

Study on Hydrothermal Cracking of Heavy Oil under the Coexisting Conditions of Supercritical Water and Non-condensate Gas

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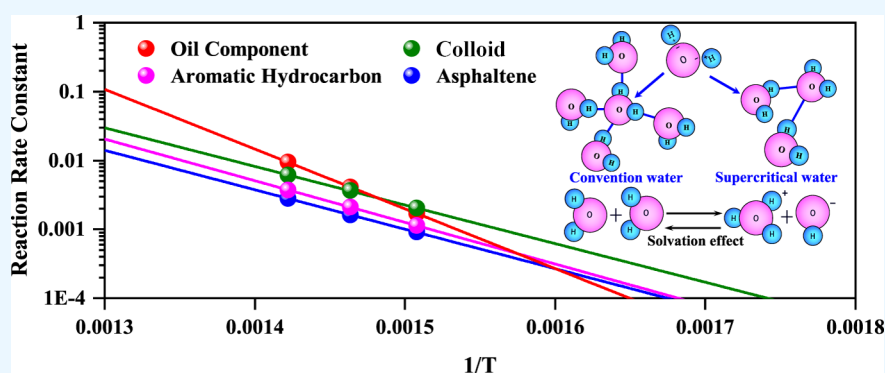


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ABSTRACT: This study looked at the effects of temperature, water–oil ratio, and the addition of non-condensable gas on the thermal cracking of extra-heavy oil in the lab. The goal was to learn more about the properties and reaction rates of deep extra-heavy oil under supercritical water conditions, which are not well understood. The changes in the composition of the extra-heavy oil were analyzed with and without the presence of non-condensable gas. The reaction kinetics of the thermal cracking of extra-heavy oil were quantitatively characterized and compared between the two conditions of supercritical water alone and supercritical water mixed with non-condensable gas. The results showed that (1) under supercritical water conditions, the extra-heavy oil underwent significant thermal cracking, which led to a significant increase in the amount of light components, the release of CH_4 , and the formation of a new component, coke, which led to a noticeable decrease in the viscosity of the oil; (2) increasing the water–oil ratio could promote the thermal cracking of extra-heavy oil and led to a significant decrease in oil viscosity, indicating a more complete thermal cracking reaction. Moreover, increasing the water–oil ratio was found to facilitate the flowability of the cracked oil; (3) the addition of non-condensable gas intensified the conversion of coke but inhibited and slowed down the thermal cracking of asphaltene, which is detrimental to the thermal cracking of extra-heavy oil; and (4) the kinetic analysis showed that the addition of non-condensable gas resulted in a decrease in the thermal cracking rate of asphaltene, which is detrimental to the thermal cracking of heavy oil.

1. INTRODUCTION

As conventional oil reserves are becoming depleted and unable to meet the growing global demand for oil, heavy oil has gradually become the focus of attention due to its significant proven reserves.^{1–4} Currently, large-scale development of heavy oil resources is achieved through thermal recovery methods, including steam stimulation,^{5–7} steam flooding,⁸ and steam-assisted gravity drainage (SAGD).⁹ For deep and extra-heavy oil reservoirs, the conventional steam injection technology is unable to inject steam into the formation due to its deep burial, high viscosity, and high pressure.^{10–12} The energy carried by injected steam will undergo significant thermal diffusion and heat exchange between the wellbore and the formation, leading to a significant decrease in the thermal efficiency of steam injection during the process.

To address the issue of low thermal efficiency in steam injection for thermal recovery of heavy oil reservoirs, injecting supercritical water (SCW) can be utilized to enhance thermal utilization.^{13–15} SCW is a special state of water.¹⁶ Under normal conditions, water can exist in four different states under different temperatures and pressures, as shown in Figure 1, which include the solid state region, the supersaturated water region, the superheated steam region, and the supercritical region. The

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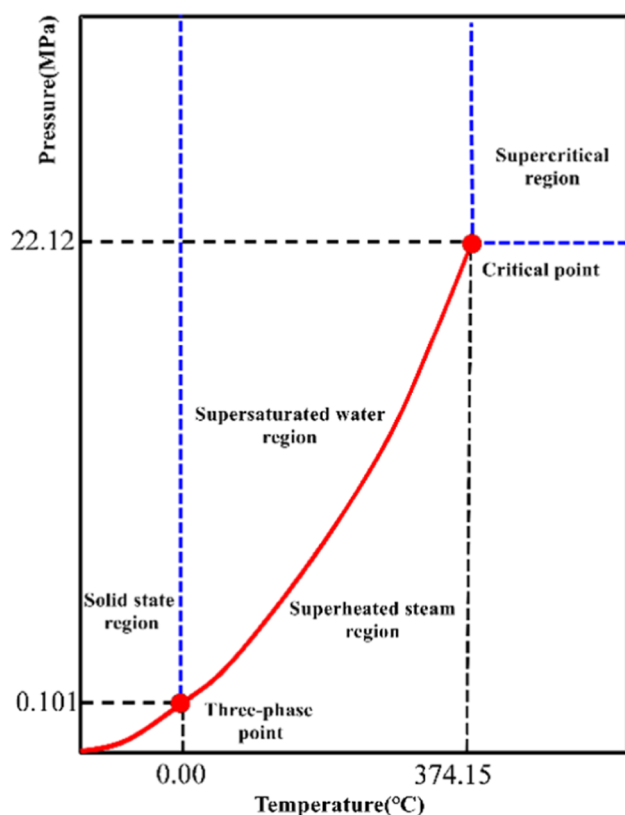


Figure 1. Phase partition of water.

boundary between the supersaturated water region and the superheated steam region is the saturation line (red line), which begins at the triple point (0 °C and 0.101 MPa) and ends at the critical point (371.15 °C and 22.12 MPa). When the temperature and pressure exceed the critical point, water will be in a supercritical state.^{17–20} Under supercritical conditions, the unique hydrogen bonds of water are almost completely destroyed (as shown in Figure 2), resulting in a very low polarity of SCW.^{21,22} It can easily dissolve in organic liquids, allowing reactions to occur in a homogeneous phase.^{23–26} Due to its high density, low viscosity, and good solubility in heavy oil, SCW has been widely studied as a potential heavy oil recovery method. In

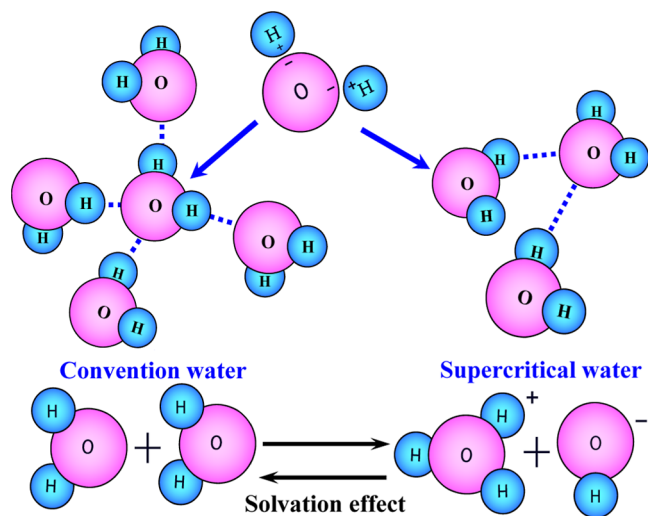


Figure 2. Structure diagram of conventional water and SCW.

particular, research has been conducted on the effective use of heavy oil, thermal cracking for upgrading, and synergies with other technologies.^{27–29} For example, Morimoto et al.³⁰ found that under the solvent effect of SCW, the formation of coke during heavy oil production was effectively inhibited. Cheng et al.³¹ conducted thermal cracking research on Gudao tar and found that SCW can increase the yield and quality of light products while reducing the coke yield. In terms of on-site application, some effects have been achieved. Yin et al.^{32,33} reported that the Lukeqin oilfield in China used SCW for thermal recovery of deep heavy oil reservoirs, and the daily oil production of wells increased significantly from 1.9 to 10 t/d. After nine consecutive cycles of thermal recovery, the production of three wells increased by 4000 t.

Non-condensable gases (NCGs) are gases that do not turn into liquids when compressed and cooled. These gases include carbon dioxide (CO₂), nitrogen (N₂), methane (CH₄), and others. During the thermal recovery of heavy oil reservoirs, mixing SCW and NCGs can make supercritical multicomponent thermal fluids. The multicomponent thermal fluid enhanced oil recovery technology is based on the way a high-pressure jet burns, which makes a mixture of N₂, CO₂, and steam when it burns in a sealed environment. The mixed fluid provides a significant oil recovery effect through the synergistic effect in the reservoir.³⁴ Due to the large amount of N₂ and CO₂ contained in the supercritical multicomponent thermal fluid, the dissolved NCGs (mainly CO₂) in the multicomponent thermal fluid can also achieve the effect of reducing crude oil viscosity, in addition to conventional heating viscosity reduction.^{35,36} Furthermore, NCGs (mainly N₂) can also reduce the reservoir heat loss, maintain the reservoir pressure, and thereby increase the recovery rate.^{37,38}

In the study of supercritical multicomponent thermal fluids, researchers gradually began to explore the research on improving recovery rates and cracking of heavy oil based on the previous research on SCW. For example, Tang et al.³⁹ realized through physical simulation experiments that the water–oil ratio (WOR) in the reactants has a significant impact on the production of multicomponent thermal fluids in the process of generating supercritical multicomponent thermal fluids. At the same time, the gas–water quality ratio also has a significant impact on the displacement efficiency of supercritical multicomponent thermal fluids. Some scholars, such as Sun, gradually focused on the hydrothermal cracking process of heavy oil by supercritical multicomponent thermal fluids and explored the reaction characteristics of the cracking process.^{40,41} Although supercritical multicomponent thermal fluids have very good production enhancement effects, the current multicomponent thermal fluid generator is heavily dependent on diesel, with high costs and strict water quality requirements that cannot directly use wastewater from heavy oil production. The single air supply method results in high combustion temperatures, severe corrosion in the local high-temperature area of the reactor, and serious heat dissipation. This makes the generation of supercritical multicomponent thermal fluids face problems such as high costs and environmental pollution.

Since the supercritical multicomponent thermal fluid is made up of SCW and NCGs and is used as a displacement medium, there are problems like high costs to make the fluid and pollution of the environment. Through lab experiments, this study looks at how SCW affects the thermal cracking of extra-heavy oil at different temperatures, WORs, and with the addition of NCGs. The behavior of extra-heavy oil during thermal cracking with

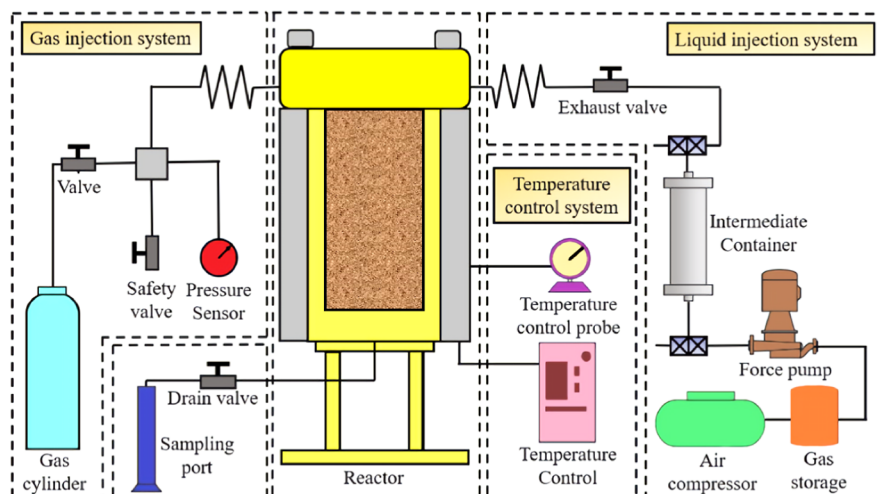


Figure 3. Experimental device of the SCW high-temperature and high-pressure reactor.

Table 1. Experimental Parameters of Cracking of Crude Oil under SCW

Tsc/°C	Php/MPa	$\rho_{scw}/(g \cdot cm^{-3})$	water oil ratio	Vhp/mL	Vw/mL	Vo/mL	Vsc/mL	Plp/MPa	note
390	25	0.25	2.5		125.0	50.0			SWC
410	25	0.15	2.5		75.0	30.0			
430	25	0.12	2.5		60.0	24.0			
390	25	0.25	2.5	175.1	125.0	50.0	18,811.68	5.11	SWC + NCG
410	25	0.15	2.5	101.0	75.0	30.0	10,427.87	2.48	
430	25	0.12	2.5	84.0	60.0	24.0	8417.98	1.94	
390	25	0.25	2.0		125.0	62.5			the influence of WOR
390	25	0.25	2.5		125.0	50.0			
390	25	0.25	3.0		125.0	41.7			

only SCW and with both SCW and NCGs was studied, and the products of thermal cracking were analyzed. The study calculated changes in reaction kinetic constants and clarified the thermal cracking characteristics of extra-heavy oil under the coexistence of SCW and NCGs. These findings deepen the understanding of the thermal cracking behavior of extra-heavy oil in the presence of SCW and provide a theoretical basis for the development of deep extra-heavy oil resources.

2. EXPERIMENTAL METHOD

2.1. Experimental Materials and Instruments. The oil utilized in the experiment was sourced from an offshore extra-heavy oil reservoir located in China. At a temperature of 50 °C, the degassed oil showed a viscosity of 29,168.1 mPa·s and a density ranging from 1.004 to 1.011 g/cm³. A comprehensive component analysis of the crude oil revealed that the target oil was comprised of 6.32% asphaltene, 31.19% saturated hydrocarbons, 30.44% naphthenic compounds, and 32.04% colloid.

The primary experimental setup is illustrated in Figure 3. The experimental equipment consisted of a supercritical high-temperature and high-pressure reactor, a constant-temperature water bath, a drying oven, an electric heating device, an analytical balance, a centrifuge, a gas cylinder, a four-component measuring device, and a rotational viscometer. The reactor had a volume of 500 mL and could withstand a maximum temperature and pressure of 450 °C and 30 MPa, respectively. Two experimental fluid conditions were considered: the first used SCW, while the second used a mixture of SCW and NCG. The NCG consisted of 13.8% CO₂ and 86.2% N₂.

2.2. Experimental Procedures. The experimental procedures are shown as following.

- (1) The PVT apparatus of high-pressure physical properties was used to measure the basic properties of the degassed crude oil, such as viscosity, density, and component content, at 50 °C.
- (2) The corresponding amounts of heavy oil and distilled water were added to the reaction vessel according to the experimental parameters listed in Table 1.
- (3) High-purity N₂ was continuously injected into the reaction vessel for 10 min to replace the air in the reaction vessel.
- (4) The reaction vessel was heated to rapidly reach the experimental temperature listed in Table 1. If the pressure in the reaction vessel exceeded the desired experimental pressure, then the pressure pump was adjusted to maintain the pressure at the design level.
- (5) The timer started when the temperature in the reaction vessel reached the preset experimental temperature value. And the power was immediately turned off when the experimental time was reached.
- (6) After the entire experimental system was cooled to 50 °C, the crude oil sample was taken out from the reaction vessel. The four-component analysis process for crude oil was used to determine the component content of the crude oil, and then the crude oil viscosity was measured at 50 °C, as shown in Figure 3.

2.3. Experimental Initial Parameter Design. Based on the experimental conditions, the physical parameters such as temperature, pressure, and density of the corresponding SCW

can be obtained. Then, the required volume of distilled water can be calculated according to the volume of the reactor (eq 1). With the volume of distilled water obtained, the required volume of crude oil can be calculated based on the WOR (R_{wo}) (eq 2). Similarly, in the study of the coexistence of SCW and NCG, the corresponding volume, pressure, and temperature parameters of the NCG at standard conditions can be obtained based on the experimental conditions. With eq 3, the initial conditions and volume of NCG at the experimental conditions can be calculated. The calculation processes are shown in Figure 4. The experimental parameters are listed in Table 1, and the calculation formulas are as follows.

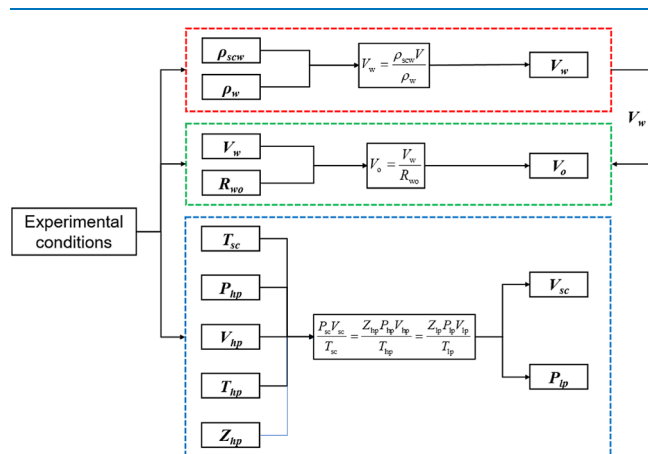


Figure 4. Calculation processes.

The volume of distilled water

$$V_w = \frac{\rho_{scw} V}{\rho_w} \quad (1)$$

The volume of crude oil

$$V_o = \frac{V_w}{R_{wo}} \quad (2)$$

Quantity of gas and initial pressure

$$\frac{P_{sc} V_{sc}}{T_{sc}} = \frac{Z_{hp} P_{hp} V_{hp}}{T_{hp}} = \frac{Z_{ip} P_{ip} V_{ip}}{T_{ip}} \quad (3)$$

where, V_w is the volume of distilled water under standard conditions, mL; ρ_{scw} is the density of SCW, g/cm³; V is the volume of the reactor, mL; ρ_w is the density of distilled water under standard conditions, g/cm³; V_o is the volume of crude oil under standard conditions, mL; R_{wo} is the water–oil volume ratio; P_{sc} is the pressure of gas under standard conditions, MPa; V_{sc} is the volume of gas under standard conditions, mL; T_{sc} is the temperature of gas under standard conditions, °C; Z_{hp} is the compression factor of gas under experimental conditions. P_{hp} is the pressure of gas under experimental conditions, MPa; V_{hp} is the volume of gas under experimental conditions, mL; T_{hp} is the temperature of gas under experimental conditions, °C; Z_{ip} is the gas compression factor under the initial experimental conditions; P_{ip} is the pressure of gas under the initial experimental conditions, MPa; V_{ip} is the volume of gas under the initial experimental conditions, mL; and T_{ip} is the temperature of gas under the initial experimental conditions, °C.

2.4. Analysis Method of Experimental Results Parameters. Upon thermal cracking by SCW, the composition of the liquid phase in the heavy oil changes. Additionally, the decomposition and transformation of asphaltene lead to the generation of gas and solid coke.⁴²

As shown in Figure 5, the reaction products were left to stand for a certain period of time, and then *n*-heptane was used to dissolve them. Insoluble products were then dissolved in toluene. If the products were soluble in toluene, they were identified as asphaltene, while insoluble products were considered solid coke. For products soluble in *n*-heptane, other solvents were used to measure the content of saturated hydrocarbons, aromatic hydrocarbons, and colloids. The four-component content of the liquid phase of crude oil, coke content, and gas content were calculated using the following formula

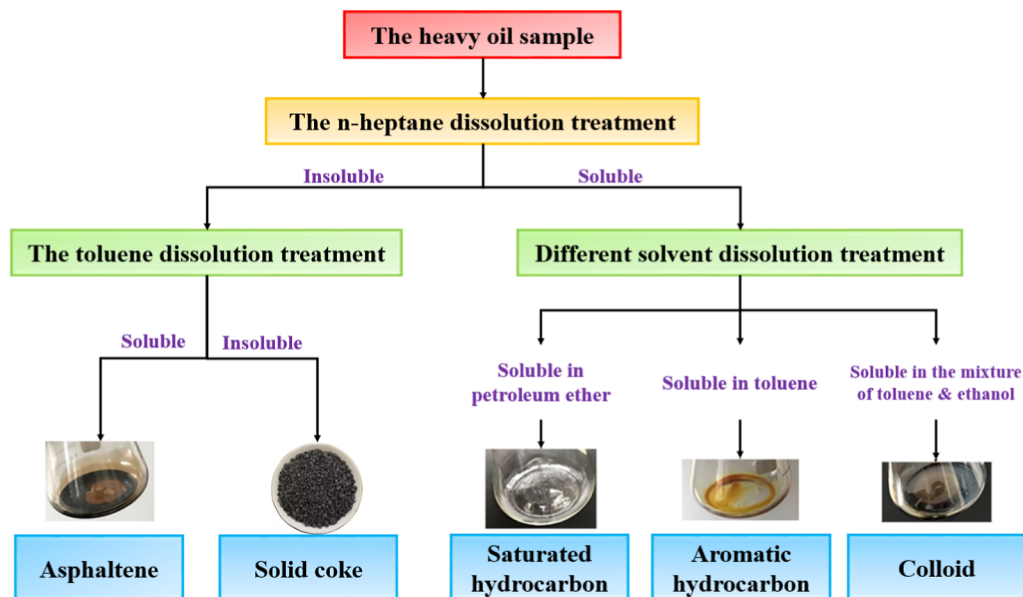
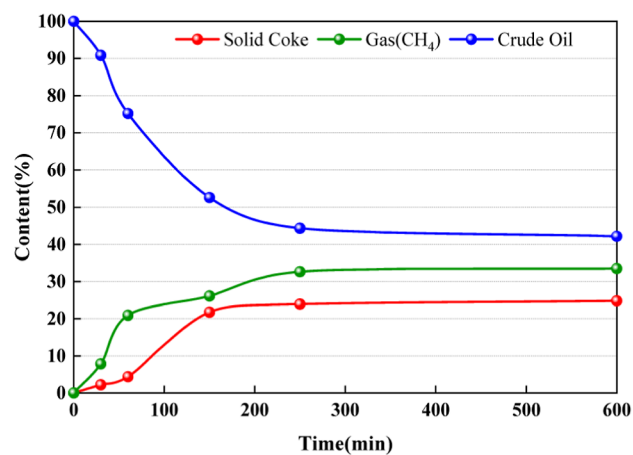
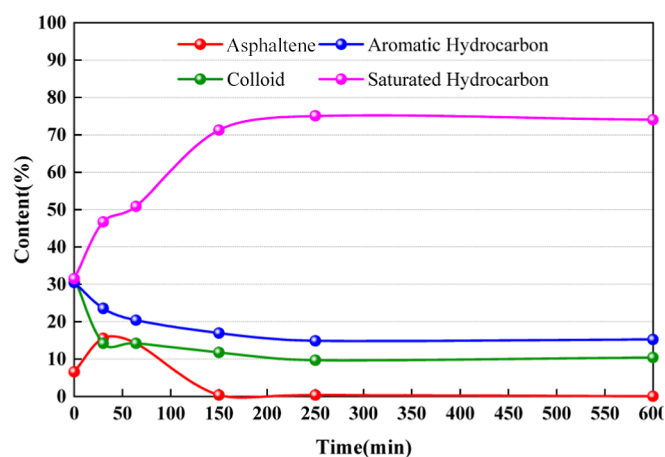


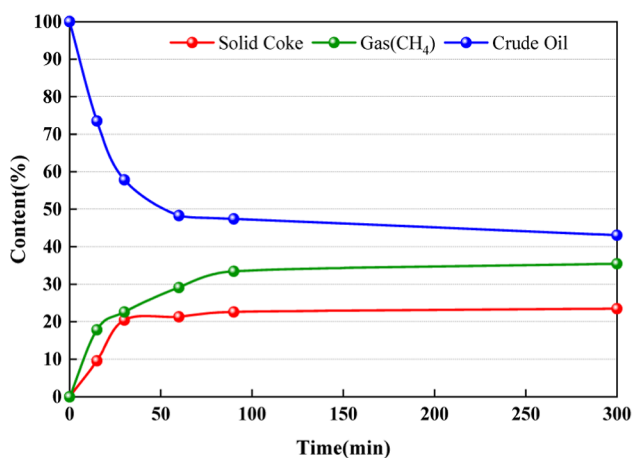
Figure 5. Flow chart of the four-component analysis of crude oil.



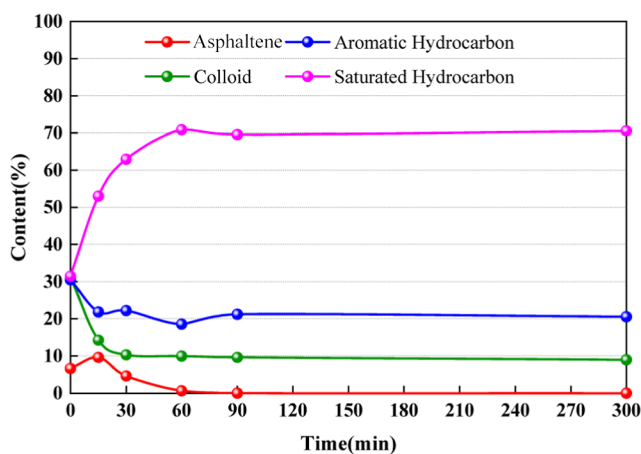
(a) The total components analysis of crude oil at 390°C



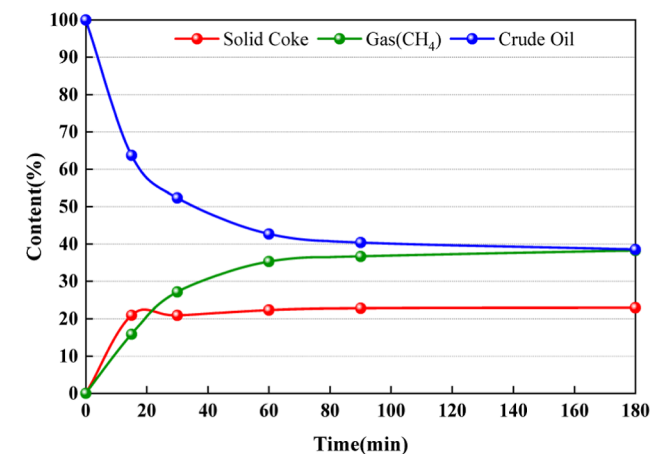
(b) The four components analysis of crude oil at 390°C



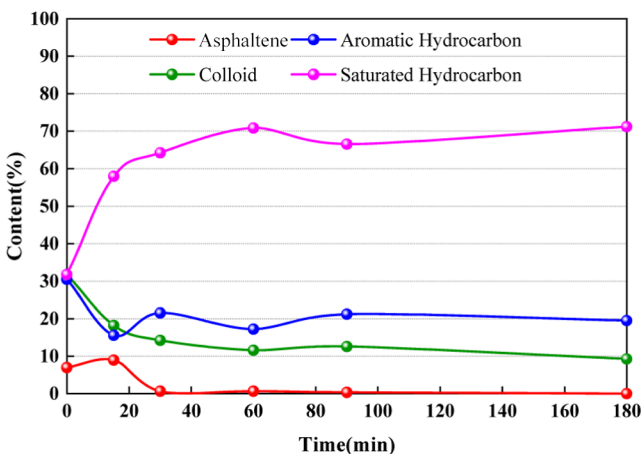
(c) The total components analysis of crude oil at 410°C



(d) The four components analysis of crude oil at 410°C



(e) The total components analysis of crude oil at 430°C



(f) The four components analysis of crude oil at 430°C

Figure 6. Effect of SCW at different temperatures on thermal cracking components of heavy oil. (a) Total components analysis of crude oil at 390 °C, (b) the four components analysis of crude oil at 390 °C, (c) the total components analysis of crude oil at 410 °C, (d) the four components analysis of crude oil at 410 °C, (e) the total components analysis of crude oil at 430 °C, (f) the four components analysis of crude oil at 430 °C.

$$Y_i = \frac{m_i}{m_L} \times 100\% \quad (4)$$

$$Y_C = \frac{m_C}{m_{Raw}} \times 100\% \quad (5)$$

$$Y_G = \frac{1 - m_L - m_C}{m_{Raw}} \times 100\% \quad (6)$$

where: Y_i is the mass percentage of each component of the crude oil liquid phase after thermal cracking, %; m_i is the mass of the crude oil liquid phase component after thermal cracking, g; m_L is

the total mass of the crude oil liquid phase after thermal cracking, g; Y_C is the mass percentage of solid coke produced after thermal cracking, %; m_C is the mass of solid coke produced after thermal cracking, g; m_{Raw} is the total mass of the crude oil sample before thermal cracking, g; and Y_G is the mass percentage of gas produced after thermal cracking, %.

According to the Arrhenius equation, which was an empirical formula for the change of chemical reaction rate constant with temperature,^{43–45} it was expressed as

$$k = Ae^{-E/RT} \quad (7)$$

Taking natural logarithms on both sides of the equation, we can get

$$\ln k = C - E/R1/T \quad (8)$$

where k is the reaction rate constant; A is the frequency factor; E is activation energy, J/mol; R is the gas constant, 8.314 J/(K·mol); T is the absolute temperature, K; and C is a constant, $C = \ln A$.

3. RESULTS AND DISCUSSION

The factors investigated in the experimental study included: (1) the effect of SCW on heavy oil thermal cracking at different temperatures (390, 410, and 430 °C); (2) the effect of adding NCG to SCW on heavy oil thermal cracking at different temperatures (390, 410, and 430 °C); and (3) the effect of different WORs (2.0:1.0, 2.5:1.0, and 3.0:1.0) on heavy oil thermal cracking.

3.1. Influence of Temperature. To investigate the effect of SCW on the thermal cracking characteristics of heavy oil, experiments were conducted under four temperature conditions: 310 °C (10 MPa, saturated state), 390 °C (25 MPa, supercritical state), 410 °C (25 MPa, supercritical state), and 430 °C (25 MPa, supercritical state). Figure 6 shows the variations in the total composition and four components of the target crude oil during the process of interacting with SCW.

Analysis of the variation characteristics revealed the following: (1) with increasing reaction time, the contents of coke and gas exhibited an overall upward trend during the cracking process. The coke generation curve exhibited an “S”-shaped feature. (2) The contents of asphaltenes and aromatic hydrocarbons in the crude oil sharply decreased in the initial stages of the reaction and remained stable after reaching a steady state, while the content of saturates reached its maximum value after the reaction stabilized and gradually tended to remain stable during the cracking process. (3) The content of colloids reached its highest value at 250 min (390 °C), 100 min (410 °C), and 30 min (430 °C) after the reaction and remained stable after the reaction stabilized. A comprehensive analysis of the thermal cracking characteristics revealed that the cracking rate of heavy oil increased with increasing temperature, and the generation time of each component became shorter. Analysis of the yield of coke and gas under high-temperature conditions (Figure 7) indicates that the yield of coke decreased while the yield of gas increased.

The experimental results are presented in Table 2 and Figure 8, where the original oil sample's four-component content, total composition content, and oil viscosity are used as comparative benchmarks.

Analyzing the thermal cracking products of the crude oil shown in Figure 8a, it can be seen that the crude oil did not undergo thermal cracking after wet steam distillation, while it underwent significant thermal cracking after SCW treatment,

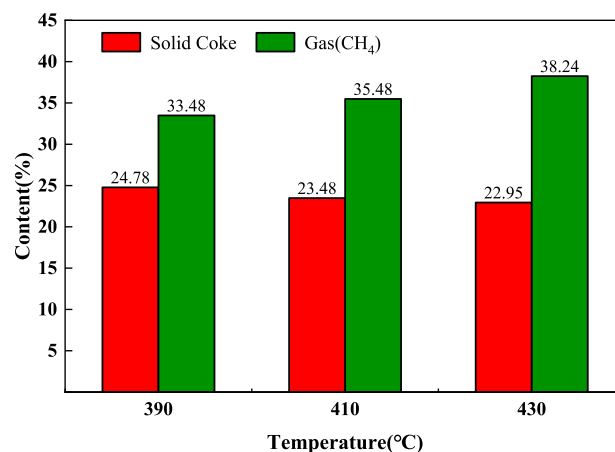


Figure 7. Production of coke and gas at different temperatures of SCW.

generating a large number of gaseous components (mainly CH₄) and a new component, solid coke. The analysis of the coke content showed that the coke content generated under three temperature conditions exceeded 23%. As coke belongs to solid-phase particles and has a great impact on the properties of crude oil, excessive deposition of coke in the reservoir will inevitably affect the pore structure of the porous medium and have adverse effects on fluid seepage.

From the analysis of the four-component content in Figure 8b, it can be concluded that after wet steam saturation, the asphaltene content of the heavy oil increased from 6.32 to 15.84%, while the content of aromatic hydrocarbons decreased from 30.44 to 23.73%. The content of saturated hydrocarbons and colloids did not change much, indicating that the light components in the extra-heavy oil were distilled out by wet saturated steam and no thermal cracking occurred. However, after a certain time of SCW hydrolysis, the asphaltene content in the crude oil became zero, and the content of saturated hydrocarbons exceeded 70%, while the content of aromatic hydrocarbons and colloids decreased significantly, indicating that the properties of the crude oil were improved, and the increase in light components came from the thermal cracking of asphaltene and colloids.

As shown in Figure 8c, it can be seen that the viscosity of the crude oil shows a slight increase due to the volatilization of light components after wet steam distillation, while the viscosity of the crude oil was only about 30% of the original value (at 50 °C) after SCW thermal cracking. As the temperature increases, the viscosity of the thermally cracked crude oil decreases, and after the experimental temperature exceeded 410 °C, the viscosity of the thermally cracked crude oil basically no longer changed (at 50 °C). Therefore, a temperature of 400 °C or above can meet the SCW thermal cracking of extra-heavy oil and make the coke conversion rate relatively low.

3.2. Influence of WOR. The WOR represents the degree of contact between the SCW and heavy oil, with a higher WOR indicating more sufficient thermal cracking of heavy oil. WOR values of 2.0:1.0, 2.5:1.0, and 3.0:1.0 were chosen for the corresponding experiments, and the experimental results are shown in Table 3 and Figure 9.

As shown in Table 3 and Figure 9, with the increase of the WOR, the viscosity of the cracked oil gradually decreases, indicating that the thermal cracking reaction of heavy oil is more sufficient under high WOR conditions. Therefore, increasing the WOR or the amount of SCW can help promote the thermal

Table 2. Effect of SCW on Thermal Cracking of Heavy Oil at Different Temperatures

test objectives	fluid type	experiment temperature/°C	experimental pressure/MPa	four components content/%				total composition content/%			oil viscosity (50 °C)/mPa·s
				asphaltene	saturated hydrocarbon	aromatic hydrocarbon	colloid	oil phase	solid coke	gas	
original oil sample				6.32	31.19	30.44	32.04	100.00	0.00	0.00	29,168.09
distillation	wet steam	310	10	15.84	30.34	23.73	30.09	100.00	0.00	0.00	35,226.47
thermal cracking	SCW	390	25	0.00	73.97	15.29	10.74	42.32	24.60	33.08	8798.54
		410	25	0.00	70.59	20.24	9.16	43.20	23.36	33.44	7605.69
		430	25	0.00	71.44	19.35	9.21	38.70	23.14	38.16	7641.97

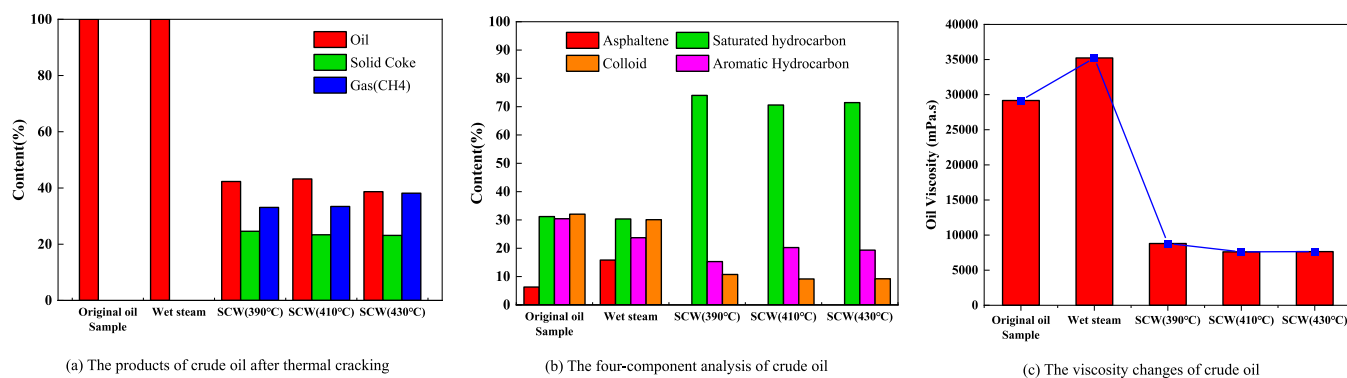


Figure 8. Effect of SCW on thermal cracking of heavy oil at different temperatures. (a) Products of crude oil after thermal cracking, (b) the four-component analysis of crude oil, (c) the viscosity changes of crude oil.

Table 3. Effect of SCW at Different WORs on the Viscosity of Crude Oil

test objectives	fluid type	WOR	experimental temperatures/°C	experimental pressure/MPa	viscosity (50°C)/mPa·s
original oil sample					29,168.09
distillation	wet steam	2.5:1.0	310	10	35,226.47
thermal cracking	SCW	2.0:1.0	390	25	16,431.17
		2.5:1.0	390	25	9622.14
		3.0:1.0	390	25	6376.01

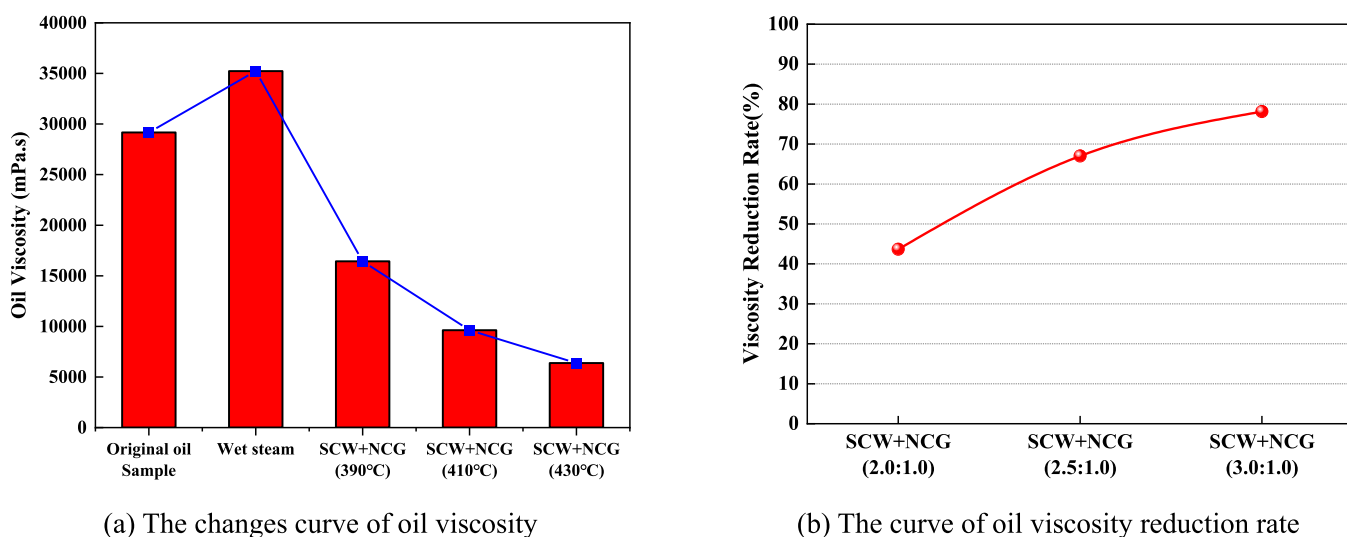
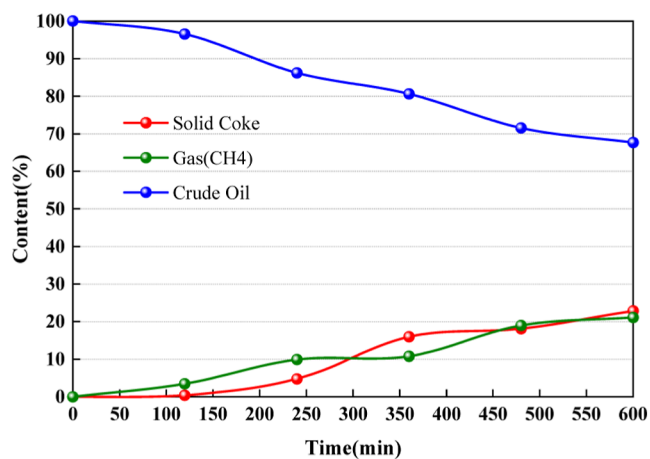


Figure 9. Viscosity changes of crude oil under different WORs. (a) Curve of changes in oil viscosity and (b) curve of oil viscosity reduction rate.

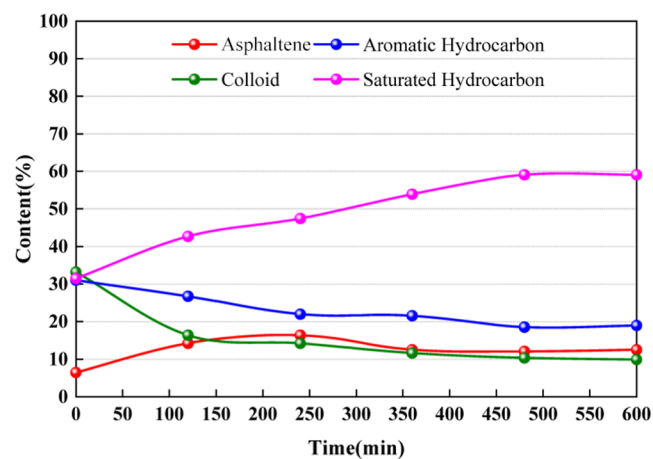
cracking reaction of heavy oil, further improving the flowability of cracked heavy oil. As shown in Figure 9b, it can be seen that the viscosity reduction rate of the cracked oil gradually increased with the WOR increasing. When the WOR exceeds 2.5:1.0, the

increasing rate gradually slows down. Therefore, the optimal WOR is above 2.5:1.0.

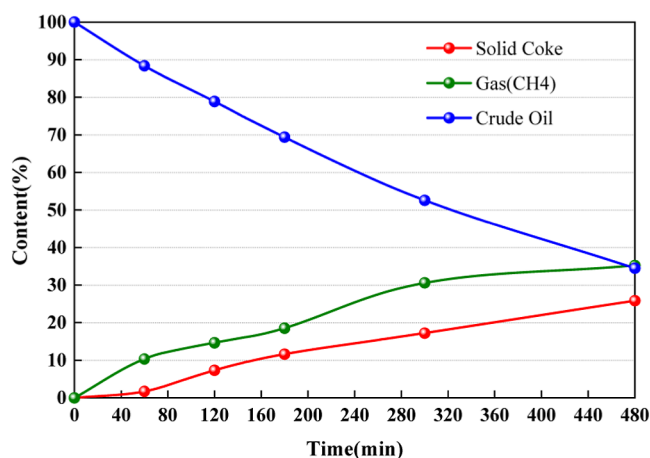
3.3. Influence of Non-condensate Gas. On the basis of conducting experiments on SCW thermal cracking of extra-



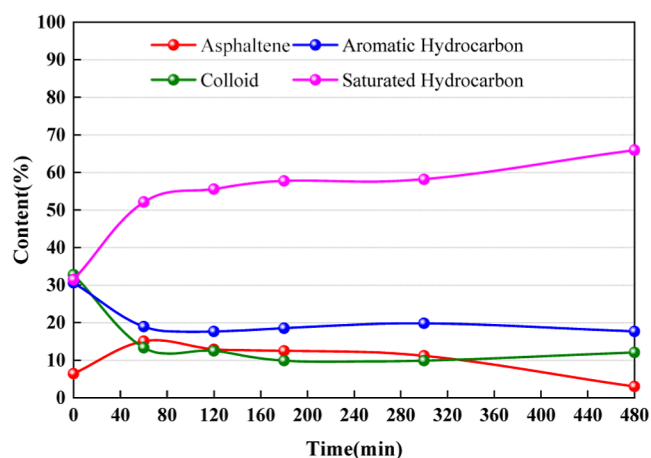
(a) The total components analysis of crude oil at 390°C



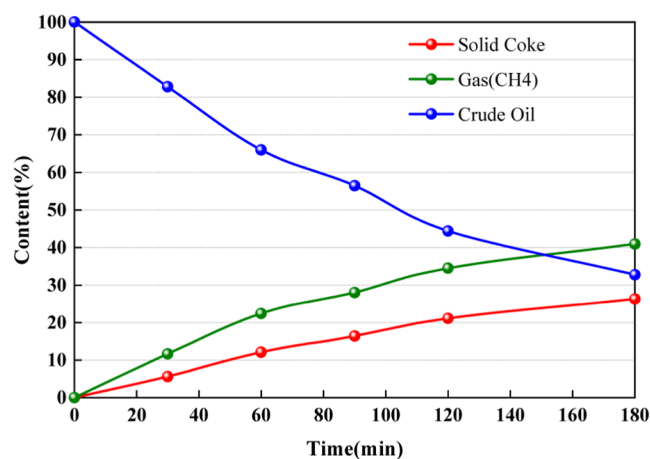
(b) The four components analysis of crude oil at 390°C



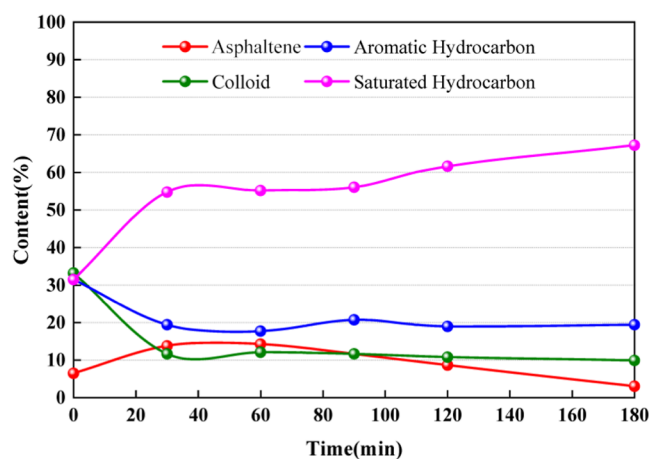
(c) The total components analysis of crude oil at 410°C



(d) The four components analysis of crude oil at 410°C



(e) The total components analysis of crude oil at 430°C



(f) The four components analysis of crude oil at 430°C

Figure 10. Effect of SCW + NCG at different temperatures on thermal cracking of heavy oil. (a) Total components analysis of crude oil at 390 °C, (b) the four components analysis of crude oil at 390 °C, (c) the total components analysis of crude oil at 410 °C, (d) the four components analysis of crude oil at 410 °C, (e) the total components analysis of crude oil at 430 °C, (f) the four components analysis of crude oil at 430 °C.

heavy oil and determining the optimal WOR, experiments were carried out on the thermal cracking of extra-heavy oil under the coexistence of SCW and NCG (SCW + NCG, gas containing 13.8% CO₂ and 86.2% N₂) at temperatures of 390, 410, and 430 °C. The changes in the components of the cracked oil and the

four components of the original oil with time during the experiment are shown in Figure 10.

Based on the analysis of the changes in the components shown in Figure 10, the following can be concluded: (1) with the increase in temperature, the time required for the thermal

cracking to reach equilibrium was shortened. Compared with saturated hydrocarbons, the asphaltene content showed an obvious trend of first increasing and then decreasing with increasing reaction time, while the saturated hydrocarbon content showed a significant increase. The aromatic hydrocarbon and colloid contents remained basically stable after a certain degree of decrease. (2) During the thermal cracking process, the liquid-phase crude oil content decreased significantly while the gas content increased sharply. This phenomenon indicated that in the later stage of thermal cracking, the cracking of saturated hydrocarbons produced smaller alkane molecules, leading to a significant increase in gas content. (3) After thermal cracking, the insoluble substance 'coke' was generated in the crude oil. Analyzing the changes in the rate of coke generation showed that the rate of coke generation was extremely slow in the early stage of cracking. In the later stage of the reaction, when a certain amount of coke was generated, the generation of coke was accelerated. The large amount of coke generated will certainly have an impact on the reservoir.

Figure 11 shows the results of an analysis of the production of coke and gas at high temperatures. Compared to the changes in

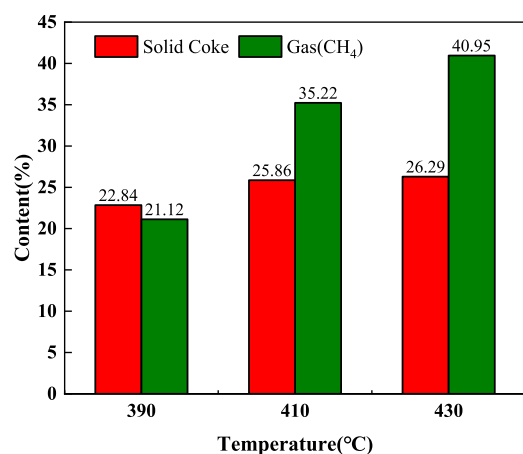


Figure 11. Change of solid coke and gas production at different temperatures under SCW + NCG.

coke production caused by SCW, the production of coke caused by SCW and NCG showed a gradual increase as the temperature increased. This was opposite to the situation where only SCW was present, indicating that the addition of NCG promotes coke production. As for gas generation, both systems showed a significant increase in gas generation.

The experimental results are summarized in Table 4, and the four groups of components, total composition, and viscosity of the oil sample under SCW conditions in Table 3 are used as a reference for comparison, as shown in Figure 12.

Analysis of the variation characteristics of each component in the oil samples in Figure 12a reveals that at 390 °C, compared with SCW, the addition of NCG to SCW reduced the extent of thermal cracking of heavy oil. After the interaction of the mixed system composed of SCW and NCG, the liquid phase of the crude oil accounted for 67.37% of the total crude composition (including the liquid, gas, and solid phases), while the liquid phase of the crude oil with SCW alone accounted for only 42.32%. By comparing the variation of the coke content after thermal cracking of heavy oil with SCW at 410 and 430 °C, it was found that the coke content in the components increased to a certain extent after the addition of NCG, and the coke content with NCG is about 3% higher than that with SCW alone.

Based on the analysis of the four components' contents in Figure 12b, it can be observed that after the interaction of SCW + NCG, the content of asphaltene in the remaining liquid phase oil sample increased to 12.20%. This indicated that the thermal conversion ability of asphaltene was reduced by the addition of NCG to SCW. Meanwhile, with increasing temperature, the thermal cracking effect of crude oil under the interaction of SCW + NCG showed a gradually increasing trend, while the content of asphaltene decreased and the amount of generated coke and gas increased.

The analysis of the viscosity changes in Figure 12c indicated that after the thermal cracking of the original oil by the mixed system of SCW and NCG, the viscosity of the crude oil showed a significant decrease. However, the post-cracking viscosity of the original oil remained above 10,000 mPa·s, which still falls within the range of extra-heavy oils, mainly due to the incomplete conversion of asphaltene. Therefore, the addition of NCG was not only unfavorable for the thermal cracking of heavy oil by SCW but also further promoted the formation of coke.

3.4. Reaction Kinetics Characteristics. Based on the Arrhenius equation, $\ln k$ is directly proportional to the inverse of the absolute temperature ($1/T$) for a substance with a constant activation energy.⁴⁶ By analyzing the experimental results, the thermal cracking characteristics of heavy oil by SCW and SCW + NCG can be analyzed, as shown in Figure 13.

Based on Figure 13, it can be observed that the logarithm of the reaction rate constant had a clear linear relationship with the inverse of temperature ($1/T$), and the reaction rate increased significantly with increasing temperature. In the SCW-heavy oil system and the SCW + NCG-heavy oil system, the reaction rate constant curves of asphaltene, colloid, and aromatic hydrocarbons showed a parallel trend because they were all cracking components of the thermal cracking reaction. However, oil components contained liquid crude oil after the removal of coke and gas. It included saturated hydrocarbons, aromatic hydrocarbons, colloids, and asphaltene, which included cracking and generating components. Although the reaction rate constant curve of oil components was still a straight line, there was a

Table 4. Effect of SCW + NCG on Thermal Cracking of Heavy Oil at Different Temperatures

test objectives	fluid type	experimental temperatures/°C	experimental pressure/MPa	four component contents/%				total composition content/%			crude oil viscosity (50° C)/mPa·s
				asphaltene	saturated hydrocarbon	aromatic hydrocarbon	colloid	oil phase	solid coke	gas	
thermal cracking	SWC + NCG	390	25	12.20	58.04	19.64	10.12	67.37	11.86	20.77	20,963.80
		410	25	3.45	65.93	17.91	12.70	34.95	26.12	38.93	13,720.76
		430	25	3.21	67.30	19.23	10.26	32.48	26.80	40.72	11,532.21

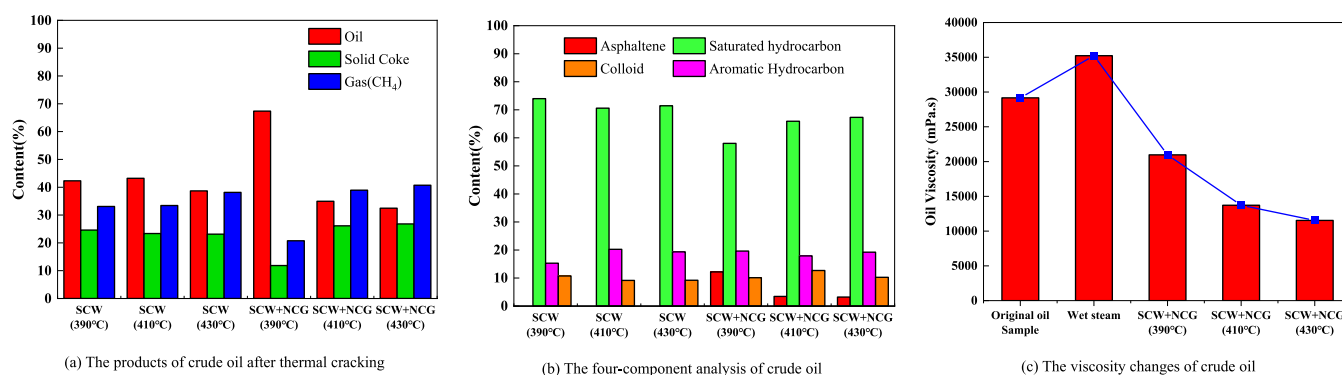


Figure 12. Effect of SCW + NCG on thermal cracking of heavy oil at different temperatures. (a) Products of crude oil after thermal cracking, (b) the four-component analysis of crude oil, (c) the viscosity changes of crude oil.

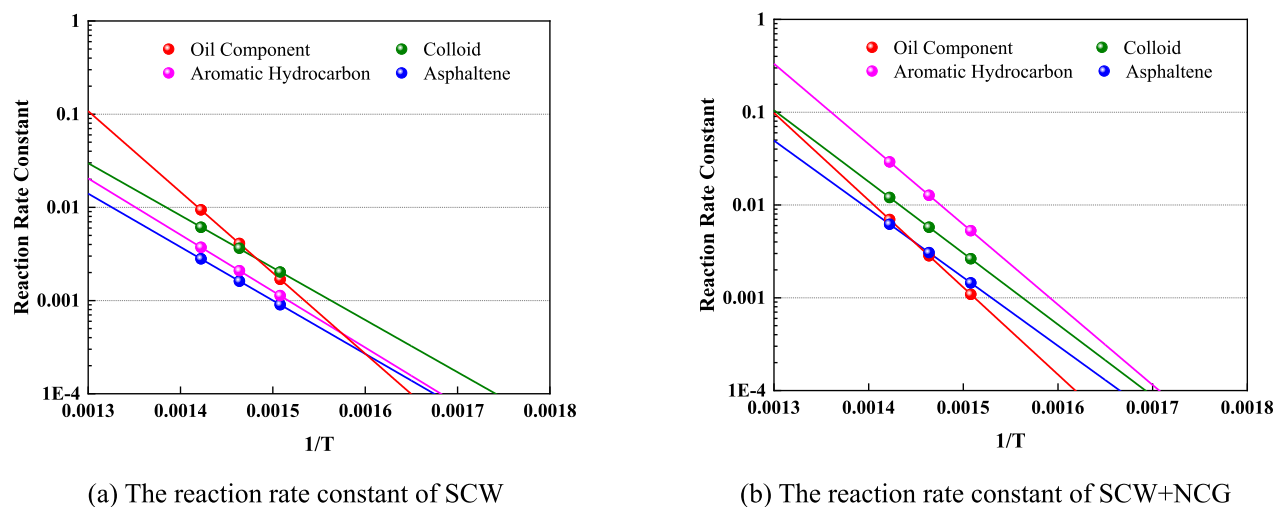


Figure 13. Changes of reaction rate constants of SCW and SCW + NCG. (a) Reaction rate constant of SCW, (b) reaction rate constant of SCW + NCG.

crossover phenomenon with the other three curves. By comparison, it can be seen that the thermal cracking rate of heavy oil samples in a SCW environment was significantly higher than that in a SCW environment with NCGs added. In the SCW environment, the reaction rate of asphaltene components was the highest, while in the SCW environment with NCG added, the reaction rate of asphaltene was lower than that of colloid. This indicated that the addition of NCG slowed down the thermal decomposition rate of asphaltene and was unfavorable to the thermal cracking reaction of heavy oil.

4. CONCLUSIONS

- (1) This study utilized laboratory experiments to thoroughly investigate the effects of different factors, including steam temperature, the presence of NCG, and WOR, on the characteristics of heavy oil thermal cracking under the influence of SCW. The reaction kinetics of heavy oil thermal cracking under SCW conditions were quantitatively analyzed using the Arrhenius formula. The findings of this study have practical implications in understanding the mechanisms of improving oil recovery in heavy oil reservoirs using SCW and promoting the application and popularization of SCW in thermal oil recovery from deep extra-heavy oil reservoirs.
- (2) Under SCW conditions, heavy oil undergoes significant thermal cracking effects, resulting in an increase in

saturated hydrocarbons and a decrease in naphthenes and colloids. The content of light components (even CH_4) and coke is increased. At 50 °C, the viscosity of the crude oil after SCW thermal cracking is only about 30% of the original value, and the properties of the crude oil are improved. SCW can exhibit thermal cracking effects above 400 °C, effectively reducing the coke conversion rate. As the WOR increases, the thermal cracking reaction of heavy oil is enhanced, and the optimal WOR is 2.5:1.0 or higher

- (3) At 390 °C, the thermal cracking effect of SCW with the addition of NCG is significantly weaker than that of SCW alone, and the addition of NCG reduces the thermal conversion ability of asphaltene. With the increase of temperature, the thermal cracking effect of the system composed of SCW and NCG gradually increases, and the content of generated gas increases significantly while the content of the target heavy oil asphaltene decreases. The addition of NCG exacerbates the conversion of coke, and the content of coke produced by the reaction is about 3% higher than that of SCW alone.
- (4) The logarithmic value of the reaction rate constant is linearly related to the inverse of the temperature. As the temperature increases, the reaction rate increases. The thermal cracking rate of heavy oil is higher under SCW conditions than under the conditions of SCW + NCG.

The reaction rate of the asphaltene component is the highest in the SCW environment, while in the mixed system environment of SCW and NCG, the reaction rate of asphaltene is lower than that of colloid. The addition of NCG slows down the thermal cracking rate of asphaltene and is not conducive to the thermal cracking reaction of heavy oil.

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Notes

The authors declare no competing financial interest.

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