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Performance of Electric Field-Enhanced Oil Recovery in Shale Kerogen Pores During CO_2 Injection: A Molecular insight

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ABSTRACT

Enhancing shale oil recovery during CO_2 injection is crucial for advancing carbon neutrality. However, the strong affinity between the surface of organic pores and hydrocarbons limits the effective oil displacement efficiency. Therefore, it is imperative to find effective methods to improve shale oil recovery. In response to this challenge, this study employs electric field technology to investigate its impact on shale oil recovery during CO_2 injection. In this study, molecular dynamics (MD) simulations were used to study the effect of an electric field on CO_2-enhanced oil recovery in shale nanopores. A composite system consisting of organic nanopores, multicomponent oil, and CO_2 was adopted. Simulations were conducted after applying different electric field intensities (0 V, 5 V, 10 V, and 20 V) to the crude oil. The results show that the electric field increases the difference in interaction energy between CO_2 - oil and oil - pore walls, enhancing the ability of CO_2 molecules to displace hydrocarbons from the pore surface. The displacement efficiency improved after different electric field intensities were applied. Specifically, the electric field intensities of 5 V, 10 V, and 20 V increased the displacement efficiency by 3.20%, 2.85%, and 1.61% respectively compared to the case of 0 V. These findings indicate that the electric field is an effective strategy to overcome oil retention at the pore scale, and its directional application is a key parameter for optimizing CO_2 - enhanced oil recovery in shale formations. This method not only improves the extraction efficiency of hydrocarbons but also supports the achievement of carbon neutrality goals by enhancing the CO_2 sequestration potential.

Keywords: Electric field; Shale oil; Carbon dioxide; Enhanced oil recovery; molecular dynamics simulation

NONMENCLATURE

Abbreviations	
APEN	Applied Energy
Symbols	
n	Year

1. INTRODUCTION

In the context of global climate change and the continuous growth of energy demand, the development of new energy sources and the improvement of the recovery rate of existing energy have become research hotspots. Under the strategic background of the "dual-carbon" goal, carbon dioxide (CO_2) flooding technology can not only significantly enhance the reservoir recovery rate but also permanently store CO_2 in the reservoir, thus achieving a synergistic effect between oil displacement and carbon sequestration. This provides unique advantages for the efficient development of shale oil reservoirs [1-2]. Currently, shale oil has attracted wide attention due to its abundant reserves and huge development potential. However, its development process faces numerous challenges, such as low recovery rates and rapid production decline. Therefore, how to develop shale oil efficiently has become an urgent problem to be solved.

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The principle of CO_2 flooding technology mainly involves injecting CO_2 into the oil reservoir to reduce the viscosity of crude oil, increase its volume, and improve the mobility ratio of the reservoir [3,4]. As a result, crude oil can more easily flow out of the reservoir pores. Nevertheless, in practical applications, especially in unconventional reservoirs like shale oil reservoirs, there is a strong affinity between the surface of organic pores and hydrocarbons. Shale oil reservoirs have a nano-scale pore structure, and the intermolecular forces between crude oil and the pore surface are relatively strong [5-6]. This causes a large amount of crude oil to be adsorbed on the pore surface and difficult to be displaced by CO_2, which greatly limits the oil-displacement efficiency of CO_2 flooding technology. According to relevant studies, in some shale oil reservoirs, even with advanced CO_2 injection technology, a considerable proportion of crude oil still cannot be effectively extracted. This has become a major challenge in improving the shale oil recovery rate.

To overcome this challenge, many scholars have carried out extensive research. Some studies focus on cooperate with CO_2 to enhance the displacement ability of crude oil [7]. However, although these methods can improve the recovery rate to some extent, they still struggle to fundamentally solve the problem of strong adsorption between the organic pore surface and crude oil.

In recent years, electric field technology has shown potential application prospects in the field of petroleum engineering. Some studies have shown that an electric field can effectively enhance the adsorption of CO_2 molecules on the shale wall surface [8-13]. In the presence of an electric field, there will be a strong interaction between CO_2 molecules and materials such as MoS_2 and graphene, which is beneficial to CO_2 capture [14-16]. Introducing electric field technology during the CO_2 injection process may break the strong adsorption state between crude oil and the pore surface by altering the interactions among CO_2, crude oil, and the pore surface, thereby improving the oil displacement efficiency. Notably, electric fields have been applied in oilfield reservoirs to improve oil and gas recovery [17-19]. Therefore, the application of electric fields in reservoirs has important practical significance. In addition, in the context of carbon neutrality, a large amount of green electricity generated by solar, wind, and photovoltaic power [20,21]. How to effectively utilize green electricity resources is also a matter worthy of attention. However, optimizing the CO_2 injection scheme, such as adopting segmented injection or alternate injection methods, to improve the distribution and displacement effect of CO_2 in the reservoir. Other studies are concerned with developing new oil - displacement agents that can there is relatively little research on the specific mechanism of electric field technology in the CO_2 flooding process. In particular, there is a lack of systematic and in-depth research on the influence of electric fields on CO_2-enhanced oil recovery in shale oil reservoirs at the nanopore scale.

Based on the above background, this study aims to use the molecular dynamics (MD) simulation method to explore the influence of electric field technology on the shale oil recovery rate during the CO_2 injection process, providing a possible approach to improve the shale oil recovery rate during CO_2 injection. By constructing a composite system composed of organic nanopores, multi-component oil, and CO_2, the displacement process of shale oil by CO_2 under different electric field intensities (0V, 5V, 10V, and 20V) is simulated. The influence of the electric field on the occurrence state, relative concentration, interaction energy, and radial distribution function of oil molecules during the CO_2 injection process is analyzed. The impact of the electric field on CO_2-enhanced crude oil recovery in shale nano-pores is clarified, providing theoretical basis and technical support for the application of electric field technology in CO_2 flooding. It is expected to open up new ways to improve the shale oil recovery rate and enhance CO_2 sequestration capacity.

2. MODELS AND METHODOLOGY

2.1 Molecular models

Shale reservoirs contain organic and inorganic substances. Kerogen is the main component of organic matter, which is an insoluble amorphous mixture. Kerogen has a complex molecular structure and mainly consists of carbon (C), hydrogen (H), and oxygen (O), along with small amounts of sulfur (S) and nitrogen (N). Kerogen slits typically represent the nanopores in shale organic matter [22-24]. Due to different temperatures and degrees of maturity, the molecular structures of kerogen also show differences. In this paper, type IIA kerogen ($C_{252}H_{294}O_{24}N_6S_3$) constructed by Unerger [25] is selected as the organic matter component, and the structure of the kerogen molecule is optimized under the polymer consistent force field (COMPASSIII).

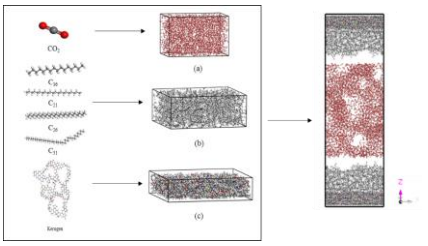

Fig. 1. The interaction energy of oil-wall and CO_2-oil

According to the results of the full - component test of crude oil, in the shale oil model before applying an electric field, the mass percentages of C_{16}, C_{21}, C_{26}, and C_{31} are set to 50.57%, 30.11%, 14.89%, and 4.43% respectively. In the model with a 5 V electric field, the mass percentages of C_{16}, C_{21}, C_{26}, and C_{31} are set to 30.25%, 55.48%, 12.60%, and 1.67% respectively. In the model with a 10 V electric field, the mass percentages of C_{16}, C_{21}, C_{26}, and C_{31} are set to 64.91%, 25.38%, 7.84%, and 1.87% respectively. In the model with a 20 V electric field, the mass percentages of C_{16}, C_{21}, C_{26}, and C_{31} are set to 61.64%, 27.32%, 9.21%, and 1.83% respectively. The Amorphous Cell module is used to build a crude - oil box, and geometric optimization and molecular dynamics simulation are carried out on the crude - oil box to make its structure reach equilibrium.

2.2 Simulation details

Kerogen Pore Model: According to the common method for constructing a kerogen slab model, the Amorphous Cell module was used to build an initial kerogen wall box. Then, its structure was optimized through geometric optimization, annealing, and molecular dynamics methods, ultimately obtaining a kerogen wall model. Subsequently, the Build layer module was employed to construct a kerogen nanopore model. The cutoff radius was set to 1.25 nm. The electrostatic force was set using the PPPM algorithm, and the van-der-Waals force was set using the Atom-based algorithm. The Berendsen method was used for pressure control, with the pressure set at 20 MPa. The geometrically optimized kerogen box was annealed under the isothermal-isobaric ensemble (NPT) to find the global minimum energy structure. The annealing simulation consisted of 10 annealing cycles, with the temperature ranging from 300 K to 800 K. The time step was set to 1 fs, and the total annealing simulation time was 1 ns. After that, a molecular dynamics simulation under the canonical ensemble (NVT) was carried out. The Andersen thermostat was used to balance the system temperature, and the simulation time was 1 ns to obtain the equilibrium structure of the final kerogen molecular configuration. Finally, graphene partitions were added around the structure - optimized kerogen matrix model, and a kerogen slab model was constructed through the extrusion mode. Considering the nanoscale effect of shale organic pores, the Build layer module was used to construct a kerogen nanopore model.

Crude Oil System and CO_2: Separate boxes for crude oil and CO_2 were built, and their structures were balanced through geometric optimization. The Smart method was used for geometric optimization, with the number of iterations set to 1×10^4, resulting in the equilibrium configuration of the CO_2 box (Fig. 1a). A molecular dynamics simulation of the geometrically optimized crude oil box was conducted under the NVT ensemble for 1 ns, obtaining the equilibrium configuration of the crude oil box (Fig. 1b).

Composite Oil-CO_2-Wall Model: The composite shale oil system, CO_2 system, and kerogen pore model were combined to construct a composite oil-CO_2-wall model, as shown in Fig. 1c. Subsequently, the wall was fixed, and the COMPASS III force field was applied to the model. The geometry of the model was optimized through the Smart algorithm to make the molecules lie on the minimum potential energy surface. Then, a molecular dynamics simulation was carried out under the NVT ensemble, and the Nosé-Hoover thermostat was used to balance the model temperature. The cutoff radius was set to 1.25 nm, the electrostatic force was set using the PPPM algorithm, and the van-der-Waals force was set using the Atom-based algorithm. The time step was set to 1 fs, and the simulation time was set to 4 ns. Notably, periodic boundary conditions were used in the model to eliminate the influence of boundary effects.

3. RESULTS AND METHODS

3.1 Effect of electric field on CO2 enhanced oil recovery in shale nanopores

This study employs electric field technology to comprehensively explore its impact on shale oil recovery during the CO_2 injection process. Shale oil recovery is a complex and crucial topic in the field of energy extraction, and understanding the underlying mechanisms of CO_2 injection in the context of electric field technology can provide valuable insights for optimizing recovery strategies. When CO_2 is injected into organic nanopores, a series of intricate physical and chemical processes occur. Some CO_2 molecules are adsorbed near the pore walls. This adsorption phenomenon is based on the principle of competitive

adsorption. The CO_2 molecules have a certain affinity for the pore - wall surface, and through this competitive adsorption mechanism, they are able to strip crude oil from the pore walls. The process of competitive adsorption is influenced by multiple factors such as the surface properties of the pore walls, the chemical composition of the CO_2 and crude oil, and the local environment within the nanopores. The other part of the CO_2 molecules, which are located far from the pore walls, have a relatively weak interaction with the pore walls. These CO_2 molecules dissolve in the crude oil. The dissolution of CO_2 in the crude oil has a significant impact on the physical properties of the crude oil. It can reduce the viscosity of the crude oil, thereby enhancing its flowability. Additionally, it can increase the diffusion coefficient of the crude oil, facilitating its movement within the nanopores. This enhancement of flow and diffusion is crucial for improving the recovery efficiency of shale oil.

The interaction energy between CO_2 and crude oil components is used to represent the positive driving force for CO_2 to strip crude oil. The stronger the interaction energy between CO_2 and crude oil, the greater the positive driving force, indicating that CO_2 can more easily strip crude oil components from the pore walls. The interaction energy between crude oil components and the wall represents the resistance that CO_2 faces when stripping crude oil from the pore walls. The stronger the interaction energy between crude oil components and the wall, the easier it is for the crude oil to be adsorbed on the pore walls, and the greater the resistance that CO_2 faces when stripping the crude oil from the pore walls, making it difficult to strip the crude oil from the wall. Therefore, the difference in interaction energy between CO_2-wall and crude oil-wall, that is, the difference between the positive driving force and the resistance, is used to describe the difficulty of CO_2 stripping crude oil components from the pore walls. The larger the difference, the easier it is for CO_2 to strip crude oil components from the pore walls; the smaller the difference, the more difficult it is for CO_2 to strip the crude oil from the wall.

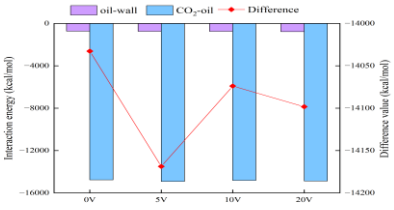

Fig. 2. The interaction energy of oil-wall and CO2-oil

Fig. 2 shows the interaction energy results of the system composed of crude oil components, pore walls, and CO_2 under different electric field intensities. The interaction energy between CO_2 and crude oil components is always greater than that between crude oil components and the wall, indicating that CO_2 can overcome the resistance to strip crude oil from the wall. After applying an electric field to the crude oil, the interaction energy between CO_2 and crude oil components increases, which means CO_2 has a stronger ability to strip different components of crude oil from the wall. The interaction energy between the crude oil and the wall gradually decreases, indicating that the adsorption of crude oil components on the wall is weakening, and the resistance that hinders the stripping of crude oil from the wall is reduced. In Fig. 2, the interaction energy differences at 0V, 5V, 10V, and 20V are -14032.6 kcal/mol, -14168.7 kcal/mol, -14073.9 kcal/mol, -14098.2 kcal/mol, and -14140.9 kcal/mol, respectively. The results show that after applying an electric field, the difference in interaction energy between CO_2 and crude oil components and that between crude oil components and the wall gradually increases, which means that the electric field makes it easier for CO_2 to strip crude oil components from the pore walls.

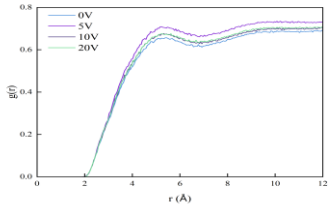

Fig. 3. Radial distribution function of CO2-oil

The radial distribution function g(r) serves as a crucial parameter that can offer profound insights into the influence exerted by varying electric field intensities on the mutual solubility of CO_2 and crude oil. The radial distribution function g(r) is a well - established concept in statistical mechanics and molecular simulations. It provides information about the probability of finding a pair of particles at a given distance r from each other. In the context of the CO_2 - crude oil system, a larger value of the radial distribution function g(r) implies a higher probability of CO_2 and crude oil molecules being in close proximity to one another. This, in turn, is strongly indicative of a better mutual solubility between the two substances. That is, when the value of g(r) is large, it

suggests that CO_2 molecules can more readily mix and dissolve within the crude oil, and vice versa. To illustrate the impact of different electric field intensities on the mutual solubility of CO_2 and crude oil, we turn to the data presented in Fig. 3. We can observe the behavior of the radial distribution function g(r) at four distinct electric field intensities: 0 V, 5 V, 10 V, and 20 V. At an electric field intensity of 0 V, which represents the absence of an external electric field, the first peak of the radial distribution function g(r) of the CO_2 - crude oil system is measured to be 0.657. This value serves as a baseline for comparison. When an electric field is applied, significant changes occur in the value of g(r). At an electric field intensity of 5 V, the first peak of the radial distribution function g(r) reaches a value of 0.709. This is the highest among the four electric field intensities considered in this study. When the electric field intensity is increased to 10 V, the first peak of g(r) drops to 0.677. Further increasing the electric field intensity to 20 V, the first peak of g(r) is 0.676, which is only slightly lower than the value at 10 V.

It is evident from these data that the radial distribution function g(r) values under different electric fields are all greater than the value obtained in the absence of an electric field. This indicates that the application of an electric field generally enhances the mutual solubility of CO_2 and crude oil. Moreover, the fact that the g(r) value at 5 V is the largest among all the tested electric field intensities clearly suggests that the mutual solubility of CO_2 and crude oil reaches an optimal state at an electric field intensity of 5 V. This finding has significant implications for practical applications, such as enhanced oil recovery techniques, where maximizing the solubility of CO_2 in crude oil can lead to more efficient extraction processes.

3.2 Effect of electric field on replacement efficiency

Fig. 4 presents the snapshot configuration structures of the kerogen - crude oil - CO_2 system under varying electric field intensities.

As depicted in Fig. 4, in the equilibrium configuration of the system when no electric field is applied, the distribution pattern of molecules of each component of the crude oil within the shale kerogen slit is highly irregular. A closer examination reveals that a relatively larger number of crude oil molecules accumulate in the vicinity of the kerogen slit wall. This accumulation is likely due to the intermolecular forces, such as van der Waals forces and electrostatic interactions, between the crude oil molecules and the kerogen surface. At the same time, a certain amount of crude oil molecules remain in the middle region, which is commonly referred to as the bulk phase of the kerogen pore. This co-existence of molecules near the wall and in the bulk phase indicates that a significant portion of the crude oil molecules are adsorbed near the kerogen wall. The adsorption process is a crucial factor influencing the mobility and recovery of crude oil in shale reservoirs.

After the shale oil is exposed to an electric field, a distinct change occurs in the distribution of crude oil molecules on the kerogen wall. The application of the electric field disrupts the existing intermolecular forces between the crude oil molecules and the kerogen wall. As a result, a greater number of oil molecules are desorbed from the wall surface. This desorption process is accompanied by a gradual increase in the number of oil molecules in the bulk phase. The shift in the distribution of oil molecules from the wall to the bulk phase implies that the adsorption amount of oil molecules near the wall decreases, while the amount in the bulk phase increases. This direct visual observation from the snapshot configuration structures has

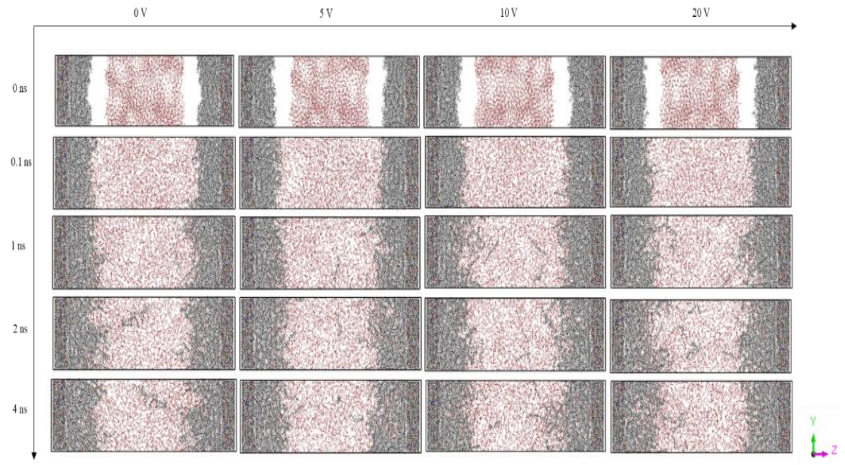

Fig. 4. Snapshot of oil molecule distribution equilibrium under different electric field strength

significant implications for the CO_2 injection process in shale oil recovery. It indicates that the crude oil, after being subjected to the action of the electric field, is more readily desorbed from the kerogen wall during the CO_2 injection.

To accurately analyze the effect of the electric field on the shale-oil recovery rate, we calculated the displacement efficiency of shale oil through the relative concentration of shale oil in the kerogen nanopores. We calculated the difference in the relative concentration distribution of shale oil in the kerogen nanopores between the initial state (T = 0.1 ns) and the equilibrium state (T = 4.0 ns). Based on this difference, we calculated the displacement efficiency of CO_2 on shale oil under different applied electric field intensities.

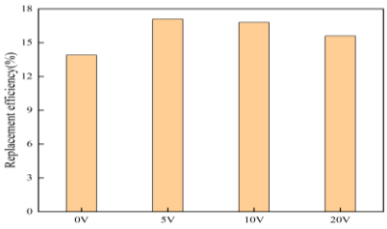

Fig. 5. Replacement efficiency with different electric fields

Fig. 5 shows that when no electric field is applied, the displacement efficiency of shale oil is 13.95%. After applying an electric field to the shale oil, the displacement efficiencies at 5 V, 10 V, and 20 V are 17.15%, 16.80%, and 15.56% respectively. Compared with the displacement efficiency without an electric field, after applying different electric fields, the displacement efficiencies at 5 V, 10 V, and 20 V increase by 3.20%, 2.85%, and 1.61% respectively. It can be seen that the displacement effect is the best when the electric field intensity is 5 V.

4. CONCLUSIONS

The interaction energy difference between CO_2 and the wall, and that between crude oil and the wall is used to represent the difficulty of CO_2 stripping crude oil from the wall. Based on the change characteristics of the interaction energy difference, after the application of an electric field, the interaction energy difference between CO_2 and crude oil components, and that between crude oil components and the wall gradually increases, indicating that the electric field has a positive impact on enhancing crude oil recovery by CO_2 in shale nanopores. From the values of the radial distribution function, at electric field intensities of 0 V, 5 V, 10 V, and 20 V, the first peak values of the radial distribution function are 0.657, 0.709, 0.677, and 0.676 respectively. It can be seen that the values of the crude oil - CO_2 system after applying an electric field are all larger than those without an electric field. This indicates that the action of the electric field promotes the mutual solubility between crude oil and CO_2 and enhances the flow and diffusion ability of crude oil.

During CO_2 injection, the relative concentration near the kerogen pore wall decreases, and the crude oil molecules on the pore wall gradually move to the bulk phase. After applying an electric field, more crude oil molecules are dislodged from the vicinity of the wall and move to the bulk phase. Under the electric field, the displacement efficiency of oil in shale nanopores increases by 3.20%, 2.85% and 1.61% at 5V, 10V, and 20V respectively, which indicates that the electric field enhances the recovery of shale oil during CO_2 injection in shale nanopores.

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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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