



Article Study on Oil Composition Variation and Its Influencing Factors during CO₂ Huff-n-Puff in Tight Oil Reservoirs

Bo Han ^{1,2,3,4}, Hui Gao ^{1,3,4,*}, Zhiwei Zhai ^{2,5,6,*}, Xiaoyong Wen ^{7,8}, Nan Zhang ⁹, Chen Wang ^{1,3,4}, Zhilin Cheng ^{1,3,4}, Teng Li ^{1,3,4} and Deqiang Wang ^{10,11}

- ¹ School of Petroleum Engineering, Xi'an Shiyou University, Xi'an 710065, China; hanbo@sxie.edu.cn (B.H.); cwangxsyu@163.com (C.W.); zhilin_cheng1992@163.com (Z.C.); liteng2052@163.com (T.L.)
- ² Faculty of Mining Engineering, Shanxi Institute of Energy, Taiyuan 030002, China
- ³ Engineering Research Center of Development and Management for Low to Ultra-Low Permeability Oil & Gas Reservoirs in West China, Ministry of Education, Xi'an 710065, China
- ⁴ Xi'an Key Laboratory of Tight Oil (Shale Oil) Development, Xi'an 710065, China
- ⁵ Technical Innovation Center for Three Gas Co-Production of Shanxi Province, Taiyuan 030008, China
- ⁶ Laboratory of Coalbed Methane Joint Extraction Ground and Underground, Shanxi Institute of Energy, Taiyuan 030002, China
- ⁷ National Engineering Laboratory for Exploration and Development of Low Permeability Oil and Gas Fields, Xi'an 710021, China; wenxy029_cq@petrochina.com.cn
- ⁸ Oil and Gas Technology Research Institute, PetroChina Changqing Oilfield Company, Xi'an 710018, China
- ⁹ Department of Electrical Engineering and Computer Science, University of Stavanger, 4036 Stavanger, Norway; nan.zhang@uis.no
- ¹⁰ State Key Laboratory of Offshore Oil Exploitation, Beijing 102209, China; wangdq23@cnooc.com.cn
- ¹¹ CNOOC Research Institute Co., Ltd., Beijing 102209, China
- * Correspondence: ghtopsun1@163.com (H.G.); zhaizw@sxie.edu.cn (Z.Z.)

Abstract: With immense potential to enhance oil recovery, CO₂ has been extensively used in the exploitation of unconventional tight oil reservoirs. Significant variations are observed to occur in the oil's composition as well as in its physical properties after interacting with CO₂. To explore the impacts of oil properties on CO_2 extraction efficiency, two different types of crude oil (light oil and heavy oil) are used in CO₂ huff-n-puff experiments. Moreover, numerical simulation is implemented to quantitatively inspect the impacts of different influencing factors including production time, reservoir pressure and reservoir temperature on physical properties as well as on the oil composition variation of the crude oil. The findings of the experiments demonstrate that, whether for the light oil sample or for the heavy oil sample, hydrocarbon distribution becomes lighter after interacting with CO₂ compared with the original state. In addition, it is also discovered that the hydrocarbon distribution variation is more significant for the light oil sample. The findings of the numerical simulation suggest that production time, reservoir pressure and reservoir temperature have significant impacts on the produced oil composition and properties. The hydrocarbon distribution of the oil becomes lighter with the increasing of production time and formation pressure, while it becomes heavier with the increasing of reservoir temperature. At the very beginning of the oil production, the properties of the produced oil are worsened. Compared with the original state, the oil density and viscosity are 25.7% and 200% higher, respectively. It is suggested that viscosity reducers are added into the well to improve the oil properties in this period. With the continuing of the oil production, the oil properties are continuously promoted. At the end of the simulation time, the oil density and viscosity are 3.5% and 15.1% lower compared with the original oil, respectively. This paper has great significance for the implementation of CO₂ huff-n-puff in tight oil reservoirs.

Keywords: tight oil; CO₂ huff-n-puff; oil composition variation; numerical simulation; influencing factors



Citation: Han, B.; Gao, H.; Zhai, Z.; Wen, X.; Zhang, N.; Wang, C.; Cheng, Z.; Li, T.; Wang, D. Study on Oil Composition Variation and Its Influencing Factors during CO₂ Huff-n-Puff in Tight Oil Reservoirs. *Processes* **2023**, *11*, 2415. https:// doi.org/10.3390/pr11082415

Academic Editors: Liang Zhang, Hongbin Yang and Yukun Du

Received: 18 July 2023 Revised: 7 August 2023 Accepted: 8 August 2023 Published: 11 August 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).

1. Introduction

As a widely distributed unconventional oil resource, tight oil has an identity of strong heterogeneity and poor properties, which creates large obstacles for reservoir development [1-3]. Due to the fact that the overburden permeability for tight formations is never more than $0.1 \times 10^{-3} \,\mu\text{m}^2$, conventional development strategies are not fully applicative and cannot achieve high oil recovery. How to develop tight oil more efficiently has always been a difficult problem for petroleum scientists and engineers [4-6]. In recent years, as energy demand is continuously increasing, tight oil is receiving more and more attention. Moreover, the emerging of advanced stimulation technology such as the horizontal well technique and the large-scale hydraulic stimulation technique make it feasible to develop tight oil [7–9]. Nowadays, the technique of horizontal wells with large-scale hydraulic stimulation is often used to promote the production of tight oil. Enhanced connectivity as well as conductivity due to this technique have led oil recovery to be achieved in an appreciably improved manner for previously unreachable tight oil. Field tests in the Ordos Basin, China, have demonstrated that oil production can be improved two-fold after engaging the horizontal well and hydraulic stimulation techniques. However, depletion without a water replenishment method is often employed because of concerns over the high risks of water channeling. Due to the lack of pressure supplementation, reservoir pressure and oil production decline very fast. The depletion implemented in tight oil is discovered to have the characteristics of high production at the very beginning of the production period, a rapid decline in the middle stages of the production period and overall low recovery factor of the oil reservoirs [10–12]. Large amounts of oil remain unrecovered after depletion. Some studies suggest that the oil recovery for tight oil reservoirs via the depletion method is always less than 8%, which is much lower compared to conventional oil reservoirs [13–15]. Accordingly, a method that can efficiently supplement reservoir pressure and hence promote oil recovery is urgently needed.

After employing water flooding, a severe water channeling problem occurred in the development of Changqing oil field via the horizontal well and hydraulic stimulation techniques, which resulted in a sharp decline in production. In response to this problem, Li et al. (2015) and Wu et al. (2017) conducted horizontal well water huff-n-puff field tests. It was discovered that daily oil production saw a significant increase, which was about 78.3% [15,16]. Qu et al. (2018) conducted static and dynamic water injection and imbibition experiments using the cores of the Chang7 tight formation in the Ordos Basin. It was presented that imbibition was of great significance to oil production for water huff-n-puff [17]. Sheng et al. (2017b) believed that water-wet reservoirs were preferable in the implementation of water huff-n-puff. With spontaneous imbibition in water-wet reservoirs, more oil can be displaced compared with oil-wet reservoirs [18]. With the help of nuclear magnetic resonance method, Li et al. (2022) quantitatively investigated microscopic oil production characteristics after implementing huff-n-puff. It was discovered that intermediate pores contributed the most to oil production, which accounted for 74.02% [19]. Wang et al. (2019) performed numerical simulation to announce the impacts of the parameters of hydraulic fracturing on water huff-n-puff for tight oil exploitation [20]. For the purpose of promoting tight oil production, many oil fields in China have implemented huff-n-puff pilot tests. However, due to compatibility issues between the injected water and the formation fluids, as well as the wettability of the reservoirs, large gaps exist in the well performance of different reservoirs [21]. The implementation of this technique is narrowed to certain types of oil reservoirs. In recent years, attempts to engage CO₂ huff-n-puff in exploiting tight oil have been tried by some scholars [22-24]. Compared to water, CO₂ has some obvious advantages such as expending oil, reducing oil viscosity and having better solubility in oil and better compatibility with the reservoir fluids, which make CO₂ achieve higher oil displacement efficiency. In addition, CO_2 can be partly buried underground during the CO_2 injection, which makes CO_2 flooding or the CO_2 huff-n-puff technique a win–win strategy of promoting oil recovery as well as reducing CO₂ emissions [25–27]. Abundant investigation has been implemented to explore the feasibility of engaging CO₂ huff-n-puff in developing tight

oil in recent years. With CO₂ and activated water as injection media, Shi et al. (2022) carried out huff-n-puff experiments using tight cores from Fuyu Oilfield. They discovered that, in comparison to activated water, CO₂ could achieve higher recovery with an additional 12.1% of oil produced [28]. Fan et al. (2021) carried out CO_2 huff-n-puff in the tight conglomerate reservoir cores of Mahu Oilfield. Nuclear magnetic resonance tests demonstrated that oil in both intermediate pores and small pores could be utilized by CO_2 [29]. Tang et al. (2021) conducted CO₂ huff-n-puff experiments with large outcrop square cores in order to explore oil production laws as well as the impact factors of huff-n-puff. The experimental findings demonstrated that oil recovery rose with the increasing of CO₂ injection volume and decreased with the increasing of production speed [13]. Wei et al. (2020) pointed out that oil recovery was mainly determined by dissolved gas driving the effect in CO₂ huff-n-puff [30]. Taking the Bakken tight formation as a research target, Afrari et al. (2022) discovered that both the bottom hole pressure and the production time were instrumental in promoting oil recovery during CO₂ huff-n-puff. Numerical simulation suggested that more than 7% incremental oil could be recovered with the implementation of huff-n-puff [31]. To promote oil production and CO_2 storage, Fakher et al. (2020) explored the feasibility of CO_2 in shale oil. They discovered CO_2 injection pressure had significant influences on both CO_2 storage and oil recovery [32]. Taking CO₂ solubility into account, Lee et al. (2020) studied the influences of CO_2 solubility in brine on huff-n-puff in shale oil reservoirs. With the employment of the simulation method, they proposed that about a third of the injected CO_2 should be dissolved in brine, which would decrease oil recovery by 4% [33]. With the employment of the NMR technique, Du et al. (2020) experimentally explored the effectiveness of CO_2 huff-n-puff for tight conglomerate reservoirs. An oil recovery efficiency of 36.85% was achieved in the experiments, which proved the feasibility of this technique in conglomerate reservoirs [34]. With the employment of low permeability cores, Du et al. (2021) explored the characteristics of oil mobilization during CO_2 huff-n-puff. The findings suggested that large pores contributed most to promoting oil production. Oil in the small pores was hardly produced with large amounts of residual oil trapped, as shown in [35]. Li et al. (2019) carried out huff-n-puff, engaging shale cores with the injection media of CO₂ and N₂, respectively. They discovered that CO₂ could significantly reduce oil viscosity, which is about 40% to 60%. Moreover, CO_2 can achieve a higher oil recovery than N_2 , with more than 26.64% additional oil produced [36]. Xue et al. (2023) established a new integrated model for fractured underground gas storage, which would offer some guidance for the numerical simulation of CO₂ huff-n-puff [37]. Zhu et al. (2020) carried out CO₂ huff-n-puff experiments with fractured shale and tight sandstone to study the effects of kerogen, injection pressure and injection time on the fracture recovery factor and the matrix recovery factor during the CO₂ huff-n-puff process. The findings demonstrated that CO₂ injectivity in shale was better than that in sandstone. However, the recovery factors for the shale samples were lower than those for sandstone samples [38].

In summary, many scholars have explored the implementation of water or CO_2 huff-n-puff to promote oil production in tight oil. Most studies advocate that CO_2 huff-n-puff has more advantages in comparison with water [39,40]. However, as to CO_2 huff-n-puff, the majority of these studies are devoted to exploring oil production characteristics along with analyzing the impact factors. A few studies have also investigated oil composition variation during CO_2 injection. Jia et al. (2023) studied oil viscosity and density variation after CH_4/CO_2 multi-component gas injection and they pointed out that CH_4 decreased the density and viscosity of the oil while CO_2 decreased the viscosity but increased the density [41]. Mojtaba Seyyedi et al. (2018) investigated strong CO_2 extraction and oil composition variation using pore-scale visualization experiments and PVT experiments. They discovered that the oil in contact with the CO_2 was heavier than the original oil [42]. Zhang et al. (2023) studied oil- CO_2 phase interaction characteristics at ultrahigh temperature and pressure conditions. They discovered that CO_2 continuously extracted light components from the oil phase, which caused the precipitation of asphaltene [43]. As far as we know, the dynamic variation of oil composition and its physical properties have not been fully

investigated yet. In our study, oil composition and oil physical property variation during CO_2 huff-n-puff is analyzed in detail with both experiments and simulation. Firstly, CO_2 huff-n-puff experiments are implemented for the purpose of studying the extraction efficiency of supercritical CO_2 on crude oil. In addition, two different oil samples are used to study the impacts of the oil properties on the produced oil composition variation and well performance, where one oil sample is a kind of light oil and the other oil sample is a kind of heavy oil. Then, different influencing factors including production time, reservoir pressure and reservoir temperature are studied using numerical simulation methods. The impacts of these influencing parameters on oil composition as well as on oil property variation are analyzed in detail.

2. CO₂ Huff-n-Puff Experiments

2.1. Experimental Materials and Equipment

Two different oil samples with diverse physical properties are employed to explore the impacts of oil properties on oil composition variation and oil recovery in this section. One oil sample is light oil derived from tight formations in the Songliao Basin, China, where the reservoir permeability ranges from $0.1 \times 10^{-3} \,\mu\text{m}^2$ to $1 \times 10^{-3} \,\mu\text{m}^2$. The other oil sample is heavy oil prepared from the above-mentioned light oil and Shengli Oilfield heavy oil in a mass ratio of 1:2. The oil density and viscosity for the light oil is $0.855 \,\text{g/cm}^3$ ($15 \,^{\circ}\text{C}$, $0.1 \,\text{MPa}$) and $23.0 \,\text{mPa} \cdot \text{s}$ ($15 \,^{\circ}\text{C}$, $0.1 \,\text{MPa}$), respectively. The oil density and viscosity for the heavy oil is $0.880 \,\text{g/cm}^3$ ($15 \,^{\circ}\text{C}$, $0.1 \,\text{MPa}$) and $115.0 \,\text{mPa} \cdot \text{s}$ ($15 \,^{\circ}\text{C}$, $0.1 \,\text{MPa}$), respectively. In addition, slim tube experiments are conducted at a reservoir temperature of $108 \,^{\circ}\text{C}$ to obtain the minimum miscibility pressure (MMP) of the two oil samples. The results demonstrate that the MMP for the light oil sample is $17.5 \,\text{MPa}$ and the MMP for the heavy oil sample is $25.6 \,\text{MPa}$. Standard saline water with a salinity of $50,000 \,\text{PPM}$ is prepared to simulate the formation water in the initial reservoir state. The purity of the CO₂ used in the experiments is 99.92%.

The experimental equipment consisted of the displacement system, the physical sand pack system, the back pressure controlling system, the temperature controlling system, the measuring system, the data acquisition system and the connecting pipelines and valves. The experiment setup is shown in Figure 1.

As the main part of the experiment system, the physical sand pack system provides the media for the CO₂ interacting with the reservoir oil, where the supercritical CO₂ will extract light components from the reservoir oil. The dimensions of the sand pack model are measured before the experiments with an inner diameter of 76.5 mm, length of 370 mm and bulk volume of 1700 cm³. In order to imitate the low permeability of the tight formation as well as simulating the actual fluid flow underground, different meshes of quartz sands and small amounts of clay are mixed together and added into the model. The quartz sands and the clay are mixed with a mass ratio of 9:1. The mixtures of the quartz sands and the clay are tamped in the axial as well as the radial direction to gain the expected permeability as well as porosity. Ultimately, the permeability and porosity are $0.3 \times 10^{-3} \ \mu m^2$ and 8.2%, respectively. As it is always defined that the permeability of tight oil reservoirs is less than $0.1 \times 10^{-3} \ \mu\text{m}^2$, the permeability of the sand pack model seems to be a little higher. However, it should be noted that $0.1 \times 10^{-3} \,\mu\text{m}^2$ is a mean value for the permeability of tight oil reservoirs. Considering the heterogeneity of the target reservoirs, the permeability of the tight formations in the Songliao Basin ranges from $0.1 \times 10^{-3} \ \mu\text{m}^2$ to $1 \times 10^{-3} \ \mu\text{m}^2$. Therefore, it is feasible to engage the sand pack model established in the laboratory to simulate the fluid flow in the actual tight porous media.

2.2. Experimental Procedures

During the experimental process, the experimental procedures below should be followed.

(1) The experiment equipment and valves are connected with the stainless steel pipelines according to the experimental flowchart shown in Figure 1. After that, the whole experimental system is vacuumed for at least for 24 h in room temperature conditions.



Figure 1. Experimental setup for CO_2 huff-n-puff in tight oil reservoirs. (a) Diagrammatic sketch of CO_2 huff-n-puff experimental setup. (b) Real experimental setup.

(2) The high-temperature oven is used to heat the model. The temperature is adjusted to the original reservoir temperature of 108 °C. For the purpose of ensuring that the temperature of the internal parts of the sand pack model reach the initial reservoir temperature and that the whole sand pack model can be heated uniformly, the heating time is set to at least 24 h.

(3) First, the sand pack model should be placed vertically inside the oven, which is essential to the saturation of the brine. Under a constant injection rate of 1 mL/min, the brine is steadily injected inside the model from the bottom end of the model. When the brine is produced at a constant rate from the top of the model, the water saturation process is terminated. With the injection volume as well as the produced volume recorded in detail, the porosity of the model can be measured after the water saturation process. Then the sand pack model is placed horizontally. At the constant injection rate illustrated above, water injection is carried out continuously. Then the permeability of the model can be calculated with the Darcy equation by recording the pressure difference between the production end and the injection end, and the water production rate.

(4) The oil saturation process is implemented to mimic the oil migration and charging process in the reservoirs. During the oil saturation process, the model is placed horizontally. At a constant injection rate of 0.5 mL/min, crude oil is gradually injected. In addition, it should be noted that back pressure for the model is controlled at 10 MPa throughout the oil saturation process. When the oil flow rate reaches a constant at the production end, the oil saturation process is suspended and the original oil reservoir environment is established. Through the oil injection process, the oil injection volume as well as the oil production volume are recorded in detail to obtain the oil saturation in the model. When the oil saturation is terminated, the model should be static for at least 24 h for oil aging.

(5) CO_2 huff-n-puff is implemented after the oil saturation process. In most cases, huff-n-puff is divided into three stages. Firstly, the CO_2 injection process (the huff stage) is carried out. At a constant injection rate of 0.5 mL/min, CO_2 is injected inside the model until the injection volume surpasses the predetermined value. With the help of the data acquisition system, the pressure inside the model is monitored and recorded continuously.

(6) After the CO_2 injection process, the second stage of soaking is carried out. During the soaking stage, all the values of the model are closed.

(7) After the termination of the soaking stage, the third stage of oil production is carried out. During this stage, the back pressure controller is used to regulate the production pressure accurately. For the sake of steady production, the oil production process is carried out at intervals. The pressure drop is controlled to be 0.5 MPa each time. When the sand pack pressure is reduced to the original pressure of 10 MPa, the huff stage is terminated. Then the produced oil is weighed and collected for composition analysis. The composition analysis is conducted by gas chromatography.

2.3. Experimental Results and Discussion

2.3.1. Oil Composition Variation during CO₂ Huff-n-Puff

In order to explore the impacts of the oil properties on the CO_2 extraction effect and the oil composition dynamic variation during huff-n-puff, two kinds of oil samples with different physical properties, as illustrated in Section 2.1, are prepared. Figure 2 illustrates the comparison between the hydrocarbon distributions of the original oil and produced oil for the light oil sample. Figure 3 illustrates the comparison between the hydrocarbon distributions of the original oil and produced oil for the heavy oil sample. For the light oil sample, it is discovered that the content of the intermediate components of C_{11} to C_{20} is increased significantly in the produced oil in comparison with the original oil. However, considering the fact that the produced gas-phase mixtures are released directly into the atmosphere and the light hydrocarbons contained in the gas-phase mixtures are not well collected, the content of the light components of C_4 to C_{10} in the produced oil is lower compared with that in the original oil. The light to intermediate components in the oil are the main extracting objectives of CO_2 , which leads to the hydrocarbon distribution of the produced oil becoming lighter in comparison with the original oil. This is responsible for the content of the intermediate components being increased while that of the heavy components is reduced in the produced oil. At the same time, it can be discovered that for heavy oil, the variation among the hydrocarbon distributions of the produced oil and original oil is not as obvious as that of the light oil sample. The oil composition does not vary a lot after interacting with the CO_2 . For the heavy oil samples, the content of heavy components is high while that of light components is low. Meanwhile, the extraction objectives of CO_2 are mainly for the light to intermediate components. Therefore, the composition variation for the heavy oil sample is not as significant as the light oil sample. Some measures such as lifting the pressure and extending the time can be adopted to improve the extraction by CO_2 . During CO_2 huff-n-puff implementation in tight formations, the extraction effect of CO_2 is non-negligible. On the one hand, the hydrocarbon distribution of the produced oil becomes lighter compared to the reservoir original oil, which is conducive to improving the oil properties and decreasing the oil density and viscosity. One the other hand, the residual oil after huff-n-puff becomes heavier at the same time that the oil density and

viscosity are increased, which causes difficulty in the development of the reservoir residual oil. Meanwhile, asphaltene deposition may be induced due to the oil composition variation, which will block the small pores and throats in the reservoir, hence reducing the reservoir permeability, ultimately causing a decrease in oil production.



Figure 2. Comparison between hydrocarbon distributions of original oil and produced oil for light oil.



Figure 3. Comparison between hydrocarbon distributions of original oil and produced oil for heavy oil.

2.3.2. CO₂ Extraction Efficiency of Oil

 CO_2 extraction efficiency is impacted by the original oil composition. To explore the impacts of oil properties and oil composition on the CO_2 extraction efficiency, the heavy oil sample as well as the light oil sample are used to conduct multiple cycles of huff-n-puff experiments. The results are shown in Figure 4. It is presented that for both the heavy oil sample and the light oil sample, if the huff-n-puff cycles are increased, the oil exchange ratio and oil recovery are decreased. The declining speed of the oil exchange ratio and the single-cycle oil recovery accelerate when the CO_2 huff-n-puff cycles surpass three. After three cycles, the oil increment of the CO_2 huff-n-puff is low. The production is characterized as low oil productivity with high gas productivity. Large amounts of CO_2 gas are produced with small amounts of oil involved. It is suggested the number of cycles should be limited to no more than three when implementing CO_2 huff-n-puff. After implementation, long periods of soaking are also advised to redistribute the water, oil and gas under capillary

force. Under the same conditions, both the oil exchange ratio and the oil recovery factor of the heavy oil are lower than those of the light oil. The fact that the content of the heavy components as well as the oil density and viscosity are higher for the heavy oil is responsible for this. In the CO_2 huff-n-puff process, the miscibility of the CO_2 with the heavy oil is poor, which leads to a lower efficiency of the CO_2 extracting for heavy oil compared to light oil under the same conditions. Meanwhile, after three cycles of implementation, the declining speed of the oil exchange ratio and the oil recovery is much faster for the heavy oil sample. Therefore, the effect of huff-n-puff cycles on the oil exchange ratio and the oil recovery should be given more attention when implementing huff-n-puff in heavy oil reservoirs. It is advised that the huff-n-puff cycles should be optimized for achieving higher economic efficiency. The oil composition has significant influences on the CO_2 extraction efficiency of oil. Light oil is preferred for the implementation of CO_2 huff-n-puff. Further studies should be conducted to quantitatively identify the effect of oil composition and oil viscosity on the oil exchange ratio as well as the oil recovery factor during implementation. Oil composition standards for the implementation of CO_2 huff-n-puff in tight oil should be established.



Figure 4. Comparison of oil exchange ratio and oil recovery between different oil samples.

3. Influencing Factors of Oil Composition and Property Variation

3.1. Reservoir Numerical Simulation Model

The experiment results imply that oil composition varies significantly during the CO_2 huff-n-puff process, which has great influence on the properties of the produced oil. However, the impact of different factors such as the production time, reservoir pressure and reservoir temperature are not fully investigated. Furthermore, oil composition and property variation need to be investigated at the field scale to offer some guidance for the implementation of CO_2 huff-n-puff in tight oil reservoirs. Considering the advantages of time saving and economic efficiency, numerical simulation is used to investigate the influences of different parameters.

For this study, the GEM compositional simulator is used to simulate CO_2 huff-n-puff in tight oil. A multi-dimensional geological model of the target reservoir is established to provide the medium for the CO_2 and oil interaction. The equation of state is employed to calculate oil composition and property variation during the process. The oil composition dynamic variation as well as its influencing factors are investigated in detail. The compositional model of huff-n-puff is established on the basis of the actual geological parameters of the tight formations in the Songliao Basin, China. Considering the fact that huff-n-puff is always implemented in a single well, the three-dimensional cylindrical geological model is used and two wells are drilled at the same position in the center of the model (see Figure 5). These two wells are set as the injection well and the production well, respectively. Furthermore, these two wells are opened alternately to imitate the operation of the huff-n-puff. The corresponding parameters used in the model are listed in Table 1. The reservoir fluid PVT model used in the numerical simulation is built on account of the Peng–Robinson equation of state [44]. The reservoir oil is divided into five pseudo-components including the volatile components (CO₂), the light components (C₄–C₆), the intermediate components (C₇–C₁₅), the transitive components (C₁₆–C₃₀) and the heavy components (C₃₁–C₄₀). The pseudo-components of the oil are acquired by matching the density, the viscosity, the gas–oil ratio and the saturation pressure of the actual reservoir oil. The comparison between the actual values and the fitting values is presented in Table 2. It can be discovered that the relative error for all the parameters is less than 5%. Therefore the reservoir fluid model can reflect the actual reservoir oil properties and is accurate enough to be used in the numerical simulation model.



Figure 5. Geological model of CO₂ huff-n-puff in tight oil reservoirs (Five layers).

Table 1. Parameter settings in the compositional model.

Parameters	Values	Parameters	Values
Radius/m	30×10	Horizontal permeability/ $10^{-3} \ \mu m^2$	0.1
Thickness/m	5×3	Vertical permeability $/10^{-3} \ \mu m^2$	0.01
Depth/m	2500	Gas injection rate/sm ³ /d	50,000
Pressure/MPa	18.0	Gas injection time/day	60
Temperature/°C	108	Soaking time/day	60
Oil saturation/%	50	Production time/day	120
Porosity/%	10	Bottom hole pressure/MPa	13.0

Table 2. Comparison between the actual and fitted properties of the crude oil.

Parameters	Actual Values	Fitting Values	Relative Error
Oil density (50 °C, 0.1 MPa) kg/m ³	855	858	0.35%
Oil viscosity (50 °C, 0.1 MPa) mPa·s	23	24	4.35%
Saturation pressure MPa	4.97	5.15	3.62%
Gas oil ratio sm ³ /m ³	19.5	20.0	2.56%

3.2. Effect of Production Time

After being injected underground, considering the special conditions underground, CO_2 will reach a supercritical state. Supercritical CO_2 has a strong ability to be extracted and will interact with the reservoir oil. The light components in the oil will be extracted, which leads to the oil composition variation. The differences between the composition of the produced oil and original oil are significant. Figure 6 illustrates the produced oil composition variation time during the CO_2 huff-n-puff. In comparison with the original oil composition (see the red box in Figure 6), the composition of the produced oil undergoes significant differences and varies with production time. At

the very beginning of production, the proportion of heavy components in the produced oil is noticeably higher than that in the original oil. The oil near the well bore is first produced at the very beginning of the production. Since the supercritical CO₂ continuously extracts the light components of the oil near the well bore when the CO_2 is injected, the proportion of the heavy components in the oil near the well bore increases, while that of the light components decreases. In the early stages of production, the oil near the well bore is preferentially displaced under the elastic effect and the gas driving effect. Therefore the content of heavy components in the oil produced at the very beginning is much higher than in the original oil. Meanwhile, the density and the viscosity of the oil produced at the very beginning are much higher than those of the original oil (see Figure 7). The properties of the produced oil are worsened, which is unfavorable for oil production as well as oil transportation. It is suggested that oil viscosity reducers need to be added to the well during the early stages of oil production for improving the produced oil properties as well as for reducing the flow resistance of the crude oil in the well bore and the surface gathering pipelines. During the production period, the oil near the well bore is gradually completely produced, which causes a decrease in the proportion of heavy components in the produced oil. Furthermore, as the reservoir pressure decreases, the effect of the elastic energy and the gas driving becomes weaker. The effect of the CO_2 extraction plays a more and more significant role in the oil production. Correspondingly, as for the produced oil, the proportion of the light and intermediate components is increased continuously, while that of the heavy components is decreased gradually. Meanwhile, the viscosity and the density of the produced oil are gradually reduced. At the later stages of oil production, the extraction effect of the CO_2 plays a dominant role in oil production. The light and intermediate components of the oil are continuously extracted by the CO₂ and are produced simultaneously, which causes the proportion of the light to intermediate components to be high in the produced oil while the content of the heavy components is low. Meanwhile, the density and viscosity of the produced oil are much lower than those of the original oil. The oil properties are significantly improved, which is advantageous for oil production and transportation.



Figure 6. Composition of produced oil varies with production time.

3.3. Effect of Reservoir Pressure

Figure 8 illustrates the produced oil composition variation under different reservoir pressure at the very beginning of production. In comparison with the original oil, the content of heavy components is significantly increased in the produced oil, while that of light components, intermediate components and transitive components is decreased. In addition, it is demonstrated that the content of the intermediate and the transitive components in the produced oil is lifted with the increasing of the reservoir pressure, while the content of the

heavy components is decreased with the increasing of the reservoir pressure. The miscibility of CO₂ with crude oil is increased with reservoir pressure. Miscibility flooding may occur during CO_2 injection under high-pressure conditions, which causes the proportion of heavy components in the oil near the well bore to decrease while the content of the intermediate and transitive components increases. This is consistent with the research results of Li et al. (2021) [45] and Cao et al. (2013) [46]. During production, the oil close to the well bore is driven out first under the effect of the elastic energy and the gas driving. Therefore, the proportion of the heavy components in the produced oil is decreased with the increasing of the reservoir pressure, while the content of the intermediate and the transitive components is increased with the increasing of the reservoir pressure. Meanwhile, the viscosity and the density of the produced oil are significantly higher than those of the original oil at the very beginning of the oil production. Furthermore, as the reservoir pressure increases, the viscosity and density of the produced oil decrease (Figure 9). At the later stages of production, the effect of the elastic energy and the gas driving is weakened gradually. The CO₂ extraction effect is of great importance to oil production. More intermediate and light components are extracted and produced, which causes the density and the viscosity of the produced oil to be much lower than that of the original oil. The oil properties are notably improved. Moreover, due to the fact the reservoir pressure tends to be consistent in different models in the later stages of oil production, the extraction effect of CO_2 is similar. Therefore, the viscosity and density of the produced oil tend to be equal.



Figure 7. Density and viscosity of produced oil varies with production time.



Figure 8. Composition of produced oil varies with reservoir pressure.



Figure 9. Viscosity and density of produced oil varies with reservoir pressure.

3.4. Effect of Reservoir Temperature

Figure 10 illustrates the produced oil composition variation under different reservoir temperatures at the early stages of oil production. Significant differences can be seen between the composition of the produced oil and the original oil. Generally, the content of the light components (C_4 – C_6) and intermediate components (C_7 – C_{15}) is decreased, while that of the transitive components (C_{16} – C_{30}) and heavy components (C_{31} – C_{40}) is increased in the produced oil. Meanwhile, the proportion of heavy components in the produced oil is decreased with the decreasing of the reservoir temperature, while the relationship between the temperature and the content of the intermediate and the transitive components is discovered to present an opposite tendency. In low temperature conditions, the miscibility effect between the CO₂ and the crude oil is strengthened. Miscibility flooding may occur near the well bore during the CO_2 injection process, which may reduce the proportion of heavy components in the oil near the well bore. This is consistent with the research results of Li et al. (2021) [45] and Zanganeh et al. (2012) [47]. During production, the oil near the well bore is produced first. Therefore, at the very beginning of the production, the proportion of heavy components in the produced oil decreases with the decreasing of the reservoir temperature. In addition, the viscosity and density of the produced oil in the early stages of production are significantly higher than those of the original oil (see Figure 11). Moreover, the viscosity and density of the produced oil increase with the reservoir temperature. At the later stages of production, the extraction of CO₂ gradually occupies a dominant position in the oil production. The light and intermediate components are extracted and produced, with the viscosity and the density of the produced oil much lower than those of the original oil. The oil properties of the produced oil are remarkably improved, which is beneficial for oil production and transportation. Compared with the impacts of the reservoir pressure, the influences of reservoir temperature on the viscosity and density of the produced oil are much more significant. There are still significant differences in the viscosity and density of the produced oil at different temperatures in the later stages of production.



Figure 10. Composition of produced oil varies with reservoir temperature.



Figure 11. Viscosity and density of produced oil varies with reservoir temperature.

4. Conclusions and Suggestions

(1) CO₂ huff-n-puff experiments demonstrate that the differences between the composition of the produced oil and the original oil are significant, which verifies that CO_2 has a strong extraction effect on the oil.

(2) CO_2 mainly extracts light to intermediate components from the oil. In comparison with the original oil, the composition of the produced oil becomes lighter both for the heavy oil sample and the light oil sample. However, the composition variation for the light oil sample is more significant. CO_2 huff-n-puff is more favorable for light oil reservoirs.

(3) The numerical simulation study demonstrates that production time, reservoir pressure and reservoir temperature are of great importance to the composition of the produced oil. The hydrocarbon distribution of the oil becomes lighter with the increasing of the production time and formation pressure, while it becomes heavier with the increasing of the reservoir temperature at the very beginning of the production.

(4) During the very beginning of production, the oil viscosity and the oil density are both much higher in comparison with the original stage, with increases of 25.7% and 200%, respectively. It is suggested that viscosity reducers can be added into the well at the very beginning of production to improve the oil properties. During the later stages of production, the properties of the produced oil are significantly improved in the light of the extraction effect of CO_2 , which causes the viscosity and density of the produced oil to be 3.5% and 15.1% lower than those of the original state, respectively.

Author Contributions: Methodology, H.G. and T.L.; software, X.W.; validation, X.W., C.W., Z.C. and T.L.; formal analysis, B.H.; investigation, B.H., C.W. and Z.C.; resources, Z.Z.; writing—original draft preparation, B.H.; writing—review and editing, N.Z. and D.W.; supervision, H.G. and Z.Z.; project administration, H.G.; funding acquisition, Z.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the financial supports from the Fundamental Research Program of Shanxi Province (202103021224333), the Higher Education Science and Technology Innovation Project of Shanxi Province (2022L600), and the Xi'an Shiyou University Graduate Innovation and Practice Ability Training Plan (YCS23112011).

Data Availability Statement: We state that the data is unavailable due to privacy or ethical restrictions of the company and university.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Fu, J.; Yu, J.; Xu, L.; Niu, X.; Feng, S.; Wang, X.; You, Y.; Li, T. New Progress in Exploration and Development of Tight Oil in Ordos Basin and Main Controlling Factors of Large-scale Enrichment and Exploitable Capacity. *China Pet. Explor.* 2015, 20, 9–19.
- Jia, Z.; Cheng, L.; Zhou, J.; Cao, R.; Pu, B.; Jia, P.; Chen, M. Upscaling simulation method of fluid flow for fracturing-shut in-flowback-production process in tight oil reservoirs: Hysteresis effects of capillary pressure and relative permeability. *Geoenergy Sci. Eng.* 2023, 226, 211792.
- Syed, F.I.; Dahaghi, A.K.; Muther, T. Laboratory to field scale assessment for EOR applicability in tight oil reservoirs. *Pet. Sci.* 2022, 19, 2131–2149. [CrossRef]
- Mohamedy, T.; Yang, F.; Mbarak, S.S.; Gu, J. Investigation on the performance between water alternating gas and water huff n puff techniques in the tight oil reservoir by three-dimensional model simulation: A case study of Jilin tight oil field. *J. King Saud* Univ.-Eng. Sci. 2022, 34, 359–367.
- Syed, F.I.; Muther, T.; Van, V.P.; Dahaghi, A.K.; Negahban, S. Numerical Trend Analysis for Factors Affecting EOR Performance and CO₂ Storage in Tight Oil Reservoirs. *Fuel* 2022, *316*, 123307. [CrossRef]
- Cao, A.; Li, Z.; Zheng, L.; Bai, H.; Zhu, D.; Li, B. Nuclear magnetic resonance study of CO₂ flooding in tight oil reservoirs: Effects of matrix permeability and fracture. *Geoenergy Sci. Eng.* 2023, 225, 211692.
- Gao, H.; Cao, J.; Wang, C.; He, M.; Dou, L.; Huang, X.; Li, T. Comprehensive characterization of pore and throat system for tight sandstone reservoirs and associated permeability determination method using SEM, rate-controlled mercury and high pressure mercury. J. Pet. Sci. Eng. 2019, 174, 514–524. [CrossRef]
- 8. Wang, W.; Su, Y.; Mu, L.; Tang, M.R.; Gao, L. Influencing factors of stimulated reservoir volume of vertical wells in tight oil reservoirs. *J. China Univ. Pet. (Ed. Nat. Sci.)* 2013, 37, 93–97.
- 9. Kang, Y.; Tian, J.; Luo, P.; You, L.; Liu, X. Technical bottlenecks and development strategies of enhancing recovery for tight oil reservoirs. *Acta Pet. Sin.* 2020, *41*, 467–477.
- 10. Han, B.; Cui, G.; Wang, Y.; Zhang, J.; Zhai, Z.; Shi, Y.; Yan, F.; Li, W. Effect of fracture network on water injection huff-puff for volume stimulation horizontal wells in tight oil reservoir: Field test and numerical simulation study. *J. Pet. Sci. Eng.* **2021**, 207, 109106.
- 11. Akbarabadi, M.; Alizadeh, A.; Piri, M.; Nagarajan, N. Experimental evaluation of enhanced oil recovery in unconventional reservoirs using cyclic hydrocarbon gas injection. *Fuel* **2023**, *331*, 125676. [CrossRef]
- 12. Huang, X.; Gao, H.; Dou, L.B. Micro pore structure and water-flooding characteristics on tight sandstone reservoir. *J. China Univ. Pet. (Ed. Nat. Sci.)* **2020**, *44*, 80–88.
- 13. Tang, X.; Li, Y.; Han, X.; Zhou, Y.; Zhan, J.; Xu, M.; Zhou, R.; Cui, K.; Chen, X.; Wang, L. Dynamic characteristics and influencing factors of CO₂ huff and puff in tight oil reservoirs. *Pet. Explor. Dev.* **2021**, *48*, 817–824. [CrossRef]
- 14. Pu, C.; Kang, S.; Pu, J.; Gu, Y.; Gao, Z.; Wang, Y.; Wang, K. Progress and development trend of water huff-n-puff technology for horizontal wells in tight oil reservoirs in China. *Acta Pet. Sin.* **2023**, *44*, 188–206.
- 15. Wu, Z.; Zeng, Q.; Li, J.; Wang, L. New effective energy-supplement development method of waterflood huff and puff for the oil reservoir with stimulated reservoir volume fracturing. *Pet. Geol. Recovery Effic.* **2017**, *24*, 78–83+92.

- 16. Li, Z.; Qu, X.; Liu, W.; Lei, Q.; Sun, H.; He, Y. Development modes of Triassic Yanchang Formation Chang 7 Member tight oil in Ordos Basin, NW China. *Pet. Explor. Dev.* **2015**, *42*, 217–221.
- 17. Qu, X.; Lei, Q.; Gao, W.; Zhang, L.; He, Y.; Wang, B. Experimental study on imbibition of Chang7 tight oil cores in Erdos Basin. J. China Univ. Pet. (Ed. Nat. Sci.) 2018, 42, 102–109.
- 18. Sheng, J.J. What type of surfactants should be used to enhance spontaneous imbibition in shale and tight reservoirs? *J. Pet. Sci. Eng.* **2017**, 159, 635–643. [CrossRef]
- 19. Li, S.; Yang, S.; Gao, X.; Wang, M.; Yu, J. Experimental study on liquid production law, oil recovery mechanism, and influencing factors of water huff-n-puff in the tight sedimentary tuff oil reservoir. *J. Pet. Sci. Eng.* **2022**, *208*, 109721. [CrossRef]
- Wang, L.; Tian, Y.; Yu, X.; Wang, C.; Yao, B.; Wang, S.; Winterfeld, P.H.; Wang, X.; Yang, Z.; Wang, Y.; et al. Advances in improved/enhanced oil recovery technologies for tight and shale reservoirs. *Fuel* 2017, 210, 425–445. [CrossRef]
- Wang, X.; Zhang, Y.; Zhang, J. EOR mechanisms of CO₂ huff and puff process for heavy oil recovery. J. China Univ. Pet. (Ed. Nat. Sci.) 2021, 45, 102–111.
- 22. Sun, L.; Li, Z.; Dou, H. Laboratory Evaluation and Parameter Optimization of CO₂ Huff-n-puff in Ultra-low Permeability Reservoirs. *Oilfield Chem.* **2018**, *35*, 268–272.
- Ren, B.; Male, F.; Duncan, I.J. Economic analysis of CCUS: Accelerated development for CO₂ EOR and storage in residual oil zones under the context of 45Q tax credit. *Appl. Energy* 2022, 321, 119393.
- Ren, B.; Duncan, I.J. Maximizing oil production from water alternating gas (CO₂) injection into residual oil zones: The impact of oil saturation and heterogeneity. *Energy* 2022, 222, 119915.
- Sun, R.; Yu, W.; Xu, F.; Pu, H.; Miao, J. Compositional simulation of CO₂ Huff-n-Puff process in Middle Bakken tight oil reservoirs with hydraulic fractures. *Fuel* 2019, 236, 1446–1457. [CrossRef]
- 26. Wang, T.; Wang, L.; Meng, X.; Chen, Y.; Song, W.; Yuan, C. Key parameters and dominant EOR mechanism of CO₂ miscible flooding applied in low-permeability oil reservoirs. *Geoenergy Sci. Eng.* **2023**, 225, 211724. [CrossRef]
- Li, L.; Zhou, X.; Wang, R.; Zhang, X.; Ma, S.; Su, Y.; Wang, C.; Luo, W.; Sun, H. Microscopic experiment study on mechanisms of oil-gas interaction and CO₂-surfactant flooding with different temperatures and pressures. *J. CO₂ Util.* 2023, *69*, 102389. [CrossRef]
- 28. Xiaodong, S.; Linghui, S.; Jianfei, Z.; Binhui, L.; Xue, H.; Huimin, L.; Chenggang, J. Carbon dioxide huff-puff technology and application in tight oil horizontal wells in the northern Songliao Basin. *Acta Pet. Sin.* **2022**, *43*, 998–1006.
- 29. Fan, X.; Pu, W.; Shan, J.; Du, D.; Qin, J.; Gao, Y. Feasibility of enhanced oil recovery by CO₂ huff-n-puff in tight conglomerate reservoir. *Pet. Reserv. Eval. Dev.* **2021**, *11*, 831–836.
- 30. Wei, B.; Zhong, M.; Gao, K.; Li, X.; Zhang, X.; Cao, J.; Lu, J. Oil recovery and compositional change of CO₂ huff-n-puff and continuous injection modes in a variety of dual-permeability tight matrix-fracture models. *Fuel* **2020**, 276, 117939. [CrossRef]
- 31. Afari, S.; Ling, K.; Sennaoui, B.; Maxey, D.; Oguntade, T.; Porlles, J. Optimization of CO₂ huff-n-puff EOR in the Bakken Formation using numerical simulation and response surface methodology. *J. Pet. Sci. Eng.* **2022**, *215*, 110552.
- 32. Fakher, S.; Imqam, A. Application of carbon dioxide injection in shale oil reservoirs for increasing oil recovery and carbon dioxide storage. *Fuel* **2020**, *265*, 116944. [CrossRef]
- 33. Lee, J.H.; Jeong, M.S.; Lee, K.S. Comprehensive modeling of CO₂ Huff-n-Puff in asphaltene-damaged shale reservoir with aqueous solubility and nano-confinement. *J. Ind. Eng. Chem.* **2020**, *90*, 232–243. [CrossRef]
- 34. Du, D.J.; Pu, W.F.; Jin, F.Y.; Liu, R. Experimental study on EOR by CO₂ huff-n-puff and CO₂ flooding in tight conglomerate reservoirs with pore scale. *Chem. Eng. Res. Des.* **2020**, *156*, 425–432. [CrossRef]
- Du, D.; Li, C.; Song, X.; Liu, Q.; Ma, N.; Wang, X.; Shen, Y.; Li, Y. Experimental study on residue oil distribution after the supercritical CO₂ huff-n-puff process in low permeability cores with Nuclear Magnetic Resonance (NMR). *Arab. J. Chem.* 2021, 14, 103355. [CrossRef]
- Li, L.; Su, Y.; Hao, Y.; Zhan, S.; Lv, Y.; Zhao, Q.; Wang, H. A comparative study of CO₂ and N₂ huff-n-puff EOR performance in shale oil production. *J. Pet. Sci. Eng.* 2019, 181, 106174. [CrossRef]
- Xue, W.; Wang, Y.; Chen, Z.; Liu, H. An integrated model with stable numerical methods for fractured underground gas storage. J. Clean. Prod. 2023, 393, 136268. [CrossRef]
- Zhu, C.F.; Guo, W.; Wang, Y.P.; Li, Y.J.; Gong, H.J.; Xu, L.; Dong, M.Z. Experimental study of enhanced oil recovery by CO₂ huf-n-puff in shales and tight sandstones with fractures. *Pet. Sci.* 2021, 18, 852–869.
- Chen, H.; Liu, X.L.; Jia, N.H.; Zhang, K.; Yang, R.; Yang, S. Prospects and key scientific issues of CO₂ near-miscible flooding. *Pet. Sci. Bull.* 2020, 3, 392–401.
- 40. Ma, Q.; Yang, S.; Chen, H.; Wang, L.; Qian, K.; Meng, Z.; Hao, L.; Wang, Z. Effect and influencing factors of CO₂ huff and puff in a tight oil reservoir—Taking the Lucaogou formation in the Xinjiang Jimsar sag as an example. *Pet. Sci. Bull.* **2018**, *4*, 434–445.
- Jia, Z.H.; Cao, R.Y.; Wang, B.Y.; Cheng, L.S.; Zhou, J.C.; Pu, B.B.; Yin, F.G.; Ma, M. Effects of CH₄/CO₂ multi-component gas on components and properties of tight oil during CO₂ utilization and storage: Physical experiment and composition numerical simulation. *Pet. Sci.* 2023, *in press.* [CrossRef]
- Seyyedi, M.; Mahzari, P.; Sohrabi, M. A comparative study of oil compositional variations during CO₂ and carbonated water injection scenarios for EOR. J. Pet. Sci. Eng. 2018, 164, 685–695. [CrossRef]

- Zhang, X.; Li, L.; Su, Y.; Da, Q.; Fu, J.; Wang, R.; Chen, F. Microfluidic investigation on asphaltene interfaces attempts to carbon sequestration and leakage: Oil-CO₂ phase interaction characteristics at ultrahigh temperature and pressure. *Appl. Energy* 2023, 348, 121518.
- 44. Peng, D.; Robinson, D.B. A New Two-Constant Equation of State. Ind. Eng. Chem. Fundam. 1976, 15, 59-64. [CrossRef]
- 45. Li, R.; Liao, X.; Zou, J.; Gao, C.; Zhao, D.; Zhang, Y.; Zhou, X. Asphaltene Deposition during CO₂ Flooding in Ultralow Permeability Reservoirs: A Case Study from Changqing Oil Field. *Geofluids* **2021**, 2021, 6626114.
- 46. Cao, M.; Gu, Y. Oil recovery mechanisms and asphaltene precipitation phenomenon in immiscible and miscible CO₂ flooding processes. *Fuel* **2013**, *109*, 157–166. [CrossRef]
- 47. Zanganeh, P.; Ayatollahi, S.; Alamdari, A.; Zolghadr, A.; Dashti, H.; Kord, S. Asphaltene Deposition during CO₂ Injection and Pressure Depletion: A Visual Study. *Energy Fuels* **2012**, *26*, 1412–1419. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.