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Molecular Transition Mechanisms of Heavy Oil in Hybrid CO_2-surfactant Thermal Systems for Post-steam Reservoirs

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ABSTRACT

A hybrid CO_2-surfactant thermal system can efficiently and eco-friendly improve the oil recovery rate for post-steam heavy oil reservoirs by modifying heavy oil characteristics. However, the complex conditions of high-temperature and high-pressure reservoirs hinder experimental investigations into the microscopic mechanisms of this system. In this study, Molecular Dynamics (MD) simulations reveal the molecular interaction mechanism between a hybrid thermal system, heavy oil, and pore surfaces. The hybrid thermal systems comprise CO_2 and a cost-effective SDS (sodium dodecyl sulfate) surfactant. The effects of surface wettability, external temperature, and CO_2 concentration on the transition of heavy oil microstructure are investigated.

Results show that the hybrid CO_2-surfactant systems can effectively improve the microstructure of heavy oil by promoting the thermal expansion process. Moreover, surface wettability and CO_2 concentration significantly affect the microstructure of heavy oil. Specifically, the thermal expansion of heavy oil is suppressed on hydrophobic surfaces compared to hydrophilic surfaces. This is because an oil-surface interaction promotes the formation of dense clusters of asphaltenes within a heavy oil layer, making the heavy oil on hydrophobic surfaces more challenging to recover. Meanwhile, the concentration of CO_2 determines the state of a hybrid thermal system and ultimately affects the distribution of heavy oil. The hybrid thermal system with moderate dynamic activity and a high effective distribution ratio of CO_2 can efficiently improve the microstructure of heavy oil for recovery and demonstrate the potential of CO_2 storage. Furthermore, an optimum CO_2 concentration of 10 wt.% is recommended for designing the hybrid thermal system.

This study provides insights into the molecular transition mechanism of heavy oil in various hybrid thermal systems. It offers valuable theoretical guidance for designing efficient and eco-friendly heavy oil recovery operations to support the transition towards carbon neutrality.

Keywords: molecular transition mechanism; hybrid CO_2-surfactant thermal system; heavy oil; molecular dynamics simulation, CCUS.

NONMENCLATURE

Abbreviations	
SDS	Sodium Dodecyl Sulfate
MD	Molecular Dynamics
PBC	Periodic Boundary Conditions
PME	Particle Mesh Ewald
Exp	Experimental
Symbols	
CH	Hydrophobic surface
OH	Hydrophilic surface
D	Diffusion coefficient
$\rho_{effective}$	Effective distribution of CO_2 in oil layer
ρ_{total}	Total distribution of CO_2

1. INTRODUCTION

A hybrid CO_2-based thermal process is a rising star among post-steam heavy oil EOR (Enhanced Oil Recovery) processes [1]. When external thermal fluids

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are simultaneously or periodically injected into a reservoir, the remaining oil in the reservoir formation can be efficiently mobilized and extracted to production wells [2]. A surfactant, viscosity reducer, and nanofluid are commonly co-injected with CO_2 as the thermal fluids in the oilfield operation [3]. The rock-fluid interaction mechanism under the reservoir conditions is complicated due to the involvement of multi-phase components. Moreover, reservoir wettability significantly impacts a distribution of remaining oil. A wettability distribution of pore surfaces becomes heterogeneous after long-term steam stimulation, which also restrains the extraction of the remaining oil [4]. Therefore, to further improve the performance of a hybrid thermal process, more detailed investigations are needed to understand the interaction behavior of heavy oil on pore surfaces under reservoir conditions.

Benefiting from the rapid development in computing technology, Molecular Dynamic (MD) simulations have been widely used to study the interaction behavior among a reservoir rock, formation fluid, and external oil displacement agent. Meghwal et al. [5] pointed out that the structure of heavy oil adjacent to a rock surface could be characterized by a dense interfacial layer followed by a bulk zone. Tetteh et al. [6] reported that a surfactant-induced wettability reversal on oil-wet surfaces was critical for recovering the remaining oil. Zhang et al. [7] demonstrated the potential of CO_2 foam to improve heavy oil recovery.

Previous studies focused on the oil adsorption behavior at normal atmospheric temperature or in a single thermal fluid. In this study, systematic MD simulations are employed to investigate a molecular transition process of heavy oil in various hybrid CO_2-surfactant thermal systems. A detailed investigation of the main controlling factors, such as temperature, wettability, and CO_2 concentration, on the heavy oil microstructure transition is performed. Overall, this study is beneficial for designing an emerging process for post-steam heavy oil reservoirs with high efficiency and environmental friendliness.

2. SIMULATION DETAILS

2.1 Model setup

An average molecular model is a feasible method to describe a heavy oil microscopic behavior regardless of its thousands of components. The heavy oil model in this paper is proposed in our previous works [8-10]. The details of the model are listed in Table 1 and Fig. 1.

Table 1 Details of the heavy oil model

Components	Chemical formula	Molecular weight	Mass distribution wt. %	
			MD	Exp.
Saturates	$C_{30}H_{62}$	422.81	20.99	21.18
	$C_{35}H_{62}$	482.87		
Aromatics	$C_{35}H_{44}$	464.72	29.17	29.32
	$C_{30}H_{46}$	406.69		
Resins	$C_{40}H_{59}N$	553.90	39.34	39.03
	$C_{40}H_{60}S$	572.97		
	$C_{29}H_{50}O$	414.71		
	$C_{36}H_{57}N$	503.84		
	$C_{18}H_{10}S_2$	290.40		
Asphaltenes	$C_{42}H_{54}O$	574.88	10.50	10.47
	$C_{66}H_{81}N$	888.36		
	$C_{51}H_{62}S$	707.10		
	$C_{56}H_{71}N$	758.17		

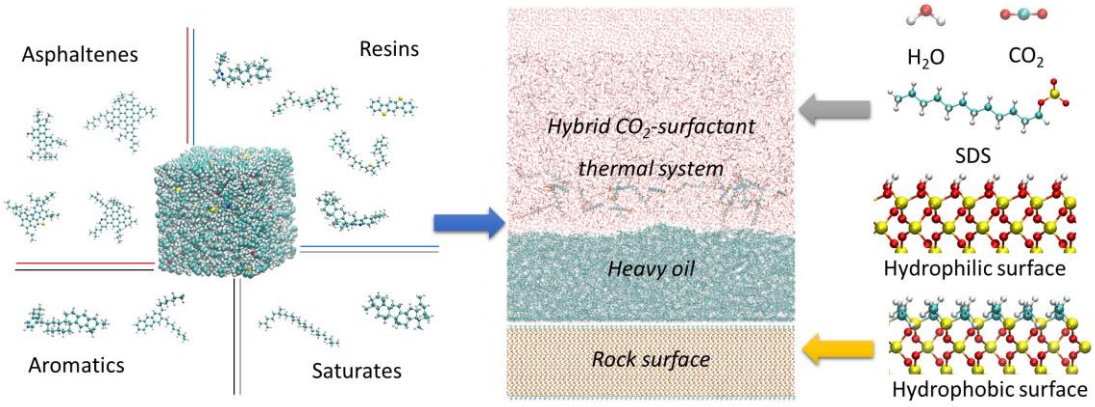

Fig. 1. Initial configuration of the MD simulation

Due to the abundance of silica in heavy oil reservoirs, the role of silica should be highlighted. Moreover, complicated heavy oil-water-rock interactions result in differences in surface wettability. Based on structural characterization experiments [11], surfaces with hydroxyl -(OH) and methyl –(CH_3) are used to simulate hydrophilic and hydrophobic surfaces, respectively. Then, Packmol [12] packs all components into a simulation box as an initial configuration. The final *xyz* dimensions of the entire model are 14.739 nm × 5.957 nm × 20.000 nm. Finally, the initial configuration of the MD simulation is shown in Fig. 1.

2.2 Simulation parameters

All the MD simulations are performed using the GROMACS 2021.6 software packages. The OPLS-AA/M [13] force field describes the heavy oil and surfactant molecules. The INTERFACE [14] force field represents the silica surfaces. The SPC/E [15] and EPM2 [16] models are employed to describe water and CO_2 in the hybrid thermal fluids, respectively. Besides, a double-pair half-ε method [17] corrected geometric mixing rules are employed to calculate the unlike molecular non-bonded interactions.

All MD simulations are employed in NPnAT ensembles. The temperature and pressure are controlled by a V-rescale thermostat and a Berendsen barostat, respectively. The simulation temperatures and pressure are set as 303K~453K and 5.0 MPa, respectively, to simulate a reservoir after a steam-based recovery process. Periodic Boundary Conditions (PBC) are applied in all directions. The Lennard-Jones 12-6 potential describes the Van der Waals interactions. Also, the Particle Mesh Ewald (PME) method is employed for long-range electrostatic interactions. The cutoff is 1.40 nm for above two interactions. The time step is 2.0 fs, and we output trajectories every 500 steps for data analysis.

Geometric optimization is performed to optimize the initial configurations with the steepest descent algorithm. Then, formal MD simulations with a 50 ns equilibrium step and a subsequent 100 ns production step are used to explore the heavy oil-fluid-surface interaction behavior. Finally, the VMD (Visual Molecular Dynamic) 1.9.3 [18] software visualizes all the MD simulation trajectories.

3. RESULTS AND DISCUSSION

3.1 Effect of the surface wettability

Fig. 2 presents a distribution transition process of heavy oil on different wettability surfaces. For clarity, the asphaltenes, SDS, and CO_2 molecules are marked in bonds, VDW, and CPK, respectively. As shown in Fig. 2, the SDS molecules distribute across the heavy oil-water interface to bridge the mass transportation, while CO_2 molecules penetrate the heavy oil layers, prompting the microstructure transition inside the heavy oil. With the temperature increasing, the oil layer swells. However, the volume of heavy oil on the hydrophobic surfaces is always smaller than that on the hydrophilic surfaces at all temperatures. It indicates that surface wettability impacts the heavy oil distribution transition.

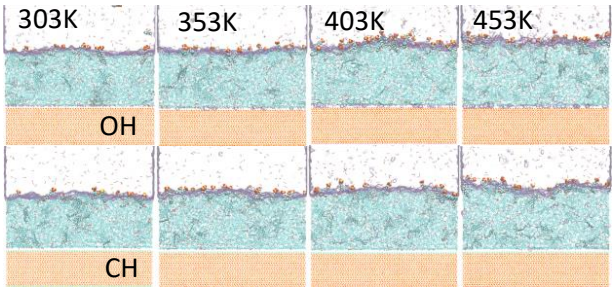

Fig. 2. The heavy oil distribution transition on hydrophilic and hydrophobic surfaces

The heavy oil-surface COM (Center of Mass) distance transition is calculated to evaluate the effect of surface wettability on a heavy oil distribution. Fig. 3 depicts that the COM distances on hydrophobic surfaces are lower than on the hydrophilic surfaces. It verifies that heavy oil on hydrophobic surfaces is more difficult to be extracted from the surfaces. Moreover, the difference between the two COM distances at 303K is significant and becomes insignificant at higher temperatures (403K-453K). It demonstrates that thermal expansion can relieve suppression from hydrophobic surfaces, which is beneficial for extracting heavy oil.

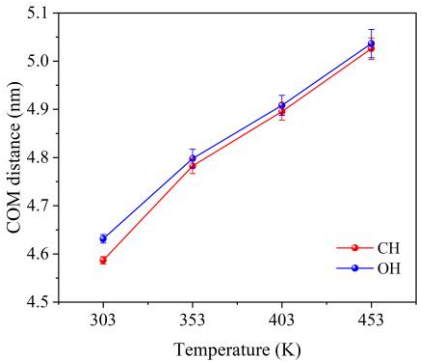

Fig. 3. The heavy oil – surface COM distance variation on different surfaces

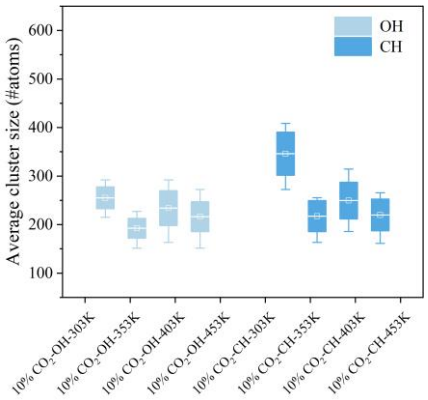

Fig. 4. The asphaltenes cluster transition on different surfaces

Meanwhile, an averaged asphaltenes cluster size is analyzed to evaluate the microstructure transition inside the heavy oil. Fig. 4 indicates that the asphaltenes inside the heavy oil tend to form a denser cluster on the hydrophobic surfaces. A dense core of asphaltenes (350 atoms) is observed on a hydrophobic surface at 303K. Like the COM distances, the cluster decomposes as the temperature rises, falling back to the same level as the hydrophilic surfaces.

3.2 Effect of CO_2 concentration

As described above, the heavy oil on a hydrophobic surface is more difficult to extract. Therefore, we focus on the performance of hybrid thermal systems on hydrophobic surfaces. In this section, the effect of CO_2 concentration on the performance of hybrid systems is evaluated. The microstructure transitions of the heavy oil layer at two typical temperatures, 353K and 453K, are presented in Fig. 5. The complete analysis results are illustrated in Figs. 7-8.

The microstructure of the heavy oil layer and the state of a hybrid system change dramatically at different CO_2 concentrations, as shown in Fig. 5. With more CO_2 introduced into the hybrid thermal systems, the volume of heavy oil increases. However, excess CO_2 separates the hybrid system into a gas-liquid immiscible system, which is not beneficial for extracting heavy oil.

The variations of a diffusion coefficient (D) and effective distribution ratio ($\rho_{effective}/\rho_{total}$) of CO_2 are used to investigate the role of CO_2 in hybrid systems. Fig. 6 exhibits that the diffusion coefficient in the 10 wt. % CO_2 systems maintains a linear growth in semi-logarithmic coordinates with increasing temperature, while the diffusion coefficient in the 20 wt. % CO_2 systems booms at higher temperatures (403K-453K).

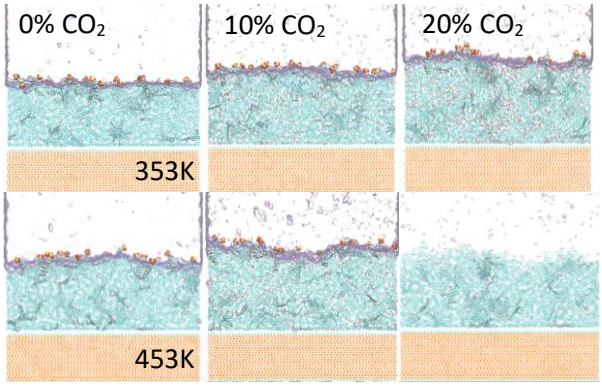

Fig. 5. The heavy oil distribution transition in various CO_2 concentrations of the hybrid thermal systems

Furthermore, an effective distribution also illustrates that most (over 60%) of CO_2 molecules can steadily distribute in the oil layer for the 10 wt. % CO_2 systems. It demonstrates that CO_2 molecules with a moderate kinetic activity can efficiently improve the microstructure of heavy oil. It also indicates that a proper design of a hybrid thermal system with a static injection process can potentially convert a post-steam heavy oil reservoir for CO_2 storage. On the contrary, the effective distribution of CO_2 for the 20 wt. % CO_2 systems sharply decreases as temperature rises. The effective distribution ratio is less than 5% when the phase separation occurs at 453K.

Additionally, an asphaltenes cluster size is calculated to evaluate the microstructure transition of the heavy oil under different CO_2 concentration conditions. Fig. 7 confirms that the asphaltenes cluster maintains the smallest size among the three conditions, which verifies that the optimum CO_2 concentration for building the hybrid thermal systems is 10wt.%.

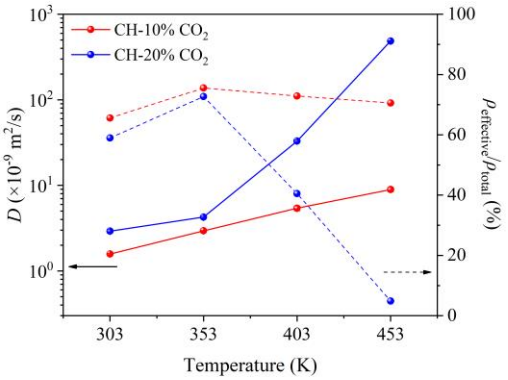

Fig. 6. The diffusion coefficient and effective distribution ratio of CO_2 in different hybrid thermal systems

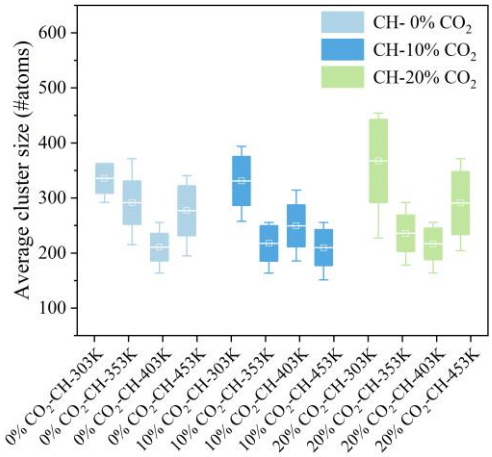

Fig. 7. The asphaltenes cluster transition in different hybrid thermal systems

3.3 Microstructure transition mechanism

The heavy oil-surface and oil-thermal fluids interaction energies are calculated to explore further the microstructure transition mechanism induced by the hybrid thermal systems. Fig. 8 shows that the heavy oil-surface interaction on a hydrophobic surface is higher than on a hydrophilic surface. It supports the above results that a pore surface with high hydrophilicity hinders heavy oil extraction. The oil-surface interaction generally decreases with temperature rising, except the 20wt. % CO_2 system at 453K for hydrophilic and hydrophobic surfaces, where asphaltenes re-precipitation occurs.

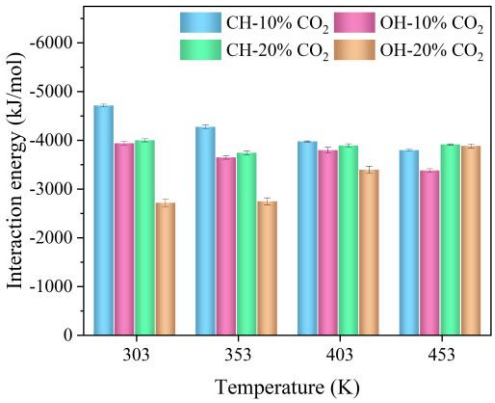

Fig. 8. The heavy oil-surface interaction energy transition on different surfaces

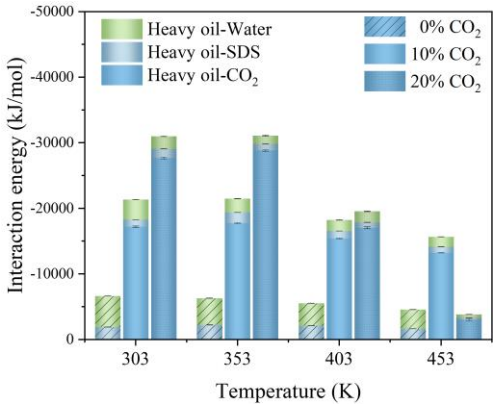

Fig. 9. The heavy oil-thermal fluids interaction energy transition in different CO_2 concentration systems

Fig. 9 exhibits the heavy oil-thermal fluids interaction energies transition in different CO_2 concentration systems. It is crystally clear that a heavy oil-CO_2 interaction dominates the heavy oil-thermal fluids interactions. Also, the results demonstrate that the heavy oil-CO_2 interaction in the 10wt. % CO_2 concentration system maintains the highest level among all conditions. It confirms that the 10 wt. % CO_2 hybrid thermal system is suitable for improving the microstructure transition of heavy oil and enhancing the performance of the hybrid system to extract heavy oil.

4. CONCLUSIONS

This study employs MD simulations to investigate the molecular transition mechanism of heavy oil in different hybrid CO_2-surfactant thermal systems. The effects of surface wettability, external temperature, and CO_2 concentration are evaluated.

1. A hybrid thermal system can effectively improve the microstructure of heavy oil, promote the extraction of heavy oil after long-term steam stimulation, and demonstrate the potential of CO_2 storage.

2. Surface wettability affects a heavy oil microstructure through oil-surface interactions. Dense asphaltene clusters are observed on a hydrophobic surface.

3. CO_2 concentration determines the state of a hybrid thermal system, which significantly changes the microstructure of heavy oil.

4. An optimum CO_2 concentration at 10 wt.% is recommended to build the hybrid thermal system for its proper kinetic activity and high effective distribution ratio.

ACKNOWLEDGEMENT

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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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