

Research Article

Phase Behavior Analysis of CO₂ and Formation Oil System

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In this paper, there are nine oil samples to explore the characteristics of formation oil at different CO₂ injection rate, and the characteristics include bubble point pressure, volume expansion coefficient, viscosity, density, and average molecular weight, composition of gas and liquid phase, and asphalt sediment. According to the experimental results of early nine oil samples of swelling tests, in high temperature and high pressure conditions, characteristics and changing rules of properties of formation oil, including bubble point pressure, volume expansion coefficient, viscosity, density, and average molecular weight, composition of gas and liquid phase, and asphalt sediment, were evaluated and analyzed at different CO₂ injection rate systematically. The research not only can provide guides for petroleum engineers when they need to adjust the injection and production programs, but also can provide comparatively comprehensive experimental rules for researches on enhanced oil recovery (EOR) mechanisms of gas miscible and nonmiscible flooding. Moreover, phase parameters of different formation oil system can be extracted for reservoir numerical simulation.

1. Introduction

Research on the phase characteristics of CO₂ and formation oil system is an indispensable access for to understand mechanisms of miscible-phase displacement. Scholars around the world have done some studies on this topic. Xiangliang mainly analyzed the changes of viscosity and density in N₂-oil system when studying the impacts of N₂ on the phase characteristics of formation oil within the Niuzhuang reservoir, a fault block reservoir. It found that elastic energy of the system is the main factor to influence the oil recovery of that reservoir [1]. Yang et al. studied the feasibility of gas injection in the third region of the western part of Wen Mi reservoir. By using tests for volume expansion coefficient and software for phase analysis, they also evaluated the change of density of the system and the molecular weight of C₇₊ [2]. After performing studies on the phase change of CO₂-oil system within Yaoying Tai oil reservoir, Shi-zhong found out that with the volume of injected CO₂ increasing, the contents of all kinds of hydrocarbon within crude oil gradually reduced. However, the CO₂ content continuously increased [3]. Xuhui et al. utilized long cores to conduct CO₂ flood-

ing tests for designing reasonable blue print to develop Tai Xing oilfield. After analyzing the reason why viscosity and density of oil apparently reduced at the outlet ends of those cores, they thought that CO₂ flooding method can more efficiently enhance oil recovery than water flooding [4]. Ma et al. evaluated the effectiveness of CO₂ huff-and-puff technology in Pu Cheng oilfield, and their results showed that CO₂ can reduce the viscosity of oil and simultaneously increase the viscosity of formation water by 20%, which effectively improves the mobility ratio of water to oil and paves ways for transformation to water flooding treatments in later period [5]. In the study of phase characteristics of light oil containing dissolved CO₂ under reservoir conditions, Li argued that CO₂ can extract light hydrocarbon from crude oil while lower the ability of formation oil to dissolve wax, and oil producers need to be reinforced with paraffin control treatments in order to operate normally [6]. Nasehi and Asghari studied the feasibility of injecting CO₂ to enhance oil recovery in heavy oil reservoirs, and they thought injecting 10%-20% of pore volume of CO₂ contributes a lot to the increase of oil recovery; meanwhile, it can also improve mobility ratio of water to oil [7]. Chung et al. pointed out in the study

Measurements and Predictions of Physical Properties Within CO₂-heavy-oil Phase System that in the process of CO₂ immiscible displacement, the viscosity of formation crude oil decreased by 30% and the volume expansion of heavy oil and dissolved gas flooding are the main factors to improve recovery. They also presented a predictive equation for phase parameters to fit the CO₂-heavy-oil system of Lick Creek reservoir [8]. The basic principle of CO₂ flooding for EOR is to use special characteristics of CO₂, including making oil expand, reducing viscosities of crude oil, lowering interfacial tension, and enhancing oil recovery by single or multiple contact miscible processes after CO₂ dissolves in crude oil. All the mechanisms are related to the changes of the phase of crude oil [9–15]. Having read and analyzed existing researches and literatures around the world, authors found that a very large fraction of those literatures simply studied changes of some parameters instead of comprehensively analyzing a series of phase parameters capable of influencing oil recovery.

In this study, according to the characteristics of crude oil of Ji Lin oilfield, representative heavy oil is selected as a research target to conduct phase behavior analyses in CO₂-oil system. Studying phase behavior in CO₂ and formation oil system in depth is key for displacement mechanisms. Researches on phase behavior in CO₂ and formation oil system can provide accurate phase parameters for design and selection of reservoir development methods, especially in different stages of gas injection. Based on various phase characteristics in CO₂-oil system, using different EOR methods and adjusting ways of injection and production can not only maintain oil recovery in a high level but also provide guides for protecting injected gas from circulating in a low even noneffective way.

2. Experimental Contents

2.1. Experiment Materials Sample. Fluid components consist of CO₂ (0.34 mol%), C₁+N₂ (18.71 mol%), C₂-C₇ (17.64 mol%), and C₇₊ (63.31 mol%). The density of formation oil is 0.8503 g/cm³. The volume factor of formation oil is 1.1723 (at 98.9°C/24.2 MPa). Gas-oil ratio is 36.7 m³/m³, and the bubble point pressure is 7.01 MPa. The injected CO₂ consists of CO₂ (99.95%) and N₂ (0.05%).

2.2. Experimental Devices Introduction. Three experimental devices are used. The experiment is conducted with the following:

- (1) The PVT device came from ST company in France, which can provide visual phase states in ultrahigh pressure. The model is PVT-240/1500FV, and equipment parameters are 150 MPa, 200°C, and 240 mL, respectively
- (2) VISCOLab, a kind of electromagnetic viscometer made by Cambridge (UK), able to work under the condition of high pressure and high temperature, is used as viscosity measuring device, whose maximum test pressure, maximum test temperature, and maxi-

imum volume are 150 MPa, 300°C, and 6 mL, respectively

- (3) The densimeter is produced by Anton Paar company, whose model number is SVM3000
- (4) The gas chromatographs are produced by Agilent company, whose model numbers are 6890N and 7890A
- (5) High-pressure sampler and other materials

2.3. Experimental Methods and Processes. First step: clean up the ST high-pressure PVT analyzer with full window at the temperature of test area and then evacuate the device.

Second step: transfer some volume of crude oil sample of test formation to the clean PTV device and maintain the inside temperature of the device for 8 hours. Note that the sample is kept in a single-phase state in the process of transferring.

Third step: test the volume of the sample under the condition of formation pressure. Inject certain amount of CO₂ in formation oil at this formation pressure to increase the pressure of the system until CO₂ dissolves completely. At this time, the system becomes single-phase state. At this state, test those parameters of the CO₂ and formation oil system, such as bubble point pressure and volume expansion coefficient.

Fourth step: transfer the mixed sample with CO₂ and formation oil into electromagnetic viscometer and measure the viscosity of the single-phase system at formation temperature. Now the first swelling test by gas injection is finished.

Repeat the four aforementioned steps to conduct the second swelling test. Note that the volume of CO₂ injected in the second time is more than that of the first time. Similarly, measure those parameters of the CO₂ and formation oil system, such as bubble point pressure, volume expansion coefficient, and viscosity. Repeat those steps for six times until the molar content of injected gas within formation oil increases to about 70%-80%.

3. Results Analysis

Through swelling tests by gas injection, this study analyzes changes of phase behavior of formation oil extracted from test area after injecting CO₂. Admittedly, although the swelling test cannot simulate the dynamic contacts between different phases in the process of CO₂ flooding, it can provide valuable data to adjust state equations. By comparatively less experimental work, wider composition of fluid can be obtained in this way.

3.1. P-X Phase Diagram of CO₂ and Formation Oil System [10]. Figure 1 presents P-X phase diagram of CO₂ and formation oil system after injecting CO₂. After injecting CO₂, the bubble point pressure of formation oil obviously increases and with the increasing of the injected CO₂, the bubble point pressure gets higher. When the content of CO₂ becomes 63.96 mol%, the bubble point pressure of the CO₂ and formation oil system is identical to initial formation pressure; when the content of CO₂ gets 80.02 mol%,

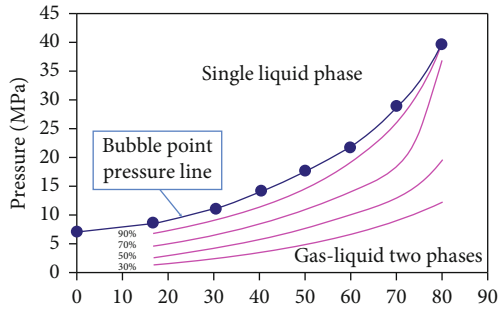


FIGURE 1: P-X phase diagram of CO₂ and formation oil system.

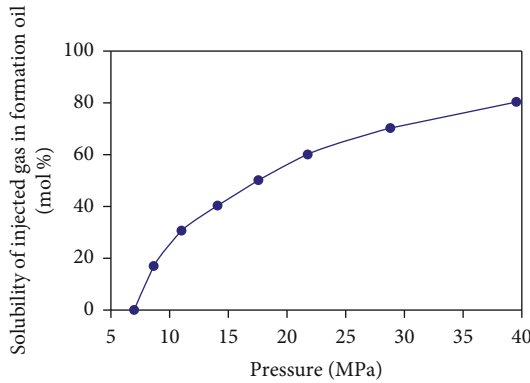


FIGURE 2: Curve of pressure versus CO₂ volume.

the bubble point pressure of the CO₂ and formation oil system becomes 39.55 MPa which is four times as high as initial pressure. Figure 2 shows correlation between the solubility of CO₂ within formation oil and pressure. With the increase of pressure, solubility of CO₂ within formation oil increases. When formation pressure becomes 24.20 MPa, the solubility of CO₂ within formation oil is 63.96 mol%. As injection pressure gets higher, the solubility of CO₂ in crude oil gets higher and meanwhile, the solubility gradient gradually reduces.

3.2. Volume Expansion Coefficient of CO₂ and Formation Oil System. Volume expansion coefficient at the formation pressure is defined as the ratio of the volume of formation crude oil under formation pressure after adding CO₂ to the volume of formation crude oil under formation pressure without adding CO₂. Volume expansion coefficient indicates swelling capacity of formation oil after adding CO₂. Figure 3 shows the changing curves of volume expansion coefficient of CO₂ and formation crude oil system with different CO₂ injection rate. The results indicate that after injecting CO₂, the volume of formation oil apparently expands and with more CO₂ been injected into crude oil, the value of volume expansion coefficient becomes bigger. When the pressure of formation is 24.20 MPa and meanwhile CO₂ reaches the saturation point in crude oil, the expansion coefficient of formation oil is 1.4200 and the formation oil expands by 42.00%. With continuously injecting CO₂, the formation oil expansion coefficient keeps increasing. When the amount of dissolved CO₂ reaches 80.02 mol%, the corresponding oil expansion coefficient is 1.8855, which means the volume of

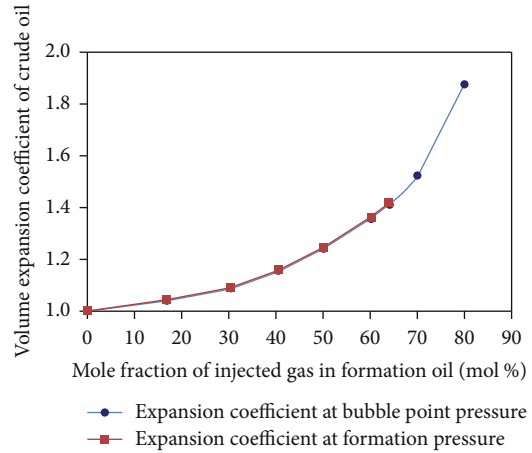


FIGURE 3: Variation curves of volume expansion coefficient.

crude oil obviously expands by 88.55%. All the results indicate that CO₂ can contribute a lot to swell crude oil and thus is very beneficial to improve productivity. Because the solubility of CO₂ in crude oil increases with the increase of injection pressure, it is useful to increase injection pressure so that oil displacement efficiency can be improved.

3.3. Viscosity Change of CO₂ and Formation Oil System. The important rationale of using CO₂ flooding to efficiently improve oil displacement efficiency is that injected CO₂ can lower the viscosity of crude oil. The oil displacement efficiency has close relationship with the effect of reducing viscosity. Figure 4 describes the relationship between viscosity of CO₂ and formation oil system and volume of injected CO₂. After injecting CO₂, the viscosity of crude oil reduces sharply and it also can be seen that although viscosity of crude oil keeps reducing as the volume of injected CO₂ increases, the degree of viscosity changes gradually reduces. When CO₂ reaches the saturation point at the formation pressure of 24.20 MPa, the viscosity of formation oil reduces by 63.24%, from initial 1.85 mPa.s to 0.68 mPa.s, showing that CO₂ can conspicuously reduce viscosity of crude oil of test area, improve mobility ratio of water to oil, and consequently improve oil displacement efficiency.

3.4. Density Change of CO₂ and Formation Oil System. Figure 5 shows the density change curves of CO₂ and formation oil system as injected CO₂ increases. With the increase of injected CO₂, the density of CO₂ and formation oil system firstly increases, then reduces to some degree, and finally increases again in the third stage. The trend of density changes of the mixed material reflects the combined effect of the change of both crude oil and CO₂ at corresponding pressures.

3.5. Average Molecular Weight Change of CO₂ and Formation Oil System. Figure 6 describes the change of average molecular weight of CO₂ and formation oil system. It can be seen that the average molecular weight of the CO₂ and formation oil system decreases as the volume of injected CO₂ increases.

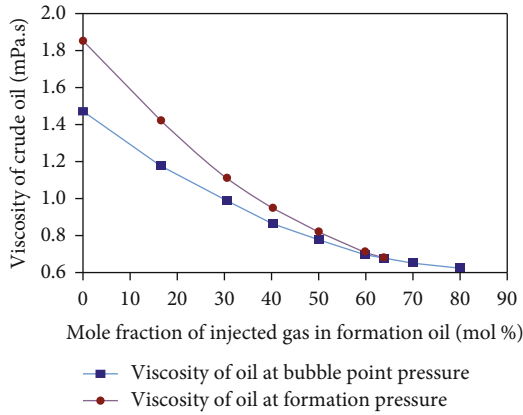


FIGURE 4: Curves of viscosity of formation oil versus CO₂ volume.

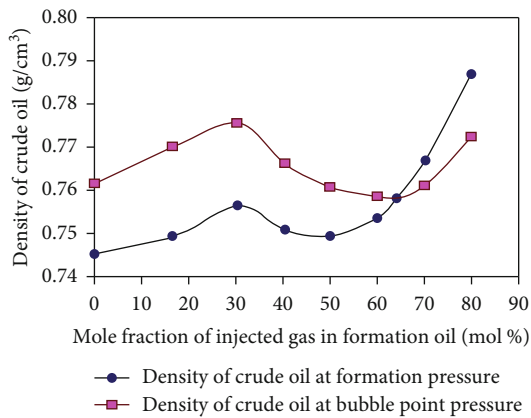


FIGURE 5: Curves of density of formation oil versus CO₂ volume.

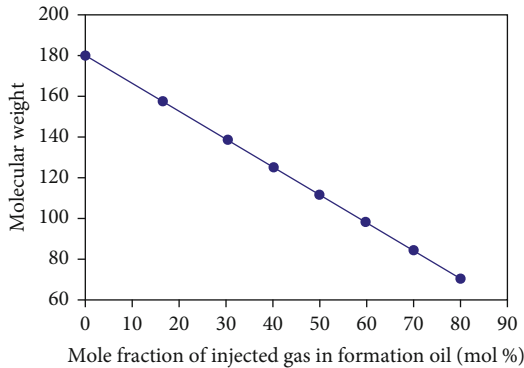


FIGURE 6: Curve of molecular weight versus CO₂ volume.

3.6. Change of Composition of Well Fluid of CO₂ and Formation Oil System. Figure 7 shows the change of composition of well fluid of CO₂ and formation oil system with the increase of injected CO₂. Among the composition of well fluid of CO₂ and formation oil system, the content of CO₂ increases while the contents of C₁-C₅, C₆-C₁₀, C₁₁-C₂₀, C₂₁-C₂₉, and C₃₀₊ all decrease as the mole percent of CO₂ increases in crude oil.

3.7. Analysis of Bitumen Precipitation Mechanisms in CO₂ and Formation Oil System. Figure 8 shows the change of

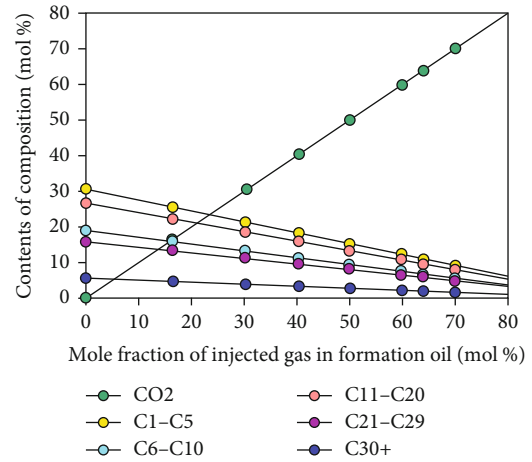


FIGURE 7: Curves of composition of well fluid.

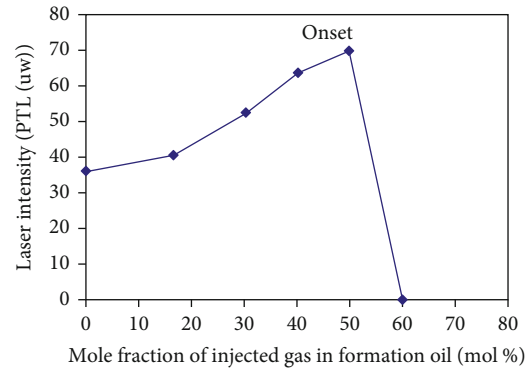


FIGURE 8: Bitumen precipitation curve of CO₂ and oil system.

laser intensity as volume of injected CO₂ increases. As we can see, laser intensity gradually increases with the volume of injected CO₂ increasing, and when the content of injected CO₂ reaches 60%, bitumen within the formation oil system begins to largely precipitate.

According to colloid theory, bitumen exists in crude oil in the form of dispersed colloids.

The core of micelles (namely core) is bituminous molecule cluster whose surface is the place that colloid molecules absorb on to generate a solvation layer. As a result, micelles generated in this way disperse in the crude oil system. A kind of peptid colloid is the key medium to make bitumen disperse in crude oil system, because molecules of colloid are able to largely reduce interface energy by generating solvation layers to keep bituminous molecule clusters from further associating when attached to the surface of bituminous molecule clusters. However, because there are spaces between colloid molecules, sometimes molecules are small enough to get close to the core. Thus, when the contents of light composition within crude oil system increase and the concentration of small molecules increases, this results in a series of responses, such as decreasing the relative concentration of small molecules, making solvation layers thin, and increasing interface energy of the system. In this case, in order to lower the interface energy, micelles will

continue associating with each other and making themselves bigger. When those micelles become big enough and reach the critical point, they will generate asphaltene precipitation [10–12].

In the process of CO₂ flooding, as injected CO₂ dissolves in crude oil in a large amount, small CO₂ molecules occupy the spaces of surfaces of bituminous molecule clusters, which makes the content of colloids decreases to the degree that colloids cannot generate micelles or solvation layers with enough thickness. Bitumen molecules will further associate with each other to generate bigger molecule clusters and finally produce flocculation and precipitation. With injected pressure increasing, solubility of CO₂ becomes stronger and the content of small CO₂ molecules increases more, leading to the fact that the concentration of colloids, namely, asphaltene stabilizer, reduces more and the asphaltene is more likely to associate with each other and generate precipitation.

When dissolved CO₂ within crude oil reaches the saturation point, the system has two phases, namely, gas and liquid. If CO₂ is continuously injected, the effect of CO₂ on crude oil changes from dissolution to evaporation. CO₂ has strong ability to extract and evaporate light composition within crude oil, making the concentrations of small molecules of light hydrocarbons within crude oil and solvation layers decrease a lot and thus discouraging asphaltene from precipitate. Note that the ability of small hydrocarbon molecules to make asphaltene precipitate is stronger than that of CO₂. Therefore, if CO₂ is continuously injected into formation oil to the degree that CO₂ reaches the saturation point and becomes gas phase, the precipitation trend of asphaltene will weaken and the volume of precipitation will also decrease.

4. Conclusion

- (1) This study systematically evaluates phase characteristics of CO₂ and formation oil system with different volume of injected CO₂ and quantitatively provides the P-X phase diagram, the change curves of volume expansion coefficient, the change curves of viscosity, change curves of density, the change curves of average molecular weight, the change curves of composition of well fluid, and the change curves of bitumen precipitation
- (2) From the experimental results, it is found that after injecting CO₂, the viscosity of the system reduces largely, which can pave the way for improving later mobility ratio of water to oil when using water flooding treatments. At the same time, after injecting CO₂, the volume of the formation oil and CO₂ system expands, which can increase elastic energy of itself and thus contribute a lot to increase of recovery
- (3) By analyzing domestic and foreign literatures, it is realized that swelling tests by injecting gas are lack of systematicness and are badly in need of industrial standards. The swelling tests not only can provide

technical supports for currently applying miscible and immiscible CO₂ flooding in large scales, but also can provide indirect supports for CO₂ huff and puff tests in some oilfields

Data Availability

The experimental data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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