Mechanism of Ultrasonic Physical–Chemical Viscosity Reduction for Different Heavy Oils

Jing Liu,* Fukang Yang, Junyong Xia, Feipeng Wu, and Chunsheng Pu

ABSTRACT: In this study, the mechanism of physical–chemical viscosity reduction of different heavy oils under ultrasonic wave is explored. Experiments of viscosity reduction and viscosity recovery of different heavy oils under ultrasonic excitation were carried out, and the optimal ultrasonic parameters, ultrasonic physical disturbance, and cavitation viscosity reduction extent of different oil samples were determined. Based on the element analysis methods, four-component analysis, gas chromatography analysis, and formation water pH value test, the micro-mechanism of the oil chemical structure change and water samples under ultrasonic wave was analyzed. The results show that the water content, temperature, and initial viscosity of heavy oil are the key to reduce the viscosity of heavy oil. The higher viscosity of the initial oil sample, the higher water content, and the temperature were needed. Compared with the lower viscosity oil sample, the higher viscosity oil sample has higher extent of cavitation viscosity reduction and lower extent of physical disturbance viscosity reduction under ultrasonic wave. After ultrasonic treatment, the contents of heteroatoms, resins, and asphaltenes in heavy oil samples with high viscosity decreased significantly, and the conversion extent of high carbon chain to low carbon chain was greater. In addition, the pH of water in heavy oils decreased after ultrasonic treatment, and the pH of water in high viscosity heavy oil decreased more significantly after ultrasonic treatment.

1. INTRODUCTION

With the increasing demand for oil and natural gas and the continuous progress of technology, unconventional heavy oil resources, which account for a large proportion of oil and gas resources, have been paid more attention. According to the statistics, heavy oil resources account for more than 20% of the total oil and gas resources in China, and the development potential has been increasingly prominent, which has become the main force of increasing oil and gas reserves and production in China. During the 13th Five-Year Plan, the highly efficient development of heavy oil resources has been listed in the national energy technology innovation and development plan.

Due to the high viscosity of heavy oil, its seepage resistance in the formation is also large, so the conventional development methods are difficult to implement. Therefore, reducing the viscosity of heavy oil and improving its liquidity are the key to the heavy oil reservoir development. At present, the heavy oil reservoir is developed mainly by injecting steam and chemical cracking viscosity reducer into the reservoir. However, in the process of injecting steam into the reservoir, due to the great difference in the mobility between steam and heavy oil, the phenomenon of steam channeling is serious, and the scope of steam sweep is small, resulting in poor effective production and low production extent. In addition, long-term steam injection to the reservoir will cause changes in the reservoir physical structure and asphaltene deposition, which will cause secondary damage to the reservoir. The main disadvantage of using chemical agents to reduce the viscosity of heavy oil is that the crack viscosity reducer does not have sufficient contact with heavy oil due to the high viscosity of heavy oil, causing a very limited reduction in viscosity. In addition, injecting chemical agents into the reservoir will also cause pollution to the reservoir. Especially in the context of advocating energy conservation and environmental protection and low oil price, a low cost, no pollution, good benefit, and strong adaptability development mode are the key to improve the development effect of heavy oil.

Ultrasonic enhanced oil recovery technology has been applied in many aspects of petroleum industry, including demulsification by ultrasonic wave, oil pollution treatment by ultrasonic...
wave, wax prevention by ultrasonic wave, plugging removal by ultrasonic wave, and viscosity reduction of heavy oil by ultrasonic wave. The main principle of ultrasonic demulsification technology is that oil and water particles continuously move to the wave belly and node due to the cavitation effect, thermal effect, and displacement effect produced by vibration, and then coalesce to generate water and oil droplets with larger diameters, and finally separate the oil and water by gravity. The application of ultrasonic technology greatly promotes the demulsification and dehydration effect of emulsion. Through ultrasonic cavitation, the macro-molecular hydrocarbons in heavy oil can be cracked into small molecular hydrocarbons, which can realize the separation of crude oil and sludge. Ultrasonic plug removal technology is widely used in China’s oilfields. The main principle of this technology is that the water plugging, organic fouling, and inorganic scale blockage, and polymer gel plugging can be removed through the cavitation and vibration of ultrasonic wave; thus, the permeability near the well area can be restored, and the effect of water injection and oil recovery can be enhanced. Ultrasonic viscosity reduction technology is a new technology to reduce crude oil viscosity by a physical method. The main principle of this technology is to produce local high temperature, high pressure, and strong physical disturbance in the fluid instantaneously through cavitation, heat, and physical shaking and thixotropy of ultrasonic wave, thus reducing the viscosity and improving the fluidity of heavy oil. This technology has the advantages of high efficiency, low cost, and low pollution. At present, the technology of reducing viscosity of heavy oil by ultrasonic wave has made some progress. These studies mainly focus on the optimization of ultrasonic parameters, the ultrasonic effect on the oxidative desulfurization of hydrocarbons in heavy oil, and the ultrasonic effect on reducing the viscosity of crude oil and the analysis of internal mechanism, and the influence of ultrasonic wave on asphaltene properties. However, for different heavy oil samples, there are few relevant researches on the extent to which ultrasonic reduces the viscosity of crude oil through physical shaking and thixotropy, the extent to which chemical cavitation reduces the viscosity of crude oil, and the microscopic mechanism of chemical action.

In this work, two different heavy oil samples and the corresponding water samples from the Shengli Oilfield were selected for ultrasonic viscosity reduction and recovery experiments under different ultrasonic parameters and reservoir conditions. The adaptability of ultrasonic wave to different heavy oil reservoir conditions were studied, and the optimal parameters of ultrasonic wave under different reservoir conditions were determined. In addition, through the experiments of element analysis, four-component analysis, gas chromatography analysis, and pH test of formation water, the influence of ultrasonic cavitation on the structure of oil and water is clarified when the crude oil viscosity is reduced by ultrasonic wave. Furthermore, the extent and microscopic mechanism of the physical—chemical action of ultrasonic wave on reducing the heavy oil viscosity are further clarified. This work indicates that the viscosity reduction of heavy oil under ultrasonic wave is composed of two parts: cavitation chemical viscosity reduction and physical disturbance viscosity reduction. The mechanism of chemical viscosity reduction by ultrasonic cavitation is the combination of the heavy oil heteroatom broken bond and ionized hydrogen radical in water. Also, this chemical viscosity reduction is irreversible. Under the optimal process parameters, the higher the viscosity of heavy oil, the higher the cavitation chemical irreversible viscosity reduction contribution and the lower the physical disturbance reversible viscosity reduction contribution under ultrasonic wave.

2. EXPERIMENTAL MATERIALS, INSTRUMENTS, AND METHODS

2.1. Experimental Materials. The materials used in the experiment are as follows: The oil sample 1 is from the Shengli Oilfield. The viscosity of crude oil at 50 °C is 2312 mPa·s. The corresponding formation water type of this oil sample is a sodium bicarbonate type, and its salinity and pH are 4500 mg/L and 8.5, respectively. The oil sample 2 is from the Shengli Oilfield. The viscosity of crude oil at 50 °C is 152,600 mPa·s. The corresponding formation water type of this oil sample is a calcium chloride type, and its salinity and pH are 15,000—20,000 mg/L and 6.7, respectively; n-heptane, methylenezene, and ethanol are also used.

2.2. Experimental Instruments. The instruments used in the experiment are as follows: ZJS-2000 type ultrasonic generator (the experimental frequencies are 15, 18, 20, 25, and 28 kHz), Brookfield DV-III type viscometer, Agilen7890A gas chromatograph, elemental variety EL cube element analyzer, PHS-3C type pH measuring instrument, high temperature and high pressure oil storage cylinder, HH-S water bath, and SF-16A crude oil four-component analyzer.

2.3. Experimental Methods. 2.3.1. Measurement of Viscosity Change of Different Crude Oils after Ultrasonic Treatment. The dehydrated crude oil is heated to 50 °C in a constant temperature water bath, and the initial viscosity of crude oil at a shear rate of 3 s⁻¹ is measured. The dehydrated crude oil and water were added into a 200 mL high temperature and high pressure vessel according to different proportions and subjected to ultrasonic treatment. The flow chart of the experiment is shown in Figure 1. The viscosity of crude oil treated with different ultrasonic parameters (frequency, power, initial temperature, water content, and time) was measured at 50 °C, and the shear rate was 3 s⁻¹.

2.3.2. Viscosity Recovery Test of Different Crude Oils after Ultrasonic Treatment. Under the optimal ultrasonic parameters, viscosity recovery experiments of heavy oil samples under different water content conditions were carried out. The specific process is as follows: The viscosity of crude oil at 0, 4, 8, 12, 24, and 36 h after ultrasonic treatment was measured at 50 °C, and the shear rate was 3 s⁻¹.

The experiment of reducing the crude oil viscosity by ultrasonic wave confirms the suitable reservoir conditions and the corresponding optimal action parameters for different oil.
samples. The effects of cavitation cracking and physical shaking and thixotropy on different heavy oil samples are illustrated by the viscosity recovery experiment of crude oil after ultrasonic treatment.

2.3.3. Elemental Analysis. The element analysis experiments of heavy oil samples under ultrasonic condition and without ultrasonic wave were carried out by using an element variety EL cube element analyzer. An appropriate amount of dehydrated heavy oil sample is burned at 1000 °C to generate CO, CO₂, NO, and H₂O, etc. First, the generated gases are purified and then brought into the chromatographic column with helium for detection. For the sulfur element in heavy oil, the heavy oil sample was oxidized in the combustion tube at high temperature to convert the sulfur element into SO₂ gas first, and then the SO₂ gas was input into a sulfur detector and it was detected using a photomultiplier tube.

2.3.4. Four-Component Analysis of Crude Oil. To study the effect of ultrasonic wave on four-component content distribution of crude oil, four components of crude oil after ultrasonic treatment and crude oil without ultrasonic treatment were analyzed. The steps of four-component analysis of crude oil are as follows: 25 mL of n-heptane was added to 0.5 g of dehydrated crude oil, heated, and refluxed for 1 h, the mixture was filtered to obtain asphaltene and then the part without asphaltene was absorbed on an alumina chromatographic column, and it was cleaned with n-heptane, toluene, and ethanol successively to obtain saturated, aromatic, and resin components.

2.3.5. Gas Chromatography Analysis. A gas chromatograph was used to test the total hydrocarbon chromatographic changes of initial heavy oil samples and heavy oil samples treated by ultrasonic wave. The processes are as follows: the gas circuit and the circuit system of the gas chromatograph were opened, the analytical conditions of the instrument and chromatographic processor were set, 0.2−1.0 μL of a sample was added to the chromatograph, and the temperature-programmed and chromatographic processor was started at the same time, and the chromatogram and original data were recorded.

The element analysis, four-component analysis, and gas chromatography analysis were carried out on the initial heavy oil samples and the heavy oil samples treated by ultrasonic wave. The influence of ultrasonic wave on the structural change of heavy oil can be clarified, and the internal mechanism and influence extent of ultrasonic wave on cracking of different heavy oil samples are expounded.

2.3.6. Analysis of Formation Water pH. The pH of initial formation water and formation water treated by ultrasonic wave were measured. The influence of ultrasonic wave on the formation water structure was studied by analyzing the change of formation water pH, and the mechanism of ultrasonic reducing crude oil viscosity was further elaborated.

3. RESULTS AND DISCUSSION

3.1. Effect of Ultrasonic Wave on Viscosity Reduction of Different Heavy Oils. 3.1.1. Optimization of Ultrasonic Parameters for Viscosity Reduction of Different Heavy Oils. According to the experimental method and process in Section 2.3.1, the influences of ultrasonic frequency (15, 18, 20, 25, and 28 kHz), power (300, 500, and 1000 W/h), water content, time, and temperature on the viscosity reduction effect of the two oil samples were studied. The optimization method is to fix four parameters, change one parameter, and gradually optimize the best parameters. The experimental results are shown in Figure 2.

![Figure 2](https://dx.doi.org/10.1021/acsomega.0c05585)

**Figure 2.** Influence of ultrasonic parameters on viscosity reduction of two different heavy oil samples: (a) the effect of ultrasonic frequency on reducing viscosity of different oil samples; (b) the effect of ultrasonic power on reducing viscosity of different oil samples; (c) the influence of water content on ultrasonic viscosity reduction of different oil samples; (d) the effect of temperature on ultrasonic viscosity reduction of different oil samples; and (e) the effect of time on ultrasonic viscosity reduction of different oil samples.

It can be seen from Figure 2 that the viscosity reduction effect tends to be stable with the increase in ultrasonic power and action time for different heavy oil systems, and the lower the ultrasonic frequency, the better the effect. The higher the initial viscosity of heavy oil, the better the effect of ultrasonic viscosity reduction. There are different favorable water contents, treatment times, and temperatures for the heavy oils with different original viscosities to reduce their viscosity. When the temperature is 40 °C, the ultrasonic frequency is 15 kHz, the power is more than 500 W/h, the treatment time is more than 20 min, and the amount of water is more than 30%; ultrasonic wave has the best viscosity reduction effect on heavy oil with a lower viscosity up to 32.8%. When the temperature is 80 °C, the ultrasonic frequency is 15 kHz, the power is more than 500 W/h, the treatment time is more than 30 min, and the amount of water is more than 40%; ultrasonic wave has the best viscosity reduction effect on heavy oil with a higher viscosity up to 47.8%.

It can be seen from Figure 2a that, with the increase in ultrasonic frequency, the viscosity reduction effect of ultrasonic wave on oil sample 1 and oil sample 2 shows a decreasing trend.
This is because of the cavitation effect of ultrasonic wave, which makes the fluid produce cavitation nuclear in the expansion stage of acoustic wave. The cavitation nuclear compressed by acoustic wave will cause the cavitation nuclear to burst, which will produce a high temperature and high pressure in an instant, and then affect the rheology of fluid. Increasing the ultrasonic wave frequency will shorten the expansion time of acoustic wave, shorten the formation and compression time of cavitation bubble, and then hinder the growth and collapse of cavitation bubble. Therefore, a low frequency should be selected when using ultrasonic wave to reduce the viscosity of heavy oil under the condition of certain other parameters.

It can be seen from Figure 2b that, with the increase in ultrasonic power, the viscosity reduction effect of ultrasonic wave on oil sample 1 and oil sample 2 increases gradually and tends to be stable. This is because of the fact that the higher the ultrasonic power is, the more energy is transferred to the oil–water system, and the cavitation phenomenon is more intense, which makes the viscosity reduction effect of heavy oil more significant. For a specific oil–water system, when the ultrasonic power reaches a certain value, the cavitation phenomenon tends to be saturated, making the effect of ultrasonic wave on reducing the viscosity of crude oil stable.

It can be seen from Figure 2c that, when the water content of heavy oil is low, it is easy to form water in oil emulsion. The emulsion has the characteristics of high viscosity and high surface tension coefficient and is less prone to cavitation. When the water content reaches a certain value to form oil in water emulsion, the viscosity coefficient of the emulsion decreases, and cavitation is easy to occur. When the water content continues to increase, due to the little change of viscosity coefficient, the hydrogen ion generation is basically stable, so there is an optimal water amount. Compared with the heavy oil with low viscosity, the macromolecular chain of heavy oil with higher viscosity is longer. To break the macromolecular chain into small molecular chain, more hydrogen ions are needed, so the optimal water content is higher than that of heavy oil with low viscosity. Due to the complex composition and structure of heavy oil, the cracking process is not completed immediately. When the ultrasonic treatment time is short, the heavy oil with high viscosity has not reached the maximum cracking degree, so the viscosity reduction rate of heavy oil with high viscosity increases significantly with the treatment time, and the higher the viscosity of heavy oil, the longer the treatment time. When the ultrasonic treatment time reaches a certain value, the cavitation phenomenon in a heavy oil system tends to be saturated. When the viscosity reduction rate of heavy oil tends to be stable, it shows that there is an equilibrium between heavy oil molecules and ultrasonic effect. The cavitation threshold of heavy oil increases with the increase in viscosity. On the one hand, increasing the temperature can improve fluid viscosity, and on the other hand, it can also reduce the cavitation threshold of heavy oil. To achieve the best cavitation effect, an appropriate temperature is needed. However, if the temperature is too high, the steam pressure will increase, which will in turn weaken the cavitation effect. Therefore, the optimal temperature for low viscosity oil sample 1 and high viscosity oil sample 2 is 40 and 80 °C, respectively.

3.1.2. Effect Analysis of Ultrasonic Cavitation and Physical Shaking and Thixotropy on Viscosity Reduction about Different Crude Oils. Ultrasonic wave is a kind of sound wave. Its main mechanism is cavitation and mechanical vibration. Therefore, the main ways to reduce the viscosity of crude oil by ultrasonic wave are irreversible viscosity reduction by cavitation and reversible viscosity reduction by mechanical vibration, which are chemical cavitation viscosity reduction and physical disturbance viscosity reduction, respectively. Physical shaking and thixotropy refers to the property that the viscosity of fluid decreases when it is subjected to shear stress and increases when the shear stops. Physical shaking and thixotropy is a reversible phenomenon, which represents the dependence of fluid viscosity on time. In short, the reversible sol phenomenon of gel under the action of mechanical force such as oscillation and compression is physical shaking and thixotropy. The mechanism is that there is a network structure in the fluid. Under the action of external force, the instantaneous change of the network structure in the fluid leads to the change of the hydrodynamic response. Therefore, the physical shaking and thixotropy effect of ultrasound on heavy oil is considered to be the part of crude oil viscosity recovery after the ultrasonic wave stopped for a period of time. Based on this, according to the experimental method and process in Section 2.3.2, the recovery of crude oil viscosity with time of oil sample 1 and oil sample 2 under the optimal ultrasonic action parameters and different water content conditions is tested, as shown in Figures 3 and 4.
macromolecular bond breaks. Therefore, under the same ultrasonic conditions, the proportion of viscosity reduction caused by physical shaking and thixotropy increases, and the viscosity recovery rate is higher. The average viscosity reduction, physical shaking and thixotropy viscosity reduction, and chemical cavitation viscosity reduction are presented in Table 1. Also, the ratio of physical viscosity reduction and the ratio of chemical viscosity reduction in different oil samples were compared. In heavy oil sample 1, the average contribution rate of crude oil viscosity reduction by physical shaking and thixotropy is about 15.7%, and that of cavitation viscosity reduction is about 84.3%; in heavy oil sample 2, the average contribution rate of crude oil viscosity reduction by physical shaking and thixotropy is about 10.3%, and that of cavitation viscosity reduction is about 89.7%. The higher the viscosity of heavy oil, the more heteroatom bond, and the bond energy of heteroatom bond is lower, and it is easier to fracture. Under the action of ultrasound, water can ionize H-radical. The H-radical is highly active and easy to combine with bond breaking, which has the effect of permanent viscosity reduction by hydrogenation. Therefore, the higher the viscosity of the heavy oil, the lower the viscosity resilience.29,31

3.2. Structural Changes of Different Heavy Oils after Ultrasonic Treatment. 3.2.1. Element Analysis. According to the experimental method in Section 2.3.3, the element analysis experiments of oil sample 1 and oil sample 2 were carried out. The results are shown in Figures 5 and 6. It can be seen from Figures 5 and 6 that the hydrogen carbon atom ratio of the two oil samples increases, but the heteroatom content decreases. It indicates that water can promote the fracture of the heteroatom bond of the C–S bond. Under the action of ultrasonic wave, the C–N bond and C–O bond transfer the hydrogen free radical in water to heavy oil components, which makes the ultrasonic wave produce a permanent cavitation viscosity reduction effect on heavy oil. Compared with oil sample 1, the content of heteroatom in oil sample 2 is higher, especially the content of sulfur, which is one of the reasons for the higher viscosity of oil sample 2. Compared with other heteroatoms, the content of heteroatom sulfur in heavy oil decreased obviously after ultrasonic treatment. This is because the C–S bond energy in heavy oil molecules is low. Under the combined action of ultrasonic wave and water, the C–S bond is easy to break and combine with hydrogen free radicals, thus achieving the purpose of C–S bond hydrogenation.29 In addition, compared with oil sample 1, element sulfur in oil sample 2 is reduced more, which indicates that ultrasonic wave has a special effect on crude oil desulfurization reaction, especially for heavy oil with a higher sulfur content.30

3.2.2. Four-Component Analysis. According to the experimental method in Section 2.3.4, four-component analysis experiments were carried out on oil sample 1 and oil sample 2. It can be seen from Figures 7 and 8 that, after ultrasonic treatment, the content of saturated hydrocarbon and aromatic hydrocarbon in oil sample 1 and oil sample 2 increased, but the content of resin and asphaltene in crude oil decreased. Among them, the saturated hydrocarbon and aromatic hydrocarbon of oil sample 1 increased by 3.95 and 1.72%, respectively, while the resin and asphaltene decreased by 3.22 and 2.45%, respectively; the saturated hydrocarbon and aromatic hydrocarbon of oil sample 2 increased by 7.86 and 3.48%, respectively, while the resin and asphaltene decreased by 6.07 and 5.27%, respectively. It can be seen from the above data that compared with oil sample 1, the content of resin and asphaltene in oil sample 2 is reduced more. This indicates that heavy components such as resin and

| oil sample | total viscosity reduction, % | physical viscosity reduction, % | chemical viscosity reduction, % | ratio of physical viscosity reduction, % | ratio of chemical viscosity reduction, % |
|------------|-------------------------------|---------------------------------|-------------------------------|----------------------------------------|----------------------------------------|
| oil sample 1 | 34.1                          | 5.4                             | 28.8                          | 15.7                                   | 84.3                                   |
| oil sample 2 | 47.6                          | 4.9                             | 42.7                          | 10.3                                   | 89.7                                   |

Figure 5. Change of element composition of oil sample 1 after ultrasonic treatment.

Figure 6. Change of element composition of oil sample 2 after ultrasonic treatment.

Figure 7. Changes of four components in crude oil after ultrasonic treatment of oil sample 1.
asphaltene in heavy oil are transformed into light components such as saturated hydrocarbon and aromatic hydrocarbon after ultrasonic treatment. It can effectively improve the quality of heavy oil and reduce the viscosity of crude oil. The conversion extent of oil sample 2 is higher than that of oil sample 1.

3.2.3. Gas Chromatography Analysis. According to the experimental method in Section 2.3.5, the gas chromatographic analysis of oil sample 1 and oil sample 2 was carried out. The results are shown in Table 2.

Table 2. Distribution of Carbon Number of Different Heavy Oils before and after Ultrasonic Treatment

| number of carbon atoms | oil sample 1 | oil sample 2 |
|------------------------|--------------|--------------|
|                        | before using ultrasonic | after using ultrasonic | before using ultrasonic | after using ultrasonic |
| 0 ≤ C ≤ 10             | 0.93         | 3.29         | 1.08          | 1.22          |
| 10 ≤ C ≤ 20            | 33.09        | 35.13        | 21.16         | 28.41         |
| 20 ≤ C ≤ 30            | 29.78        | 28.48        | 29.80         | 27.63         |
| 30 ≤ C ≤ 40            | 36.07        | 33.11        | 46.51         | 42.33         |
| 40 ≤ C ≤ 43            | 0.13         | 0.00         | 1.27          | 0.42          |
| 43 ≤ C ≤ 45            | 0.00         | 0.00         | 0.19          | 0.00          |

It can be seen from Table 2 that, after ultrasonic treatment, the content of hydrocarbon (0 ≤ C ≤ 10) in oil sample 1 increases from 0.93 to 3.29%, the content of hydrocarbon (10 ≤ C ≤ 20) increases from 33.09 to 35.13%, the content of hydrocarbon (30 ≤ C ≤ 40) decreases from 36.07 to 33.11%, and the content of hydrocarbon (40 ≤ C ≤ 43) decreases from 1.27 to 0.42%. In oil sample 2, the content of hydrocarbon (0 ≤ C ≤ 10) increased from 1.08 to 2.22%, the content of hydrocarbon (10 ≤ C ≤ 20) increased from 21.16 to 28.41%, the content of hydrocarbon (30 ≤ C ≤ 40) decreased from 46.51 to 42.33%, the content of hydrocarbon (40 ≤ C ≤ 43) decreased from 1.27 to 0.42%, and the content of hydrocarbon (43 ≤ C ≤ 45) decreased from 0.19% to 0. The above data indicate that, after ultrasonic treatment, a series of C-C bond fracture reactions (such as chain breaking reaction of long chain alkanes, side chain reaction of aromatic ring dealkylation, etc.) occurred in hydrocarbons in heavy oil, which made part of large carbon number hydrocarbons crack into small carbon number hydrocarbons, thus reducing the viscosity of heavy oil and improving the quality of heavy oil. However, for different heavy oil samples, there were 4.4% of macromolecular hydrocarbons transformed into small molecular hydrocarbons. In oil sample 2, there were 7.39% of macromolecular hydrocarbons transformed into small molecule hydrocarbons. This further indicates that ultrasonic wave has better viscosity reduction effect on heavy oil with higher viscosity.

3.3. pH Change of Formation Water after Ultrasonic Treatment. After ultrasonic treatment, the pH of formation water in oil sample 1 and oil sample 2 were measured to further reveal the microscopic mechanism of ultrasonic wave on reducing viscosity of heavy oil. The experimental results are shown in Figure 9.

![Figure 9. Formation water pH changes after ultrasonic treatment.](https://dx.doi.org/10.1021/acsomega.0c05585)

It can be seen from Figure 9 that the formation water pH decreases after ultrasonic treatment. The pH value of oil sample 1 decreases by 0.4, and that of oil sample 2 decreases by 0.6. Thus, it can be seen that the formation water pH in the oil sample with higher viscosity is greatly reduced. When the oil sample is treated by ultrasonic wave, many small bubbles will appear in the oil sample, which indicates that the cavitation phenomenon is quite severe. Under the action of ultrasonic wave, the chemical bond of hydrocarbon in heavy oil and formation water will be destroyed, forming new free radicals:

\[
\begin{align*}
H_2O & \rightarrow H + OH^- \\
M_1M_2 & \rightarrow M_1^- + M_2^- \\
H^- + M_1^- & \rightarrow HM_1 \\
H^- + M_2^- & \rightarrow HM_2 \\
OH^- + OH^- & \rightarrow H_2O_2
\end{align*}
\]

After ultrasonic treatment, the water produces hydrogen free radicals (H·) and hydrogen oxygen radicals (OH·). After ultrasonic treatment, the heteroatom bond in heavy oil is broken and free radicals M_1· and M_2· are formed. Hydrogen free radicals combine with M_1· and M_2· radicals, which transforms macro-molecules into small molecules in heavy oil, and hydrogen oxygen radicals combine with hydrogen oxygen radicals to form hydrogen peroxide. Usually, hydrogen peroxide shows weak acidity, so the pH value decreases after ultrasonic treatment.

For heavy oil with high viscosity, more hydrogen free radicals can be consumed and more hydrogen peroxide can be generated due to more heteroatom bond breaking after ultrasonic treatment. Therefore, compared with oil sample 1, the water pH in oil sample 2 is greatly reduced.

4. CONCLUSIONS

(1) An ultrasonic viscosity reduction experiment shows that ultrasonic wave can reduce the viscosity of heavy oil, and the optimal ultrasonic parameters corresponding to different initial viscosities of heavy oils are different.
When the temperature is 40 °C, the ultrasonic frequency is 15 kHz, the power is more than 500 W/h, the treatment time is more than 20 min, and the amount of water is more than 30%; ultrasonic wave has the best viscosity reduction effect on heavy oil with a lower viscosity up to 32.8%. When the temperature is 80 °C, the ultrasonic frequency is 15 kHz, the power is more than 500 W/h, the treatment time is more than 30 min, and the amount of water is more than 40%; ultrasonic wave has the best viscosity reduction effect on heavy oil with a higher viscosity up to 47.8%.

(2) Based on the viscosity recovery experiment, the contribution rates of physical shaking and thixotropy and chemical cavitation in different heavy oil samples were analyzed. In heavy oil sample 1, the average contribution rate of crude oil viscosity reduction by physical shaking and thixotropy is about 15.7% and that of cavitation viscosity reduction is about 89.7%. In heavy oil sample 2, the average contribution rate of crude oil viscosity reduction by physical shaking and thixotropy is about 10.3% and that of cavitation viscosity reduction is about 89.7%.

(3) Through the experiments of element analysis, four-component analysis, gas chromatography analysis, and formation water pH test, the influence of ultrasonic wave on the oil sample structure and formation water structure change is studied, and the chemical mechanism and action extent of ultrasonic wave reducing heavy oil viscosity are explored. The results show that the higher the viscosity of heavy oil, the better the effect of ultrasonic wave on reducing the viscosity of crude oil. Compared with the heavy oil with lower viscosity, the heavy oil with higher viscosity has more heteroatomic bond fracture. Compared with the heavy oil with lower viscosity, the higher viscosity heavy oil has more heteroatom bond fracture. Moreover, the content of the sulfur atom in the heteroatom decreases more obviously than that of the oxygen atom and the nitrogen atom, which increases the proportion of a heavy component and high carbon chain converted into a light component and low carbon chain in heavy oil. For heavy oil with high viscosity, after ultrasonic treatment, the heteroatom bond breaks more easily, which makes it easier to combine more hydrogen free radicals in water, resulting in more hydrogen oxygen free radicals remaining in water. These hydrogen oxygen free radicals combine with each other to form hydrogen peroxide, which makes formation water show weak acidity. Therefore, as compared with oil sample 1, the formation water pH in oil sample 2 decreases more significantly after ultrasonic treatment.

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**Notes**

The authors declare no competing financial interest.

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