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Comparison of the Reaction Characteristics of Different Fuels in the Supercritical Multicomponent Thermal Fluid Generation Process

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Abstract: Supercritical multicomponent thermal fluid technology is a new technology with obvious advantages in offshore heavy oil recovery. However, there is currently insufficient understanding of the generation characteristics of the supercritical multicomponent thermal fluid, which is not conducive to the promotion and application of this technology. In order to improve the economic benefits and applicability of the supercritical multicomponent thermal fluid thermal recovery technology, this article reports on indoor supercritical multicomponent thermal fluid generation experiments and compares the reaction characteristics of different fuels in the supercritical multicomponent thermal fluid generation process. The research results indicate that the main components of the products obtained from the supercritical water–crude oil/diesel reaction are similar. Compared to the supercritical water–crude oil reaction, the total enthalpy value of the supercritical multicomponent thermal fluid generated by the supercritical water–diesel reaction is higher, and the specific enthalpy is lower. When the thermal efficiency of the boiler is the same, the energy equilibrium concentration of crude oil is lower than that of diesel. The feasibility of using crude oil instead of diesel to prepare supercritical multicomponent thermal fluids is analyzed from three aspects: reaction mechanism, economic benefits, and technical conditions. It is believed that using crude oil instead of diesel to prepare supercritical multicomponent thermal fluids has good feasibility.

Keywords: heavy oil; supercritical multicomponent thermal fluid; thermal recovery

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1. Introduction

China has abundant heavy oil resources, with offshore heavy oil resources mainly concentrated in the Bohai Bay. The conventional heavy oil thermal recovery technology has achieved good results on land, but its adaptability is poor in sea [1–5]. The problems are mainly concentrated in the following aspects: First, conventional thermal recovery technologies mostly use steam as the heat carrier, which has high requirements for water quality. The water treatment process on offshore platforms is complex, and the costs for water treatment and pipeline maintenance are very high. Second, the preparation of steam heavily relies on diesel fuel, which is costly and emits a large amount of carbon dioxide. Third, there is severe heat loss during the steam injection process, resulting in low thermal efficiency.

Therefore, in 2017, Zhou et al. proposed the supercritical multicomponent thermal fluid technology [6]. Supercritical multicomponent thermal fluids are a type of mixed fluid generated by the reaction of supercritical water with diesel or crude oil, primarily consisting of supercritical water, nitrogen, and carbon dioxide. Due to the strong reactivity of supercritical water, supercritical multicomponent thermal fluid exhibits the following three characteristics: Firstly, it has high solubility for organic compounds and gases in oil and can approximate miscible flooding, improving the efficiency of heavy oil displacement;

Secondly, it has high diffusivity, low surface tension and dynamic viscosity, large swept volume after injection into the formation, and a good displacement effect; Thirdly, it has high reactivity and can significantly reduce the conversion temperature of long-chain macromolecular hydrocarbons in heavy oil, thereby improving the properties of heavy oil in the formation and enhancing its flow capacity.

Supercritical multicomponent thermal fluids are primarily composed of supercritical water, carbon dioxide (CO_2), and nitrogen (N_2). Their production predominantly utilizes techniques such as supercritical water gasification and supercritical water oxidation. Leveraging the exceptional solubility and diffusivity of supercritical water, a wide array of organic waste liquids, including diesel and oily effluents, can be completely dissolved and rapidly vaporized under the extreme temperature and pressure characteristics of supercritical conditions. This process converts them into gasification products primarily consisting of hydrogen (H_2) and carbon dioxide (CO_2). Subsequently, these products are combusted with oxygen-enriched gases that are also dissolved in supercritical water, culminating in the formation of supercritical multisource, multicomponent thermal fluids. This approach harnesses the unique properties of supercritical water to efficiently transform waste into a potent source of energy [6–10]. During the supercritical water gasification process, this unique medium significantly enhances the conversion efficiency of the feedstock. It diminishes the coke formation within the system and exerts a profound impact through its solvent and dispersive capabilities, hydrogen donation, and acid-catalytic functions. These attributes lead to remarkable desulfurization, denitrification, and the removal of heavy metals, thereby contributing to a cleaner and more efficient gasification outcome. The transformative power of supercritical water lies in its ability to act as a potent solvent that breaks down complex organic molecules, while its capacity to transfer hydrogen and catalyze reactions accelerates the gasification process, yielding a more refined end product [11,12].

In the oxidation process of supercritical water, higher content of organic matter brings greater heat release [13–16]. Additionally, once the concentration of organic material in the reaction mixture crosses a specific threshold, the exothermic nature of the reaction can be harnessed to maintain the heat balance, thereby enabling an energy-self-sustaining process. This innovative approach significantly enhances the economic viability of the entire operation. Preliminary findings from our research indicate that an oxygen surplus exceeding 10% is sufficient to ensure the complete dissociation of all substances involved in the reaction. Beyond this point, an increase in oxygen levels does not exert any additional influence on the reaction's progress [17]. Furthermore, it is observed that when the organic matter concentration in the supercritical water oxidation reaction exceeds 2%, the reaction becomes self-heating. This is attributed to the substantial heat liberated during the reaction process, which is sufficient to sustain the reaction's temperature requirements without the need for external heating sources. This self-sustaining characteristic is a significant advantage, as it contributes to the overall energy efficiency and cost-effectiveness of the process [18–21]. Experiments on wastewater with different chemical oxygen consumption ranges show that as long as the chemical oxygen consumption ranges from 183 to 437 g/L and the mass flow rate ranges from 20.83 to 104.17 kg/h, the reaction can be maintained entirely by the heat released from its own reaction [21].

Previous work mainly focuses on the supercritical water treatment of wastewater, and the research on the reaction mechanism of supercritical water and the products after the reaction is relatively mature. However, there is currently little discussion on using different fuels to generate supercritical multicomponent thermal fluids under different conditions, let alone comparing the similarities and differences of different fuels in the process of generating supercritical multicomponent thermal fluids and the substitutability between fuels. However, these are precisely the things that oil field engineers are very concerned about. In view of this and to better understand the process of generating supercritical multicomponent thermal fluids using different fuels and clarify the differences brought about by various fuels, in this study, we conducted experiments on the generation of supercritical multicomponent thermal fluids using diesel and crude oil under

different conditions. Based on the experimental results, the characteristics of supercritical multicomponent thermal fluids prepared using different fuels under different conditions were compared and analyzed, and the feasibility of using crude oil instead of diesel to generate supercritical multicomponent thermal fluids was tested. This study marks the first comprehensive comparison of the differences in generating supercritical multicomponent thermal fluids using various fuels. It holds significant guiding importance for the rational selection of fuels for the generation of supercritical multicomponent thermal fluids.

2. Materials and Methods

(1) Experimental materials

The diesel used in these experiments is 0# diesel, and the crude oil is from the L block of Bohai Bay, China. At reservoir temperature (50 °C), the viscosity of crude oil is 1756 MPa·s, which belongs to ordinary heavy oil. The SARA analysis results of crude oil are shown in Table 1.

Table 1. SARA analysis results of crude oil.

No.	Component	Wt.%
1	Asphaltenes	25.99
2	Resins	8.14
3	Aromatics	19.65
4	Saturates	46.22
5	Total	100.00

(2) Apparatus

As illustrated in Figure 1, the experimental setup is anchored by a supercritical multicomponent thermal fluid generation system and a chromatographic analysis apparatus. The former includes a high-temperature, high-pressure reactor (as shown in Figure 2), an ISCO pump, a check valve, and an intermediate holding vessel, all meticulously designed to facilitate the generation process. The chromatographic analysis apparatus, on the other hand, is equipped with both a gas chromatograph and a liquid chromatograph, ensuring a comprehensive analysis of the thermal fluid components. This sophisticated arrangement of equipment ensures a seamless workflow from the production of supercritical fluids to their detailed characterization.

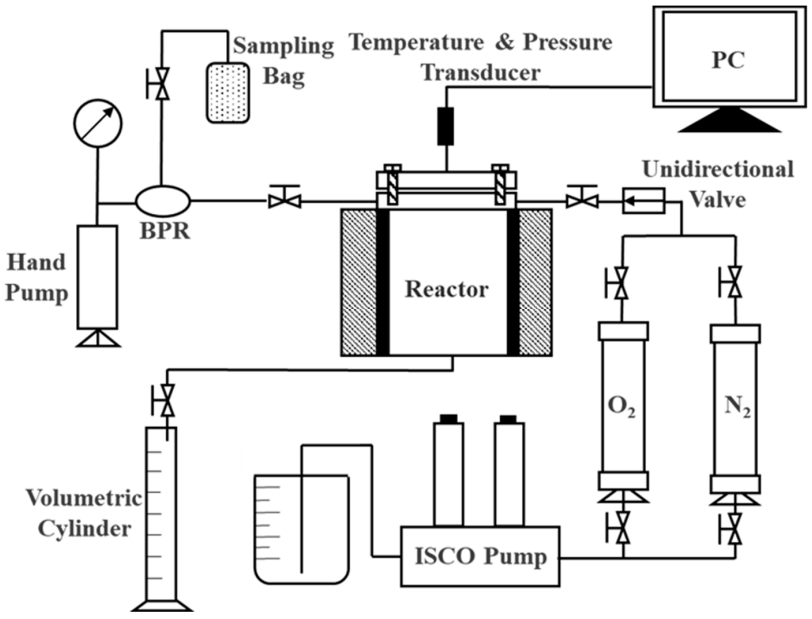


Figure 1. Experimental flow of supercritical multicomponent thermal fluid generation.



Figure 2. High temperature and pressure reactor.

(3) Procedures

①Analyzing diesel oil/crude oil samples by liquid chromatography before the experiment.

② Checking the status of experimental equipment and repairing faulty components.

③ Connecting the experimental equipment according to the experimental flow chart.

④ Carefully measuring diesel oil or crude oil sample and water according to the predetermined ratio; the mixture is introduced into the high-temperature, high-pressure reactor, ensuring a secure seal to contain the process within. The experimental vessel is crafted from HC276 alloy, a material renowned for its durability and resistance to extreme conditions. It is designed to withstand a maximum working pressure of up to 40 MPa and can operate effectively at temperatures reaching as high as 600 °C, providing a robust platform for conducting experiments under demanding thermal and pressure regimes.

⑤ Opening the air inlet and outlet, charging nitrogen for more than 10 min through the air inlet with a large displacement to ensure that the air in the reactor is cleared, and then closing the air outlet.

⑥ Filling nitrogen into the reactor up to the design pressure and then turning on the reactor power supply and the heating mode.

⑦ Upon attaining the supercritical state within the reactor, as indicated by the optimal temperature and pressure thresholds, the heating process is gradually discontinued, and the agitation function is engaged. Throughout the entirety of the reaction experiment, the reactor is continuously supplied with oxygen, ensuring a steady progression of the reaction to its conclusion. Concurrently, the fluctuating temperatures and pressures within the reactor during the experiment are meticulously monitored and documented in real time, capturing the dynamic essence of the supercritical transformation.

⑧ Once the reaction is complete, the reactor is allowed to cool, descending from its supercritical temperatures to a safe, ambient level. As the reactor's temperature returns to normalcy, the air outlet is cautiously opened, facilitating the collection of gas samples that have been formed within the vessel. Subsequently, the pressure within the reactor is gradually relieved, and the reactor itself is opened to carefully harvest any remaining liquid and solid residues, if present, ensuring that all components are accounted for in the post-reaction analysis.

⑨ Analyzing the collected gas–liquid samples by chromatography.

The parameters determined for the experiment are shown in Table 2. Given the specific conditions on the oil field, two types of fuels, three temperature conditions, and two pressure conditions are being considered.

Table 2. Experimental parameters of supercritical water–oil reaction.

Case	Reactant	Initial Temperature and Pressure
1	45 mL water + 5 mL diesel oil	400 °C/23 MPa
2	45 mL water + 5 mL diesel oil	400 °C/25 MPa
3	45 mL water + 5 mL diesel oil	450 °C/25 MPa
4	45 mL water + 5 mL diesel oil	500 °C/25 MPa
5	45 mL water + 5 mL diesel oil	500 °C/23 MPa
6	45 mL water + 5 mL diesel oil	400 °C/25 MPa
7	28.3 mL water + 5 mL diesel oil	400 °C/25 MPa
8	20 mL water + 5 mL diesel oil	400 °C/25 MPa
9	15 mL water + 5 mL diesel oil	400 °C/25 MPa
10	11.67 mL water + 5 mL diesel oil	400 °C/25 MPa
11	45 mL water + 5 mL crude oil	400 °C/23 MPa
12	45 mL water + 5 mL crude oil	400 °C/25 MPa
13	45 mL water + 5 mL crude oil	450 °C/25 MPa
14	45 mL water + 5 mL crude oil	500 °C/25 MPa
15	45 mL water + 5 mL crude oil	500 °C/23 MPa
16	45 mL water + 5 mL crude oil	400 °C/25 MPa
17	28.3 mL water + 5 mL crude oil	400 °C/25 MPa
18	20 mL water + 5 mL crude oil	400 °C/25 MPa
19	15 mL water + 5 mL crude oil	400 °C/25 MPa
20	11.67 mL water + 5 mL crude oil	400 °C/25 MPa

3. Results and Discussion

3.1. Comparison of Reaction Product Composition, Product State, and Reaction Mechanism of Supercritical Water–Crude Oil and Water–Diesel Oil

Following the completion of the supercritical water–oil (encompassing diesel oil and crude oil) reaction experiment, which was conducted under various oil–water ratios and a range of temperature and pressure settings, the reactor was allowed to cool down to ambient temperature. Subsequently, the gaseous contents within the reactor were extracted and subjected to chromatographic analysis. This process was undertaken to ascertain the precise makeup of the supercritical multicomponent thermal fluid.

The chromatographic analysis results (Figures 3 and 4) indicate that the primary constituents of the gaseous byproducts from the reactions involving diesel oil and heavy oil (at room temperature) are largely identical. This implies that the primary components are carbon dioxide, nitrogen, and oxygen that were not utilized in the reaction process. However, when contrasting the reaction outputs of diesel oil with those of heavy oil, it is evident that the latter reaction yields a higher concentration of impurity gases, including sulfur dioxide and nitrogen dioxide. This disparity is attributed to the fact that heavy oil, unlike diesel oil, contains asphaltene, which is composed of heteroatom elements, such as sulfur and nitrogen. These elements, upon undergoing complete combustion in an oxygen-rich environment, transform into sulfur dioxide and nitrogen dioxide.

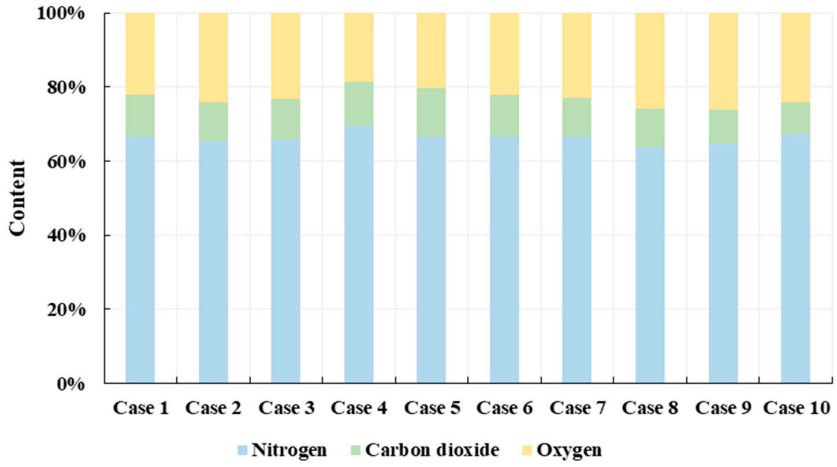


Figure 3. Gas chromatography analysis of supercritical water–diesel oil reaction products.

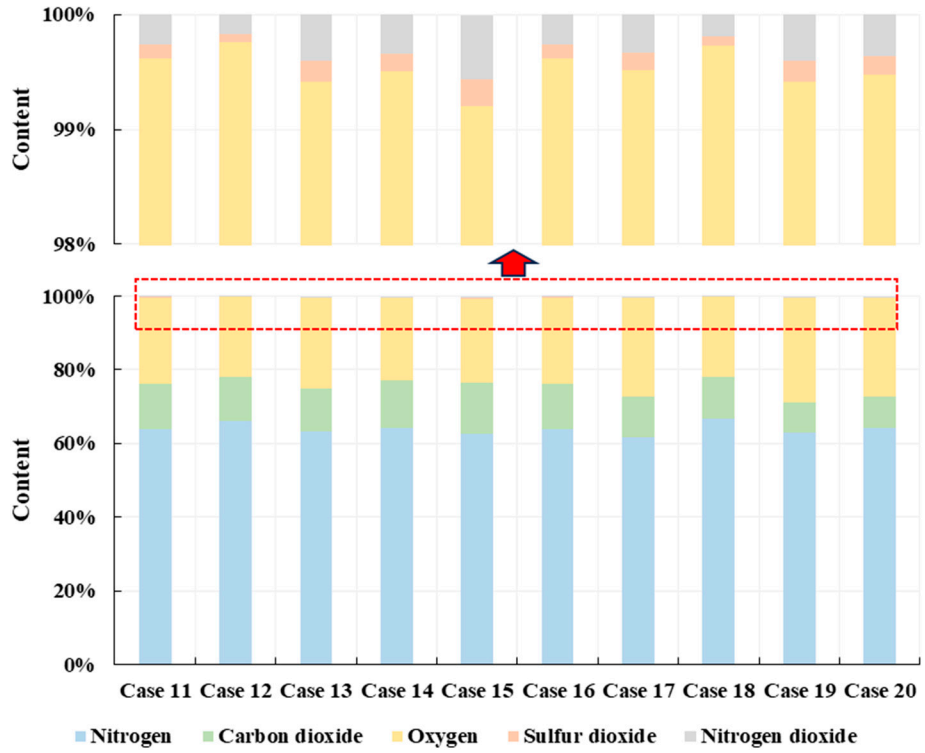


Figure 4. Gas chromatography analysis of supercritical water–crude oil reaction products.

The influence of the oil–water ratio in the reactants is more pronounced on the chromatographic outcomes. In the experiments, while the overall quantity of oil was kept constant, the oil–water ratio was modified by varying the volume of water. Given a fixed reactor size, the amount of nitrogen required to achieve the same initial pressure varied depending on the oil–water ratio. Specifically, a higher oil proportion, which corresponds to a lower water volume, results in a smaller combined volume of oil and water. Consequently, more nitrogen is needed to reach the same starting pressure compared to other experiments with different oil–water ratios. As a result, the examination of the chromatograms from the gases collected post-reaction reveals a clear trend: as the oil ratio increases, the concentration of carbon dioxide diminishes, and the concentration of nitrogen increases. Since the quantity of oil in the reaction is constant, the amount of oxygen introduced is roughly equivalent across experiments. Thus, the residual oxygen's proportion in the chromatographic results remains essentially consistent.

The reaction between supercritical water and diesel oil as well as the reaction between supercritical water and crude oil can be roughly divided into two stages, i.e., the supercritical water first disperses the continuous oil, and then the oil is oxidized and reacted completely under the joint action of supercritical water and oxygen, and intermediates will be generated in the oxidation process. However, since crude oil has more long-chain compounds, it is not only physically dispersed in the first stage of reaction with supercritical water but also has an obvious cracking process, which is the difference between the supercritical water–diesel oil reaction and the supercritical water–crude oil reaction mechanisms.

3.2. Enthalpy Comparison of Supercritical Water–Crude Oil/Diesel Oil Reactions to Generate Supercritical Multicomponent Thermal Fluids

Generally speaking, a thermal fluid with greater enthalpy indicates a higher heat transfer capacity, which is more beneficial for the extraction of viscous oil. Thus the enthalpy of the thermal fluid produced through the reaction is a very intriguing metric. It should be noted that due to constraints of the experimental methodology and procedures employed in this study, the quantities of nitrogen and oxygen introduced into the reactor do

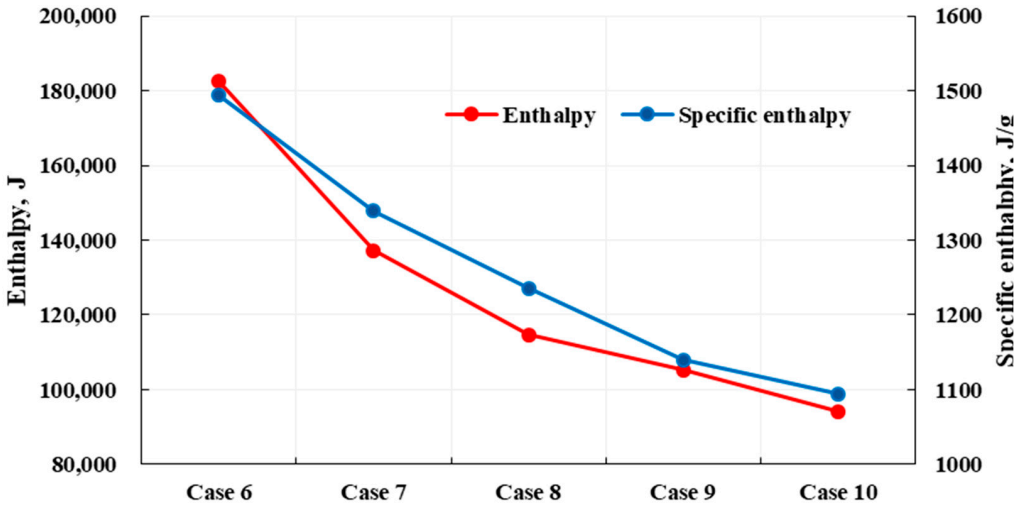
not mirror the natural ratio found in air. In mining operations, the gas typically introduced into the reaction is air itself. To ensure that the calculated enthalpy of the supercritical multicomponent thermal fluid has broad applicability and is comparable, the enthalpy of the supercritical multicomponent thermal fluid generated in various reactions can be determined using the output fluid chromatography results. This process involves adjusting the nitrogen content to align with the air's nitrogen–oxygen ratio and disregarding the reaction's residual oxygen. The calculation formula is as follows:

$$h = \frac{w_i}{\sum_{i=1}^{n} w_i} h_i \tag{1}$$

$$\overline{h} = \frac{h}{\sum_{i=1}^{n} w_i} \tag{2}$$

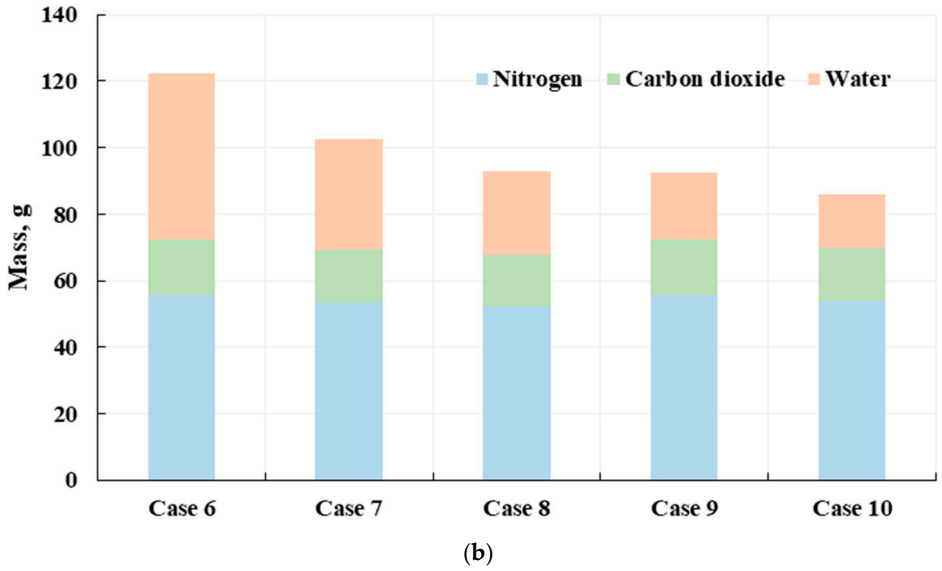
where h is the enthalpy of the supercritical multicomponent thermal fluid, J. h_i is the enthalpy of the component i in the supercritical multicomponent thermal fluid, J. w_i is the mass of the component i in the supercritical multicomponent thermal fluids, g. i is any component in the supercritical multicomponent thermal fluids; $\overline{h}$ is the specific enthalpy, which is the enthalpy value of a supercritical multicomponent thermal fluid per unit mass.

Viewing through the lens of specific enthalpy (Figures 5 and 6), an inverse relationship is observed between the proportion of diesel and the specific enthalpy of the thermal fluid—it increases as the diesel content diminishes and the water content grows. This phenomenon can be attributed to the predominant heat-carrying role of supercritical water within the thermal fluid. An elevated proportion of supercritical water correlates with a higher enthalpy in the resultant supercritical multicomponent thermal fluid. Employing the method previously described, we calculated the specific enthalpy values of supercritical multicomponent thermal fluids produced under various initial temperatures and pressures. As alluded to earlier, the initial conditions of temperature and pressure exert a negligible influence on the reaction products' composition. Consequently, when normalized to a uniform temperature and pressure (400 °C, 25 MPa), the total and specific enthalpy values for the thermal fluids, derived from experiments under differing initial states, are strikingly similar. The computed average values are 180,934.940 J for total enthalpy and 1506.448 J/g for specific enthalpy.



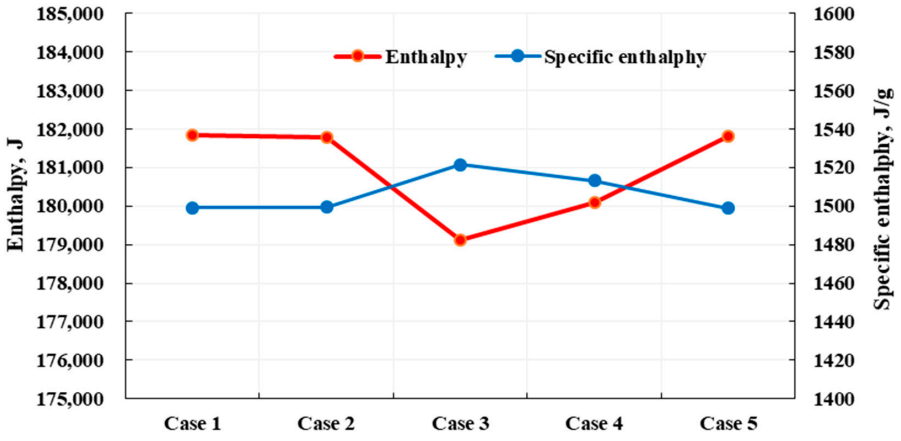
(**a**)

Figure 5. *Cont.*

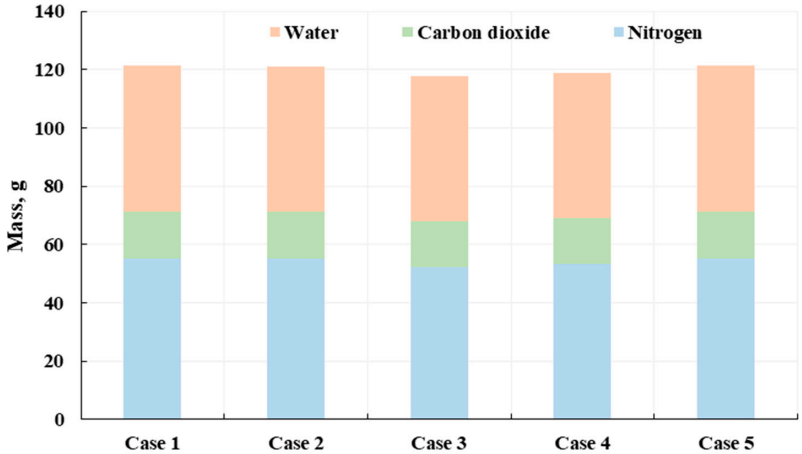


(**b**)

Figure 5. The supercritical multicomponent thermal fluid generated by supercritical water–diesel reaction under different oil–water ratios. (**a**) Enthalpy and specific enthalpy of the supercritical multicomponent thermal fluid; (**b**) Mass composition of supercritical multicomponent thermal fluid.



(**a**)



(**b**)

Figure 6. The supercritical multicomponent thermal fluid generated by supercritical water–diesel reaction under different initial temperature and pressure conditions. (**a**) Enthalpy and specific enthalpy of the supercritical multicomponent thermal fluid; (**b**) Mass composition of supercritical multicomponent thermal fluid.

Consistent with the earlier methodology, the specific enthalpy values of the supercritical multicomponent thermal fluids produced from the reaction between supercritical water and crude oil were calculated based on the composition of the output fluid components. Solely from the perspective of specific enthalpy, the trend is similar to the reaction between supercritical water and crude oil. Specifically, as the water proportion increases, the proportion of supercritical water in the resulting products also rises, leading to higher specific enthalpy values in the thermal fluid.

Using the previously described approach, the specific enthalpy values of supercritical multicomponent thermal fluids produced under varying initial temperature and pressure conditions were determined. When these values are adjusted to a consistent temperature and pressure (400 °C, 25 MPa), the total and specific enthalpy values for the thermal fluids produced under different initial conditions are found to be quite similar, with average totals of 168,630.034 J and 1593.106 J/g, respectively (Figures 7 and 8).

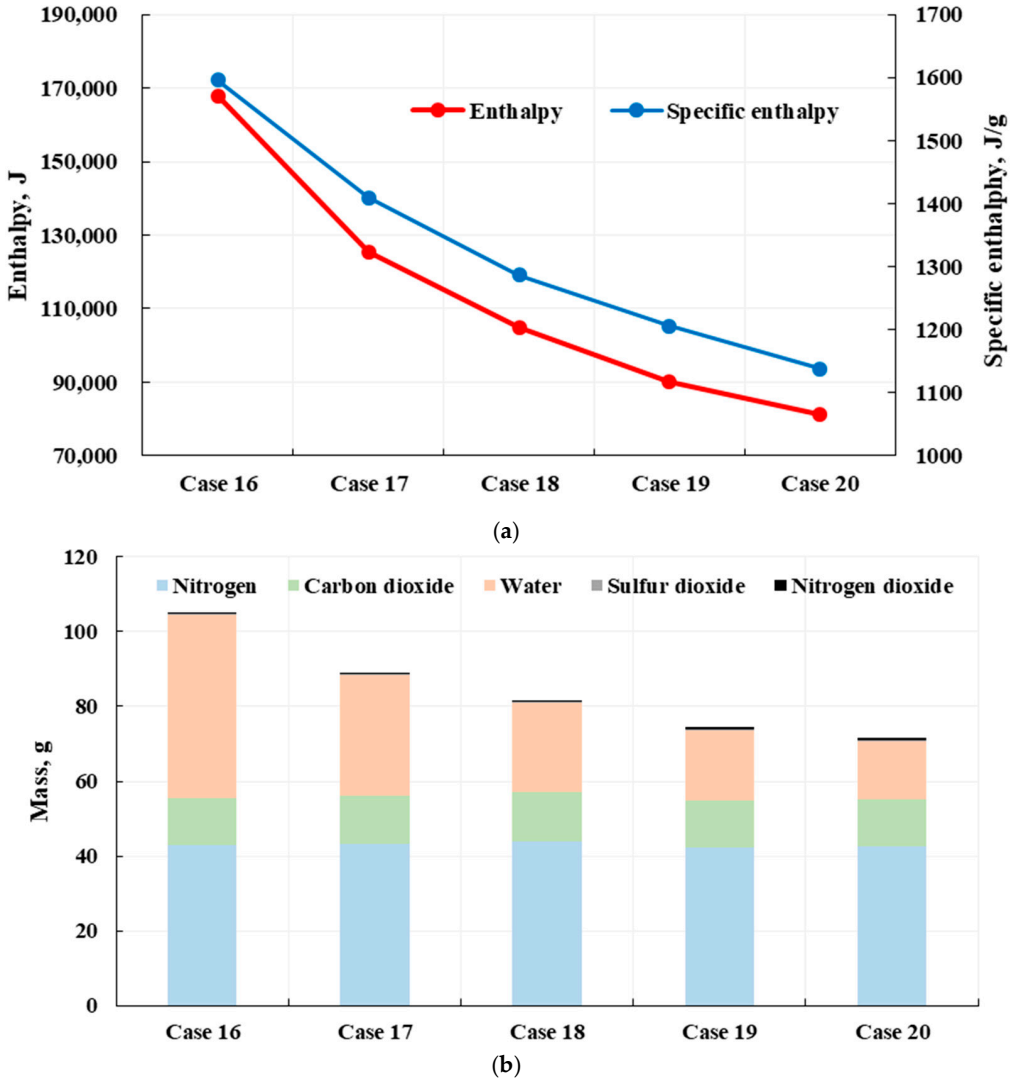


Figure 7. The supercritical multicomponent thermal fluid generated by supercritical water–crude oil reaction under different oil–water ratios. (**a**) Enthalpy and specific enthalpy of the supercritical multicomponent thermal fluid; (**b**) Mass composition of supercritical multicomponent thermal fluid.

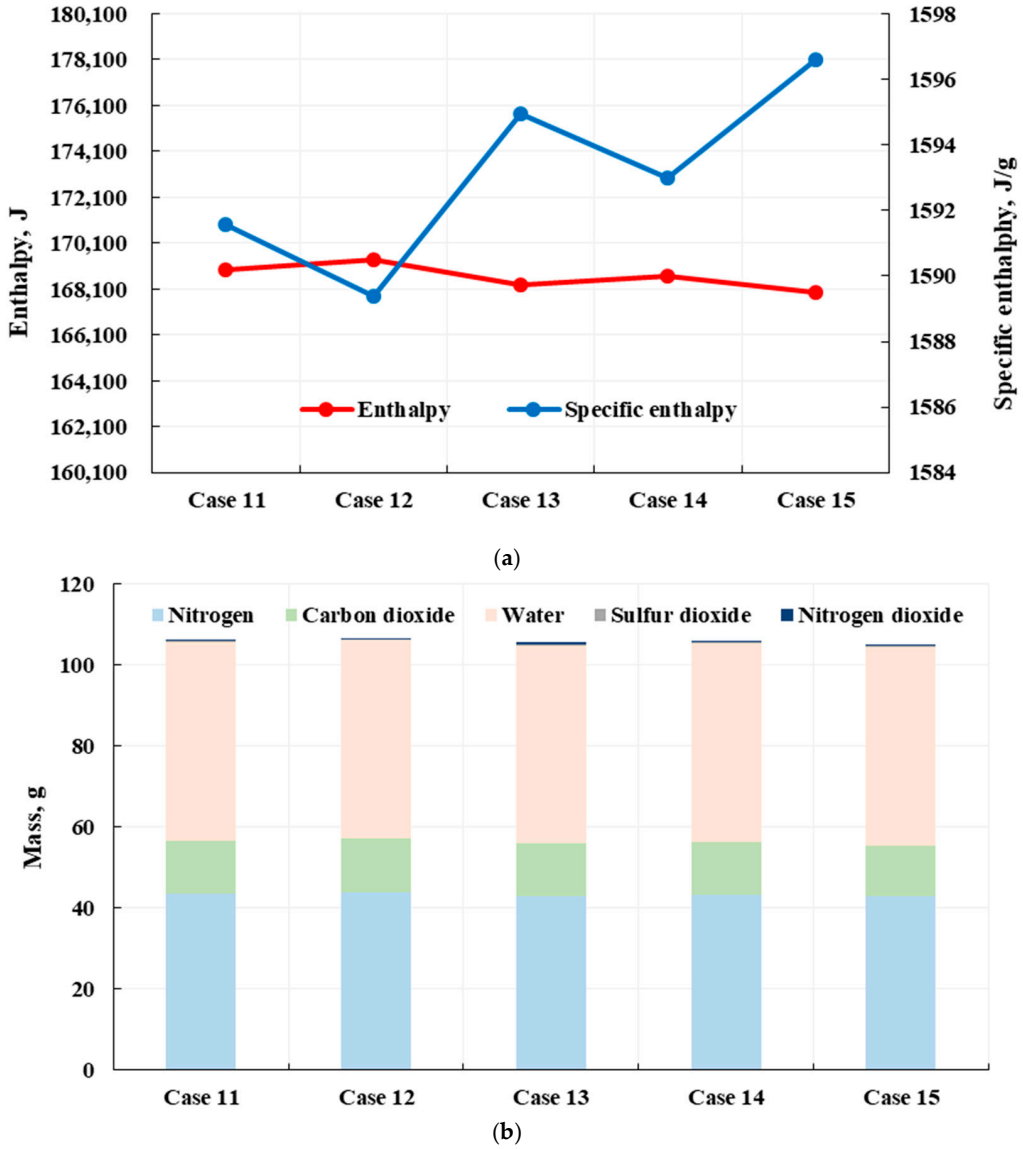


Figure 8. The enthalpy of supercritical multicomponent thermal fluid generated by supercritical water–crude oil reaction under different initial temperature and pressure conditions. (**a**) Enthalpy and specific enthalpy of the supercritical multicomponent thermal fluid; (**b**) Mass composition of supercritical multicomponent thermal fluid.

Analyzing the results from the four preceding figures, it is clear that the total enthalpy of supercritical multicomponent thermal fluids resulting from the reaction between diesel and supercritical water exceeds that of the reaction with heavy oil. Conversely, the specific enthalpy values show an opposite trend. For instance, in the 10% diesel and 10% heavy oil reaction experiments, both initiated at 400 °C and 25 MPa, the diesel reaction yields more carbon dioxide and water, with the excess carbon dioxide being more significant than the excess water. Further analysis indicates that diesel, which is over 95% hydrocarbons with 90% of those being saturated hydrocarbons, has a lower density than heavy oil. The mass of 5 mL of diesel is slightly less than the mass of 5 mL of heavy oil. However, due to the higher oxygen consumption of hydrocarbons, especially the saturated ones, the reaction with diesel consumes more oxygen, leading to an increased production of carbon dioxide and water.

Since oxygen is sourced from air, higher oxygen consumption in the diesel reaction results in a higher nitrogen content in the resulting thermal fluid, which contributes to a greater mass of gas and, consequently, a higher total mass and total enthalpy. On the other

hand, heavy oil, with a hydrocarbon content of less than 70% and a saturated hydrocarbon content about half that of diesel, consumes less oxygen during the reaction. This results in lower nitrogen content in the thermal fluid from the heavy oil reaction, leading to less gas mass, total mass, and total enthalpy.

Given that the thermal fluid is predominantly composed of supercritical water and that gases have significantly lower heat capacity than water, their contribution to the overall enthalpy is minor. Therefore, for the supercritical multicomponent thermal fluids produced in the reaction with heavy oil, the proportion of water per unit mass of the thermal fluid is higher, resulting in a higher specific enthalpy compared to those produced in the reaction with diesel (Figures 9 and 10).

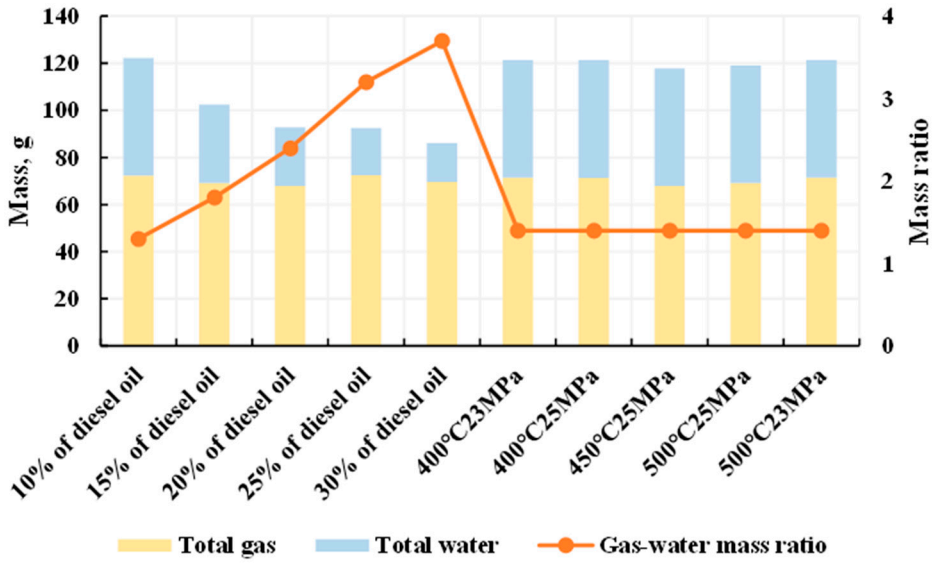


Figure 9. Gas-water mass ratio of supercritical multicomponent thermal fluid generated by supercritical water-diesel reaction under different conditions.

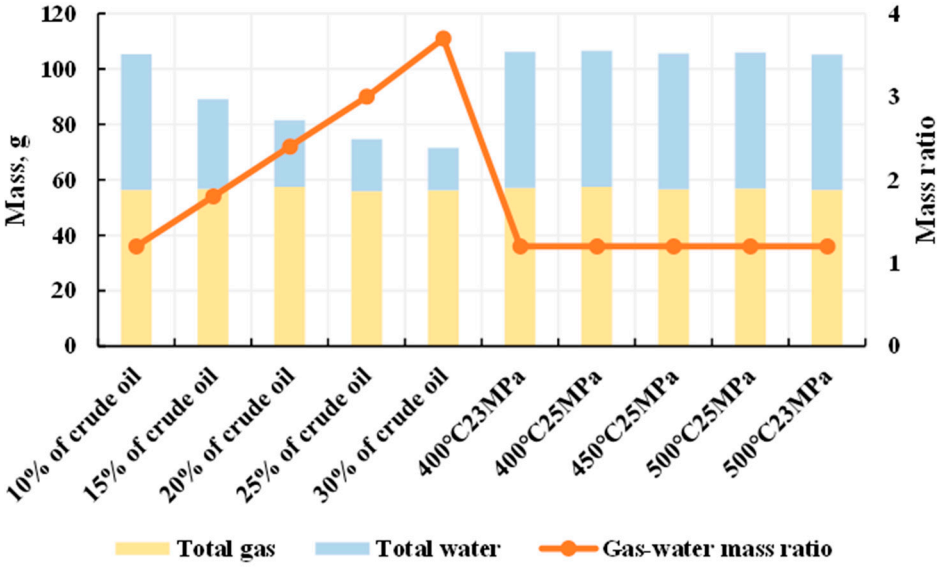


Figure 10. Gas-water mass ratio of supercritical multicomponent thermal fluid generated by supercritical water-crude oil reaction under different conditions.

4. Energy Equilibrium Point in Supercritical Water–Diesel/Crude Oil Reaction Process

In practical applications within oil fields, the preparation of supercritical multicomponent thermal fluids is achieved through the utilization of supercritical multicomponent

thermal fluid generators. In this preparation process, the energy balance point of the supercritical water–diesel/crude oil reaction needs to be taken into consideration.

Generally, the energy balance point refers to the equilibrium relationship between the incoming and outgoing heat in the operation of a generator. Typically, the incoming heat in a generator operation is considered to be the low calorific value of the fuel, and the outgoing heat includes the heat utilized in generating steam (or hot water) and the heat lost without utilization.

Based on this definition, for the oil field preparing supercritical multicomponent thermal fluids through a supercritical multicomponent thermal fluid generator, the following statement should uphold: when reaching an energy balance, the heat released per unit time from the supercritical water–diesel/crude oil reaction should be equal to the sum of lost heat (the heat carried by the generated supercritical multicomponent thermal fluid) and the heat absorbed per unit time by the incoming materials heated to the supercritical state inside the generator.

Although several sets of experiments involving supercritical multicomponent thermal fluid–diesel/crude oil reactions have been conducted, no new reactants were added during the laboratory reaction experiments. The heat loss from the laboratory reaction vessel is also irrelevant for the generators used in oil fields. Therefore, the generator thermal efficiency is introduced here to address the issue of heat loss in generators. In other words, when achieving energy balance, the heat released per unit time from the supercritical water–diesel/crude oil reaction multiplied by the generator thermal efficiency should be equal to the sum of the heat carried by the generated supercritical multicomponent thermal fluid and the heat absorbed per unit time by the incoming materials heated to the supercritical state inside the generator. This relationship can be expressed as follows:

$$\mathrm{E} \cdot \eta = H + \Delta h \tag{3}$$

where E is the total heat dissipation of fuel. η is the generator's thermal efficiency. H is the enthalpy of the generated supercritical multicomponent thermal fluid. Δh is the heat absorbed by the new material when heated to the reaction condition.

Since the calculation of this method requires trial calculation, the calculation flow is shown in Figure 11:

Following this approach and computational procedure, calculations were conducted for both the supercritical water-diesel reaction and the supercritical water-crude oil reaction. The thermal efficiency of the generator was varied across five scenarios: 0.5, 0.6, 0.7, 0.8, and 0.9. Utilizing the energy balance relationship mentioned above, the concentrations of diesel and crude oil at the energy balance point can be computed. This provides guidance for the efficient preparation of supercritical multicomponent thermal fluids in oil fields. The parameter values and calculation results are listed below.

From Figure 12, it is evident that despite the similar combustion heats of the crude oil and diesel used, the energy balance concentration for crude oil is lower than that for diesel when the generator efficiency is the same. In other words, if the crude oil from this project is used to prepare supercritical multicomponent thermal fluids in oil fields, the required concentration would be lower than that of diesel, meaning less quantity would be needed.

It is important to note that the energy balance is influenced by various factors. Different fuels will alter the combustion heat, consequently changing the energy balance point. Changes in the generator or generator efficiency will also impact the energy balance point. Moreover, alterations in the temperature and pressure of the output thermal fluid will result in changes in the energy balance point. To better address this issue, calculations of the combustion heat for different fuels were conducted (Figures 13 and 14). The combustion heat for crude oil was determined when its energy balance concentration matched that of diesel, as well as when the combustion heat for crude oil was equivalent to that of diesel with the same cost.

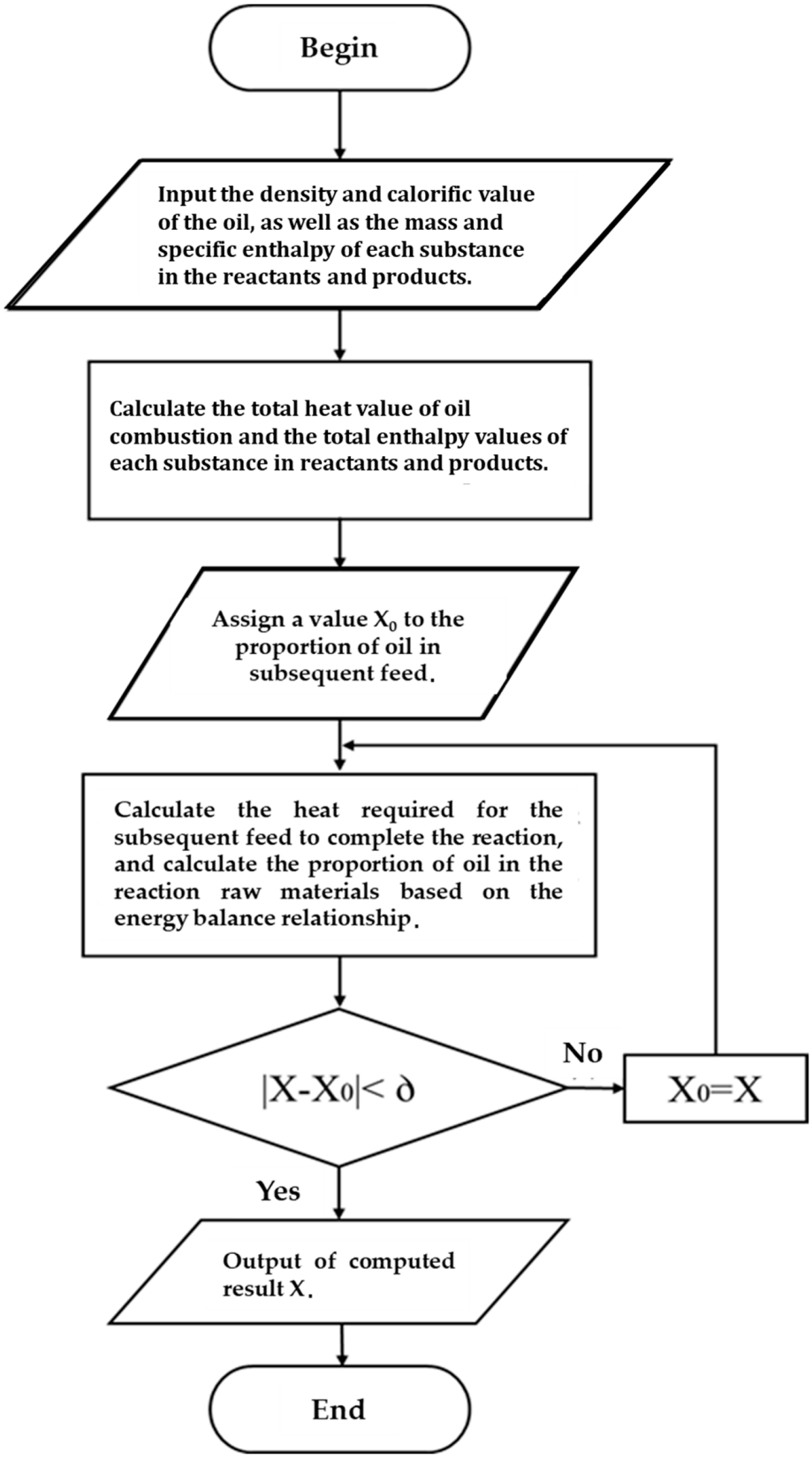


Figure 11. Flow for calculating energy balance concentration of supercritical water-diesel/crude oil reaction.

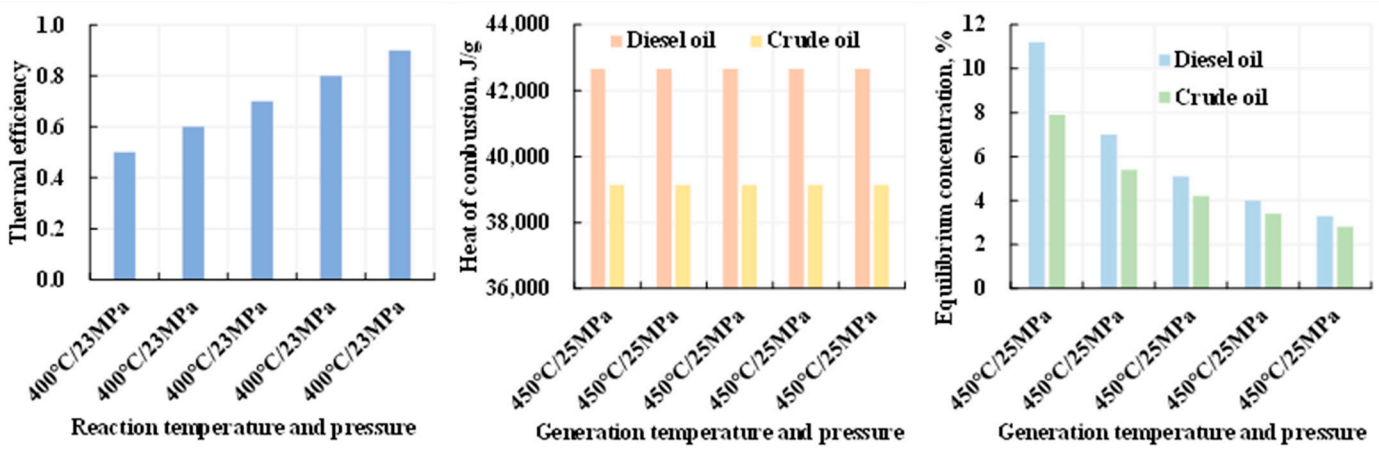


Figure 12. Energy balance concentration of supercritical water–diesel/crude oil reaction.

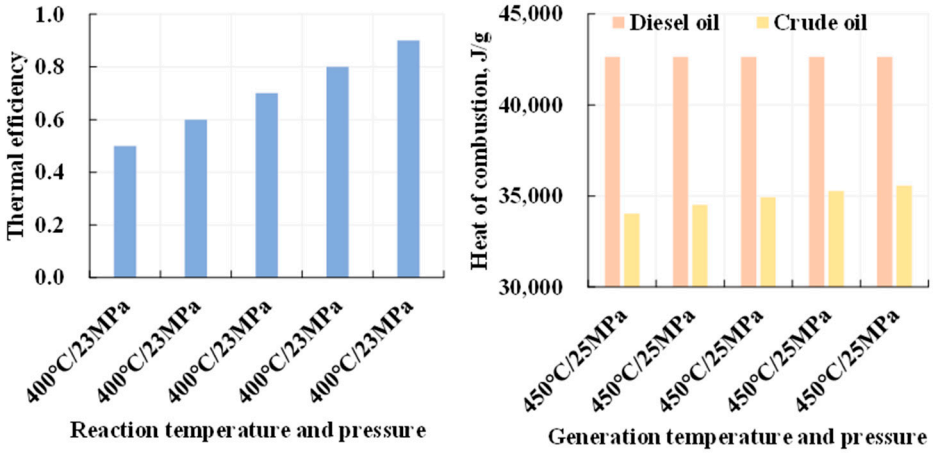


Figure 13. Heat of combustion in supercritical water–diesel/crude oil reaction with the same crude oil equilibrium concentration and diesel equilibrium concentration.

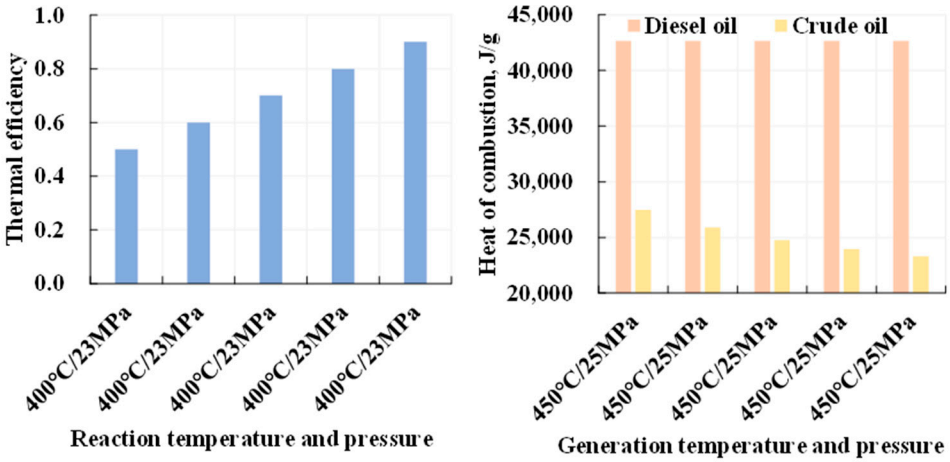


Figure 14. Heat of combustion in supercritical water–diesel/crude oil reaction with the same cost of crude oil diesel.

5. Feasibility Analysis of Crude Oil Replacing Diesel Oil to Prepare Supercritical Multicomponent Thermal Fluid

5.1. Reaction Mechanism Feasibility

From the various research results mentioned earlier, it is evident that the mechanisms of the reactions between supercritical water and diesel, as well as supercritical water and

crude oil, are generally similar and can be divided into two stages. In the first stage, supercritical water disperses the continuous diesel/crude oil, and in the second stage, under the combined action of supercritical water and oxygen, the oil undergoes complete oxidation. Intermediate products are generated during the oxidation process. However, due to the presence of more long-chain compounds in crude oil, during the first stage of the reaction with supercritical water, there is not only physical dispersion but also a noticeable cracking process. This is the key distinction between the mechanism of the reaction between supercritical water and diesel, and the one between supercritical water and crude oil.

Therefore, it can be considered that utilizing crude oil as a substitute for diesel in the preparation of supercritical multicomponent thermal fluids is feasible and viable at a mechanistic level.

5.2. Economic Feasibility

Based on the current international oil prices and domestic refined oil prices, it is apparent that the price of 0# diesel is 8.13 yuan per liter, while the international Brent crude oil is equivalent to approximately 3.92 yuan per liter. This implies that the unit price of diesel is roughly twice that of crude oil. However, as calculated in the previous section using the energy balance point, under the same generator efficiency, the energy balance point for crude oil is lower. As long as the combustion heat of crude oil is not lower than 27,000 J/g and the generator efficiency is above 50%, it is economically feasible. Therefore, solely from the perspective of fuel consumption, the use of crude oil demonstrates favorable economic feasibility.

5.3. Technical Feasibility

From the aforementioned research results, it is evident that regardless of whether it is the supercritical water–diesel reaction or the supercritical water–crude oil reaction, there will be coke as an intermediate product. Moreover, notably, the amount of coke in the intermediate products of the supercritical water–crude oil reaction is higher than that in the supercritical water–diesel reaction. Additionally, experimental tests indicate that the oxygen consumption of diesel is higher than that of crude oil.

In the actual preparation of supercritical multicomponent thermal fluids in oil fields, when using diesel, more air needs to be injected into the generator, resulting in a higher flow rate and a further reduction in the likelihood of coke generation and deposition in the generator. However, for crude oil, the possibility of coke generation and deposition in the generator exists, especially when using high carbon–hydrogen ratio crude oil (i.e., high viscosity crude oil).

In summary, when preparing supercritical multicomponent thermal fluids using crude oil, at the technical level, attention should be paid to inject a sufficient amount of air into the generator. This is to ensure that the crude oil reacts completely, thereby reducing the generation of coke.

6. Conclusions

(1) In reactions involving supercritical water with crude oil or diesel, an increased proportion of water among the reactants results in a greater share of supercritical water in the resulting products. This, in turn, leads to an elevated specific enthalpy within the thermal fluid. The total enthalpy of the supercritical multicomponent thermal fluid produced from the interaction between diesel and supercritical water has an average value of 180,934.940 J, which exceeds the total enthalpy of the fluid produced from the reaction with crude oil, with an average value of 168,630.034 J. Conversely, the specific enthalpies of these two scenarios are inversely related.

(2) The combustion heat of crude oil is close to that of diesel, but when the generator efficiency is the same, the energy balance concentration for crude oil is lower than that for diesel. In other words, if the crude oil is used to generate supercritical

multicomponent thermal fluids in oil fields, the required concentration would be lower than that for diesel, meaning less quantity would be needed.

(3) Considering the reaction mechanisms, economic benefits, and technical conditions, using crude oil instead of diesel to generate supercritical multicomponent thermal fluids is feasible and has favorable potential.

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