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Mechanisms and Production Enhancement Effects of CO_2/CH_4 Mixed Gas Injection in Shale Oil

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Abstract: Shale oil, a critical unconventional energy resource, has received substantial attention in recent years. However, systematic research on developing shale oil using mixed gases remains limited, and the effects of various gas compositions on crude oil and rock properties, along with their potential for enhanced oil recovery, are not yet fully understood. This study utilizes PVT analysis, SEM, and core flooding tests with various gas mixtures to elucidate the interaction mechanisms among crude oil, gas, and rock, as well as the recovery efficiency of different gas types. The results indicate that increasing the mole fraction of CH_4 substantially raises the oil saturation pressure, up to 1.5 times its initial value. Pure CO_2, by contrast, exhibits the lowest saturation pressure, rendering it suitable for long-term pressurization strategies. CO_2 shows exceptional efficacy in reducing interfacial tension, though the viscosity reduction effects of different gases exhibit minimal variation. Furthermore, CO_2 markedly modifies the pore structure of shale through dissolution, increasing porosity by 2% and enhancing permeability by 61.63%. In both matrix and fractured cores, the recovery rates achieved with mixed gases were 36.9% and 58.6%, respectively, demonstrating improved production compared to single-component gases. This research offers a theoretical foundation and novel insights into shale oil development.

Keywords: shale oil; mixed gas injection; oil phase behavior; gas dissolution effects; production enhancement

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1. Introduction

As global energy demand continues to rise, shale oil has attracted substantial attention as a critical unconventional energy resource [1–3]. Developing and utilizing shale oil can alleviate the energy crisis while also playing a pivotal role in fostering economic growth and strengthening national energy security [4–6]. Currently, shale oil extraction predominantly relies on techniques such as hydraulic fracturing and gas displacement [7,8]. These approaches enhance recovery by improving reservoir permeability or injecting displacement gases. Conventional enhanced oil recovery (EOR) techniques generally employ single gases (e.g., CO_2 [9], natural gas [10], and N_2 [11]) or single chemicals (e.g., surfactants [12], low salinity water [13], and nanofluids [14]), achieving production enhancement via single-well flooding. However, conventional single-gas flooding faces challenges such as low miscibility efficiency, channeling along dominant flow paths, limited displacement coverage, and preferential gas adsorption, which collectively impede further recovery improvements [15]. Consequently, the development of synergistic injection fluid strategies has garnered growing attention.

Recent studies have highlighted the interactions between gas and crude oil as a critical factor influencing gas-enhanced production [16,17]. These interactions primarily involve the extraction of light components from crude oil and the dissolution of gas into oil, which alters its properties [18,19]. These interactions ultimately determine the degree of production enhancement achieved with different injected gases [20]. Numerous researchers attribute variations in the recovery rates of different gases to their distinct capacities for expanding crude oil and reducing its viscosity, as evidenced by swelling factor and viscosity measurement experiments [21–23]. Ding et al. [24] elucidated the interactions among CO_2, natural gas, and crude oil through extraction and dissolution experiments, as well as core flooding tests, and explored their implications for EOR processes. Yassin et al. [25] analyzed production data from field fracturing wells and simulations, concluding that interactions between multiphase oil and gas significantly influence oil production increases following well shut-ins. They further noted that oil swelling and increased compressibility are key factors contributing to enhanced oil permeability after shut-ins. Investigations into the interactions between injected gases and reservoir rocks predominantly utilize microscopic techniques, including scanning electron microscopy, nuclear magnetic resonance, and CT scanning [26–28]. From a physical perspective, gas injection markedly modifies the properties of reservoir rocks through mechanisms such as diffusion, dissolution, and permeability enhancement [29,30]. Studies have shown that gas injection generally increases the effective porosity and permeability of rocks, thereby enhancing the flow performance of oil and gas [31–33]. Additionally, the chemical interactions between gas and rock merit significant attention. Gas injection, particularly with acidic gases like CO_2, can induce complex chemical reactions that modify the mineral composition and pore structure of rocks [34]. Studies indicate that CO_2 injection facilitates the dissolution of carbonate minerals, generating additional pore space and improving reservoir recoverability [29,35]. The types and proportions of injected gases play a critical role in influencing chemical reactions within the reservoir, underscoring the importance of systematic studies for optimizing production efficiency [36]. Gas injections can also induce mechanical effects on the rock stress field. The pressure generated by injected gases alters stress distribution, promoting fracture formation and propagation, which enhances fluid flow pathways. This effect is particularly pronounced in shale oil development [37]. This effect is particularly significant in the development of shale oil. On the other hand, some scholars have found through related experiments that adding methane to CO_2 reduces the miscibility with oil and gas [38]. Adding 5% of light gases (C_2–C_6) effectively lowers the miscibility pressure and enhances crude oil recovery through synergistic effects between gas phases [39]. Dong et al. evaluated the recovery enhancement capabilities and breakthrough times of a CO_2/N_2 mixture through laboratory experiments, revealing that this mixed system can delay CO_2 breakthrough time while reducing oil and gas miscibility, thus affecting core recovery rates. After four rounds of CO_2/N_2 flooding in different cores, the recovery rates were 43.54%, 37.85%, and 55.12%, respectively, which are higher than those achieved with pure CO_2 flooding (37.00%, 33.57%, and 47.92%) [40,41]. Huang et al. [42] studied the production enhancement effects of various gases (flue gas, CO_2, CH_4, and oxygen-reduced air) in single-well injection, finding that the combination of flue gas and oxygen-reduced air yielded the highest enhancement in production. Bender and Akin [43] analyzed gas injection cases in U.S. shale oil blocks and concluded that using CO_2 after flue gas injection enhances the overall economic benefit of the block. Their study demonstrated the production enhancement potential of mixed gases in shale oil development, with the ultimate recovery rate reaching up to 12%. Shi et al. [44] confirmed that combined extraction of CH_4 and CO_2 can improve the recovery rate of heavy oil. Liu et al. [45] used simulation software to validate the production enhancement potential of CH_4/CO_2 mixed gases for low-permeability and

rhythmic oil reservoirs. For tight or shale reservoirs with low porosity and permeability, experimental results from several scholars indicate that multi-component gas development outperforms single-component gas, further supporting the effectiveness of using mixed gases in low-porosity, low-permeability reservoirs. The final oil recovery efficiency of mixed gas injection in tight reservoirs is above 50%, with the highest recovery efficiency of 60.31% achieved when the ratio of CH_4 to CO_2 is 1:1 [46–48]. These studies demonstrate that optimizing gas combinations can significantly enhance oil and gas recovery efficiency, providing critical theoretical foundations and practical guidance for the development of shale oil and other unconventional resources.

Currently, there is limited systematic research on the use of mixed gases for shale oil development. The effects of varying gas component concentrations on crude oil and rock properties, as well as their potential to enhance production, remain unclear. To address this, this study will first employ PVT experiments to investigate the impact of different injected gases on the phase behavior of crude oil. Subsequently, the interactions between injected gases and reservoir rocks will be examined under in situ temperature and pressure conditions to analyze their effects on rock microstructure, porosity, and permeability, thereby elucidating the underlying micro-mechanisms. Finally, core-scale injection experiments will be conducted with various gas types to evaluate their production enhancement potential. This research aims to provide critical experimental insights and a robust theoretical foundation for the efficient development of shale reservoirs.

2. Experiments and Materials

2.1. Experimental Equipment and Samples

This study investigates the production enhancement mechanisms and influencing factors of shale oil under mixed gas flooding in the C7 shale reservoir of the Ordos Basin, China. The C7 reservoir is a laminated shale formation primarily composed of sandstone and mudstone, with a formation temperature of 80 °C and a current formation pressure of 20 MPa. The reservoir exhibits porosity ranging from 5% to 12% and permeability between 0.011 and 0.3 mD. Previous pilot tests employing water injection flooding and CO_2 energy supplementation techniques have yielded promising results. Consequently, the identification and implementation of more efficient production technologies remain a key focus for advancing field applications in this block. To address these challenges, this study has developed a comprehensive experimental system utilizing various advanced equipment. Specifically, PVT apparatus is employed to analyze the physical properties of shale oil samples under different pressure, volume, and temperature conditions. This setup includes a high-precision, high-pressure reactor to simulate reservoir conditions; pressure and temperature sensors for real-time monitoring; and a volume measurement device to assess sample expansion and dissolved gas volume changes. A schematic diagram of the experimental setup is presented in Figure 1.

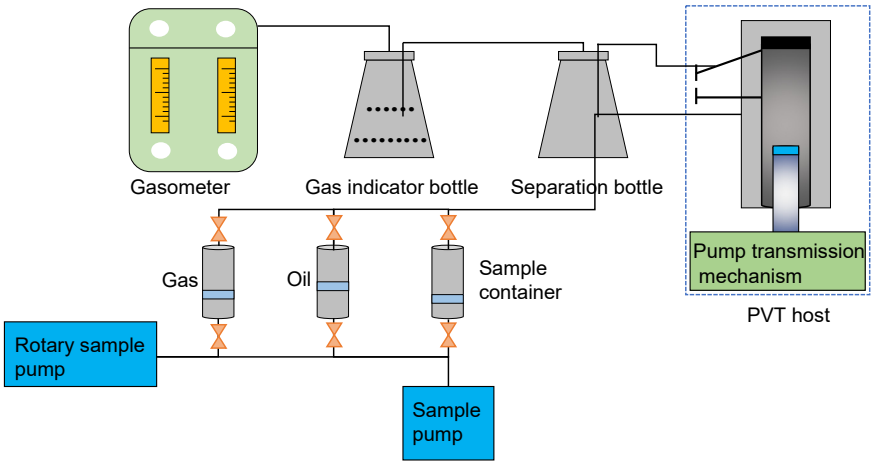


Figure 1. The schematic diagram of PVT experimental equipment.

A scanning electron microscope (SEM) is utilized to observe the microstructure of shale samples in detail, focusing on pore morphology and fracture network characterization. By comparing SEM images of the rock's microstructure before and after gas injection, we can visually evaluate structural changes and the connectivity of the pore network during the injection process. This comparison helps clarify the effects of gas injection and the underlying micro-mechanisms of oil and gas flow. The SEM equipment employed in this study is a field-emission dual-beam electron microscope, model FEI Helios Nanolab 600i, manufactured by FEI Company (Hillsboro, OR, USA) and purchased from SEIR Network Co., Ltd. (Beijing, China). The porosity of the shale samples is determined by measuring the mass difference in saturated dodecane liquid, while permeability is assessed using the helium pulse method. The dodecane used is sourced from China National Pharmaceutical Group Chemical Reagents Co., Ltd. (Shanghai, China), with a purity of 99.99%, and the helium gas is provided by Qingdao Xinke Yuan Gas Co., Ltd. (Qingdao, China), also with a purity of 99.99%. A schematic diagram of the core-scale mixed gas injection experimental setup is shown in Figure 2. The main components of this setup include a core holder, a high-pressure vessel, a displacement pump, and micro gas and liquid measuring devices.

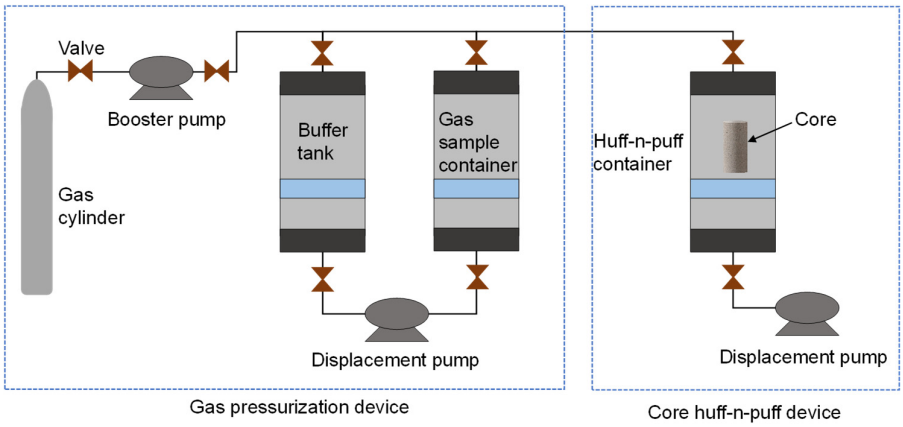


Figure 2. The schematic diagram of the mixed gas huff and puff core experimental device.

The cores used in the experiments to assess the enhanced recovery effects of different mixed gas injections were sourced from the C7 reservoir, with the core properties provided in Table 1. The cores were classified into two types: matrix and fractured, with the matrix cores exhibiting well-developed microfractures. The crude oil used in the experiment

was a simulated oil formed by blending reservoir-degasified crude oil with kerosene. The composition of the reservoir crude oil is shown in Figure 3.

Table 1. Core basic parameter data.

Core No.	Diameter (mm)	Length (mm)	Weight (g)	Permeability (mD)	Porosity (%)	Core Category
1	24.65	58.36	61.91	0.106	6.23	Matrix core
2	24.96	55.11	58.85	201.95	5.33	Fractured core

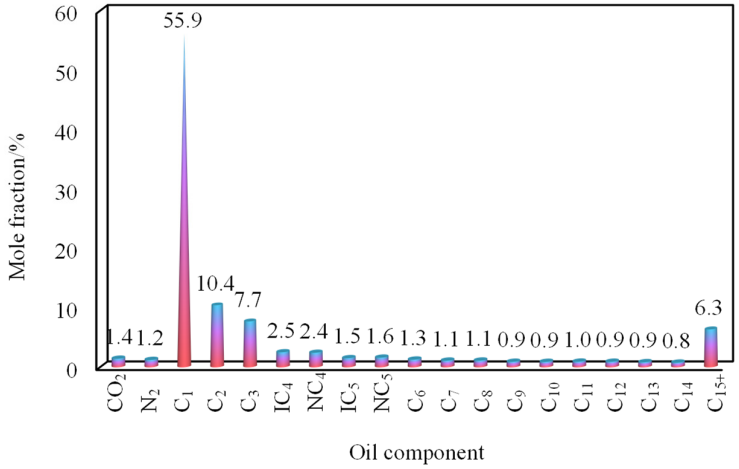


Figure 3. Composition of formation oil composition.

2.2. Experimental Process

2.2.1. PVT Experimental Process of Mixture Gas and Oil

Using the PVT experimental setup, reservoir crude oil samples were prepared by restoring the gas-to-oil ratio to reservoir conditions at the bubble (or dew) point. Several gas injections were conducted to investigate the changes in crude oil properties and to determine the effects of different gas types on the volume expansion coefficient, viscosity, and saturation pressure of the crude oil. The main experimental process is outlined as follows:

(1) The surface-degassed crude oil was placed in a high-pressure vessel, with gradual adjustments to pressure and temperature to match reservoir conditions. This was primarily achieved by mixing with produced gas to restore the dissolved gas content and pressure environment in the crude oil.

(2) Different types of injection gases were prepared based on the mass ratios of the various mixtures. The gases used in this study included CO_2, CH_4, a mixture of CH_4 and CO_2 at a 2:1 mass ratio, and a mixture of CH_4 and CO_2 at a 1:2 mass ratio.

(3) A high-pressure gas storage device was used to pre-treat the different gas types to achieve conditions matching the pressure and temperature of the reservoir crude oil, ensuring that gas–oil interactions could simulate real reservoir conditions.

(4) Before injecting the gases, the PVT apparatus was used to conduct baseline property tests on the crude oil restored to reservoir conditions, measuring key parameters such as initial volume, viscosity, saturation pressure, and dissolved gas content. These initial data served as a baseline for subsequent comparative analyses of changes in crude oil properties under different gas injection scenarios.

(5) Different types of gases were injected into the reservoir crude oil, with real-time recording of volume changes, pressure fluctuations, and gas dissolution during the injection process.

(6) The changes in crude oil properties following the injection of different gas types were analyzed. The parameters included the volume expansion coefficient, viscosity, and saturation pressure of the crude oil. The volume expansion coefficient was calculated by measuring the change in oil sample volume before and after gas injection, while viscosity was measured in real time using a viscometer. Saturation pressure was determined by controlling and adjusting the system pressure to find the pressure at which gas began to separate from the oil sample. After each round of gas injections, the pressure was gradually reduced, and the gas separation was monitored to establish the new saturation pressure.

2.2.2. Experimental Process of Gas–Rock Interaction

The impact of mixed gas injection on the pore structure and flow capacity of the rock was analyzed by measuring porosity, permeability, and SEM images before and after interaction with the rock. The main experimental process is outlined as follows:

(1) Organic solvents (a mixture of petroleum ether and ethanol in a 1:1 volume ratio) were used to wash the reservoir core, removing any residual oil. After cleaning, the core was placed in a vacuum drying oven and dried at a constant temperature of 100 °C for 12 h, ensuring all moisture and residual solvents were completely evaporated.
(2) The rock samples were cut into 5 × 5 × 5 mm cubes, followed by argon ion polishing and gold spraying before SEM imaging to observe the initial microstructure of the rock.
(3) The permeability of the dried core samples was measured using a pulse permeability tester, and the dry weight of the core was recorded. After saturation with dodecane under 20 MPa pressure for 7 days, the wet weight of the core was measured to calculate the initial porosity. The core was then dried at a constant temperature of 100 °C for 12 h.
(4) After saturating the rock cubes and cylindrical cores with aqueous fracturing fluid (slick water) for 5 days, they were placed in a high-pressure reactor. Different types of gases were injected at 80 °C and 20 MPa for a reaction time of 10 days.
(5) After the reaction, the rock cubes were dried at 100 °C for 24 h, then polished and gold-coated before undergoing SEM scanning. The same regions as in the initial scan were selected to observe the changes in the micro-pore structure of the core.
(6) The porosity and permeability of the cylindrical cores were measured again using the same testing equipment and methods as in the initial stage. A comparative analysis was performed to assess the effects of gas injection on the core's pore structure and fluid flow performance.

2.2.3. Experimental Process of Mixed Gas Core Huff and Puff

By conducting core throughput experiments with different types of gases, the enhanced oil recovery effects of mixed gas injection in shale oil were evaluated. The main experimental process is outlined as follows:

(1) The dried core was cut using wire-cutting techniques to create fractures. The cut core was placed into heat-shrink tubing, sealing it to prevent damage during the experiment.
(2) The fundamental physical parameters of both fractured and matrix cores were measured, including dry weight, length, permeability, and porosity, as shown in Table 1.
(3) The core was saturated with crude oil using a vacuum saturation device at a saturation pressure of 20 MPa for 7 days. After saturation, the wet weight of the core was recorded to calculate the initial oil content.

(4) The core was placed in the shale oil core throughput experiment setup, where a gas pressurization device injected mixed gas into the intermediate container holding the core, stabilizing at the specified pressure for 6 h.
(5) After stabilization, the intermediate container was depressurized, and the remaining oil in the core was measured using a weighing method to calculate the oil recovery rate.
(6) Steps (4) and (5) were repeated for multiple cycles to determine the degree of oil extraction at each round.

3. Results and Discussion

3.1. Gas–Oil Interaction Mechanism of Shale Oil

Based on the gas composition provided by the oilfield (Figure 4), mixed gases were formulated in the laboratory using gas state equations and mixing compressibility factors. The crude oil was then mixed with a gas-to-oil ratio of 90 m^3/m^3 to closely replicate the actual reservoir oil composition.

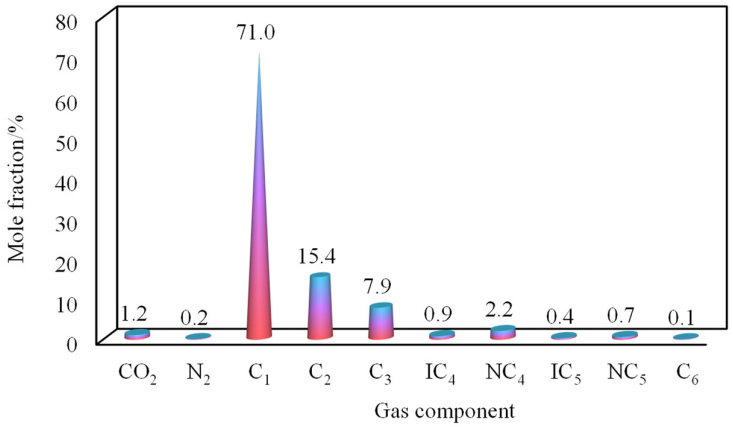


Figure 4. Composition of produced gas components.

Isothermal constant composition expansion experiments (Figure 5a) determined the saturation pressure of the crude oil to be 20.1 MPa. When the system pressure dropped below this value, gas bubbles formed in the oil, causing rapid volume expansion. Results from constant composition expansion experiments with various injected gases (Figure 5b) indicated that the saturation pressure increased with the molar fraction of the injected gas, although the effects varied significantly across different gas combinations. The study by Li et al. [49] also confirmed this conclusion, showing that when the CO_2 mole fraction increased from 0% to 45%, the crude oil saturation pressure increased by approximately 1.6 times. However, this study found significant differences in the impact of different gas combinations on saturation pressure. Among these, pure CH_4 resulted in the highest saturation pressure, with the most pronounced pressure increase as the mole fraction rose. When the mole fraction of the injected gas reached 80%, the saturation pressure was 1.5 times higher than in the initial state. This characteristic makes pure CH_4 particularly effective in scenarios requiring rapid pressure enhancement and improved reservoir displacement. In contrast, pure CO_2 exhibited the lowest saturation pressure at the same molar fraction. At an 80% molar fraction, the saturation pressure of pure CH_4 was 1.24 times that of pure CO_2. Furthermore, the increase in saturation pressure for pure CO_2 was more gradual as the molar fraction rose. This suggests that CO_2 has high solubility, enabling effective diffusion under low-pressure conditions and progressively enhancing oil recovery, making it suitable for stable, long-term pressurization strategies. In the case of mixed gases, a higher CO_2 ratio (CO_2 at 2:1) resulted in a saturation pressure close to that of pure CO_2, albeit slightly higher, indicating that the presence of CH_4 enhanced the compressibility

of the mixed gas. Conversely, increasing the CH_4 ratio significantly raised the saturation pressure, approaching that of pure CH_4, further highlighting the pressure-enhancing role of CH_4 in gas injection development. By comparing different gas combinations, it can be inferred that in actual reservoir development, selecting appropriate gas injection ratios based on specific needs allows for flexible adjustment of reservoir pressure enhancement rates and magnitudes, leveraging the rapid pressure boost of pure CH_4, the stable pressure effects of pure CO_2, or achieving an optimal balance through judicious mixed gas ratios for effective and economical oil recovery.

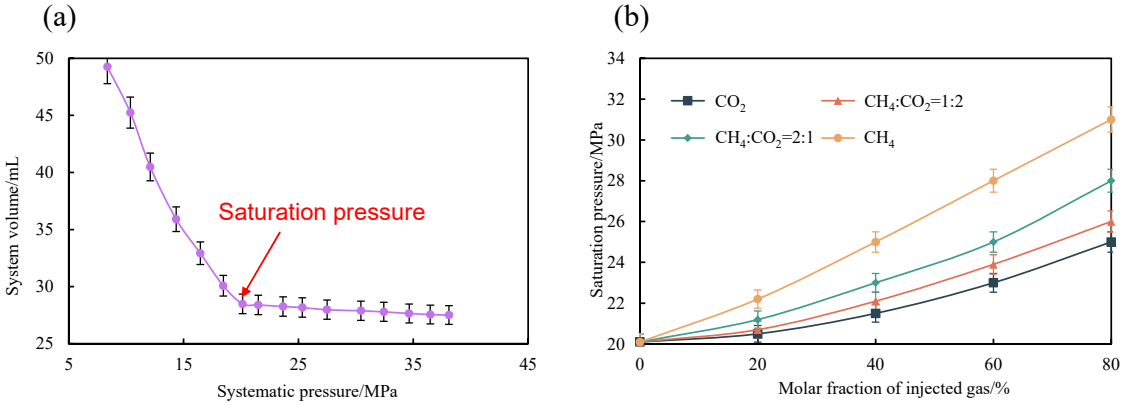


Figure 5. The results of the constant mass expansion experiment: (**a**) the results of the isothermal constant mass expansion experiment of crude oil and (**b**) the comparison of saturation pressure between different injected gases and crude oil.

The variation in the crude oil expansion coefficient and viscosity under different gas media is shown in Figure 6. As the molar fraction of injected gas increases, the crude oil expansion coefficient gradually rises across different gas media. Specifically, when the CO_2 molar fraction in the crude oil system increases from 0 to 80%, the expansion coefficient increases by 39%, while for CH_4, it rises by 21%. The effect of the CH_4/CO_2 mixed gas lies between those of the two pure gases, with the expansion coefficient decreasing as the molar ratio of CH_4 in the mixed gas increases. This suggests that a higher proportion of CH_4 in the mixed gas leads to an effect more similar to that of CH_4, resulting in a reduction in the overall expansion coefficient. This can be attributed to CO_2's high solubility and strong dissolving capability, which interact significantly with CH_4 molecules in the crude oil, causing notable volume expansion. In contrast, CH_4 has a relatively minor expansion effect. When the molar ratio of CH_4 and CO_2 in the mixed gas changes, the expansion coefficient reflects a value between those of the two pure gases. As the molar ratio of CH_4 increases, the expansion coefficient approaches that of pure CH_4, indicating that the addition of CH_4 diminishes the expansion effect of CO_2, reducing the overall expansion coefficient of the mixed gas. At the same time, the study by Habibi et al. [50] showed that the expansion factor of crude oil in contact with gas is also time-dependent. Through visualized PVT experiments, they found that during the CO_2 injection phase, the system pressure reached 13.8 MPa, and the expansion factor of crude oil was 1.23. After stopping CO_2 injection, the system pressure decreased to 11.8 MPa after 5 h, while the crude oil expansion factor increased to 1.32. On the other hand, as the molar fraction of injected gas increases from 0 to 40%, a significant decrease in crude oil viscosity is observed, indicating that gas dissolution effectively alters the oil's flowability during this stage. Within this range, both pure CO_2 and CH_4 substantially reduce the viscosity of crude oil through gas dissolution. Specifically, pure CO_2 reduces crude oil viscosity by 94.4%, while pure CH_4 reduces it by 94%. The effects are very similar, suggesting that the composition of mixed gases does not significantly affect the degree of viscosity reduction. This is consistent with

the findings of Wang et al. [51], who noted that while the addition of gases like C_2 to CO_2 reduced the viscosity-reducing effect, the decrease was relatively small. However, when the molar fraction of injected gas exceeds 40%, the viscosity of crude oil remains largely unchanged, indicating that further gas dissolution approaches saturation, and the oil's flowability has reached its maximum improvement.

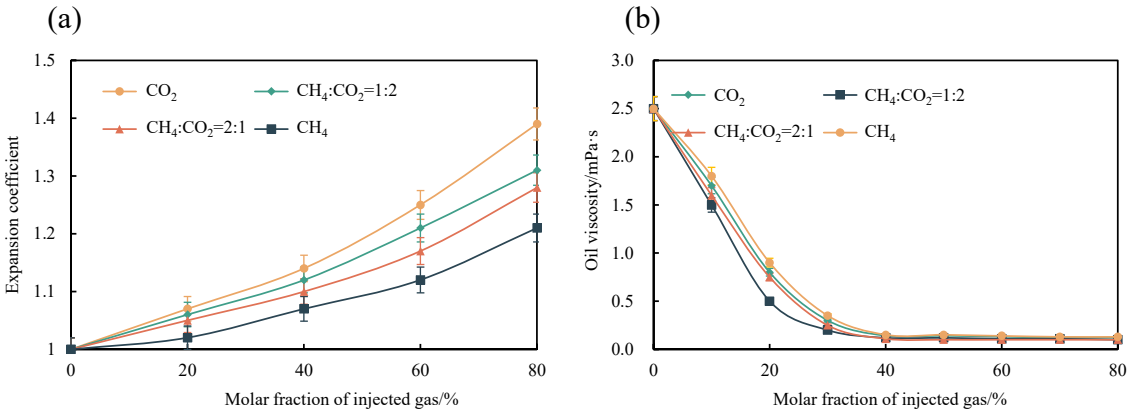


Figure 6. The experimental results of expansion coefficient and viscosity of crude oil with different gases: (**a**) curves of expansion coefficient of different injected gases with molar fraction and (**b**) curves of viscosity of crude oil with different injected gases with molar fraction.

The changes in interfacial tension and miscibility pressure of oil and gas under different gas media are shown in Figure 7. As the molar fraction of injected gas increases, the interfacial tension between the gas and crude oil gradually decreases, indicating a significant impact of gas dissolution on interfacial behavior. Pure CO_2 demonstrates the strongest capability in reducing interfacial tension, with a 54.54% reduction when its molar fraction reaches 80%, highlighting its robust regulatory influence on interfacial behavior. In contrast, pure CH_4 exhibits a weaker effect, reducing interfacial tension by only 31.82% at 80% molar fraction. For CH_4/CO_2 mixed gases, the ability to reduce interfacial tension falls between those of the two pure gases, with this effect diminishing as the molar proportion of CH_4 increases. This indicates that a higher CH_4 component weakens the ability of the mixed gas to reduce interfacial tension, causing its behavior to align more closely with that of CH_4. Consequently, under reservoir conditions, an increase in the CH_4 ratio of the mixed gas leads to a rise in the minimum miscibility pressure (MMP), making it more difficult for the gas to achieve complete miscibility with crude oil. This is because CH_4 is less effective than CO_2 in reducing interfacial tension and promoting gas–oil mixing, requiring higher pressures to overcome interfacial tension for miscibility at higher CH_4 ratios. Therefore, as the CH_4 proportion in the mixed gas increases, the gas faces greater difficulty in achieving miscibility with crude oil, thereby affecting reservoir displacement efficiency and the overall effectiveness of gas injection. The miscibility of CO_2 with crude oil involves two main physical and chemical processes: first, CO_2 dissolves in the crude oil, and then CO_2 extracts lighter CH_4 components from the crude oil. This is the process of CO_2 miscibility with crude oil [9,52]. Al Hinai et al. [53] also measured the interfacial tension between crude oil and CO_2-associated gas mixtures. They explained that the high miscibility pressure of associated gas is due to its significantly lower extraction effect on the light CH_4 components in crude oil compared to pure CO_2.

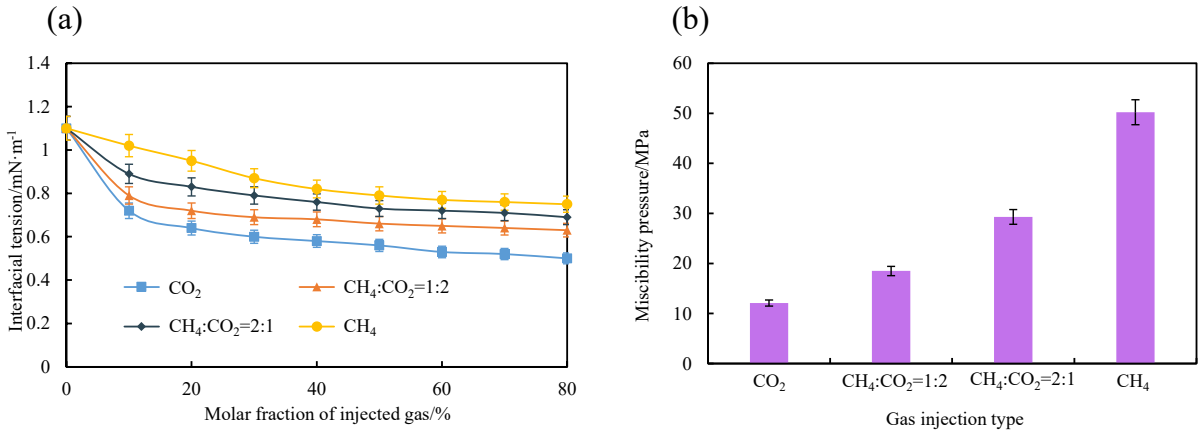


Figure 7. The experimental results of miscibility with crude oil in different gas media: (**a**) curves of interfacial tension of different injected gases with mole fraction and (**b**) comparison of miscible pressure of different injected gases.

3.2. Interaction Mechanisms Between Gas and Shale Rock

This study focuses on mixed gas components primarily composed of CO_2 and CH_4, and the SEM experiments specifically examine the effects of these gases on the microstructure of the rock. The original appearance of the rock sample is shown in the SEM image (Figure 8a), while the SEM images after treatment with pure CO_2 and CH_4 are depicted in Figures 8b and 8c, respectively. It is evident that, following treatment with different gases, the shale surfaces exhibit varying degrees of dissolution. Specifically, the shale surface treated with CH_4 appears smoother and denser, indicating a weaker dissolutive effect of CH_4 and the preservation of a relatively intact rock surface structure. In contrast, the shale surface treated with CO_2 displays a rougher, looser structure, with a greater generation of micropores, indicating a more pronounced dissolutive effect of CO_2 and a higher degree of dissolution on the shale surface. Therefore, it is clear that the impact of different gas treatments on the shale structure varies significantly, with CO_2 demonstrating a stronger dissolutive capacity that notably alters the microstructure of the shale.

Thus, this study focuses on the changes in the rock's microstructure before and after CO_2 treatment. SEM images illustrating the effects of CO_2 treatment on various regions of the rock are shown in Figure 9. It is evident that significant dissolution occurs in the pores surrounding the organic matter in the shale following CO_2 treatment. Under the dissolutive action of CO_2, some intergranular and intragranular micropores have expanded in size, while others have reduced due to the filling of detached minerals, resulting in pore sizes ranging from 0.4 to 1.2 times their original dimensions. Concurrently, the dissolution of minerals has increased pore sizes by 1.5 to 3 times, thereby enhancing the shale's porosity. Additionally, several microfractures have formed, further altering the internal structure of the shale. These observations indicate that CO_2 not only significantly impacts the pore structure around the organic matter but also markedly alters the pore network and microfracture distribution within the shale through its dissolutive action.

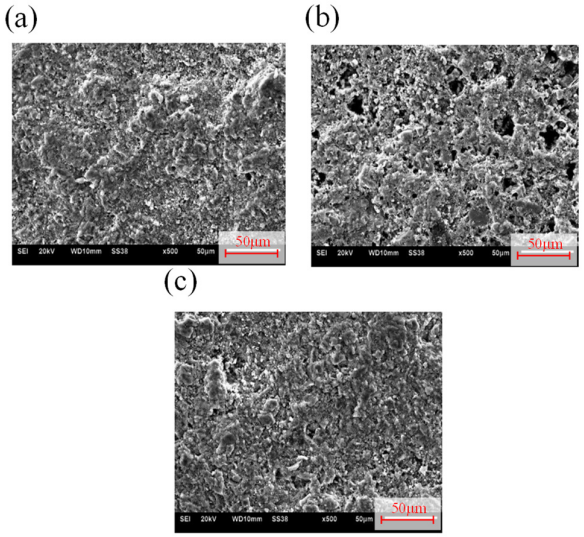


Figure 8. The SEM experimental images of rock at different times: (**a**) the original overall appearance of the rock, (**b**) the SEM image after CO_2 treatment, and (**c**) the SEM image after CH_4 treatment.

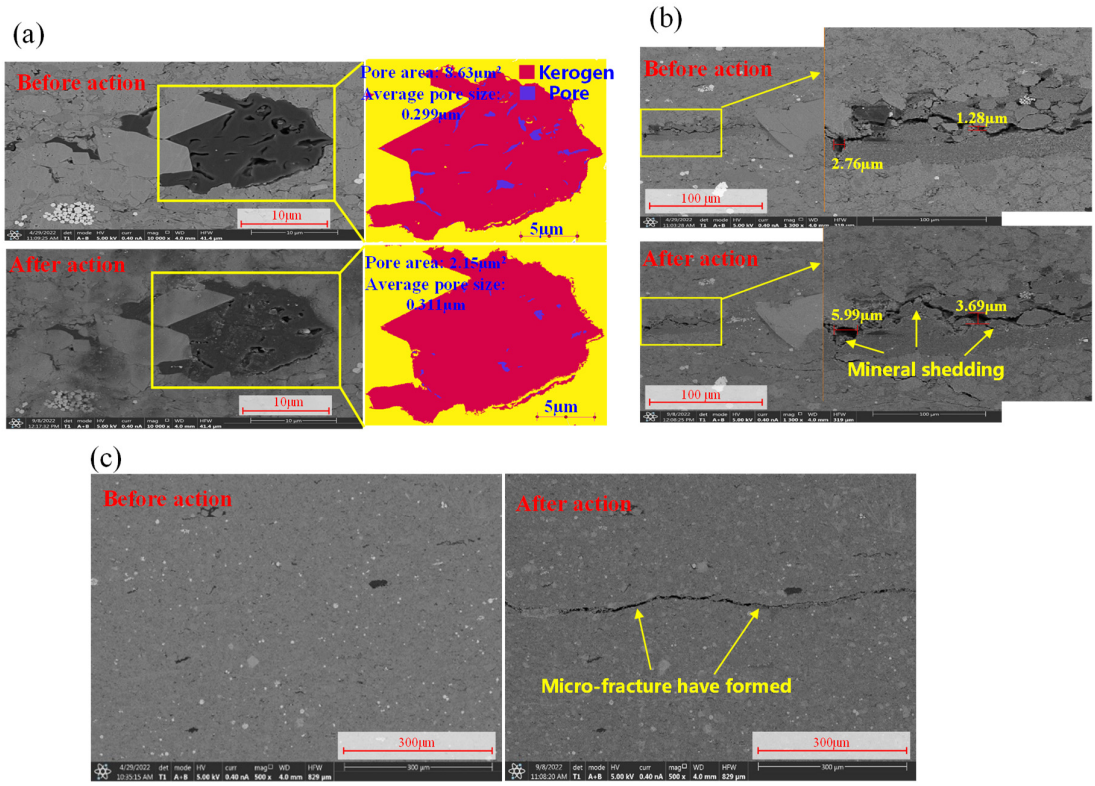


Figure 9. SEM images of different parts of rock: (**a**) SEM images before and after CO_2 action, (**b**) SEM images before and after CO_2 action, and (**c**) SEM images before and after CO_2 action.

Figure 10 illustrates the changes in porosity and permeability of shale cores before and after the application of different gases. The experimental results indicate that CO_2 injection significantly enhances the porosity of the reservoir, increasing it from 2.5% to 4.5% over 10 days, a 2% increase. This demonstrates that CO_2 molecules can effectively diffuse into the rock's pores, promoting the expansion and reorganization of the pore structure, thereby improving the overall porosity of the reservoir. Furthermore, mixed gases of CH_4 and CO_2 (at ratios of 1:2 and 2:1) also influenced porosity, with the mixture containing a higher proportion of CO_2 showing better results, achieving a 1.2% increase in porosity. In contrast, the mixture with a higher CH_4 proportion resulted in a smaller porosity increase of only 0.7%.

The porosity of pure CH_4 increased slightly, from 2.3% to 2.5% over 10 days, indicating that CH_4 struggles to significantly improve the pore structure of the reservoir in a short period. This limitation may be due to the larger molecular size and weaker diffusion capability of CH_4 compared to CO_2, which restricts their permeability and effectiveness within the pores. On the other hand, the changes in permeability further highlight the impact of gas injection on the reservoir's flow capacity. CO_2 injection increased the permeability from an initial 0.00967 mD to 0.01563 mD, a 0.00596 mD increase, demonstrating that CO_2 injection can significantly enhance the flow pathways within the reservoir. This improvement may be attributed to the formation of larger free volumes and flow paths in the pores created by the CO_2 gas. In comparison, mixed gases of CH_4 and CO_2 resulted in moderate increases in permeability, with increments of 0.003 mD and 0.00112 mD, respectively. This indicates that a higher proportion of CH_4 significantly reduces the improvement in permeability. The effect of CH_4 on permeability was the weakest, with an increase of only 0.00064 mD, which is almost negligible, further supporting the notion that pure CH_4 is ineffective in enhancing the permeability of the reservoir.

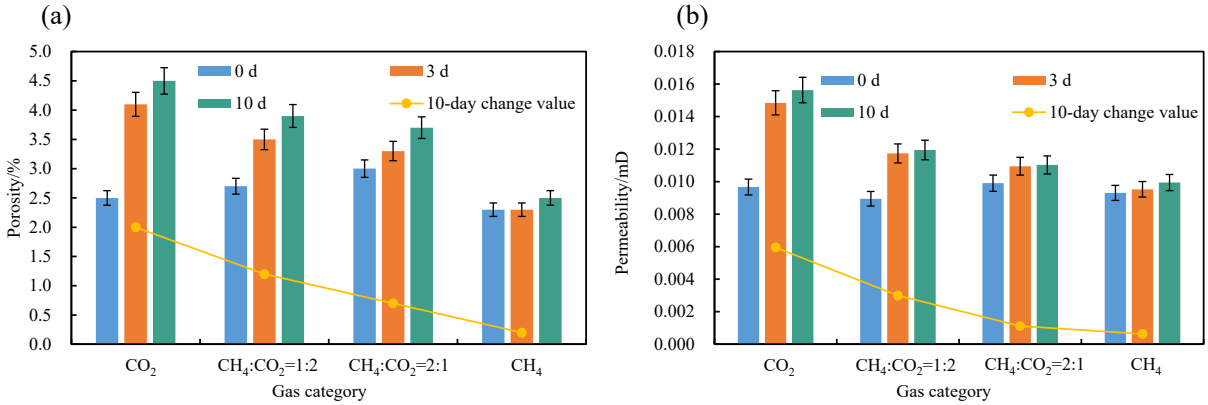


Figure 10. The change in shale physical properties under different gas effects: (**a**) the change in porosity under different gas effects and (**b**) the change in permeability under different gas effects.

3.3. Evaluation of Core Experiments on the Production Enhancement Effects

Figure 11 illustrates the production enhancement effects of various injection gases on the matrix core. In the matrix core production experiments, the CO_2 recovery rate increased from 10.237% in the first round to 32.0379% in the sixth round. CO_2 demonstrated a significant production enhancement effect in the initial rounds, particularly in the first and second rounds, with increases of 10.237% and 7.109%, respectively. However, as the rounds progressed, the production increase gradually diminished, with the sixth round showing a modest increase of only 1.8009%. This phenomenon is closely related to the low permeability, pore structure, and the physicochemical properties of the gas in the matrix core. CO_2, as a highly diffusive gas with a small molecular size and excellent solubility in oil, can effectively penetrate deeper micro-pores in the matrix core, promoting crude oil flow. However, the oil recovery effect of CO_2 is limited by the complex pore structure and high capillary pressure of the low-permeability core, resulting in a slower increase in recovery efficiency. Chen et al. conducted CO_2 injection experiments on shale cores from the Jimusaer Luchao Gou Formation. The recovery rates for each cycle followed a consistent trend, with the final recovery rate from CO_2 injection in cores with similar porosity and permeability being approximately 30% [54,55]. In comparison, the mixed gas of CH_4 and CO_2 outperformed pure CO_2 in production enhancement during each cycle. Specifically, the gas mixture of CH_4 and CO_2 in a 2:1 ratio exhibited the highest production enhancement potential, achieving a final recovery rate of 36.9%, 1.15 times higher than that of pure CO_2

and 1.25 times higher than pure CH_4. The production enhancement was particularly notable in the first three cycles, with increases of 10.9%, 9.5%, and 7.8%, respectively. This phenomenon is primarily attributed to the CH_4 component in the mixed gas. Although CH_4 is less effective at reducing interfacial tension, they enhance CO_2 diffusion and improve the solubility of gas in the oil phase, further promoting oil–gas displacement and fluid mobility. During the miscible oil displacement process, the addition of CH_4 improved gas permeability, thereby increasing fluid displacement efficiency. Furthermore, the high proportion of CH_4 increased the pressure difference in the oil–gas mixture, reducing capillary resistance and thereby enhancing overall fluid displacement efficiency. The oil displacement effect of pure CH_4 was relatively weak, mainly due to the larger molecular structure of CH_4, which resulted in slower diffusion in low-permeability cores, making it difficult to penetrate fine pores and limiting the recovery improvement.

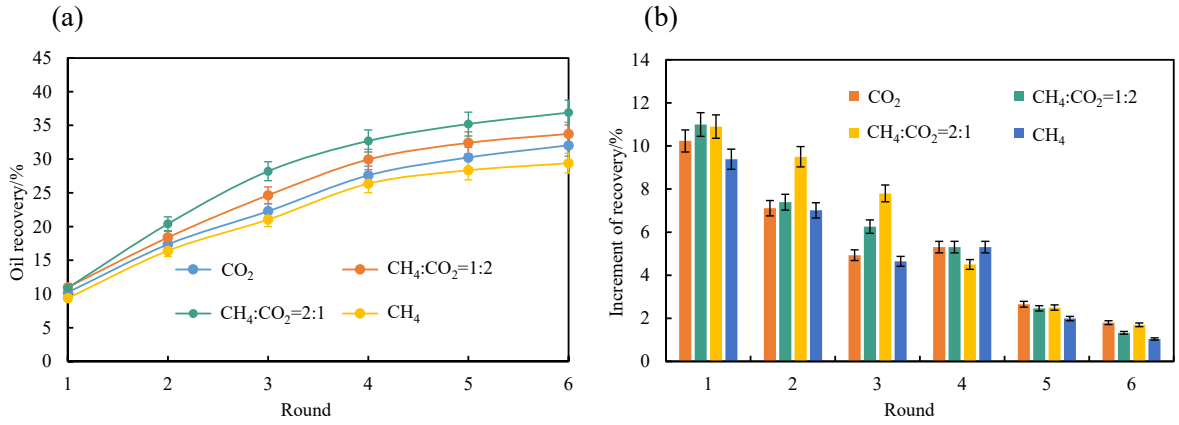


Figure 11. The effect of different gas injection huff and puff on the matrix core: (**a**) different rounds of gas injection recovery and (**b**) different rounds of gas to improve the recovery rate.

Figure 12 shows the experimental results for different injected gases in fractured cores. Compared to matrix cores, the production enhancement effect of gas injection in fractured cores is more pronounced. Specifically, CO_2 injection in fractured cores led to an 18.87% increase in recovery, while pure CH_4 resulted in a 16.42% increase. The gas mixture in a 2:1 mass ratio demonstrated a 21.7% increase. This is due to the fracture structure, which significantly enhances gas permeability and diffusion, providing a more direct flow path for the gas. As a result, the sweep area increases, capillary pressure reduces, and recovery ultimately improves. Peng et al. argued that during CO_2 injection in fractured cores, the gas phase becomes saturated in the fracture zone, and the matrix crude oil is primarily displaced by CO_2 diffusion [56]. Therefore, the more fractures there are and the longer they are, the greater the contact area between CO_2 and the matrix, leading to a higher final recovery. Li et al. found through core experiments that recovery in fractured cores was approximately 16% higher than in matrix cores, and that recovery improvement increased with the number of fractures [57]. In fractured cores, the production enhancement from different gas mixtures varied significantly across cycles. For example, pure CO_2 resulted in a final recovery of 50.9%, which was 1.11 times higher than that of pure CH_4. However, when the mass ratio of CH_4 to CO_2 in the mixed gas was 2:1, the recovery was even higher at 58.6%. Additionally, as the number of cycles increased, the production enhancement gradually decreased for all injected gas conditions, but the overall enhancement remained higher than that observed in matrix cores. Therefore, in fractured structures, a higher proportion of CH_4 further enhances the diffusion and oil displacement effects of the gas. However, during later injection cycles, the oil displacement efficiency of the gas is relatively lower than that of CO_2. These results suggest that in fractured cores, the use of mixed

gas can more effectively improve recovery. In the later stages of injection, reducing the proportion of CH_4 in the gas mixture may optimize oil recovery.

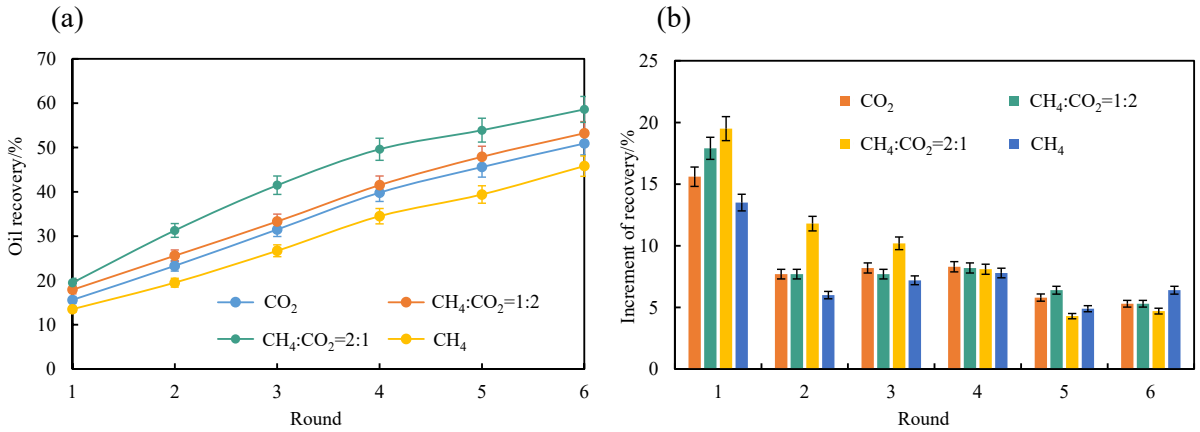


Figure 12. The effect of different gas injection huff and puff in fractured core: (**a**) different rounds of gas injection recovery and (**b**) different rounds of gas to improve the recovery rate.

4. Conclusions

This study investigates the impact of different gas combinations on shale oil extraction and reveals the mechanisms by which gas injection enhances reservoir performance. The results show that the composition and ratio of injected gases significantly influence oil properties, rock microstructure, and production enhancement effects. The main conclusions of this study are as follows:

(1) An increase in the molar fraction of CH_4 in the injected gas causes a significant rise in the saturation pressure of crude oil, reaching up to 1.5 times the initial level, while the saturation pressure with pure CO_2 is the lowest, making it more suitable for long-term pressurization strategies.

(2) The presence of CH_4 inhibits the expansion of crude oil. Pure CO_2 reduces the viscosity of crude oil by 94.4%, while pure CH_4 reduces it by 94%, indicating a nearly identical effect on viscosity reduction.

(3) Pure CO_2 is the most effective at reducing interfacial tension, achieving a 54.54% reduction when the CO_2 molar fraction reaches 80%. As the proportion of CO_2 in the gas mixture increases, the MMP decreases, highlighting CO_2's strong ability to control interfacial behavior.

(4) CO_2 significantly affects the pore structure around organic matter in shale, altering the pore network and microfracture distribution through dissolution. In contrast, CH_4 has a weaker dissolution effect, preserving a more intact rock surface structure.

(5) CO_2 injection increases the porosity of the rock from 2.5% to 4.5%, representing a 2% increase; permeability also rises by 0.00596 mD. In comparison, pure CH_4 has little effect on improving reservoir permeability.

(6) In matrix cores, recovery with a 2:1 mixed gas ratio reaches 36.9%, which is 1.15 times that of pure CO_2 and 1.25 times that of pure CH_4. In fractured cores, recovery is higher with a 2:1 mass ratio of CH_4 to CO_2, reaching 58.6%. However, in the later stages of production cycles, pure CO_2 demonstrates a strong ability to enhance.

This study offers valuable insights into the mechanism and recovery enhancement of CO_2/CH_4 gas injection in shale oil production through core experiments. However, several limitations exist. First, the experimental conditions were somewhat idealized and did not fully account for the complex multiphase environment caused by fracturing fluid residues in the reservoir, which may lead to discrepancies between experimental results and real-

world applications. Second, while the experiments primarily focus on macroscopic recovery enhancement, they lack a detailed analysis of the microscopic mechanisms underlying gas–oil–rock interactions. Additionally, the experimental equipment's pressure and temperature range has limited adaptability, making it insufficient to simulate the actual conditions of high-temperature, high-pressure reservoirs. Therefore, future research should incorporate advanced microscopic characterization techniques and conduct visualization experiments to study the diffusion, adsorption, and flow behavior of CO_2/CH_4 mixtures within shale pores, aiming to reveal the mechanisms behind gas injection-enhanced recovery. Furthermore, integrating nuclear magnetic resonance (NMR) experiments into subsequent core studies could help monitor the interactions between the injected gas, oil, and rock, providing detailed data on fluid distribution, flow dynamics, and pore-filling states, thereby enabling a more comprehensive understanding of the recovery enhancement mechanisms.

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