil shale using supercritical CO₂ (sCO₂) with different co-solvents and observed that sCO₂ along with other co-solvents (such as hexane and acetone) interacted with the kerogen. This led to the dissolution of organic fragments because of an increase in solubility and mass transfer. Jarboe et al. [5] used sCO₂ to extract n-aliphatic hydrocarbons from core samples of Marcellus shale with total organic carbon (TOC) content ranging from 1.5 to 6.2 wt%. They concluded that sCO₂ is able to mobilize residual organic matter present in over-mature shales. Zhang et al. [6], conducted simulation experiments on sCO₂ fracturing in shale and showed that compared with hydraulic fracturing, using sCO₂ as the fracturing fluid reduces the pressure needed to initiate fractures by more than 50%. This reduction is due to the increased percolation and pore pressure effects of using sCO₂. Jin et al. [8] performed comprehensive rock-fluid characterization and supercritical CO₂ extraction experiments on Bakken shale samples. Their measured CO₂ adsorption isotherms showed that the Bakken Formation has a considerable capacity to adsorb CO₂ under reservoir conditions and the formation could be a promising target for permanent storage of large quantity of CO₂.

In nanopores, dynamical and thermodynamical behavior of fluids differ from their bulk counterparts. The transport properties in nanopores is of diffusive nature and affected by fluid-fluid and fluid rock interactions [10], which can result in inhomogeneous density distributions across the pores. Liu et al. [9] performed nonequilibrium molecular dynamics (NEMD) simulations to study adsorption and translocation of sCO₂/dodecane in shale inorganic nanopores at different sCO₂ injection rates. Their result showed that injected sCO₂ preferentially adsorbs in proximity of the surface and form layering structures due to hydrogen bonds interactions between CO₂ and -OH groups.

In this work, Molecular dynamics (MD) provide powerful tool to investigate the phase behavior of hydrocarbons and miscibility of CO₂ in oil trapped in organic nanopores.

2. Methodology

2.1. System Setup

In order to investigate the physics behind huff-n-puff process in organic rich shales, a kerogen molecular structure is created (discussed in section 2.3). The kerogen structures include a channel with 5 nm height (Fig. 1). The channel is closed from the left side with a repulsive wall. The fluid molecules (hydrocarbons) are placed in kerogen channel. On the other end of kerogen channel, a reservoir is created to store the carbon dioxide. At the beginning of the simulations, a wall is placed between the carbon dioxide reservoir and kerogen channel to equilibrate the hydrocarbons and carbon dioxide separately. Once the system reached to equilibrium, the middle wall is deleted and carbon dioxide and hydrocarbons can interact with each other using Equilibrium Molecular Dynamics (EMD) simulations in canonical ensemble (constant number of molecules (N), constant volume (V), constant temperature (T)) or NVT. The equation of motion is integrated using the Verlet algorithm [11] with a timestep of 1 femtosecond. Temperature of the system is kept constant using Nosé-Hoover thermostat. The number of carbon dioxide molecules entering the kerogen channel and also the number of dodecane molecules producing from it are recorded with time. The carbon dioxide is let to

interact with dodecane for a several soaking times. After each of soaking periods, the repulsive wall at the right end of the system is opened in order to create a pressure gradient (production period). As a result, effect soaking time on hydrocarbon recovery from kerogen is investigated. Furthermore, the interaction of carbon dioxide with kerogen channel is studied. All the simulations are performed using Large Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [12] with GPU package [13,14,15]. The cut-off radius is selected to be 30 Å as it is necessary for this type of force field. The average of various properties of the system are determined over 5 ns after the equilibration is reached. All simulations are performed at temperature of 343 K.

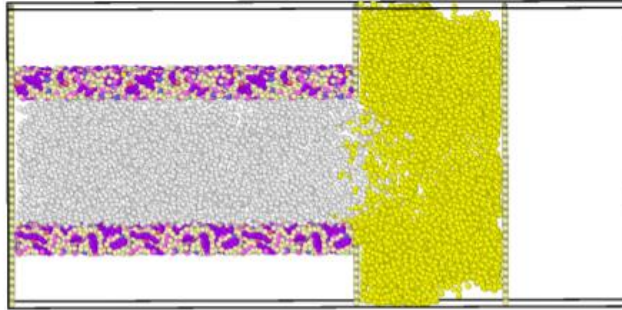


Fig. 1. Schematic of huff-n-puff molecular simulation structure. The yellow and gray molecules are carbon dioxide and dodecane, respectively. Dodecane molecules are confined within the kerogen channel which closed from the left side.

2.2. Kerogen Molecular Structure

Kerogen unit molecules with different maturities, prepared by Ungerer et al. [16] are used in this study. To build a representative solid-state model of kerogen, eight kerogen molecules are placed in a $10 \times 10 \times 10$ nm periodic cubic cell using Moltemplate software. The Lennard-Jones diameter of dummy particles is selected to be 15 Å. The COMPASS (Condensed-Phase Optimized Molecular Potentials for Atomistic Simulation Studies) class2 force field is used to describe the interactions between atoms, bonds, and angles. Once the initial configuration of kerogen molecules is prepared, constant-temperature constant-volume (NVT) simulations are performed at 900 K for 3 ns. Several conformations are sampled from NVT simulations. Each sampled conformation goes under successive constant-temperature constant pressure (NPT) simulations for a temperature range of 900 to 338 K at 20 MPa pressure. The produced structure is duplicated to create a channel shown in Fig. 1. In this work, we use kerogen type IIC to perform simulations.

3. Results

3.1. Dodecane Soaking with CO_2

As discussed in methodology section, carbon dioxide is let to interact with dodecane for 23 nanoseconds (ns). The pressure of carbon dioxide is set to 100 atm and the pressure of dodecane is 68 atm. Fig. 2 shows the number of these two components in kerogen channel and CO_2 reservoir at different soaking times. As shown for the case of 15 ns soaking, the number of CO_2 increases in kerogen and the number of dodecane molecules decreases. While soaking, dodecane molecules move out of the kerogen channel.

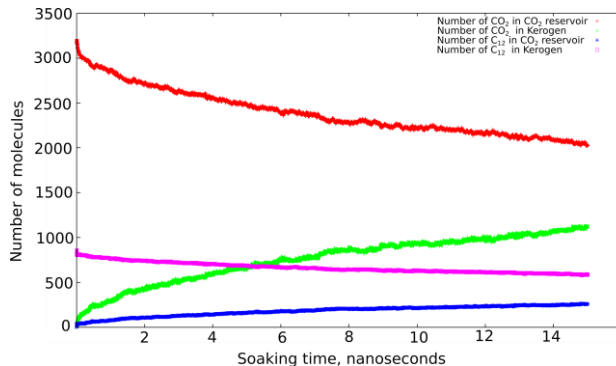


Fig. 2. Number of molecules in kerogen channel and CO₂ reservoir with soaking time.

Fig. 3 shows the number density profiles of CO₂ and C₁₂ along the channel height (Y) at two different soaking times, i.e. zero and 15 ns. It can be observed that the number of carbon dioxide molecules significantly increase inside channel specifically near the kerogen walls while the number dodecane molecules reduce as soaking time increases to 15 ns.

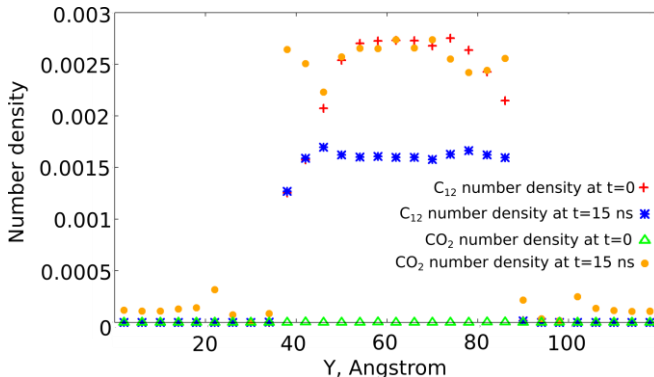


Fig. 3. Number density profiles of CO₂ and C₁₂ along the channel height at different soaking times.

Fig. 4 demonstrates the carbon dioxide and dodecane density profiles along the channel (x-axis) at 0 and 15 ns of soaking. Initially at time zero, all of CO₂ molecules are in middle reservoir and all of dodecane molecules are placed inside kerogen. Therefore, CO₂ density peak happens between 150 to 200 A. After soaking for 15 ns, the CO₂ molecules move to kerogen channel and some of dodecane molecules move out of channel due to viscosity reduction. Therefore, we can see that the density of C₁₂ increased while density of CO₂ reduced in the middle reservoir.

The soaking process was performed for 23 ns. In order to investigate the effect of soaking on dodecane production from kerogen, we started production stage (discussed in methodology section) at different soaking time and the recovery factor from kerogen channel was determined. Fig. 5 shows the recovery factor obtained as a function of soaking time.

Initially (t=0), we do not let CO₂ and C₁₂ to interact and we start the production stage right away. This minimizes the effect of carbon dioxide soaking. Only 8 percent of dodecane move out of kerogen channel with zero soaking time. As we increase the soaking time, the recovery factor increases until 10 ns of soaking. After this soaking time, the change in recovery factor is not huge. Therefore, an optimal soaking time period exists after which the recovery factor will not increase significantly. In our case (a channel with 5 nm height), a maximum recovery factor of 22% was achieved which is within the range reported by EOG Resources Company for enhanced oil recovery of Eagle Ford shale. Our research group are performing further studies to investigate the effect of oil composition, pore size, and pressure on enhanced oil recovery of organic nanopores.

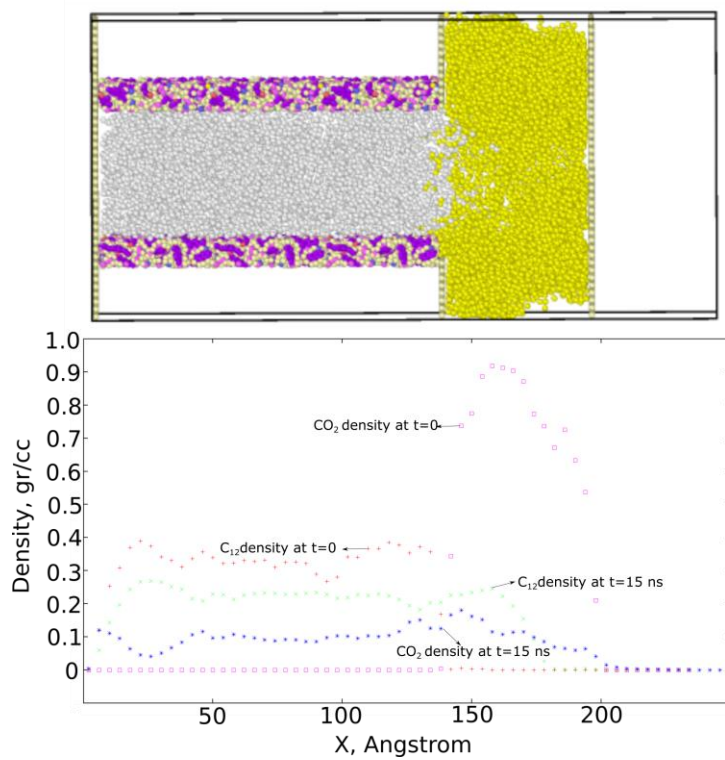


Fig. 4. Density profiles of carbon dioxide and dodecane along x-axis at two different soaking times.

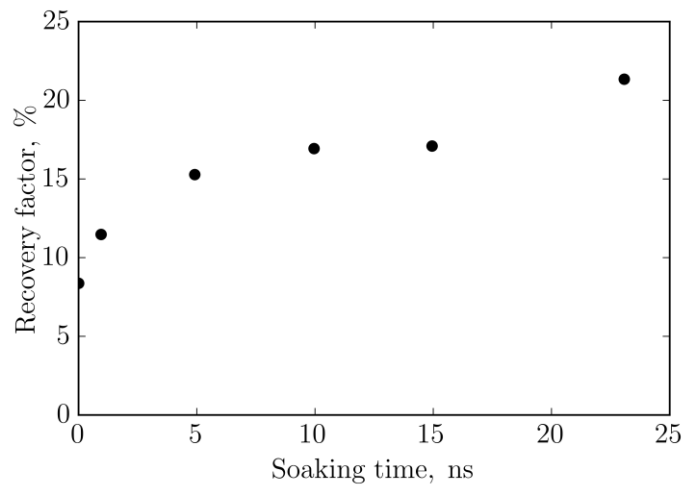


Fig. 5. Recovery factors from production stage for different soaking times.

4. Conclusions

Simulations of phase behavior and CO₂ EOR were performed using molecular dynamics simulations. Since the experimental measurements and investigation of enhanced oil recovery in tight shale reservoirs are cumbersome,

molecular simulations can be very fruitful in understanding of physics behind the huff-n-puff process. Simulation results demonstrated that the carbon dioxide have higher adsorption capability as its number density near the kerogen walls were higher than dodecane. It takes a long time for carbon dioxide molecules to reach the end of kerogen pore as diffusion process is slow. Our simulations showed that there is an optimal soaking time after which the production is not affected significantly by soaking. Further studies are required to investigate the effect of pore size, oil composition, and injection pressure on CO₂ enhanced oil recovery in organic nanopores.

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