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Impact of Pentanol on CO_2-Oil MMP: A Molecular Dynamics Study for Enhanced Oil Recovery

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ABSTRACT

It is important to improve CO_2 miscible flooding efficiency by using additives for CO_2 enhanced oil recovery (EOR). To bridge the gap, this study aims to investigate the effect of pentanol additives on the Minimum Miscibility Pressure (MMP) of CO_2-oil systems under reservoir conditions.

Molecular dynamics (MD) simulations were conducted in this work by using LAMMPS software to model the interactions between CO_2, crude oil, and pentanol molecules under reservoir conditions. The force field parameters were carefully calibrated and validated against experimental data. The vanishing interface method was employed to determine the MMP by observing changes in the gas-liquid interface and assessing miscibility under different conditions. The impact of pentanol concentration (0-10 wt%) on MMP was thoroughly analyzed.

The simulation results reveal that pentanol significantly reduces the MMP of CO_2-oil systems. The MMP decreases as the concentration of pentanol increases, reaching an optimal point before leveling off. In addition, CO_2 molecules preferentially cluster around the hydroxyl groups of pentanol, enhancing their interaction with the oil phase and facilitating the disruption of oil molecular cohesion. This interaction effectively reduces the MMP, demonstrating pentanol's potential as a powerful additive for CO_2 miscible flooding.

The findings provide valuable insights for optimizing the processes of CO_2 enhanced oil recovery and storage, offering a practical approach for achieving carbon neutrality through improved reservoir exploitation techniques.

Keywords: Minimum Miscibility Pressure (MMP), CO_2 Miscible Flooding, Molecular Dynamics Simulations, Pentanol, EOR

NONMENCLATURE

Abbreviations	
MD	Molecular dynamics
EOR	Enhanced oil recovery
MMP	Minimum miscibility pressure
CCUS	Carbon capture, utilization, and storage
IFT	Interface tension
Symbols	
wt	Mass fraction
K	Kelvin
Å	Angstrom
ns	Nanoseconds
MPa	MegaPascals

1. INTRODUCTION

The global pursuit of carbon neutrality and the increasing urgency of addressing climate change have driven the development of advanced carbon capture, utilization, and storage (CCUS) technologies[1]. Among these, CO_2-enhanced oil recovery (CO_2-EOR) stands out for its dual benefits: it not only sequesters CO_2 but also significantly enhances oil production [2]. By injecting CO_2 into oil reservoirs, CO_2-EOR can reduce oil viscosity, decrease interfacial tension, and improve oil mobility, leading to higher recovery rates. A key parameter in this process is the minimum miscibility pressure (MMP), which determines whether the injected CO_2 can fully mix with crude oil to achieve miscible flooding conditions. Achieving a lower MMP is crucial as it enhances the efficiency and feasibility of CO_2-EOR, particularly in reservoirs with high MMP requirements.

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Numerous methods have been explored to reduce MMP, including increasing the purity of the injected CO_2 and using mixed gas injections. However, these approaches often come with limitations, such as high operational costs and potential reductions in miscibility effectiveness. Chemical additives, particularly alcohols, have shown promise in reducing MMP by altering the interfacial properties between CO_2 and crude oil [3]. Alcohols like pentanol have been found to be effective due to their ability to form hydrogen bonds with CO_2 molecules, enhancing CO_2 solubility in the oil phase and reducing interfacial tension [4].

Previous studies have demonstrated that alcohol additives can lower MMP, with the effectiveness depending on the concentration of the alcohol used. However, the specific mechanisms by which these alcohols reduce MMP and the optimal concentrations required for maximum effect are still under investigation.

This study aims to investigate the impact of pentanol on the Minimum Miscibility Pressure (MMP) of CO_2-oil systems using molecular dynamics (MD) simulations. Pentanol is selected for its potential to form strong hydrogen bonds with CO_2, enhancing miscibility and reducing MMP. By utilizing MD simulations with LAMMPS software [5], the study will model interactions between CO_2, crude oil, and pentanol under reservoir conditions, providing a detailed molecular-level understanding. The force field parameters will be calibrated and validated against experimental data to ensure accuracy. The vanishing interface method will be employed to determine MMP by observing gas-liquid interface changes and assessing miscibility under different conditions. The impact of pentanol on MMP will be analyzed, focusing on its concentration and molecular interactions. The study will explore how pentanol enhances CO_2-oil interactions, disrupts oil molecular cohesion, and improves the CO_2-enhanced oil recovery (EOR) process. The insights gained will contribute to optimizing CO_2-EOR techniques, making them more efficient and cost-effective, and supporting broader efforts to achieve carbon neutrality.

This study aims to elucidate the impact of pentanol on the MMP of CO_2-oil systems under reservoir conditions by conducting molecular dynamics simulations. This section details the construction and validation of these models, as well as the simulation settings used to achieve reliable results.

2. SIMULATION SETTING

2.1 Molecular model

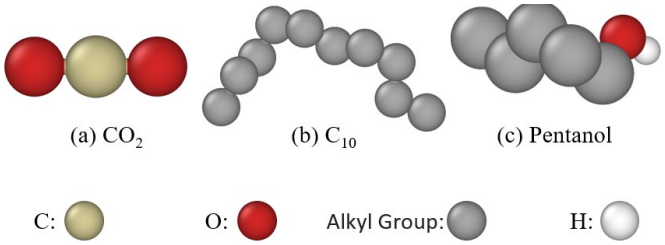

Fig. 1. Molecular models

In this study, molecular dynamics (MD) simulations were conducted using the LAMMPS software to investigate the impact of pentanol additives on the MMP of CO_2-oil systems. In the simulations, CO_2 was modeled using an all-atom model, ensuring a detailed and accurate representation of its behavior. Conversely, n-decane and pentanol were represented using a united atom model, where the hydrogen atoms in the alkane molecules are combined with the carbon atoms, simplifying the calculations while accurately describing the phase behavior of these molecules. However, the oxygen and hydrogen atoms in the hydroxyl group (-OH) of pentanol were treated as separate entities to accurately capture their interactions.

This approach balances computational efficiency with the need for accuracy in describing molecular interactions, particularly the critical interactions between CO_2 and the hydroxyl groups of pentanol.

2.2 Force fields

State the objectives of the work and provide an adequate background, avoiding a detailed literature survey or a summary of the results.

Currently, the flexible molecular force field for CO_2 is primarily based on the EPM2 [6] molecular model and the TraPPE [7] molecular model, with molecular model parameters proposed through quantum chemistry methods. This study uses the ZHU [8] force field, which is established based on the EPM2 force field. The total potential energy function is shown in Formula 1:

$$V_{tot} = \sum_{\text{bonds}} \frac{k_{ij}^{b}}{2}(r_{ij} - b_{ij})^2 + \sum_{\text{angles}} \frac{k_{ijk}^{\theta}}{2}(\theta_{ijk} - \theta_{ijk}^{0})^2 + \sum_{\text{dihedrals}} \left[V_0 + \frac{1}{2}(V_1(1+\cos\psi) + V_2(1-\cos(2\psi)) + V_3(1+\cos(3\psi))) \right] + \sum_{\text{nonbonded},1-2,1-3\text{excl}} f_{ij} \left[4\varepsilon_{ij}\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} + \frac{q_i q_j}{4\pi\varepsilon_0\varepsilon_r r_{ij}} \right] \quad (1)$$

When the interaction between atoms is a 1-4 no-bond interaction, f_{ij} is set to 0; otherwise, it is set to 1.

2.3 Simulation setting

All molecular simulations in this study were performed using LAMMPS, with periodic boundary conditions applied in the x, y, and z directions. To

simulate reservoir conditions, the simulation temperature was maintained at 343.15 K, 363.15 K, and 383.15 K. Referencing the guidelines of [9], the simulation box was designed with dimensions of 60 Å × 60 Å × 350 Å to ensure reasonable molecular simulations under different temperature and pressure conditions. As shown in Figure 2, the initial system snapshot displays an initial oil phase width of 90 Å, with CO_2 phases on both sides each measuring 130 Å.

Since the initial molecular simulation model often deviates significantly from equilibrium, a series of preparatory steps are necessary before starting the simulation. First, the conjugate gradient method is used for energy minimization to bring the system to a minimum energy state and optimize the configuration. Then, atoms are randomly assigned initial velocities following the Maxwell-Boltzmann distribution. The leapfrog integration method is used to solve the equations of motion.

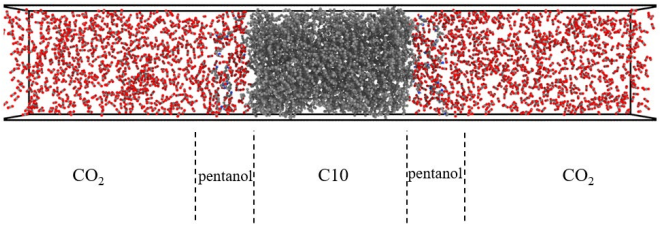

Fig. 2. Initial configuration in the simulation box

During the simulation, the NVT ensemble is used for control. Trajectory data is recorded at fixed time intervals of 1 ps, generating one data point per 1 ps for subsequent analysis. In the NVT simulation, temperature control is implemented using a Nosé-Hoover thermostat with a relaxation time of 200 fs. Long-range electrostatic interactions are calculated using the particle-particle particle-mesh (PPPM) method. The cutoff radius for non-bonded interactions is set to 20 Å, and the time step is fixed at 2 fs. The total simulation time is 10 ns, with the first 5 ns used to reach equilibrium. After completing the 5 ns equilibrium period, data collection is performed from 6 ns to 10 ns.

This simulation setup ensures that the interactions and behaviors of CO_2, n-decane, and pentanol molecules under reservoir conditions are accurately captured, providing a robust foundation for analyzing the impact of pentanol on the MMP of CO_2-oil systems.

2.4 Simulation case setup

In this study, the CO_2-n-decane-alcohol system is set up to include 800 n-decane molecules, a certain number of alcohol molecules, and a certain number of CO_2 molecules. For example, in base case without alcohol, the system contains 1882 CO_2 molecules. The alcohol molecules are distributed on both sides of the n-decane system, with 20 molecules on each side, making the molar fraction of alcohol relative to n-decane 2.5%. The number of CO_2 molecules is determined based on the pressure, allowing for the investigation of the dynamics and interactions of the system under different pressure conditions.

3. RESULT AND DISCUSSIONS

3.1 *Molecular motion process of the CO_2-n-Decane system with pentanol*

Taking the base case as an example, this study captured snapshots of the simulation system at 0 ns, 5 ns, and 10 ns to observe the dynamic behavior of the molecules, as illustrated in Figure 3. Initially, pentanol molecules were placed in the CO_2 phase close to the n-decane molecules to ensure quick contact with the oil phase and reduce the time required for the system to reach equilibrium.

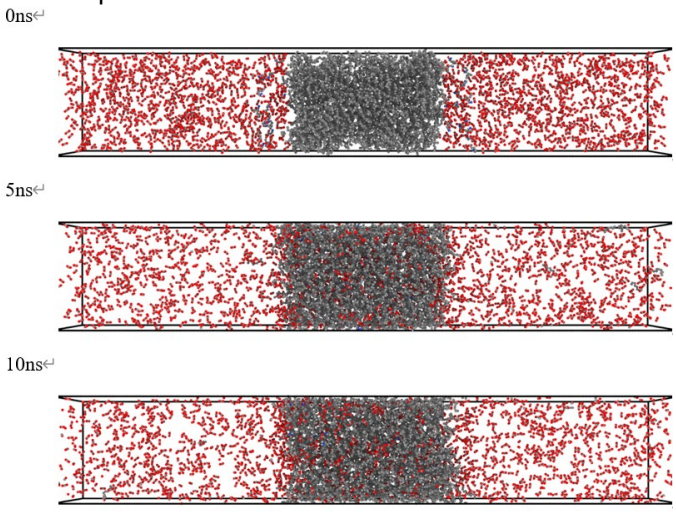

Fig. 3. Snapshots of the CO_2-n-Decane system with pentanol at 0 ns, 5 ns, and 10 ns

As the simulation progresses, CO_2 molecules gradually migrate towards the central oil phase. By 5 ns, most pentanol molecules have entered the oil phase, and CO_2 molecules begin to accumulate around the oil phase. This indicates that pentanol molecules effectively facilitate the penetration and distribution of CO_2 into the oil phase. By 10 ns, the system's distribution stabilizes, indicating that equilibrium has been reached.

3.2 *Interaction energy analysis*

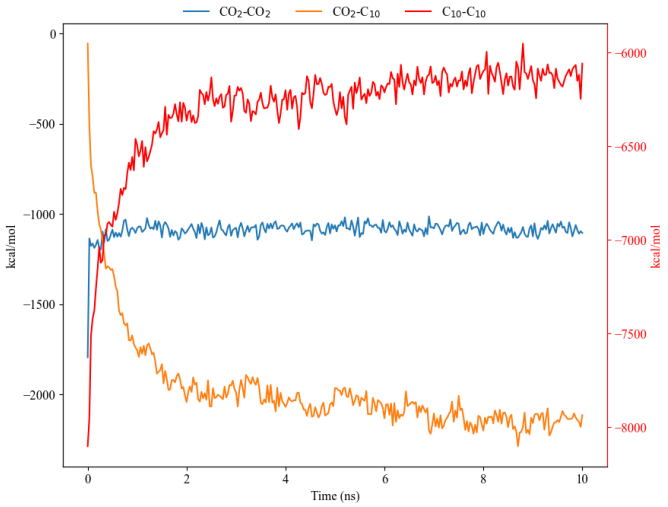

Fig. 4 Interaction energy analysis of the CO_2-pentanol-n-Decane system

The changes in interaction energy between different molecules in the system were analyzed over time. As the simulation progresses, the interaction energy between CO_2 and n-decane molecules continuously decreases, while the interaction energy between CO_2-CO_2 and n-decane-n-decane molecules increases. This phenomenon indicates that CO_2 molecules gradually penetrate the n-decane system and aggregate around n-decane molecules, leading to a decrease in interaction energy between them.

Additionally, by analyzing the interaction energy at different time points, the diffusion process of CO_2 molecules in the n-decane system and their impact on the system's equilibrium state can be clearly observed. After 5 ns, the interaction energy between CO_2 and n-decane molecules no longer changes significantly, indicating that the system has reached equilibrium.

3.3 *Density distribution and phase analysis*

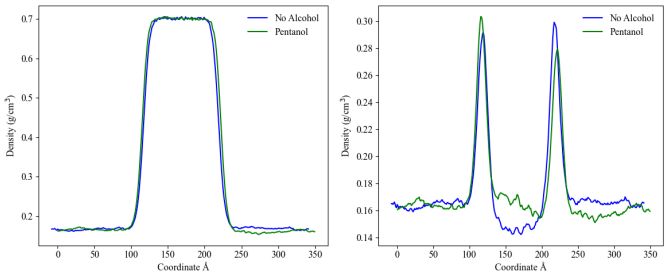

Fig.5 Density distribution of CO_2-n-Decane system and CO_2 density distribution along the Z-axis.

To evaluate the impact of pentanol on the density distribution and phase behavior of the CO_2-n-decane system, this study analyzed the system's density distribution and CO_2 density distribution before and after the addition of pentanol, as shown in Figure 5. The results indicate that after adding pentanol, the oil phase region of the system expanded, and the density of CO_2 in the oil phase increased.

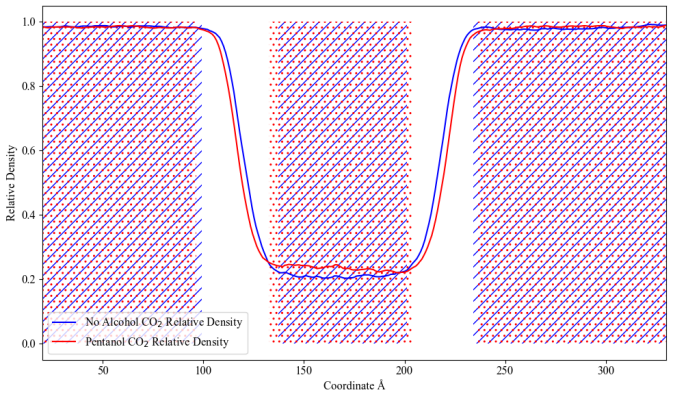

Fig.6 CO_2 relative density distribution

The relative density distribution of CO_2 at various positions within the model was calculated, and the average rate of change within 1 nm was obtained using a convolution method. If this rate exceeds 0.005, a phase transition is considered to have occurred. As shown in Figure 6, the analysis revealed the positions and thicknesses of the gas and oil phases within the system, and the average relative density of CO_2 in both phases was determined. The results indicate that after adding pentanol, the relative density of CO_2 in the oil phase significantly increased, and the thickness of the oil phase also increased, while the thickness of the gas phase decreased. This suggests that the addition of pentanol promotes the dissolution and diffusion of CO_2 into the oil phase, leading to the expansion of the oil phase.

3.4 *MMP analysis*

The minimum miscibility pressure (MMP) was determined using the method by Müller et al. [9], which involves calculating the interfacial tension (IFT) and applying the interface disappearance method. Interfacial tension is a crucial physical quantity that describes the interactions at the interface between the liquid and gas phases. By simulating the interfacial tension of the CO_2-n-decane system under different pressures and performing linear fitting, the pressure corresponding to zero interfacial tension was determined as the MMP.

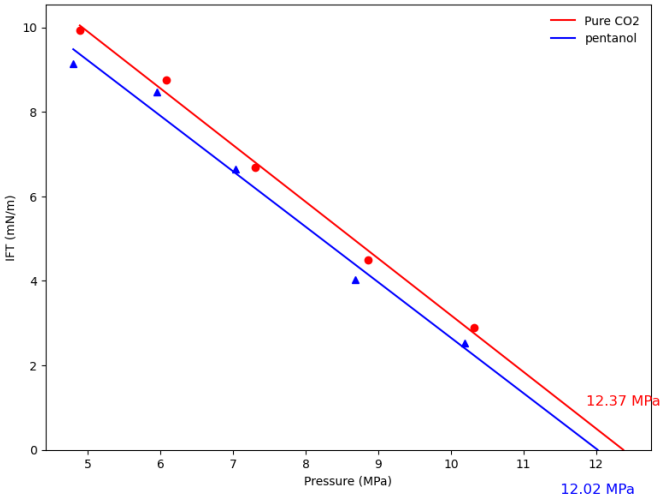

Fig.7 Interfacial tension and MMP determination of the CO_2-n-Decane system with and without pentanol

At a temperature of 343.15 K, with the addition of pentanol at a mass fraction of 3% relative to the oil phase, the simulation results, as shown in Figure 7, indicate that the addition of pentanol reduces the MMP of the CO_2-n-decane system by approximately 2.8% compared to the system without alcohol additives. This reduction is attributed to the enhanced interaction between CO_2 and n-decane molecules facilitated by pentanol, which disrupts the cohesion within the oil phase and lowers the MMP.

3.5 *Influence of pentanol content*

This section further explores the effect of pentanol content on the MMP of the CO_2-n-decane system. As shown in Figure 12, under the condition of 343.15 K, the MMP value of the CO_2-n-decane system continuously decreases with the increase in pentanol content, but the rate of decrease gradually diminishes.

When 40 molecules of pentanol were added to the CO_2-n-decane system, the MMP value decreased from 12.37 MPa (without pentanol additive) to 12.02 MPa, a reduction of approximately 2.8%. Increasing the pentanol content to 80 molecules further reduced the MMP value to 11.18 MPa, a reduction of 9.6% compared to the system without the additive. When the number of pentanol molecules was further increased to 160, the MMP value dropped to 10.86 MPa, a reduction of 12.2% compared to the system without the additive.

This phenomenon indicates that pentanol, as an additive, can continuously lower the MMP value of the CO_2-n-decane system within a certain range. However, as the amount of pentanol increases, its effect on reducing the MMP value gradually weakens, showing a diminishing trend.

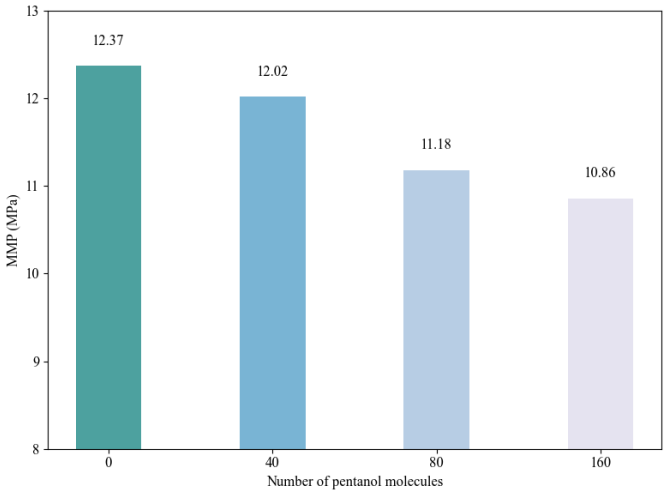

Fig. 8 MMP with different numbers of pentanol molecule

4. CONCLUSIONS

This study demonstrates that pentanol significantly reduces the Minimum Miscibility Pressure (MMP) of CO_2-oil systems through molecular dynamics simulations. Key findings include:

1. The addition of pentanol reduces MMP by up to 12.2%, with higher concentrations yielding greater reductions.
2. Pentanol increases CO_2 density within the oil phase and expands the oil phase region, promoting CO_2 diffusion.
3. Increasing the amount of pentanol continuously lowers MMP, though the rate of reduction diminishes with higher concentrations.

DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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