



# Article Mechanism and Main Control Factors of CO<sub>2</sub> Huff and Puff to Enhance Oil Recovery in Chang 7 Shale Oil Reservoir of Ordos Basin

Tong Wang <sup>1,2</sup>, Bo Xu <sup>1,2,\*</sup>, Yatong Chen <sup>1,2</sup> and Jian Wang <sup>3</sup>

- <sup>1</sup> School of Petroleum Engineering, Xi'an Shiyou University, Xi'an 710065, China; wangtong214@126.com (T.W.); c12370904@126.com (Y.C.)
- <sup>2</sup> Key Laboratory of Special Stimulation Technology for Oil and Gas Fields in Shaanxi Province, Xi'an 710065, China
- <sup>3</sup> Research Institute of Exploration and Development, Shengli Oilfield Co., Sinopec, Dongying 257015, China; dkywj@163.com
- Correspondence: xsyuxb@126.com

Abstract: The Chang 7 shale oil reservoir has low natural energy and is both tight and highly heterogeneous, resulting in significant remaining oil after depletion development. CO<sub>2</sub> huff and puff (huff-n-puff) is an effective way to take over from depletion development. Numerous scholars have studied and analyzed the CO<sub>2</sub> huff-n-puff mechanism and parameters based on laboratory core sample huff-n-puff experiments. However, experimental procedures are not comprehensive, leading to more general studies of some mechanisms, and existing CO<sub>2</sub> huff-n-puff experiments struggle to reflect the effect of actual reservoir heterogeneity due to the limited length of the experimental core samples. In this paper, CO<sub>2</sub> huff-n-puff laboratory experiments were performed on short (about 5 cm) and long (about 100 cm) core samples from the Chang 7 shale oil reservoir, and the microscopic pore fluid utilization in the short samples was investigated using a nuclear magnetic resonance (NMR) technique. We then analyzed and discussed the seven controlling factors of CO<sub>2</sub> huff-n-puff and their recovery-enhancing mechanisms. The experimental results show that the cumulative recovery increased with the number of huff-n-puff cycles, but the degree of cycle recovery decreased due to the limitation of the differential pressure of the production. The significant increase in recovery after the CO<sub>2</sub> mixed-phase drive was achieved by increasing the minimum depletion pressure as well as the gas injection amount. The soaking time was adjusted appropriately to ensure that the injected energy was thoroughly utilized; too short or too long a soaking time was detrimental. The pressure depletion rate was the main factor in the CO<sub>2</sub> huff-n-puff effect in shale. If the pressure depletion rate was very high, the effective permeability loss was larger. In the CO<sub>2</sub> huff-n-puff process of the Chang 7 shale oil reservoir, the improvement in oil recovery was mainly contributed to by mesopores and small pores. The huff-n-puff experiments using long cores could better characterize the effect of heterogeneity on the huff-n-puff effect than short cores.

Keywords: Chang 7 shale oil reservoir; CO<sub>2</sub> huff-n-puff; enhance oil recovery (EOR); heterogeneity

## 1. Introduction

This paper investigates the potential of  $CO_2$  huff-n-puff to enhance oil recovery in the challenging context of the Chang 7 shale oil reservoir, characterized by low natural energy and high heterogeneity. Most shale oil reservoirs are depleted using horizontal wells and hydraulic fracturing technology, which typically yield recoveries of less than 10%, and are less effective at improving recovery [1–3].  $CO_2$  has a low density and excellent all-around performance, and it is easy to obtain at a low cost. Its solubility in crude oil is extremely good, it can reduce the viscosity of crude oil, and it can increase the expansion coefficient of crude oil [4,5]. Therefore,  $CO_2$  huff-n-puff can be used as an efficient way to take over



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**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/). from the development of depletion. Proper utilization and storage of CO<sub>2</sub> play an essential role in shale oil development [6,7].

In recent years, numerous researchers have extended the related research on CO<sub>2</sub> huff-npuff techniques and achieved some interesting results. Gamadi and Li et al. [8–10] conducted CO<sub>2</sub> huff-n-puff laboratory experiments on shale cores and set various parameters such as soaking time, experimental pressure, and huff-n-puff cycles. They found that the  $CO_2$  huffn-puff technique significantly improved the recovery of shale oil after adjusting parameters. Li and Wan et al. [11,12] conducted a  $CO_2$  huff-n-puff laboratory experiment with shale oil to study the influence of permeability, injection pressure, and soaking time on the huffn-puff effect. Tang et al. [13,14] conducted a core CO<sub>2</sub> huff-n-puff laboratory experiment and investigated the influences of CO<sub>2</sub> injection amount, soaking time, production rate, and  $CO_2$  injection rate on the  $CO_2$  huff-n-puff effect. They concluded that the amount of  $CO_2$  injected and the production rate were the main factors. Yu and Zhang et al. [15,16] investigated the effects of injection pressure, soaking time, and huff-n-puff cycles on the  $CO_2$  sweep range using numerical simulation technology. They concluded that the huff-npuff cycle had a minor effect and that the injection pressure was the main factor affecting the  $CO_2$  sweep. Liu et al. [17] used NMR technology to monitor the real-time migration of core matrix crude oil at different stages of  $CO_2$  huff-n-puff. The effects of injection pressure, soaking time, huff-n-puff cycle, and shut-in time on the CO<sub>2</sub> huff-n-puff effect were investigated. It was concluded that simply increasing the injection pressure could improve the oil displacement efficiency without increasing the sweeping range.

At present, numerous scholars have carried out laboratory experiments on  $CO_2$  huffn-puff with good results. However, the considered influences are not comprehensive, the mechanism studies are more general, and the interpretation of the experimental results is not clear enough. Most of the laboratory experiments use a short core (about 5 cm) for  $CO_2$  huff-n-puff experiments, and  $CO_2$  breakthrough is extremely common in laboratory experiments on the short core but rarely occurs in actual field development. Due to the limited total amount of crude oil in the short core, the measurement error of the experimental setup has a large impact, which cannot accurately reflect the mechanism of  $CO_2$  huff-n-puff in the actual formation [18–20]. Moreover, there is also a difference between long and short cores, characterizing the effect of heterogeneity on the huff-n-puff effect in real formations. Finally, most of the studies based on shale oil  $CO_2$  huff-n-puff focus on the improvement in shale oil recovery and optimization of injection production parameters, and very few of them explain the reasons for the improvement in shale oil  $CO_2$ huff-n-puff from the mechanism study side.

Based on the above problems, this paper used a long core (about 100 cm) to conduct  $CO_2$  huff-n-puff experiments. Then, seven groups of experiments were established to comprehensively compare the influence mechanisms of huff-n-puff cycles, minimum depletion pressure, pressure depletion rate, soaking time, gas injection method,  $CO_2$  injection amount, and  $CO_2$  injection rate on the effect of  $CO_2$  huff-n-puff. We also used NMR to characterize the fluid utilization after a short-core huff-n-puff experiment. A comparison of huff-n-puff experiments in short and long cores was performed to clarify the mechanism and main controlling factors of  $CO_2$  huff-n-puff in shale oil reservoirs. The primary objective of this study is to analyze the mechanisms and main control factors influencing  $CO_2$ -huff-n-puff-enhanced oil recovery in the Chang 7 shale oil reservoir.

#### 2. Experimental Instruments and Methods

#### 2.1. Experimental Material

The core used in the experiment is taken from the natural core of the reservoir section of the Chang 7 shale oil reservoir, which belongs to the black shale of the Yanchang 7 formation in the Ordos Basin. According to previous fine tube experiment results, the minimum miscible pressure (MMP) of  $CO_2$  and crude oil in the Chang 7 shale oil reservoir is 13.4 MPa. The crude oil used for the experiment is simulated oil, which is proportioned according to the original formation crude oil (the density of the ground crude oil is

0.89 g/cm<sup>3</sup>, and the viscosity of the crude oil at 60 °C is 3.98 mPa·s). The gas used in the experiment is CO<sub>2</sub>, which has a purity of 99.99%. Twenty short cores of the Chang 7 shale oil are concatenated into a long core in a certain form. The detailed physical parameters of the cores are given in Table 1. The total length of the long core is calculated to be 975.31 cm, and the average permeability is  $0.151 \times 10^{-3} \,\mu\text{m}^2$ .

Table 1. Core sample parameters table.

Sample Number	Length /mm	Diameter /mm	Permeability /(10 <sup>-3</sup> μm <sup>2</sup> )	Porosity /%
1	53.20	25.28	0.065	1.20
2	50.41	25.23	0.115	1.85
3	55.25	25.22	0.234	4.02
4	35.80	25.21	0.142	2.56
5	30.42	25.35	0.175	2.80
6	45.25	25.20	0.232	3.75
7	43.55	25.35	0.162	2.02
8	54.20	25.23	0.121	2.15
9	48.12	25.15	0.085	1.88
10	53.25	25.13	0.065	1.15
11	45.32	25.02	0.078	1.45
12	46.25	25.52	0.295	4.20
13	56.46	25.25	0.280	4.75
14	51.20	25.35	0.142	4.35
15	55.62	25.42	0.120	1.79
16	50.24	25.16	0.076	1.89
17	54.25	25.16	0.089	1.63
18	49.63	25.24	0.213	3.98
19	47.25	25.16	0.203	3.03
20	49.64	25.18	0.126	2.20

#### 2.2. Experimental Device

The long-core CO<sub>2</sub> huff-n-puff experimental device consists mainly of a core support, ISCO displacement pump, thermostat, back pressure pump, hand crank pump, and collection device. The maximum length of the core that can be inserted is 1 m. The temperature of the thermostat is up to 150 °C. The maximum pressure of the core holder system is 70 MPa. The flow accuracy of the pump is 0.01 mL. The experimental device is shown in Figure 1. The model of the NMR device is a Mini-MR, the magnetic field strength is set to 0.5 T, and the frequency of the RF pulse can be controlled from 1 to 30 MHz. Additional devices used in this experiment are an electronic balance, caliper gauge, gas flow meter, and CO<sub>2</sub> cylinder.



**Figure 1.** Flow chart of  $CO_2$  huff-n-puff experimental device. The red numbers 1–6 denote six different valves in the six-way valve.

The consistency of the  $CO_2$  huff-n-puff experimental device for the short core is the same as that for the long core, with the only difference being the shortening of the core support. The core support of the short-core experimental device can be inserted up to a maximum length of 30 cm. A rubber cylinder exists in the annulus between the core support and the core, and the diameter of the core that can be inserted in the core support ranges from 2.5 cm to 3.5 cm.

## 2.3. Experimental Principle (NMR)

NMR technology was mainly used in the medical field in its early stage and was introduced into oil and gas field development later on. It has been widely used and has clear advantages over other techniques in the study of pore structures and pore fluids in reservoirs [21]. The principle of the NMR technique is to determine the response parameter of a hydrogen nucleus in a magnetic field. Then, by detecting the hydrogen nuclei in the reservoir fluid distribution in the pore structure, porosity, permeability, mobile fluid distribution pore throat structure, and other related parameters can be obtained. With this technology, the position of the pore fluid before and after CO<sub>2</sub> huff-n-puff can be determined, and the mobilization of the reservoir oil and gas resources can be studied from a microscopic point of view, thus evaluating the effect of oil displacement.

At the start of the experiment, the core to be tested is placed in a uniformly distributed magnetic field generated by the instrument. A vector of magnetized hydrogen nuclei is then created in the reservoir fluid. A specific frequency is then applied to the core and the NMR phenomenon occurs [22]. The transverse relaxation time  $T_1$  and longitudinal relaxation time  $T_2$  of the hydrogen nuclei undergoing the relaxation motion are analyzed in terms of the parameters. It follows that the pore radius is inversely proportional to the relaxation rate of the hydrogen nucleus, i.e.,

$$\frac{1}{T_2} = \rho(\frac{S}{V})_{\text{pore}} \tag{1}$$

where  $\rho$  is the relaxation strength constant and S/V is the specific surface of the throat. S/V is proportional to the pore radius r;  $S/V = F_S/r$ .  $F_S$  is the pore shape factor (dimensionless), and its magnitude varies with the pore model. Therefore, the core pore throat T relaxation time can be expressed as

$$T_2 = T_{2S} = \frac{1}{\rho F_S} r \tag{2}$$

Since  $\rho$  and  $F_S$  are dimensionless constants, it can be concluded from the equation that the value of  $T_2$  is proportional to the radius of the pore throat of the reservoir rock, and its larger value reflects the larger pore throat.

## 3. Experiments

#### 3.1. Experimental Preparation

The selected core samples were thoroughly washed and dried, after which the porosity and permeability of the core samples were determined. The appropriate cores were selected as the experimental cores, and the cores were sorted according to their length and permeability according to Burra's rule. In addition, a layer of thermal filtration membrane was added in the middle of the core so that the pore channels between the two different cores could be connected.

## 3.2. Experimental Procedure

(1) We configure simulated formation water (salinity of 20,000 mg/L) according to the reservoir geological data and place the experimental core in the simulated formation water, covering the top of the core. The experimental core is then vacuumed for 48 h so that it is fully saturated with simulated formation water. The core porosity

is calculated using the difference in weight between the core samples before and after saturation.

- (2) We inject simulated oil into the core, record the amount of water produced, and calculate the bound water saturation. When the core pressure reaches the formation pressure, we close the inlet end and age the core for 24 h.
- (3) At a temperature of 60 °C, in the "huffing" stage, CO<sub>2</sub> is injected into the core at a certain rate with a displacement pump, and the pressure is raised to the design value. Then, the inlet end is closed. When the soaking time meets the experimental requirements, the inlet end is opened to enter the "puffing" stage, and four rounds of huff-n-puff are repeated.
- (4) We investigate the effect of these parameters on CO<sub>2</sub> huff-n-puff recovery by adjusting the parameters of gas injection amount, minimum depletion pressure, soaking time, pressure depletion rate, gas injection method, and gas injection rate.
- (5) After the experiments are completed, we select 6 contrasting cores out of the 20 cores and group them to perform the core huff-n-puff experiment and measure the NMR T<sub>2</sub> spectrum. This is used to study crude oil utilization before and after huff-n-puff in terms of microporosity.

## 4. Results and Discussions

According to the requirements of reservoir development and the study of the huff-npuff mechanism, seven experimental groups were designed, each with four huff-n-puff cycles (Table 2). We investigated the impact of the  $CO_2$  huff-n-puff cycle, minimum depletion pressure, pressure depletion rate, soaking time, gas injection method,  $CO_2$ injection amount, and gas injection rate on the  $CO_2$  huff-n-puff. In contrast to previous experiments, the experimental parameters in this paper were more comprehensive, and the mechanism and main controlling factors of the  $CO_2$  huff-n-puff EOR in the Chang 7 shale oil were investigated in depth.

		Conditions			Results			
Exp No.	Oil Saturation (%)	Gas Injection Rate (mL/min)	Pressure Depletion Rate (MPa/h)	Min Depletion Pressure (MPa)	Max Pressure (MPa)	Gas Injection Amount	Recovery (%)	Cycle Soaking Time
1	60.32	6	3	0.1	11.5	0.2 PV	20.81	Pressure stabilized
2	61.59	10	3	2	13.55	0.3 PV	26.42	Pressure stabilized
3	60.63	10	2	2	13.48	0.3 PV	28.25	Pressure stabilized
4	61.36	10	3	2	13.5	0.3 PV	25.04	1 h
5	60.98	10	3	2	12	-	23.98	Pressure stabilized
6	61.91	6	3	2	12	-	24.75	Pressure stabilized
7	61.82	6	3	0.1	8.5	0.1 PV	8.86	Pressure stabilized
	Fir	First Cycle Second Cycle		Third	Cycle	Fourth Cycle		
Exp No.	Max Pressure	Recovery	Max Pressure	Recovery	Max Pressure	Recovery	Max Pressure	Recovery
	(MPa)	(%)	(MPa)	(%)	(MPa)	(%)	(MPa)	(%)
1	11.5	9.65	6.22	5.12	5.83	3.41	4.94	2.63
2	13.55	12.95	9.12	6.19	8.19	4.12	7.39	3.16
3	13.48	13.69	8.67	6.54	7.83	4.96	6.93	3.06
4	13.43	11.86	8.59	5.32	7.24	4.85	6.32	3.01
5	12	9.85	12	7.14	12	4.32	12	2.67
6	12	10.06	12	7.86	12	3.96	12	2.87
7	8.5	8.86	-	-	-	-	-	-

Table 2. Experimental conditions and results of CO<sub>2</sub> huff-n-puff in the long core.

## 4.1. Huff-n-Puff Cycle

In Experiment 1, the gas injection rate was set to 6 mL/min, the well was soaked until the pressure was stabilized, the pressure depletion rate was 3 MPa/h, and the minimum depletion pressure was 0.1 MPa. The influence of huff-n-puff cycles on the  $CO_2$  huff-n-puff

effect was investigated. In the second cycle of Experiment 1, the production pressure decreased significantly from 11.5 MPa to 6.22 MPa compared with the first cycle, and the cyclic recovery decreased from 9.65% to 5.12% (Figure 2a). As the huff-n-puff cycle progressed, the CO<sub>2</sub> advanced to the distal end of the core, the CO<sub>2</sub> sweep increased, and the effective utilization radius increased, but the recovery increase decreased. Based on previous N<sub>2</sub> adsorption experiments, the pore sizes of the shale in the core hole ranged from 1.59 nm to 161.89 nm, and the molecular diameter of the CO<sub>2</sub> gas was 0.33 nm. Under experimental conditions, the CO<sub>2</sub> gas reached a supercritical state with little interfacial tension with crude oil, excellent oil washing efficiency, and small capillary resistance. It could enter the pore throat where water could not enter and drove out crude oil [23,24].



**Figure 2.** (a) Experiment 1 huff-n-puff cycle oil displacement effect relationship curve; (b) Experiment 1 huff-n-puff cycle rate of oil production.

After the first huff-n-puff cycle of crude oil in the pore of the long core, the easily flowable crude oil in one of the larger pores was returned and drained out. The second cycle, in which an equal amount of  $CO_2$  gas was injected, was limited by the reduction in the pore fluid, which prevented the development of higher pressure. The reduction in the production of differential pressure limited the flow of  $CO_2$ , did not significantly improve the sweep coefficient, and made it difficult to utilize the crude oil in the small pores, which in turn affected the recovery of the core. In actual production, the remaining oil content in the near-well zone decreased, and the relative content of light components in the remaining oil decreased, which ultimately led to weaker  $CO_2$  extraction capacity [25]. When the cycle pressure dropped to 2 MPa, the oil recovery was zero, so the depletion pressure (wellhead pressure in the extraction stage) should be set as a lower limit.

The maximum oil production rates were 0.061, 0.055, 0.041, and 0.025 g/min over the four cycles of Experiment 1. The peak oil production rate decreased more as the number of cycles increased (Figure 2b). In the production stage with pressure decrease, the oil production rate quickly reached the peak and then began to decrease. The amount of oil recovered in each cycle decreased rapidly and then increased. This was mainly due to the microscopic pore structure, and the  $CO_2$  gas could not advance uniformly. Since the oil production rate was higher in the first cycle and the highest recovery was eventually achieved, the production time should be extended. By slowing down the pressure depletion rate at the outlet to maintain production pressure in the range of 4–10 MPa for a long time, oil was produced at a higher rate, and cumulative recovery was increased. In actual production, the number of cycles should be minimized considering the development cost.

Figure 3a shows that the cycle recovery measured in Experiment 1 decreased exponentially with an increasing number of huff-n-puff cycles, with a recovery of only 2.63% in the fourth cycle. This indicates that the CO<sub>2</sub> huff-n-puff effect gradually deteriorates under the influence of the decrease in residual oil content and the increase in mobilization difficulty. Figure 3b shows that the cumulative cycle recovery measured in Experiment 1 increased with an increasing number of huff-n-puff cycles, but the magnitude of the increase decreased. The above experimental phenomena indicate that the effective development cycle of shale oil reservoirs is about five cycles or so, which is consistent with previous research results [26].



**Figure 3.** (a) Recovery of different CO<sub>2</sub> huff-n-puff cycles; (b) cumulative recovery from the huff-n-puff process.

#### 4.2. Minimum Depletion Pressure

In Experiment 2, the gas injection rate was set to 10 mL/min, the well was soaked until the pressure was stabilized, the pressure depletion rate was 3 MPa/h, and the minimum depletion pressure was 2 MPa. A comparison of Experiment 1 was performed to analyze the effect of different minimum depletion pressures on the CO<sub>2</sub> huff-n-puff effect. The maximum pressure in the first cycle reached the CO<sub>2</sub> MMP (13.4 MPa) due to the injection of a greater amount of gas (from 0.2 PV to 0.3 PV) and the increase in the lower limit of the production pressure (from 0.1 MPa to 2 MPa). The experiments showed that increasing the minimum depletion pressure during CO<sub>2</sub> huff-n-puff as well as the CO<sub>2</sub> injection amount resulted in a 5.61% increase in recovery. In addition, the first huff-n-puff cycle had an important influence on the total huff-n-puff cycle, which increased the recovery by 3.3%.

After implementing the  $CO_2$  huff-n-puff mixed-phase oil drive, the comparison with the non-mixed-phase huff-n-puff oil drive was better. The viscosity of crude oil was significantly reduced, the interfacial tension was lowered, the flow resistance was reduced, and the sweep efficiency and oil washing efficiency were improved [27]. After increasing the minimum depletion pressure and injecting the same amount of  $CO_2$  gas, the subsequent cycles can reach a higher production pressure up to the  $CO_2$  near-mixed-phase pressure [28]. In real production, the minimum depletion pressure can be appropriately increased in conjunction with economic feasibility issues.

## 4.3. Pressure Depletion Rate

In Experiment 3, the gas injection rate was set to 10 mL/min, the well was soaked until the pressure was stabilized, the pressure depletion rate was 2 MPa/h, and the minimum depletion pressure was 2 MPa. A comparison with Experiment 2 was performed to analyze the effect of different pressure depletion rates on the CO<sub>2</sub> huff-n-puff effect. The pressure depletion rate was 3 MPa/h and 2 MPa/h for Experiment 2 and Experiment 3, and the recovery was 26.42% and 28.25%, respectively (Figure 4a). By reducing the pressure depletion rate, the recovery of the first cycle of Experiment 3 was high, reaching 13.69%, which was the highest among the seven experimental groups, and an increase of 0.74% compared to Experiment 2. From the analysis, it could be concluded that the pressure depletion rate, the production time of the first cycle was considerably extended (from 175 min to 350 min). The CO<sub>2</sub> gas could more completely play the role of viscosity reduction and extraction and carry back additional crude oil for discharging.



**Figure 4.** (a) Effect of pressure depletion rate on cycle recovery; (b) effect of soaking time on cycle recovery.

When the well was opened for production, the elastic energy of the formation worked with the expansion energy of the crude oil to produce the crude oil. If the pressure depletion rate was too high, the flow rate at the outlet end was fast, and the  $CO_2$  gas dissolved in the crude oil was rapidly expelled. The pressure depletion rate affects the sequence of elastic energy release, leading to a large loss of effective permeability of the core at the outlet end. After the  $CO_2$  gas in dissolved crude oil was rapidly discharged, the viscosity-reducing effect of dissolved gas on crude oil was weakened, which affected the flow of crude oil [29,30]. Experiment 3 shows a higher recovery for the first three cycles than Experiment 2. It can be concluded that decreasing the pressure depletion rate improves recovery.

#### 4.4. Soaking Time

In Experiment 4, the gas injection rate was set to 10 mL/min, the well was soaked until the pressure was stabilized, the pressure depletion rate was 3 MPa/h, and the minimum depletion pressure was 2 MPa. A comparison of Experiment 2 was performed to analyze the effect of different soaking times on the  $CO_2$  huff-n-puff effect. The peak oil production rates in the first two cycles of Experiment 4 were extremely close to each other (0.0796 and 0.0799 g/min, respectively), whereas in Experiment 2, the oil production rate in the second cycle decreased significantly compared to the first cycle. The reason for this difference was the reduction in the soaking time. The first and second cycles of Experiment 2 involved soaking for 550 and 210 min, respectively, with recovery of 12.95% and 6.19%. In Experiment 4, the soaking time was reduced to 60 min, and the corresponding recovery for the first two cycles was 11.86% and 5.32%, respectively (Figure 4b), which indicated that the soaking time had a greater effect on the recovery in the first and second cycles. Especially in the first cycle, in which the recovery decreased by 1.09% after reducing the soaking time. The importance of proper soaking time was evident from the experiments, where the optimal soaking time resulted in a 3.21% increase in recovery.

During the CO<sub>2</sub> huff-n-puff process, there are two main parts of the sweep of crude oil, the flow sweep and the diffusion sweep [31,32]. The flow sweep refers to the fraction of CO<sub>2</sub> that enters the reservoir due to the effect of the pressure difference in production; the diffusion sweep refers to the part of the crude oil that depends on the molecular diffusion effect controlled by the concentration difference. The area utilized by the two sweep effects is called the effective utilization radius. In the gas injection phase, due to the large pressure difference, the flow sweep dominates, while in the soaking phase, after the formation pressure is restored to equilibrium, the diffusion sweep dominates. The amount of CO<sub>2</sub> dissolved in the crude oil is positively correlated with the soaking time because the molecular diffusion effect is time-dependent [33]. The effective radius of CO<sub>2</sub> utilization during the soaking stage is the flow sweep dominated by the differential pressure before the formation pressure is returned to equilibrium, as well as the diffusion sweep in the presence of differential molecular concentration. If the soaking time is short and production occurs before the formation pressure returns to equilibrium, the injected energy cannot be thoroughly utilized, which affects the ultimate recovery. If the soaking time is too long after the formation pressure returns to equilibrium, it only relies on the molecular diffusion effect of the  $CO_2$  concentration difference to increase the sweep area, which affects the field development efficiency. Crude oil expansion, which is constantly present during the soaking process, also causes a certain depletion of formation energy and is detrimental to the recovery of crude oil.

In actual production, there should be an upper limit on the soaking time. After the upper limit is reached, the viscosity reduction and extraction reactions of  $CO_2$  with crude oil are sufficient and the amount of  $CO_2$  dissolved in crude oil reaches its maximum value. As illustrated by Fick's law, while extending the soaking time increases the diffusion region, the diffusion rate slows as  $CO_2$  penetrates deeper into the formation. Moreover, crude oil stored deeper in the formation matrix requires extra energy to move. Continuing to increase the soaking time is not appropriate from a field development perspective, resulting in a delay in the production time of opened wells. Therefore, in actual field production, the soaking time should be adjusted to ensure that in the first cycle, the injected  $CO_2$  gas is used to produce crude oil after the formation to be completely utilized. In the subsequent huff-n-puff cycles, the soaking time can be flexible to suit.

#### 4.5. Gas Injection Method

In Experiment 5, the gas injection rate was set to 10 mL/min, the well was soaked until the pressure was stabilized at 12 MPa, the pressure depletion rate was 3 MPa/h, and the minimum depletion pressure was 2 MPa. A comparison with Experiment 4 was performed to analyze the effect of different gas injection methods on the  $CO_2$  huff-n-puff effect. The production pressure of each cycle of Experiment 5 was the same, 12 MPa. The peak oil production rate of the second cycle was a maximum 0.0755 g/min (Figure 5a), and the recovery was 7.14%, which was higher than that of the quantitative gas injection method. Overall, the recovery of Experiment 5 decreased by 1.06% compared to Experiment 4, indicating that constant-pressure gas injection is worse than quantitative gas injection. In the first cycle, the saturation of the crude oil in the pore was so high that only a limited amount of  $CO_2$  needed to be injected to reach the set pressure. For the same soaking time, the swelling and viscosity reduction effects of the  $CO_2$  gas on the crude oil during the first huff-n-puff cycle were not sufficiently exerted due to the limited amount of CO<sub>2</sub> dissolved in the crude oil and the poor effect of sweeping in the formation. In the second cycle, more  $CO_2$  gas had to be injected to reach the set pressure of 12 MPa, due to the reduction in the saturation of the crude. In other words, the "huffing" stage was longer, and a large amount of  $CO_2$  gas came into contact with the crude oil and dissolved, which considerably increased the sweeping area due to the existence of the production pressure difference. In the third and fourth cycles, even if more CO<sub>2</sub> gas was injected, there was no significant increase in recovery because a significant amount of crude oil had been displaced from the near-well zone in the previous two cycles.

The recovery in the first cycle of this experimental group was 9.85%, and the cumulative recovery was 23.98%, which was low compared to the previous four experimental groups. This indicates that constant-pressure gas injection was not suitable for shale  $CO_2$ huff-n-puff to improve recovery. Compared to the quantitative injection of  $CO_2$  gas for production, the degree of utilization of the constant pressure gas injection production was small. In the subsequent third and fourth cycles of injecting a lot of  $CO_2$  gas, the recovery was limited, which led to its economic feasibility.



**Figure 5.** (a) Experiment 5 huff-n-puff oil displacement effect relationship curve; (b) effect of gas injection rate on cycle recovery.

#### 4.6. Gas Injection Rate

In Experiment 6, the gas injection rate was set to 6 mL/min, the well was soaked until the pressure was stabilized, the pressure depletion rate was 3 MPa/h, and the minimum depletion pressure was 2 MPa. The production pressure of each cycle of Experiment 6 was the same, 12 MPa. A comparison with Experiment 5 was performed to analyze the effect of different gas injection rates on the  $CO_2$  huff-n-puff effect. The gas injection rates were 10 mL/min and 6 mL/min for Experiment 5 and Experiment 6, respectively. Experiment 6, compared with Experiment 5 with other conditions unchanged, recovery increased in other huff-n-puff cycles except the third cycle (Figure 5b). It was shown that Experiment 6 increased the recovery by 0.77% after reducing the gas injection rate. This indicates that under the condition of a lower injection rate,  $CO_2$  gas could better overcome the effect of heterogeneity in the core model [34] (the effect of heterogeneity was mainly reflected in the following: the injected  $CO_2$  could not uniformly propel the crude oil, the leading edge of repulsion was unstable, and the sweep efficiency was low).

Since the injection rate of  $CO_2$  affected its viscosity reduction and dissolving effect on crude oil, the contact between  $CO_2$  and crude oil was more sufficient when the injection rate was lower. The gas injection time in Experiment 6 was 30% longer than that in Experiment 5, which maintained the formation pressure gradient for a long time and drove the flow sweep to a broader area. After increasing the gas injection rate, the  $CO_2$  gas chose to enter the large pore with less resistance and could not fully contact the crude oil in the small pore, which affected the efficiency of  $CO_2$  oil washing. In the actual production at the well site, even the crude oil near the near-well zone may be pushed into the pore in the deep part of the formation [35]. Therefore, it was necessary to minimize the influence of gas finger inlet and select the appropriate gas injection rate for production.

#### 4.7. CO<sub>2</sub> Injection Amount

By comparing the experimental results of Experiment 1, Experiment 2, and Experiment 7, the influence of  $CO_2$  injection rate on the huff-n-puff effect was analyzed. As shown in Figure 6a, the maximum experimental pressure continued to increase as the amount of  $CO_2$  gas injected increased, as did the final cumulative recovery. This was because as the amount of injected gas increased, the pressure of the model continued to increase. In addition, driven by the production pressure difference,  $CO_2$  was more easily dissolved in the crude oil, improving its extraction and viscosity reduction and improving the efficiency of oil washing. The effective utilization radius of the  $CO_2$  sweep was increased and the oil recovery rate was improved. In field application, it was necessary to consider the oil displacement efficiency of  $CO_2$  for crude oil, and appropriately increase the injection amount of  $CO_2$  gas based on economic benefits.



**Figure 6.** (a) CO<sub>2</sub> injection amount related to recovery and max pressure; (b) relationship between cycle production time and rate of oil production.

#### 4.8. Declining Contrast

A comparison of the five groups of experiments behind the production decline law found that the production decline law was a linear decline, the slope represented the rate of oil production rate decay, and the larger the absolute value of the slope, the steeper the decay curve and the faster the production decline. From Figure 6b, it can be seen that the peak oil production rate of Experiment 3 was the largest, reaching 0.0812 g/min, the production time reached 350 min, the rate of production decline was the slowest, the slope of the declining section curve was 0.00021, and the final effect of oil increase was the best. The difference between Experiment 3 and the other groups was mainly the reduction in the pressure depletion rate from 3 MPa/h to 2 MPa/h, which indicates that the pressure depletion rate was the main controlling factor of  $CO_2$  huff-n-puff to improve the recovery.

## 4.9. CO<sub>2</sub> Microscopic Huff-n-Puff Oil Displacement Effect

To investigate the recovery-enhancing effect of  $CO_2$  huff-n-puff on shale cores at the microscopic level, six cores were selected from the long core of the above seven experimental groups to conduct short-core huff-n-puff experiments under the set conditions. Then, the NMR T<sub>2</sub> spectrum of the cores was measured before and after huff-n-puff, and the experimental conditions and results are shown in Table 3. The short cores were divided into two experimental groups with soaking times of 12 h and 48 h, the CO<sub>2</sub> injection amount was set to 0.25 PV, and three cycles of huff-n-puff were performed.

Core Number	Permeability /10 <sup>-3</sup> μm <sup>2</sup>	Pressure /MPa	Soaking Time/h	Cycle Injection Volume/PV	First Cycle/%	Second Cycle/%	Third Cycle/%
2	0.115	8	12	0.25	14.13	22.61	24.98
7	0.162	12	12	0.25	20.13	28.63	30.19
11	0.078	16	12	0.25	21.32	30.26	32.26
14	0.142	8	48	0.25	19.35	25.91	28.23
20	0.126	12	48	0.25	25.34	29.87	32.16
9	0.085	16	48	0.25	28.64	31.69	35.32

**Table 3.** Experimental conditions and cumulative oil recovery for different cycles.

Assuming that the initial saturated crude oil volume in the core borehole throat is represented by the  $(S_o + S_i)$  region and the saturated crude oil content after the CO<sub>2</sub> huff-n-puff process is represented by  $S_i$ , the driving efficiency is calculated by calculating

the difference between the  $T_2$  spectrum of the crude oils before and after the huff-n-puff experiments and by calculating the oil displacement efficiency *E*.

$$E = \frac{S_o}{S_o + S_i} \times 100\% \tag{3}$$

where *E* is the oil displacement efficiency, %; *S*<sup>0</sup> is the frequency range difference between the initial remaining oil content and the secondary saturated oil content  $T_2$  spectrum; and  $S_i$  is the secondary saturated oil content  $T_2$  spectrum frequency range. The initial remaining oil content before huff-n-puff is represented by the area covered under the  $T_2$  spectrum curve, and the oil displacement efficiency is represented by the difference between the area covered by the  $T_2$  spectrum curve after the huff-n-puff cycle and the area of the amplitude curve before huff-n-puff (Figure 7a). As the number of huff-n-puff cycles increased, the amplitude value of the  $T_2$  spectrum decreased continuously, which was due to the reduced crude oil content in the core. The relationship between the NMR  $T_2$  spectrum and pore size was classified as follows:  $T_2$  relaxation time <1 ms for micropores, 1–10 ms for small pores, 10–100 ms for mesopores, and >100 ms for macropores [36]. The Chang 7 shale oil reservoir had small pore throats structures, which were dominated by micropores and small pores. CO<sub>2</sub> gas was a strongly non-wetting phase, and after entering the shale core,  $CO_2$  preferentially entered the large pores with less resistance and contact and react with the crude oil in them. Then, in the soaking phase, the  $CO_2$  in the large pores diffused into the meso-small pores. In the production stage, the crude oil in the large pore was also driven out first, and the crude oil in the meso-small pore flowed into the large pore under the effect of dissolved gas driving and expansion, and finally be driven out. The crude oil in micropores was subjected to weak diffusion, and a trace amount of crude oil was also driven out [37,38]. As can be seen in Figure 7b, the  $T_2$  spectrum of the cores showed a double-peaked feature, but the left peak was higher than the right one, indicating that the macropore was poorly developed.



**Figure 7.** (a) Schematic diagram of quantitative evaluation of oil displacement efficiency; (b)  $T_2$  spectrum before and after huff-n-puff of core sample No. 2.

From the decreasing amplitude of the  $T_2$  spectrum, it could be concluded that the recovery in the first huff-n-puff cycle was mainly contributed to by the macropore. After three huff-n-puff cycles, the amplitude values of the  $T_2$  spectrum of the small pores decreased more than those of the macropores, and the recovery of the core was dominated by the contribution of the meso–small pores. At the end of the huff-n-puff experiment, the remaining oil in the core was mainly stored in the micropores and small pores. The  $T_2$  spectrum of core No. 2, which had a shorter soaking time, had a smaller decrease, and the cumulative recovery was only 24.98%. On the other hand, the recovery of core 14 increased to 28.23% with the increase in soaking time. This indicated that under the condition of the same experimental pressure, increasing the soaking time could effectively improve the recovery.

By analyzing the recovery of two groups of cores with soaking times of 12 h and 48 h under different experimental pressures, it was concluded that the recovery increases with the increase in the experimental pressure if other conditions remain unchanged. Then, it was found that the recovery of the two groups of cores at an experimental pressure of about 12 MPa had a greater increase compared to that of 8 MPa. This was since the CO<sub>2</sub> huff-npuff process changed from non-mixed-phase flow to near-mixed-phase flow at a pressure of about 12 MPa, which reduced the viscosity of the crude oil as well as the interfacial tension and increased the degree of crude oil utilization. After reaching the mixed-phase pressure (13.4 MPa), the increase in recovery decreased as the experimental pressure increased. Because the experimental pressure was higher than the minimum mixed-phase pressure, it was more likely to cause reservoir plugging. At higher experimental pressures, light components such as aromatics were extracted by  $CO_2$  and asphaltenes were deposited in large quantities, forming plugs. This ultimately resulted in a smaller increase in  $CO_2$ huff-n-puff recovery at 16 MPa compared to 12 MPa huff-n-puff recovery [39,40].

As the pressure increased from 12 MPa to 16 MPa, the large and small pores gradually completed the mixed phase, and the small pores had a higher minimum mixing pressure due to the higher capillary resistance [41,42]. In the non-mixed-phase replacement, the interfacial tension was relatively high, and  $CO_2$  gas as a strong non-wetting phase replaced the crude oil in the large pore in a segmented plug, and the interface between the two phases of oil and gas was extremely obvious. Moreover, it was difficult for  $CO_2$  to enter the small pore, and it could only be driven out by the flow into the large pore driven by the dissolved gas. After the MMP was reached, the interfacial tension and viscosity were considerably reduced, and  $CO_2$  could separate and carry out the fine oil film adsorbed on the edge of the pore. Moreover,  $CO_2$  could easily enter the small pore and improve the recovery of crude oil in it.

#### 5. Comparison of Huff-n-Puff Effects of Long and Short Core

Under the same conditions, the short cores had a large uncertainty in the pore structure due to their limited length, which could not accurately reflect the degree of influence of the reservoir pore structure on the  $CO_2$  huff-n-puff effect. The heterogeneity of the short cores was weak, and the heterogeneity of the short cores could even be ignored when compared with the actual formation. Long cores, on the other hand, were better able to reflect the heterogeneity of the actual formation due to the dispersed well locations of the cores. Second,  $CO_2$  breakthroughs, which were easy to achieve in laboratory experiments with short cores, barely occur in actual field huff-n-puff development, making it difficult to guide actual production in the field. Finally, the short cores were limited by the amount of crude oil in the pore, the amount of crude oil returned to the outlet end was extremely small, and the error in the measurement method had a greater impact, which affected the calculation of recovery.

At the macroscopic level, the heterogeneity of the Chang 7 shale was mainly reflected in the development of the interlayer [43]. The macroscopic heterogeneity of the reservoir complicated the hydrocarbon flow path, and the presence of a muddy interlayer affected the flow of crude oil. At the microscopic level, the permeability heterogeneity of the Chang 7 shale oil reservoir samples was very strong. It was mainly manifested in the differences in fluid flow caused by the heterogeneity in the microscopic pore throat structure, which mainly included pore heterogeneity, filler heterogeneity, and particle heterogeneity. These factors control the characteristics of oil and water seepage and the efficiency of microscopic oil displacement, and the high heterogeneity easily forms a high pore/throat ratio, which was unfavorable to the  $CO_2$  huff-n-puff effect. When the huff-n-puff experiments were carried out with a long core, the heterogeneity of the reservoir could be fully characterized.

In the following, the long and short core that were used to performed  $CO_2$  huff-npuff at the experimental pressure of 12 MPa in this paper were selected (Table 4). The comparison showed that the huff-n-puff recovery of the short core was larger than that of the long core, and although only three cycles of huff-n-puff were performed in the short core, the cumulative recovery was larger than that of the long core with four cycles of huff-n-puff. This indicated that the short core had a larger sweep and weaker heterogeneity, while the long core had stronger heterogeneity, which could truly reflect the huff-n-puff process of the underground reservoir.

**Table 4.** Long and short core sample huff-n-puff recovery comparison.

Core	Pressure	First Cycle	Second Cycle	Third Cycle	Fourth Cycle
Samples	(MPa)	Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)
Short core	12	20.13	8.5	1.56	-
Long core	12	10.06	7.86	3.96	2.87

Therefore, the  $CO_2$  huff-n-puff laboratory experiments with long cores are of some significance for actual oil field production. This study provides valuable insights into the nuanced mechanisms and critical control factors affecting  $CO_2$ -huff-n-puff-enhanced oil recovery. By utilizing both short- and long-core experiments, we extend the understanding of the technique's effectiveness across different scales of reservoir heterogeneity.

#### 6. Conclusions and Recommendations

In this paper, seven injection production parameters of  $CO_2$  huff-n-puff were investigated through long-core laboratory experiments, among which pressure depletion rate, soaking time, and  $CO_2$  injection amount were important control factors. These studies were instructive and useful for field development, and long cores could better characterize the heterogeneity of the actual reservoir. The findings underscore the importance of tailoring  $CO_2$  huff-n-puff strategies to reservoir-specific conditions, such as pressure depletion rate and gas injection amount, to maximize recovery potential.

- (1) In the long-core huff-n-puff experiments, the pressure depletion rate was the main controlling factor in improving the recovery of CO<sub>2</sub> huff-n-puff. The highest recovery was obtained by appropriately reducing the pressure depletion rate. If the pressure depletion rate was too large, it affected the sequence of elastic energy release and led to excessive permeability loss at the outlet end.
- (2) The first huff-n-puff cycle was critical to the overall huff-n-puff process. As the number of huff-n-puff cycles increased, the final cumulative recovery increased. However, the cycle recovery decreased due to the decrease in production differential pressure and the difficulty of utilizing the crude oil in the small pore. By fitting the recovery and cumulative recovery, the number of cycles for effective development of the Chang 7 shale oil reservoir was found to be four.
- (3) CO<sub>2</sub> mixed-phase drive was realized by increasing the minimum depletion pressure as well as the gas injection amount. The viscosity of the crude oil was reduced, the flow resistance was reduced, the sweeping coefficient and the oil washing efficiency were improved, and the recovery rate was substantially increased. After increasing the above parameters, the near-mixed-phase pressure could be reached in subsequent cycles, which was also beneficial for the development of the reservoir.
- (4) Increasing the soaking time before the formation pressure returned to equilibrium was conducive to recovery. If the soaking time was overly long, after the formation pressure reached equilibrium, it was difficult to play a role in the flow sweep, relying only on the diffusion sweep of the molecular concentration difference to improve the effective utilization radius, which affected the actual development efficiency of the oil field. If the soaking time was overly short, the injected energy would not be sufficiently utilized, which was also unfavorable to the recovery improvement. If the soaking time was too short, the energy injected was not fully utilized, which affected the final recovery.
- (5) At a lower injection rate, the CO<sub>2</sub> gas could better overcome the effect of nonhomogeneity of the core model. If the injection rate was too high, the CO<sub>2</sub> gas chose to enter the macropore, which was less effective in driving the crude oil in the

small pore; in the actual production, it would even push the crude oil in the near-well zone to the deeper pore of the formation.

- (6) At the microscopic level, the Chang 7 shale oil reservoir is characterized by strong heterogeneity, extremely low permeability, and poor physical properties. The crude oil recovery was mainly contributed to by the meso–small pores, but the overall effect was not excellent. The analysis of the NMR T<sub>2</sub> spectrum showed that the recovery was significantly increased when the experimental pressure reached the CO<sub>2</sub> near-mixed-phase driving pressure; however, when the experimental pressure was higher than the minimum mixed-phase pressure, reservoir plugging might occur.
- (7) Comparison of short- and long-core huff-n-puff experiments: The short core length was limited, the measurement error had a large impact, and it was difficult to reflect the heterogeneity of the actual formation. The long core could better reflect the influence of reservoir heterogeneity on the CO<sub>2</sub> huff-n-puff effect, which was a certain guidance for the field.
- (8) Future research could explore the applicability of the identified mechanisms and control factors in other shale oil reservoirs and investigate the integration of CO<sub>2</sub> huff-n-puff with other enhanced oil recovery techniques.

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## References

- 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 CO<sub>2</sub> Huff-n-Puff in Tight Oil Reservoirs. *Processes* 2023, *11*, 2415.
- Meng, X.; Meng, Z.; Ma, J.; Wang, T. Performance Evaluation of CO<sub>2</sub> Huff-n-Puff Gas Injection in Shale Gas Condensate Reservoirs. Energies 2019, 12, 42.
- 3. Yuan, J.; Luo, D.; Feng, L. A Review of the Technical and Economic Evaluation Techniques for Shale Gas Development. *Appl. Energy* **2015**, *148*, 49–65.
- 4. Ren, B.; Zhang, L.; Huang, H.; Ren, S.; Chen, G.; Zhang, H. Performance Evaluation and Mechanisms Study of Near-Miscible CO<sub>2</sub> Flooding in a Tight Oil Reservoir of Jilin Oilfield China. *J. Nat. Gas Sci. Eng.* **2015**, *27*, 1796–1805.
- Zhou, J.; Yang, K.; Tian, S.; Zhou, L.; Xian, X.; Jiang, Y. CO<sub>2</sub>-water-shale interaction induced shale microstructural alteration. *Fuel* 2019, 263, 11664.
- Song, Y.L.; Song, Z.J.; Zeng, H.W.; Tai, C.L.; Chang, X.L. N<sub>2</sub> and CO<sub>2</sub> Huff-n-Puff for Enhanced Tight Oil Recovery: An Experimental Study Using Nuclear Magnetic Resonance. *Energy Fuels* 2022, *36*, 1515–1521.
- Wang, D.; Li, Y.; Wang, B.; Shan, J.; Dai, L. Re-Fracturing vs. CO<sub>2</sub> Huff-n-Puff Injection in a Tight Shale Reservoir for Enhancing Gas Production. Front. *Energy Res.* 2023, 10, 922860.
- Gamadi, T.D.; Sheng, J.J.; Soliman, M.Y.; Menouar, H.; Watson, M.C.; Emadibaladehi, H. An experimental study of cyclic CO<sub>2</sub> Injection to Improve shale oil recovery. In Proceedings of the SPE Improved Oil Recovery Symposium, Tulsa, OK, USA, 12–16 April 2014.
- Li, L.; Sheng J, J. Gas Selection for Huff-n-Puff FOR in Shale Oil Reservoirs Based upon Experimental and Numerical Study. In Proceedings of the SPE Unconventional Resources Conference, Society of Petroleum Engineers, Calgary, AB, Canada, 15–16 February 2017.
- 10. Wei, B.; Lu, L.; Pu, W.; Wu, R.; Zhang, X.; Li, Y.; Jin, F. Production dynamics of CO<sub>2</sub> cyclic injection and CO<sub>2</sub> sequestration in tight porous media of Lucaogou formation in Jimsar sag. *J. Petrol. Sci. Eng.* **2017**, *157*, 1084–1094.
- 11. Li, L.; Su, Y.; Hao, Y.; Zhan, S.; Lv, Y.; Zhao, Q.; Wang, H. A comparative study of CO<sub>2</sub> and N<sub>2</sub> huff-n-puff EOR performance in shale oil production. *J. Pet. Sci. Eng.* **2019**, *181*, 106174.
- 12. Wan, T.; Sheng, J. Compositional Modelling of the Diffusion Effect on EOR Process in Fractured Shale-Oil Reservoirs by Gas flooding. *J. Can. Pet. Technol.* **2015**, *54*, 2248–2264. [CrossRef]
- 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 CO<sub>2</sub> huff and puff in tight oil reservoirs. *Petrol. Explor. Dev.* **2021**, *48*, 946–955.

- 14. Wan, T.; Sheng, J.; Soliman, M. Evaluation of the EOR Potential in Shale Oil Reservoirs by Cyclic Gas Injection. Master's Thesis, Texas Tech University, Lubbock, TX, USA, 2013.
- 15. Yu, H.; Qi, S.; Chen, Z.; Cheng, S.; Xie, Q.; Qu, X. Simulation Study of Allied In-Situ Injection and Production for Enhancing Shale Oil Recovery and CO<sub>2</sub> Emission Control. *Energies* **2019**, *12*, 3961. [CrossRef]
- 16. Zhang, Y.; Hu, J.; Zhang, Q. Simulation Study of CO<sub>2</sub> Huff-n-Puff in Tight Oil Reservoirs Considering Molecular Diffusion and Adsorption. *Energies* **2019**, *12*, 2136. [CrossRef]
- 17. Liu, J.; Li, H.; Tan, Q.; Liu, S.; Zhao, H.; Wang, Z. Quantitative study of CO<sub>2</sub> huff-n-puff enhanced oil recovery in tight formation using online NMR technology. *J. Pet. Sci. Eng.* **2022**, *216*, 110688.
- 18. Li, L.; Wang, C.; Li, D.; Fu, J.; Su, Y.; Lv, Y. Experimental investigation of shale oil recovery from Qianjiang core samples by the CO<sub>2</sub> huff-n-puff EOR method. *RSC Adv.* **2019**, *9*, 28857–28869.
- 19. Or, C.; Sasaki, K.; Sugai, Y.; Nakano, M.; Imai, M. Swelling and viscosity reduction of heavy oil by CO<sub>2</sub>-gas foaming in immiscible condition. *SPE Reserv. Eval. Eng.* **2016**, *19*, 294–304.
- Jia, B.; Tsau, J.S.; Barati, R. Role of molecular diffusion in naturally fractured shale reservoirs during CO<sub>2</sub> huff-n-puff. J. Petrol. Sci. Eng. 2018, 164, 31–42.
- Li, J.; Jin, W.; Wang, L.; Wu, Q.; Lu, J.; Hao, S. Quantitative evaluation of organic and inorganic pore size distribution by NMR: A case from the Silurian Longmaxi Formation gas shale in Fuling area, Sichuan Basin. *Oil Gas Geol.* 2016, 37, 129–134.
- 22. Liu, J.; Sheng, J.J. Experimental investigation of surfactant enhanced spontaneous imbibition in Chinese shale oil reservoirs using NMR tests. *J. Ind. Eng. Chem.* **2018**, 72, 414–422. [CrossRef]
- 23. Nguyen, P.; Carey, J.W.; Viswanathan, H.S.; Porter, M. Effectiveness of supercritical-CO<sub>2</sub> and N<sub>2</sub> huff-and-puff methods of enhanced oil recovery in shale fracture networks using microfluidic experiments. *Appl. Energy* **2018**, 230, 160–174.
- 24. Li, L.; Zhou, X.; Su, Y.; Xiao, P.; Cui, M.; Zheng, J. Potential and challenges for the new method supercritical CO<sub>2</sub>/H<sub>2</sub>O mixed fluid huff-n-puff in shale oil EOR. *Front. Energy Res.* **2022**, *10*, 1041851.
- Li, S.; Zhang, S.; Zou, Y.; Zhang, X.; Ma, X.; Wu, S. Experimental Study on the Feasibility of Supercritical CO<sub>2</sub>-gel Fracturing for Stimulating Shale Oil Reservoirs. *Eng. Fracture Mech.* 2020, 238, 5–11.
- Pu, W.; Wei, B.; Jin, F.; Li, Y.; Jia, H.; Liu, P.; Tang, Z. Experimental investigation of CO2 huff-n-puff process for enhancing oil recovery in tight reservoirs. *Chem. Eng. Res. Des.* 2016, 111, 13256–13271. [CrossRef]
- 27. Czarnota, R.; Janiga, D.; Stopa, J.; Wojnarowski, P.; Kosowski, P. Minimum miscibility pressure measurement for CO<sub>2</sub> and oil using rapid pressure increase method. *J. CO<sub>2</sub> Util.* **2017**, *21*, 156–161. [CrossRef]
- Zhou, T.; Liu, X.; Yang, Z.; Li, X.; Wang, S. Experimental analysis on reservoir blockage mechanism for CO<sub>2</sub> flooding. *Pet. Explor.* Dev. 2015, 42, 502–506. [CrossRef]
- 29. Song, C.; Yang, D. Experimental and numerical evaluation of CO<sub>2</sub> huff-n-puff processes in Bakken formation. *Fuel* **2017**, 190, 145–162. [CrossRef]
- Solarin, S.A.; Gil Alana Luis, A.; Lafuente, C. An investigation of long range reliance on shale oil and shale gas production in the U.S. market. *Energy* 2019, 195, 116933.
- 31. Hawthorne, S.B.; Gorecki, C.D.; Sorensen, J.A.; Steadman, E.N.; Harju, J.A.; Melzer, S. Hydrocarbon mobilization mechanisms from upper, middle, and lower Bakken reservoir rocks exposed to CO<sub>2</sub>. *SPE* **2013**, *2*, 920–928.
- Hoffman, B.T.; Rutledge, J.M. Mechanisms for huff-n-puff cyclic gas injection into unconventional reservoirs. In Proceedings of the SPE Oklahoma City Oil and Gas Symposium, Oklahoma City, OK, USA, 9 April 2019.
- 33. Jiang, C.; Liu, Q.; Zhang, Z.; Gao, J.; Chen, X. Influence of low pressure area on the spread range of carbon dioxide in the process of carbon dioxide huff and puff in tight reservoir. *Sci. Technol. Eng.* **2023**, *23*, 183–188.
- 34. Hu, S.; Zhao, W.; Hou, L.; Yang, Z.; Zhu, R.; Wu, S.; Bai, B.; Jin, X. Development potential and technical strategy of continental shale oil in China. *Pet. Explor. Dev.* **2020**, *47*, 819–828. [CrossRef]
- 35. Nojabaei, B.; Johns, R.T.; Chu, L. Effect of capillary pressure on phase behavior in tight rocks and shales. *SPE Res. Eval. Eng.* **2013**, 16, 281–289. [CrossRef]
- Zhu, J.; Chen, J.; Wang, X.; Fan, L.; Nie, X. Experimental Investigation on the Characteristic Mobilization and Remaining Oil Distribution under CO<sub>2</sub> Huff-n-Puff of Chang 7 Continental Shale Oil. *Energies* 2021, 14, 2782. [CrossRef]
- 37. Sheng J, J. Enhanced oil recovery in shale reservoirs by gas injection. J. Nat. Gas. Sci. Eng. 2015, 22, 252–259. [CrossRef]
- Qiao, R.; Li, F.; Zhang, S.; Wang, H.; Wang, F.; Zhou, T. CO<sub>2</sub> Mass Transfer and Oil Replacement Capacity in Fractured Shale Oil Reservoirs: From Laboratory to Field. *Front. Earth Sci.* 2022, *9*, 794534. [CrossRef]
- 39. Peng, X.; Wang, Y.; Diao, Y.; Zhang, L.; Yazid, I.M.; Ren, S. Experimental investigation on the operation parameters of carbon dioxide huff-n-puff process in ultra low permeability oil reservoirs. *J. Pet. Sci. Eng.* **2019**, *174*, 903–912. [CrossRef]
- Zhou, X.; Yuan, Q.; Rui, Z.; Wang, H.; Feng, J.; Zhang, L.; Zeng, F. Feasibility study of CO<sub>2</sub> huff 'n' puff process to enhance heavy oil recovery via long core experiments. *Appl. Energy* 2019, 236, 526–539. [CrossRef]
- 41. Cui, J.; Cheng, L. A theoretical study of the occurrence state of shale oil based on the pore sizes of mixed Gaussian distribution. *Fuel* **2017**, *206*, 564–571. [CrossRef]

- 42. L., S.; L., P. Experimental and simulation determination of minimum miscibility pressure for a Bakken tight oil and different injection gases. *Petroleum* **2017**, *3*, 79–86.
- 43. Qiao, J.; Baniasad, A.; Zieger, L.; Zhang, C.; Luo, Q.; Littke, R. Paleo-depositional environment, origin and characteristics of organic matter of the Triassic chang 7 member of the Yanchang Formation throughout the mid-western part of the Ordos Basin, China. *Int. J. Coal Geol.* **2021**, 237, 103636. [CrossRef]

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