Review Article

Supercritical hydrothermal combustion: Basic principles, characteristics and applications and development in energy and environment

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Abstract: Supercritical hydrothermal combustion technology is a new homogeneous combustion technology with high potential in the fields of efficient removal of organic waste, clean utilization of conventional fossil energy, and efficient recovery of heavy oil. This manuscript reviews the literature related to supercritical hydrothermal combustion in recent years, and focuses on evaluating the current status of experimental and numerical simulation studies on the characteristics of supercritical hydrothermal combustion, as well as the latest progress in engineering. It is pointed out that the reduction of ignition temperature and extinction temperature is the key to promoting the application of supercritical hydrothermal combustion technology, and the consideration of the real-fluid effects and turbulence-reaction interactions can correctly reflect the combustion process. In addition, supercritical hydrothermal combustion technology, as a source of heat and reaction medium supply, can realize the efficient removal of highly concentrated organic wastewater, the clean combustion of coal and in-situ hydrogen production, as well as the thermal recovery of heavy oil by multi-thermal fluids. At present, supercritical hydrothermal combustion forced ignition technology, reactor design guidelines, and corrosion prevention of key equipment are still the focus of future research, which is of great significance to promote the application.

Keywords: supercritical hydrothermal combustion; combustion characteristics; numerical simulation; waste treatment; in-situ coal gasification; heavy oil thermal recovery

1. Introduction

The continuously growing energy demand and organic waste pollution have brought huge challenges to China’s goal of achieving “carbon neutrality” and promoting the construction of ecological civilization. Low-carbonization is the transformation and development direction of China’s energy structure, but coal and oil are still the main components of China’s current energy structure. According to reports, in 2022, coal and oil will account for 56.2% and 17.9% of China’s total energy consumption respectively[1]. The efficient and clean development and utilization of coal and crude oil is a key part of China’s goal of sustainable development and “carbon neutrality”. However, limited by the formation environment and technical level, traditional well engineering technology is difficult to exploit deep (1000–3000 m) coal resources and high-viscosity heavy oil resources. About 3.77 × 10¹² t of deep coal resources[2] and 2.3 billion t of heavy oil resources in the Bohai Oilfield[3] are facing difficulties in efficient exploitation. At the same time, the traditional coal mining and combustion process will inevitably produce large amounts of CO₂, SOₓ, NOₓ and smoke, posing a huge threat to environmental safety. The higher cost of CO₂ capture and desulfurization, denitrification, and dust removal equipment also increase the burden on enterprises. In addition, the efficient and thorough treatment of high-concentration and high-salt organic waste liquids is a key and difficult issue that needs to be solved urgently.
in the environmental field, causing great pollution risks to water bodies, soil and other resources. However, traditional chemical oxidation, incineration, biological treatment and other treatment methods are difficult to completely degrade organic wastewater and may even produce secondary pollutants. Supercritical hydrothermal combustion technology has been used in the complete harmless treatment and energy utilization of high-concentration and high-salt organic waste, super thermal recovery of deep underground or submarine heavy oil, supercritical multi-heat flow assisted in-situ gasification or modification of underground fossil fuels, etc. The fields of energy and environment have shown great application value and technological prospects, and are expected to promote the transformative development of related technologies. The application and development progress of supercritical hydrothermal combustion technology in different fields are detailed in the fourth part of this paper.

Supercritical hydrothermal combustion (SCHC) technology is a new homogeneous combustion method in which organic matter and oxidants undergo a violent oxidation reaction in a supercritical water environment to produce a supercritical hydrothermal flame (SHF). The supercritical water environment is a homogeneous system with extremely small mass transfer resistance, which allows the oxidation reaction of organic matter and oxygen to be completed within milliseconds. The degradation rate of organic matter reaches more than 99.9%, realizing direct heat transfer between molecules. Compared with conventional combustion, supercritical hydrothermal combustion technology has extremely strong adaptability, can directly burn high-humidity organic pollutants, and completely convert C, H, O, N and other elements in the organic matter into H$_2$O, CO$_2$, N$_2$ and other harmless substances, elements such as S and Cl are converted into corresponding inorganic acid salts, heavy metals are mineralized into stable solid phases, and there is no production of secondary pollutants such as SO$_x$, NO$_x$, and dioxins. Therefore, supercritical hydrothermal combustion technology can efficiently process organic waste and achieve clean combustion of coal. At the same time, after supercritical hydrothermal combustion occurs, the main components of the product are CO$_2$ and supercritical water. In the subsequent process flow, H$_2$O (liquid state) and CO$_2$ (gaseous state) can be separated by just cooling and reducing pressure, thereby realizing CO$_2$ capture. At the same time, no SO$_x$, NO$_x$, dust and other substances are produced in the combustion products, and there is no need to install additional desulfurization, denitrification and dust removal devices, further reducing the cost of the CO$_2$ capture process. Furthermore, supercritical hydrothermal combustion technology can be used to generate in-situ combustion in the formation to generate a multi-element thermal fluid with supercritical water as the main component, thereby converting deep coal and high-viscosity crude oil into H$_2$ and low-viscosity light oil. Crude oil, thereby, achieves efficient and clean mining of fossil resources.

Because supercritical hydrothermal combustion has many unique advantages, it has received extensive attention and research from various fields such as organic waste treatment, clean utilization and conversion of fossil fuels, and development of unconventional oil and gas resources. In 1988, Franck et al.\cite{4} systematically elaborated on the reactor structure and reaction conditions used to generate supercritical hydrothermal flames for the first time, and used optical methods to obtain supercritical hydrothermal flame images. Since then, research institutions such as Sandia National Laboratories in the United States\cite{5} and McGill University in Canada\cite{6} have focused on exploring the supercritical hydrothermal combustion and ignition characteristics of organic matter such as methane and methanol under semi-intermittent conditions; ETH Zurich in Switzerland\cite{7-9}, University of Valladolid in Spain\cite{10-12}, NASA\cite{13}, Xi’an Jiaotong University\cite{14,15} and other research institutions have used experimental and numerical simulation methods to study the flow conditions under continuous flow conditions. The ignition and combustion characteristics and mechanisms of supercritical hydrothermal combustion, and a variety of supercritical hydrothermal combustion reactors and process systems have been further developed.
This article summarizes the relevant literature in recent years, focusing on the technical principles, key combustion characteristics and rules of supercritical hydrothermal combustion, and the application and development status of this technology in different fields. It also further looks into the prospects of supercritical hydrothermal combustion technology to provide guidance and reference for subsequent research and development of supercritical hydrothermal combustion technology.

2. Supercritical hydrothermal combustion principles, flame types and related equipment

2.1. Basic principles of supercritical hydrothermal combustion

Supercritical water (SCW) refers to water in a special state whose temperature and pressure are both higher than its critical point (Tc = 374.15 °C, Pc = 22.129 MPa). It has excellent physical and chemical properties such as low density, low viscosity, and low dielectric constant \(^{[16-21]}\). For example, for supercritical water with a temperature of 600 °C and a pressure of 24.6 MPa, its dielectric constant is only 1.2. Therefore, the properties of supercritical water are closer to non-polar solvents. The solubility of inorganic salts in supercritical water is extremely small, while non-polar substances such as organic matter and oxygen can be almost completely dissolved in supercritical water, resulting in supercritical hydrothermal homogeneity. reaction. When the concentration of organic matter exceeds a certain value, the oxidation reaction becomes more intense and can further produce a luminous supercritical hydrothermal flame, as shown in Figure 1. Generally, the reaction process in which supercritical hydrothermal flame exists is called supercritical hydrothermal combustion\(^{[22,23]}\).

![Figure 1](image-url)

**Figure 1.** The supercritical hydrothermal flame generation process of 50% ethanol solution in a supercritical water environment of 23.8 MPa and 425 °C\(^{[13]}\). (a) 0 s; (b) 0.033 s; (c) 0.100 s; (d) 0.133 s; (e) 0.166 s.

One of the key features that distinguishes supercritical hydrothermal combustion from ordinary combustion is that supercritical water serves as both reaction medium and reactant. Supercritical water provides a homogeneous reaction environment, eliminates heat transfer and mass transfer resistance, and realizes direct heat transfer between molecules, allowing the reaction to be completed within milliseconds. At the same time, during the transcritical process from subcritical heating to supercritical, the strong buoyancy effect caused by the sudden drop in water density strengthens the diffusion and mixing of fuel and oxidant, and promotes oxidation and combustion reactions. Since the ionic product of supercritical water decreases rapidly as the density decreases or the temperature increases, elementary reactions dominate in supercritical water environments rather than ionic reactions\(^{[24]}\). Henrikson et al.\(^{[25]}\) believe that water as a reactant affects the oxidation of fuel by increasing the production rate of OH\(^{-}\) radicals. The key elementary reactions are as
shown in Equations (1) and (2). Holgate et al.\cite{26} further explained that changes in water density will also affect the chain branching elementary Equation (3). Fujii\cite{27} further speculated through experiments that supercritical water promotes the generation of OH- radicals through Equation (3).

There are many elementary reactions involved in the supercritical hydrothermal combustion process. Boock and Klein\cite{28} reviewed the existing research content and summarized eight types of key elementary reactions according to the order of chain reactions, as shown in Table 1. It can be seen from Table 1 that the supercritical hydrothermal combustion/oxidation reaction is caused by dehydrogenation between organic matter and oxidant. In the subsequent chain development stages, free radicals generate new free radicals through oxygen addition reactions, hydrogen absorption reactions, isomerization- intramolecular hydrogen absorption reactions, β-fragmentation reactions, etc. The disproportionation reaction converts RO₂⁻ into RO⁻, resulting in reaction chain transfer. ROOH will decompose to produce RO⁻ and OH⁻, effectively increasing the concentration of free radicals in the system. Eventually, free radicals such as RO⁻ and ROO⁻ react to form stable substances, terminating the reaction. In addition, in the rapid reaction stage, H₂O₂ is the main source of OH⁻ free radicals, which decomposes through Equation (4) to produce a large amount of OH⁻ free radicals, which are the most active components in the reaction process, which quickly reacts with organic matter through dehydrogenation Equation (5) and quickly reduces the concentration of organic matter.

\[
\begin{align*}
\text{CH}_3\text{H}_2\text{O}=\text{CH}_4+\text{OH}^- & \quad (1) \\
\text{H}^- + \text{H}_2\text{O}=\text{H}_2+\text{OH}^- & \quad (2) \\
\text{HO}_2^- + \text{H}_2\text{O}=\text{H}_2\text{O}_2+\text{OH}^- & \quad (3) \\
\text{H}_2\text{O}_2+(\text{M})=2\text{OH}^-+(\text{M}) & \quad (4) \\
\text{RH}+\text{OH}^- = \text{R}^- + \text{H}_2\text{O} & \quad (5)
\end{align*}
\]

<table>
<thead>
<tr>
<th>Reaction stage</th>
<th>Reaction type</th>
<th>Reaction formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chain initiation</td>
<td>Dehydrogenation reaction</td>
<td>RH+O₂→R⁻+HO₂⁻</td>
</tr>
<tr>
<td>Chain development</td>
<td>Oxygen addition reaction</td>
<td>R⁻+O₂→RO₂⁻</td>
</tr>
<tr>
<td></td>
<td>Hydrogen absorption reaction</td>
<td>RO₂⁻+RH→ROOH</td>
</tr>
<tr>
<td></td>
<td>Isomerization</td>
<td>RO₂⁻→HOOR⁻</td>
</tr>
<tr>
<td></td>
<td>β fragmentation reaction</td>
<td>R⁻→R⁻+C=RH</td>
</tr>
<tr>
<td>Chain transfer</td>
<td>Disproportionation reaction</td>
<td>2RO₂⁻→O₂+2RO⁻</td>
</tr>
<tr>
<td>Chain branching</td>
<td>Decomposition reaction</td>
<td>ROOH→RO⁻+OH⁻</td>
</tr>
<tr>
<td>Chain termination</td>
<td>Free radical polymerization reaction</td>
<td>RO₂⁻+RO₂→Stable substances</td>
</tr>
</tbody>
</table>

2.2. Supercritical hydrothermal flame types and related generating equipment

According to the different injection and combustion methods of fuel and oxidant during the supercritical hydrothermal combustion process, supercritical hydrothermal flames can be divided into semi-intermittent supercritical hydrothermal flames, diffusion supercritical hydrothermal flames and premixed supercritical water flames. There are three types of hot flames, and the principle is shown in Figure 2. Semi-intermittent supercritical hydrothermal flame is mainly used to explore the fuel types and conditions under which
A typical supercritical hydrothermal combustion semi-batch reactor is shown in Figure 3. Figure 3(a) shows the intermittent supercritical hydrothermal combustion reactor developed by Franck et al.\cite{4} of Karlsruhe Institute of Technology. Its main body is a cylindrical corrosion-resistant high-strength nickel-based alloy with an outer diameter of 80 mm and an inner diameter of 30 mm, there is a 30 mL combustion chamber in the middle, with a design pressure of 200 MPa. To facilitate observation of the supercritical hydrothermal flame, sapphire windows are installed at both ends of the reactor. The semi-batch hydrothermal combustion reactor shown in Figure 3(b) was developed by Sandia National Laboratories in the United States\cite{5}. The reactor is made of chromium-nickel alloy Inconel 718 and is surrounded by three sapphire windows, allowing researchers to observe and detect of supercritical hydrothermal combustion through optical cameras and Raman scattering. In the study of Franck et al.\cite{4}, water was first injected into the reactor and the temperature and pressure were raised to supercritical temperature and pressure, and then methane was introduced to form a 30 mol% methane solution. When the fuel is evenly mixed, oxygen is injected from the bottom interface, and then the oxygen and fuel diffuse and mix, and the oxidation reaction generates active free radicals and releases heat. As the concentration and temperature of active free radicals in the reactor continue to rise, the supercritical water-fuel-oxidant reaches thermal self-ignition conditions, and a hydrothermal flame appears. Experimental results show that under the conditions of 30 MPa and 500 °C, a supercritical hydrothermal flame with a height of 1.2 mm and a width of 0.5 mm can be generated. The flame image is shown in Figure 4. Although oxygen continues to be introduced, the methane in the reactor is gradually consumed as the reaction proceeds, and is eventually completely consumed, and the supercritical hydrothermal flame is extinguished, so it is called a semi-intermittent supercritical hydrothermal flame.

**Figure 2.** Typical supercritical hydrothermal flame generation modes: (a) semi-intermittent flame; (b) diffusion flame; (c) premixed flame\cite{23}. 

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Figure 3. Typical semi-batch supercritical hydrothermal combustion reactor. (a) Karlsruhe institute of technology semi-batch reactor\cite{4}; (b) Sandia national laboratories semi-batch reactor\cite{5}.

For the diffusion supercritical hydrothermal flame and the premixed supercritical hydrothermal flame, both of them generate a supercritical hydrothermal flame in the reactor by continuously injecting fuel and oxidant. The main difference between the two is that in the former, the fuel and oxidant enter the reactor separately and diffuse and mix, forming a flame front at the interface where the fuel and oxidant contact, producing a hydrothermal flame; however, in the latter case, the fuel and oxidant are already mixed before entering the reactor. Research on diffusion supercritical hydrothermal flames and premixed supercritical hydrothermal flames aims to explore the feasibility of continuous supercritical hydrothermal flames in engineering applications and the typical continuous type of continuous supercritical hydrothermal flames. The supercritical hydrothermal combustion reactor is shown in Figure 5. Continuous supercritical hydrothermal combustion reactors include tubular reactors, transpiring wall reactor (TWR) and water-cooled hydrothermal burner (WCHB). Figure 5(a) shows the tubular hydrothermal combustion reactor of the University of Valladolid in Spain. It consists of a straight tube made of nickel alloy C-276. The straight tube is 2000 mm long and 3.86 mm in diameter. The volume is 18.5 mL. Cabeza et al.\cite{29} used this tubular reactor to study the degradation effect of a supercritical hydrothermal flame formed by isopropyl alcohol and oxygen on high concentrations of refractory substances (acetic acid and ammonia). Figure 5(b) shows the evaporation wall reactor developed by the above team. The pressure-bearing wall of the reactor is made of stainless steel, the upper and lower ends of the porous wall are made of nickel-based alloy 625, and the central porous part is sintered from nickel-based alloy 600. The center of the reaction device is a tubular mixer, which is used to input fuel and oxidant into the reaction chamber. The periphery of the reaction chamber is an evaporation wall formed by porous media. The evaporated water forms a water film on the inner surface of the evaporation wall to dissolve the inorganic salts present in the fuel. Prevent salt deposition and subsequent scaling\cite{10}; Figure
Figure 5. Typical continuous supercritical hydrothermal combustion reactor. (a) Schematic diagram of a tubular reactor[29]; (b) Schematic diagram of an evaporating wall reactor[10]; (c) Schematic diagram of a water-cooled wall reactor[7].

3. Supercritical hydrothermal combustion characteristics and rules

3.1. Experimental study on supercritical hydrothermal combustion characteristics

Current experimental research on supercritical hydrothermal combustion focuses on exploring the macroscopic combustion characteristics of organic matter in a supercritical water environment, such as ignition temperature, flameout temperature. The ignition temperature and flameout temperature respectively refer to the minimum preheating temperature at which the incident fuel can induce supercritical hydrothermal combustion and maintain supercritical hydrothermal combustion. They are of great significance in supporting the development, promotion and application of supercritical hydrothermal combustion technology and
equipment. A detailed discussion of ignition/quenching temperatures and other indicators of hydrothermal combustion characteristics is provided below.

3.1.1. Ignition temperature

The ignition temperature refers to the lowest preheating temperature at which the incident fuel can induce a supercritical hydrothermal combustion reaction. Lower ignition temperature means lower ignition energy consumption of supercritical hydrothermal combustion, which helps to promote the application of supercritical hydrothermal combustion technology. According to current research, it can be seen that the ignition temperature is mainly affected by key parameters such as fuel concentration, reactant flow rate, and reaction pressure. Steeper et al.\cite{5} used a batch reactor to study the limits of thermal spontaneous ignition of methanol and methane at different concentrations, and obtained the relationship between ignition temperature and fuel concentration, as shown in Figure 6. Research results show that the ignition temperature of methane and methanol in supercritical water is 370–480 °C. When the concentration of methane or methanol is less than 6 mol%, no flame can be generated even if the temperature increases. This phenomenon indicates that there is a fuel concentration threshold at which the energy released by the oxidation of organic matter in the fuel is insufficient to form a hydrothermal combustion flame\cite{30}. Wellig et al.\cite{8} studied hydrothermal flame thermal spontaneous ignition when the methanol concentration in TWR was 15–22.1 wt %, and they observed that the ignition temperature ranged from 465–490 °C. Cabeza et al.\cite{10} used isopropanol with a concentration of 4 wt % and ignited a hydrothermal flame at a preheating temperature of 400 °C. Existing research literature shows that ignition can be achieved at 400 °C with a minimum concentration of 1.5 wt.% isopropyl alcohol. When the isopropyl alcohol concentration is increased by 1 wt %, the final reaction temperature increases by 150 °C\cite{29}. Zhang et al.\cite{31} also conducted studies using an evaporating wall reactor and concluded that increasing fuel concentration will lead to a decrease in ignition temperature. In addition, it can be seen from Figure 6 that as the fuel concentration increases, the decreasing trend of ignition temperature gradually slows down and will eventually stabilize within a certain temperature range.

![Figure 6](image.png)

Figure 6. The relationship between ignition temperature and fuel concentration of supercritical hydrothermal combustion of methane and methanol\cite{5}. (a) The methane ignition concentration changes with temperature; (b) The methanol ignition concentration changes with temperature.

Generally speaking, the ignition temperature of supercritical hydrothermal combustion increases with the increase of reactant flow rate. In the study of Bermejo et al.\cite{32}, it was found that for an isopropyl alcohol solution with a concentration of 4 wt.%, when the flow rate increased from 6 kg·h⁻¹ to 18 kg·h⁻¹, the ignition temperature increased from 380–395 °C up to 415 °C. Sobhy et al.\cite{33} found that for the methanol-air diffusion flame in a semi-batch reactor, when the air flow rate is higher than 1.5 ml·min⁻¹, the flame boundary is unstable.
and flickers and is quickly extinguished. It is worth noting that Zhang et al.\cite{31} used high-temperature softened water as the auxiliary thermal fluid to heat the reactant, and carried out a study on the effect of fuel flow on ignition temperature. The experimental results are shown in Figure 7. As the fuel flow rate increases from 2.1 kg·h\(^{-1}\) to 5.0 kg·h\(^{-1}\), the ignition temperature decreases from 569 °C to 478 °C. It seems that the above researchers have reached opposite conclusions about the effect of flow rate on ignition temperature, but in fact both conclusions reflect that reactant mixing has an important impact on ignition temperature. In the experiment of Zhang et al.\cite{31}, fuel and oxidant were injected into the reactor at room temperature, and the combustible mixture was completely heated to the ignition temperature by auxiliary thermal fluid. Therefore, an increase in fuel flow can cause a more intense heat and mass exchange between the combustible mixture and the auxiliary heating fluid, resulting in a decrease in the ignition temperature. At the same time, Reddy et al.\cite{34} pointed out that the microscopic and macroscopic mixing of reactants plays a crucial role in supercritical hydrothermal combustion ignition. Experimental studies have shown that achieving complete micromixing at subcritical temperatures is difficult, whereas micromixing can be improved with increasing temperature. Therefore, a higher reactant preheating temperature will be beneficial to ignite the hydrothermal flame under higher flow conditions\cite{34}.

![Figure 7. Zhang et al. studied the effect of fuel flow on ignition temperature\cite{31}.](image)

In addition, existing research results also show that the ignition temperature is closely related to the pressure of the reaction system. Schilling and Franck\cite{4} used a semi-batch reactor to measure the ignition temperature of 30 mol% methane using pure oxygen as the oxidant at different pressures. Experiments found that when the reactor system pressure increased from 20 MPa to 100 MPa, the ignition temperature decreased from 420 °C to 400 °C, which was significantly lower than the methane ignition temperature (550 °C) under gas phase conditions. Hirth et al.\cite{35} used a semi-batch reactor to measure the ignition temperature of methane with different concentrations under different pressures. The results show that when the pressure increases from 30 MPa to 100 MPa, the ignition temperature of 30 mol% methane decreases from 425 °C to 390 °C. Under supercritical conditions, as the pressure increases, the density of supercritical water increases, resulting in an increase in the concentration of reactants and an increase in the chemical reaction rate, so the ignition temperature will also decrease accordingly. It is worth noting that although literature\cite{36} pointed out that an increase in pressure will cause an increase in the ion product of water, thereby hindering the free radical reaction during supercritical hydrothermal combustion, the above experimental results show that the increase in pressure to a certain extent, it is beneficial to reduce the ignition temperature.
Some typical fuels under supercritical water conditions can be seen in Table 2. Summarizing the current research results on thermal spontaneous ignition of supercritical water thermal combustion, it can be seen that the thermal spontaneous ignition temperature of fuels such as methanol and isopropyl alcohol is usually 400–450 ℃. Higher preheating temperature causes thermal autoignition ignition to consume more energy, and may also cause inorganic salts in the reactants to precipitate during the preheating process, blocking the reactor inlet pipeline, which seriously limits supercritical hydrothermal combustion technology. Therefore, researchers studied the ignition characteristics of another ignition method, forced ignition. Compared with thermal spontaneous ignition, the ignition temperature under forced ignition conditions is more sensitive to changes in fuel concentration. Stathopoulos[9] and Meier et al.[37] used Cr 60/15 coils to make a hot surface ignition device. The heating part of the device is 30 mm long, and the structure is shown in Figure 8. Stathopoulos[9] and Meier et al.[37] used a hot surface ignition device to study the effect of fuel concentration on the forced ignition temperature of ethanol-water-oxygen mixture. During the experiment, the pressure and flow rate were both 26 MPa and 20 kg·h⁻¹. When the fuel concentration is 12.5 wt.% and 17.5 wt.%, the fuel preheating temperatures required for ignition are 310–340 ℃ and 305–330 ℃, respectively, and the corresponding hot surface temperatures are 450–800 ℃[9]; when the fuel concentration increased to 22.5–32.5 wt.%. The experimental results are shown in Figure 9. The fuel only needs to be preheated to 23–83 ℃ before it can be ignited by the hot surface with a temperature of 360 ± 40 ℃[37], which is significantly reduced. The energy consumed in preheating the fuel. At the same time, in the ignition experiment of Stathopoulos[9], the minimum power consumed by the hot surface during firing was only about 60 W. This study proves that forced ignition technology can significantly reduce the dependence of supercritical hydrothermal combustion ignition on preheated fuel, and is of great significance to the promotion of the application of supercritical hydrothermal combustion technology.

![Figure 8](image1.png)

**Figure 8.** Hot surface ignition device produced by Stathopoulos[9] and Meier et al.[37].

![Figure 9](image2.png)

**Figure 9.** The relationship between hot surface temperature and preheating temperature during supercritical hydrothermal combustion of 2.5–32.5 wt.% ethanol solution[37].
Table 2. Summary of supercritical hydrothermal combustion ignition and flameout experiments.

<table>
<thead>
<tr>
<th>Fuel/oxidizer</th>
<th>Fuel concentration /wt.%</th>
<th>Fuel flow rate /kg·h⁻¹</th>
<th>Ignition temperature /℃</th>
<th>Extinguishing temperature /℃</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol/oxygen</td>
<td>15–22.1</td>
<td>5.4–5.76</td>
<td>460</td>
<td>224–284</td>
<td>[38]</td>
</tr>
<tr>
<td>Methanol/oxygen</td>
<td>6</td>
<td>17</td>
<td>419</td>
<td>/</td>
<td>[39]</td>
</tr>
<tr>
<td>Methanol/oxygen</td>
<td>30–35</td>
<td>2–4.95</td>
<td>/</td>
<td>&gt;354</td>
<td>[40]</td>
</tr>
<tr>
<td>Ethanol/oxygen</td>
<td>7.5–20</td>
<td>20, 30</td>
<td>Fuel preheat temperature 370–420; igniter surface temperature 450–800</td>
<td>/</td>
<td>[9]</td>
</tr>
<tr>
<td>Ethanol/oxygen</td>
<td>20–32.5</td>
<td>20</td>
<td>Fuel preheat temperature 23–83; igniter surface temperature 360 ± 40</td>
<td>/</td>
<td>[37]</td>
</tr>
<tr>
<td>Isopropanol/air</td>
<td>8</td>
<td>21–65.6</td>
<td>&gt;400</td>
<td>173–350</td>
<td>[10]</td>
</tr>
<tr>
<td>Isopropanol/air</td>
<td>6.5</td>
<td>/</td>
<td>420</td>
<td>/</td>
<td>[41]</td>
</tr>
<tr>
<td>Isopropanol/air</td>
<td>2.5–7.5</td>
<td>2.99</td>
<td>&gt;470</td>
<td>/</td>
<td>[42]</td>
</tr>
<tr>
<td>Isopropanol/air</td>
<td>7–8.5</td>
<td>/</td>
<td>&gt;400</td>
<td>20–200</td>
<td>[43]</td>
</tr>
<tr>
<td>Isopropanol/air</td>
<td>8–9.5</td>
<td>/</td>
<td>&gt;400</td>
<td>50, 150, 300</td>
<td>[11]</td>
</tr>
</tbody>
</table>

The reason why supercritical hydrothermal combustion forced ignition has a lower ignition temperature is its special ignition process. According to the research of Stathopoulos et al. [9], during the forced ignition process, the temperature of the combustible mixture near the hot surface is close to the temperature of the hot surface. Especially when the fluid preheating temperature is near the quasi-critical temperature, transfer occurs between the hot surface and the fluid. Thermal strengthening allows heat to be transferred between the hot surface and the fluid with a small temperature difference. If the hot surface temperature exceeds the fuel thermal auto-ignition temperature, the high-temperature combustible mixture near the hot surface will first undergo an oxidation reaction, releasing heat to heat the surrounding fluid to the ignition temperature and further ignite. The supercritical hydrothermal combustion heat spontaneous ignition process requires that all reactants be heated to the supercritical ignition temperature before ignition can occur, so the ignition temperature is relatively high.

3.1.2. Flameout temperature

The flameout temperature refers to the lowest fuel inlet temperature that maintains the supercritical hydrothermal flame without extinguishing. The lower the flameout temperature means that the stable operation of the reaction device is less dependent on the fuel preheating temperature. Researchers are committed to reducing the flameout temperature, enabling incident fuel to be injected at room temperature and maintaining stable combustion of the hydrothermal flame. It can be seen from the current research content that key parameters such as fuel concentration and feed flow rate will affect the flameout temperature.

The flameout temperature is extremely sensitive to changes in fuel concentration. The experiment of Prikopsky [44] showed that with the increase of mass fraction, the flameout temperature dropped significantly from 380 °C at 12 wt.% to 340 °C at 20 wt.%. Furthermore, when the fuel concentration exceeds 27 wt.%, the flameout temperature will drop to 92 °C, which means that there is the possibility of maintaining hydrothermal flame stability without preheating. Wellig et al. [8] also found the same phenomenon through research. When the methanol concentration increased from 6 wt.% to 28 wt. %, the flameout temperature dropped from 444 °C to 92 °C. Zhang et al. [31] plotted the obtained flameout temperature as a function of fuel concentration and found that the higher the fuel concentration, the lower the flameout temperature. The experimental data of Wellig [8] and Zhang et al. [31] are shown in Figure 10, showing the same pattern of flameout temperature.
changing with concentration. The difference in values may be due to the different reactor structures and experimental operations.

Another factor that has a greater impact on the flameout temperature is the fuel flow. The flameout temperature will increase as the fuel flow rate increases. According to the experimental results of Bermejo et al.\(^{[10]}\), when the fuel flow rate decreases from 14 kg·h\(^{-1}\) to 6 kg·h\(^{-1}\), the flameout temperature will drop from 388 °C to 354 °C. Zhang et al.\(^{[31]}\) also obtained the same rule. When the fuel flow rate is 2.10 kg/h, the flameout temperature is 350 °C; when the fuel flow rate increases to 4.90 kg·h\(^{-1}\), the flameout temperature rises to 400 °C. The results are shown in Figure 11. The research on the flameout temperature of some typical fuels under supercritical water conditions can be seen in Table 2. The stable combustion of supercritical hydrothermal flame is a macroscopic manifestation of the matching relationship between the propagation speed of the supercritical hydrothermal flame and the flow rate of the combustible mixture. Regarding flame propagation Speed will be discussed in the next section.

![Figure 10. Wellig\(^{[8]}\) and Zhang et al.\(^{[31]}\) studied the influence of fuel concentration on flameout temperature.](image1.jpg)

![Figure 11. Effect of fuel flow on flameout temperature\(^{[31]}\).](image2.jpg)
3.1.3. Flame propagation speed

In gas phase combustion, the flame propagation speed is defined as the speed of the flame front in the normal direction relative to the unburned gas at infinity, which essentially represents the amount of combustible mixture burned per unit area of the flame front per unit time. It characterizes the spatial movement speed of the flame front during the combustion process and is an important piece of data for studying flame stability. The flame front propagation speed mainly depends on the properties of the combustible material itself, pressure, temperature, excess air coefficient, flow state and heat dissipation conditions. According to the boundary velocity gradient theory, when the flame propagation velocity is equal to the component of the material flow velocity in the normal direction of the flame front, the flame can remain stable; when the former is smaller than the latter, the flame will be blown downstream, and in severe cases, the flame will be extinguished; when the former is larger than the latter, the flame will move upstream, and for premixed flames, backfire will occur. Therefore, in order to ensure stable hydrothermal combustion, the flame propagation speed should match the material flow rate.

Hicks\textsuperscript{[13]} obtained the propagation speed of laminar diffusion flame under two air flow speed conditions of 2 ml·min\textsuperscript{−1} and 7 m·min\textsuperscript{−1} through a visualization method. For low air flow rate conditions, the average flame propagation speed is about 4.6 cm/s; for higher air flow speed conditions, the average flame propagation speed is about 9 cm·s\textsuperscript{−1}, and the propagation speed is not monotonic, as shown in Figure 12. Combined with the combustion images, it is believed that the minimum flame speed at high air flow rates corresponds to the local flameout, which is caused by the lack of reactants. Due to the mixing effect, the reactants are replenished, and the downstream flame speed increases at the minimum value; the high upstream value is mainly because the high heat released by the reaction is enough to maintain the ignition of the reactants at the high flow rate at the nozzle exit.

Bermejo et al.\textsuperscript{[10]} used the laminar flame velocity formula to calculate the laminar flow propagation velocity of supercritical hydrothermal flames generated by 4 wt.% and 8 wt.% isopropanol at a preheating temperature of 300–600 °C. The results are shown in Figure 13. The results show that the flame propagation velocity increases with the increase of incident temperature and fuel concentration, and compared with the higher flame propagation velocity of 0.4–3 m·s\textsuperscript{−1} under atmospheric conditions, the flame propagation velocity range in the volumetric reactor is 0.01–0.1 m·s\textsuperscript{−1}. Therefore, for situations where the fuel flow rate is high, a higher fuel concentration or preheating temperature is required to ensure that the flame propagation speed matches the fuel flow rate, thereby ensuring flame stability.

![Figure 12](image.png)

**Figure 12.** Flame propagation velocity as a function of x/d, which is defined as the ratio of the axial height x above the burner outlet plane to the burner diameter\textsuperscript{[13]}.

![Figure 13](image2.png)

**Figure 13.** Flame propagation velocity as a function of x/d, which is defined as the ratio of the axial height x above the burner outlet plane to the burner diameter\textsuperscript{[13]}.
3.2. Research on numerical simulation of supercritical hydrothermal combustion

Limited by the harsh experimental conditions of supercritical hydrothermal combustion and the difficulty of manufacturing reaction devices, current research related to supercritical hydrothermal combustion mainly involves macroscopic characteristics such as ignition temperature and flameout temperature. There is a lack of research on the process and mechanism of ignition and combustion, and it is impossible to further study it. Guide the practical application of supercritical hydrothermal combustion technology. In order to further explore the mechanism of supercritical hydrothermal combustion, researchers established supercritical water oxidation/combustion chemical reaction kinetic models of various organic substances, making full use of the convenience of computational fluid dynamics (CFD) to explore supercritical hydrothermal combustion and microscopic mechanisms in the combustion process, and then guide experiments and reaction device manufacturing design.

3.2.1. Reaction kinetics under supercritical water conditions

The supercritical hydrothermal combustion chemical reaction kinetic model mainly includes a turnkey reaction kinetic model and a detailed elementary reaction kinetic model based on experimental data fitting. Schanzenbächer et al.[45] studied the first-order global reaction kinetics of supercritical water oxidation of ethanol at a temperature of 433–494 °C, a reaction pressure of 24.6 MPa, a reaction time of 2–12 s, and an ethanol concentration of 1 mmol·L⁻¹. The activation energy was obtained as 163.9 ± 3.3kJ·mol⁻¹ and the pre-exponential factor was 10¹¹.¹ ± 4.5. Vogel et al.[46] summarized the kinetic equations of typical organic turn-key reactions and found that the chemical reaction kinetic parameters of turn-key reaction kinetics are affected by factors such as reaction pressure, reaction temperature, reactant concentration, etc., so the reaction rate constants are highly dispersed. Generally cannot be extrapolated beyond the range of experimental conditions. Detailed elementary reaction kinetics includes all intermediate products and elementary reactions in the reaction process, and has been widely used in current gas-phase combustion theory[47]. In addition, since the ion product of supercritical water decreases rapidly with the decrease of density and increase of temperature, elementary reactions dominate in supercritical water environment rather than ionic reactions[24]. In the current study, the researchers mainly studied the supercritical hydrothermal combustion process of organic matter by establishing a detailed elementary chemical reaction kinetic model.

Brock et al.[48] constructed a detailed kinetic model for supercritical water oxidation of methane, methanol, carbon monoxide, and hydrogen, which adopted the kinetic parameters recommended by Baulch et al.[49,50] and considered the kinetic parameters of the pressure-dependent reaction changes, providing kinetic data at the relevant high-pressure limit, which can predict the reaction order of the above four organic compounds to a certain extent. At the same time, the study pointed out that HO₂⁻ free radicals are important free radicals in the...
supercritical water oxidation reaction process. Further understanding of the reaction rate constants of chemical reactions containing HO$_2$· free radicals and the thermochemical data of HO$_2$· free radicals can further improve the model’s prediction accuracy. Based on the ethanol gas-phase combustion model proposed by Marinov$^{[52]}$, Rice et al.$^{[51]}$ established the supercritical water oxidation of ethanol by correcting the decomposition rate of H$_2$O$_2$, adding the reaction mechanisms of CH$_3$O and CH$_3$CHO, and supplementing the HOCO reaction mechanism. The detailed elementary reaction kinetic model well predicts the total conversion rate of ethanol as well as the formation and consumption of intermediate products, and summarizes the ethanol supercritical water oxidation reaction path, as shown in Figure 14. Ploeger et al.$^{[53]}$ added the reaction mechanism of methylphosphonic acid to Rice et al.$^{[51]}$ and constructed a detailed elementary reaction kinetic model for the co-oxidation of methylphosphonic acid and ethanol in supercritical water, successfully reproducing the experiment. This model also observed the trend in the conversion of methylphosphonic acid with ethanol. A summary of existing research on detailed chemical reaction kinetics of supercritical water oxidation/hydrothermal combustion is shown in Table 3.

**Figure 14.** Ethanol reaction pathway proposed by Rice et al.$^{[51]}$.

Summarizing the above related research, it can be seen that the supercritical water oxidation/combustion chemical reaction kinetic model research:

1) Since the reaction pressure of supercritical hydrothermal combustion is much greater than the reaction pressure of conventional gas-phase combustion, when the detailed chemical kinetic model established by gas-phase combustion is applied to a supercritical water environment, the reaction rate constant of the partial pressure-dependent reaction reaches high pressure limit, the original reaction kinetic parameters need to be corrected. One of the authors of this paper, Ren Mengmeng et al.$^{[54]}$, based on the methanol gas-phase combustion model proposed by Princeton University Li et al.$^{[55]}$, analyzed the four pressure-dependent reactions involving OH·, CH$_2$O, CH$_3$O, CH$_2$OH and other reactants. The low-pressure limit kinetic parameters were replaced, and the reaction kinetic parameters of two sensitive reactions in which CH$_3$OH and HO$_2$· and CO and OH· were preferred as reactants were replaced. At the same time, new reaction paths for CH$_3$OH and the intermediate product HOCO were supplemented, thereby constructing a detailed free radical chemical reaction kinetic model for supercritical water combustion of methanol and oxygen in a water environment, and achieved good predictions of the ignition temperature and flameout temperature of supercritical combustion of methanol at different concentrations. The results are shown in Figure 15.
<table>
<thead>
<tr>
<th>Research subject</th>
<th>Research pressure and temperature</th>
<th>Specific study content</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane, methanol, carbon monoxide, and hydrogen</td>
<td>24–25 MPa 450–650 ℃</td>
<td>A detailed chemical reaction kinetics model for the supercritical water oxidation of methane, methanol, carbon monoxide, and hydrogen was developed, achieving good prediction of reaction orders and activation energy.</td>
<td>[48]</td>
</tr>
<tr>
<td>Methanol, ethanol</td>
<td>24.7 MPa 520–530 ℃</td>
<td>Detailed chemical reaction kinetics for the supercritical water oxidation of a methanol-ethanol binary mixture was developed. Results indicate that ethanol promotes the conversion of methanol, while methanol slightly delays the oxidation of ethanol.</td>
<td>[56]</td>
</tr>
<tr>
<td>Methanol</td>
<td>25 MPa 100–550 ℃</td>
<td>Based on the methanol gas-phase combustion model, a detailed chemical reaction kinetics model for methanol supercritical hydrothermal combustion was developed, which successfully predicts the conversion rate of methanol supercritical hydrothermal combustion, ignition delay time, flame temperature, and laminar flame propagation speed.</td>
<td>[54]</td>
</tr>
<tr>
<td>Ethanol</td>
<td>24.5 MPa 10–470 ℃</td>
<td>Developed a detailed chemical reaction kinetics model for ethanol supercritical water oxidation based on the ethanol gas-phase combustion model, which accurately predicts the yield of the intermediate product acetaldehyde.</td>
<td>[51]</td>
</tr>
<tr>
<td>Ammonia, ethanol</td>
<td>24.6 MPa 655–700 ℃</td>
<td>Established a detailed chemical reaction kinetics model for the supercritical water co-oxidation of ammonia-ethanol. By modifying the reaction mechanism including H₂NNOX, it achieved good prediction of the N₂O yield.</td>
<td>[57]</td>
</tr>
<tr>
<td>Methylphosphonic acid and Ethanol</td>
<td>24.6 MPa 473 ℃</td>
<td>Combined the reaction mechanisms of methylphosphonic acid and ethanol to develop a detailed chemical reaction kinetics model suitable for supercritical water oxidation, accurately predicting the trend of increased methylphosphonic acid conversion rate with increased ethanol concentration.</td>
<td>[53]</td>
</tr>
<tr>
<td>Methylamine</td>
<td>25 MPa 400–500 ℃</td>
<td>Based on Brock’s C1 chemical reaction kinetics model, a detailed chemical kinetics model for methylamine supercritical water oxidation was developed, indicating that the degradation of methylamine primarily originates from the reaction with OH· radicals.</td>
<td>[58]</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>24.6 MPa 495–600 ℃</td>
<td>Obtained a first-order kinetics model for hydrogen supercritical water oxidation based on experimental results; developed a detailed chemical reaction kinetics model for hydrogen supercritical water oxidation based on the gas-phase combustion model of hydrogen.</td>
<td>[26]</td>
</tr>
<tr>
<td>Benzene</td>
<td>24.6 MPa 540 ℃</td>
<td>Developed a detailed chemical reaction kinetics model for benzene supercritical water oxidation based on the benzene combustion mechanism and the mechanism of key intermediate oxidation.</td>
<td>[59]</td>
</tr>
</tbody>
</table>
2) Commercial CFD software simulates gas-phase combustion based on the ideal gas model, and the environmental pressure of supercritical hydrothermal flames is extremely high, resulting in material properties that are significantly different from those in the ideal state. If the ideal gas is still used for processing, it will produce larger errors. In order to consider the influence of real fluid effects on supercritical hydrothermal flames, Gao et al.\cite{60} replaced the ideal gas state equation with the P-R state equation, used the deviation function to calculate the real fluid enthalpy value and constant pressure specific heat capacity, and used Chung et al.\cite{61} The method calculates the viscosity and thermal conductivity under high pressure conditions, while the diffusion velocity and diffusion coefficient are calculated by the mixture averaging method. The research results show that after replacing the ideal gas equation of state with the real fluid equation of state, the position of the opposing flame is more accurate and is closer to the central area than the result of the ideal gas equation of state. This is attributed to the inability of the ideal gas equation of state to accurately calculate low-temperature and high-pressure states. Lower material density; for premixed flames, the real fluid effect has a significant impact on the flame speed, and the error can reach 35% when using the ideal gas model.

3.2.2. Research on turbulence-chemical reaction interaction

Under actual combustion conditions, supercritical hydrothermal flames are usually in a turbulent state. The turbulence will cause the temperature and component concentration distribution in the reactor to pulsate instantaneously, which will in turn cause the chemical reaction rate to pulsate; on the other hand, chemical The reaction releases a large amount of heat, which will further enhance the turbulent flow state in the reactor. In short, during the supercritical hydrothermal combustion process, turbulence and chemical reactions will interact and promote each other. Therefore, an appropriate flow-reaction interaction model needs to be selected to study the supercritical hydrothermal combustion process.

Narayanan et al.\cite{62} and Sierra et al.\cite{63} both used two-dimensional models to study supercritical hydrothermal combustion in coaxial burners. In order to reflect the real physical properties of fluids, both use the P-R equation of state to calculate the density, specific heat capacity and specific enthalpy of the substance. The material viscosity and thermal conductivity models of Chung et al.\cite{61} and Lucas et al.\cite{64} were applied in the studies of Narayanan et al.\cite{62} and Sierra et al.\cite{63} respectively. The mass diffusion coefficient models of the two substances are respectively derived from the research of He et al.\cite{65} and Mathur et al.\cite{66}. In considering the turbulence-chemical reaction interaction, both adopt the eddy dissipation model. The eddy dissipation model considers that the reaction is controlled by turbulent mixing, and only uses the turbulent dissipation rate...
to calculate the chemical reaction source term. The numerical models proposed by both of them can well predict the temperature field, flow field, substance type and concentration distribution in the reactor when the fuel inlet temperature is high. However, when the fuel inlet temperature is the thermal autoignition temperature, the model tends to overestimate the reactor temperature. Sierra et al.\textsuperscript{[63]} attributed this phenomenon to the fact that chemical kinetics and mixing kinetics compete with each other at the autoignition temperature, and the numerical model does not consider the impact of reaction rate on supercritical hydrothermal combustion.

Combining the eddy dissipation model with the turnkey chemical reaction kinetics model can improve the accuracy of simulation results to a certain extent. Ren\textsuperscript{[47]}, one of the authors of the paper, compared the simulation results of the simple eddy dissipation model and the global-reaction finite rate/eddy dissipation model for supercritical hydrothermal combustion of 25 MPa, 628 K, and 16 wt.% concentration methanol solution, as shown in Figure 16. It can be seen from Figure 16 that the high-temperature region of the eddy dissipation model is in direct contact with the fuel nozzle, while the high-temperature region of the global-reaction finite rate/eddy dissipation model appears some distance downstream of the nozzle. The fundamental reason for this phenomenon is that the eddy dissipation conceptual model directly uses the turbulent eddy dissipation reaction rate as the turbulent combustion rate, while the global-reaction finite rate/eddy dissipation model takes the eddy dissipation reaction rate and arrhenius chemistry. The smaller one of the reaction rates is used as the turbulent combustion rate. Therefore, the results of the global-reaction finite rate/eddy dissipation model are more reasonable. The combination of a detailed chemical reaction kinetic model of supercritical hydrothermal combustion of methanol and a conceptual model of eddy dissipation will allow further study of the concentration distribution of key components such as OH- radicals during the combustion process\textsuperscript{[54]}.

Zhang et al.\textsuperscript{[67]} further used the above-mentioned detailed chemical reaction kinetics/eddy dissipation conceptual model to study and optimize the structures of coaxial nozzles and cross-jet nozzles in supercritical hydrothermal combustion reactors. The researchers compared the combustion conditions of three nozzles with different central flow cross-sectional areas. The central fluid cross-sectional areas of TEST1, 2, and 3 conditions were 7.07 mm\textsuperscript{2}, 0.79 mm\textsuperscript{2}, and 3.14 mm\textsuperscript{2} respectively. The simulation results are shown in Figure 17. The TEST2 operating condition with the smallest central flow cross-sectional area has the largest reflow area near the wall, while the TEST1 operating condition has the smallest reflow area near the wall. The Craya-Curtet number is defined as the square root of the momentum ratio between the annulus jet and the core jet. The range of the reflow zone increases as the Craya-Curtet number decreases. If the reflow zone is too small or too large, it is not conducive to flame stability. In the study the recommended Craya-Curtet number is given as 0.17. The cross-jet nozzle simulation results are shown in Figure 18. Combustion mainly occurs in the
oxygen-rich recirculation zone. After the central jet changes from fuel to oxidant, the oxygen-rich recirculation zone changes from near the wall to the center of the reactor, reducing heat loss and flame Greater stability.

In addition, direct numerical simulation is another numerical simulation method that can accurately describe the combustion process. Its characteristic is that it directly solves the N-S equation without making any assumptions, and has higher requirements on the computing platform. Song\cite{68} conducted a direct numerical simulation study of supercritical hydrothermal combustion using hydrogen as fuel. The reaction mechanism is derived from the hydrogen and oxygen reaction mechanism proposed by Tester\cite{26}. In order to reflect the true physical properties of the multi-element mixture, the temperature, pressure, and volume relationships between fluids are established through the Volume-Translated Peng-Robinson state equation. Specific enthalpy, specific entropy, thermal properties such as specific heat capacity are calculated by the Departure Functions method, the diffusion coefficient is calculated by the uniform Lewis number, and the viscosity and thermal conductivity are calculated by the calculation formula proposed by Chung et al.\cite{61}. Through a series of numerical simulation studies, it was revealed that the supercritical hydrothermal combustion flame has a unique two-branch flame structure instead of the typical three-branch flame structure, that is, it lacks the combustion-rich side flame branch. The ignition process is divided into pre-ignition stage, ignition stage and post-ignition stage. In the pre-ignition stage, the key intermediate products HO$_2$· and H$_2$O$_2$ are greatly enriched, and the high-temperature chemical reaction marker component OH-free radical concentration is low; while in the ignition stage, stage, H$_2$O$_2$ is rapidly consumed, and HO$_2$· and OH-free radicals are enriched near the flame front and in the rear high-temperature zone respectively.

**Figure 17.** Comparison of temperature and velocity distribution generated by three nozzles with different central flow cross-sectional areas\cite{47}. The size of the central flow cross-sectional area is TEST2 < TEST3 < TEST1. (a–c) Temperature distribution, (d–f) Velocity distribution.

**Figure 18.** Material and temperature distribution in the reactor when the central jets of the cross-jet nozzle are fuel and oxygen respectively\cite{47}. (a–e) The central jet is fuel, (d–f) the central jet is air.
4. Application and development of supercritical hydrothermal combustion technology

4.1. Efficient treatment and energy utilization of high-concentration organic waste

With the continuous development of modern industrialization, people’s material living standards have been greatly improved, but at the same time, a large amount of organic waste has been produced, which has put great pressure on the ecological environment. At present, chemical, petrochemical, papermaking, textile printing and dyeing, pharmaceutical and other industries produce a large amount of sludge, organic wastewater, leakage and other organic wastes, resulting in frequent cases of soil, groundwater, air and other resources being contaminated, seriously threatening human life. health and safety.

Characteristics of high-concentration organic waste such as high moisture content and poor biochemical properties reduce the efficiency of treatment methods such as incineration, coagulation, and chemical oxidation, increase energy consumption, and may produce secondary pollutants. Supercritical water oxidation technology is an international cutting-edge technology for processing highly concentrated organic waste. High-moisture content organic waste and oxidants undergo a homogeneous oxidation reaction in a supercritical water environment, completely removing C, H, O, N and other elements in the organic waste by converting them into harmless substances such as H_2O, CO_2, and N_2, S, Cl and other elements are converted into corresponding inorganic salts, and heavy metals are mineralized into stable solid phases, and no secondary pollutants such as SO_x, NO_x, and dioxins are produced during the reaction process. However, supercritical water oxidation technology currently faces bottlenecks such as high energy consumption, salt deposition, and corrosion. In order to maintain the supercritical water oxidation reaction, the reactants need to be heated to above the supercritical temperature and pressure before entering the reactor. On the one hand, the supercritical preheating temperature leads to an increase in system energy consumption. On the other hand, when processing high-salt organic waste, inorganic salts will precipitate at the reactor inlet, block or even corrode the pipeline, seriously affecting the safety of the system.

Solving the technical bottleneck of supercritical water oxidation of high-concentration and high-salt organic waste is an important driving force for the development of supercritical hydrothermal combustion technology. Compared with supercritical water oxidation technology, the existence of hydrothermal flame allows organic matter to enter the reactor at subcritical temperature or even room temperature, reducing the dependence of the reaction on fuel preheating and avoiding the risk of inorganic salts precipitating in the inlet pipe. , which is more suitable for high concentration and high salt. A large number of scholars have found that supercritical hydrothermal combustion can completely remove almost all pollutants, including stubborn compounds, or control the reaction rate at relatively mild reaction temperatures (700–800 °C) and shorter residence times (minutes or even seconds). Intermediate products, such as sludge\textsuperscript{69}, quinoline\textsuperscript{70}, naphthalene\textsuperscript{60}, toluene\textsuperscript{35}, acetic acid\textsuperscript{29} and ammonia nitrogen\textsuperscript{29}. Aromatic compounds and nitrogen-containing organic matter are often considered refractory substances. Ren et al.\textsuperscript{70} conducted research on supercritical water oxidation and supercritical hydrothermal combustion of a typical nitrogen-containing organic compound, quinoline. The temperature rise curve and product distribution of the reaction process when the quinoline concentration is 1–10 wt.\% are shown in Figure 19. At the preheating temperature of 450 °C, when the quinoline concentration was 10 wt.\%, a sudden temperature rise of about 100 °C was detected, indicating that a certain concentration of quinoline can spontaneously generate a supercritical hydrothermal flame, and the CO_2 yield is much higher than other concentration conditions. Further comparison of the CO_2 yields at 1 wt.\% and 10 wt.\% quinoline concentrations shows that the former requires 10 min at a preheating temperature of 510 °C to reach the maximum CO_2 yield of 0.63. The latter only needs 3 min to achieve a CO_2
yield of 0.85 at a preheating temperature of 450 °C. This phenomenon is attributed to the fact that the combustion heat of the reactants increases the reaction temperature, which improves the reaction rate control steps such as the pyridine ring-opening reaction, thereby achieving efficient degradation of quinoline at a relatively mild preheating temperature and a short reaction time.

For substances such as NH$_3$-N that cannot spontaneously combust to produce supercritical hydrothermal flames, researchers add easily reactive substances such as methanol and ethanol to initiate a co-oxidation reaction, and improve their degradation rate through both chemical reaction kinetics and thermodynamics. Qian et al.\textsuperscript{[69]} studied the effect of 0%–20% methanol content on the ammonia nitrogen removal rate in sludge at 450–600 °C. The results show that at each preheating temperature, the residual amount of NH$_3$-N in the presence of methanol is lower than that in the absence of methanol. When the preheating temperature is 600 °C and the methanol content is 20%, the remaining amount of NH$_3$-N is less than 500mg·L$^{-1}$. Zhang et al.\textsuperscript{[71]} believe that easily reactive substances such as methanol first generate a large amount of free radicals such as HO$_2^-$, H$_2$O$_2$ and OH$^\cdot$ through Equations (6–9), and OH$^\cdot$ further reacts with NH$_3$, shortening the NH$_3$ reaction time. The induction time promotes the degradation efficiency of NH$_3$. In general, methanol accelerates the reaction of ammonia through the generated OH$^\cdot$. According to a study by Zhang et al.\textsuperscript{[71]}, when the methanol concentration is 800 mmol·L$^{-1}$, the preheating temperature is 415 °C, and the oxidation coefficient is 1.5, the inlet temperature of the tubular reactor rises rapidly by about 500 °C, and the NH$_3$ conversion rate reaches up to 97.5%, close to complete conversion. This phenomenon shows that the relatively high concentration of methanol rapidly oxidizes and releases a large amount of heat in the reactor, which accelerates the degradation efficiency of NH$_3$. In another document by Zhang et al.\textsuperscript{[72]}, it was also observed that the temperature of the mixture of NH$_3$ and methanol increased by about 100 °C at the reactor inlet, indicating that the mixture of NH$_3$ and methanol underwent supercritical hydrothermal combustion, causing the conversion of NH$_3$ The rate reaches 98%.

\[
\begin{align*}
H-\text{CH}_2\text{OH}+\text{O}_2 & \rightarrow \text{CH}_2\text{OH}+\text{O}_2 \\
\text{CH}_2\text{OH}+\text{HO}_2^- & \rightarrow \text{CH}_2\text{O}+\text{H}_2\text{O}_2 \\
H-\text{CH}_2\text{OH}+\text{HO}_2^- & \rightarrow \text{CH}_2\text{O}+\text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 & \rightarrow 2\text{OH}^\cdot
\end{align*}
\]

Supercritical water oxidation technology can achieve efficient degradation of nearly 80% of 37 types and 157 categories of hazardous wastes, including mother liquor, organic solvents, waste liquids and sludge produced in the pharmaceutical industry, chemical industry, petroleum mining and
refining and other industries. Its market space is huge, exceeding 100 billion yuan. In the field of organic waste treatment, supercritical hydrothermal combustion technology is regarded as an upgraded version of supercritical water oxidation technology. It has the advantages of shorter reaction time, low-temperature incident material, and avoidance of salt deposition and corrosion. Therefore, supercritical hydrothermal combustion technology will be more reliable, with lower investment and operating costs and better economic benefits. It is a key development direction in the future for efficient treatment of high-concentration and high-salt organic waste.

4.2. Clean utilization and conversion of fossil energy

China’s fossil energy resource endowment shows the characteristics of “rich coal, little oil, and lack of gas”, which determines that China’s coal-dominated energy structure will be difficult to fundamentally change in a short period of time. China has put forward the “dual carbon” goals of “striving to achieve carbon peak before 2030” and “achieving carbon neutrality before 2060”, which puts forward urgent requirements for the green and low-carbon transformation and development of traditional fossil energy. Therefore, capturing, utilizing and storing CO\(_2\) generated by the combustion of traditional fossil energy, and converting traditional fossil energy into green and clean energy are important means to achieve the “dual carbon” goal.

Research by Fujie et al.\(^{[73]}\) shows that during the supercritical water oxidation process of lignite, elements such as C, H, O, and N can be completely converted into green, non-polluting substances such as CO\(_2\), H\(_2\)O, and N\(_2\). In sufficient time, the S element is converted into SO\(_4^{2-}\) at a lower temperature, and no pollutants such as dust are emitted into the atmosphere during the reaction process. Therefore, supercritical hydrothermal combustion technology can eliminate the tail gas desulfurization and denitrification processes necessary in conventional coal combustion, and achieve CO\(_2\) capture at a lower cost. It has great potential in the field of clean coal utilization. Ma\(^{[74]}\) used semi-coke, a solid product after coal gasification, as the research object and explored its oxidation/combustion mechanism and process in supercritical water. They found that the reaction only proceeds in the radial direction on the particle surface, and the semi-coke particles are oxidized. Heat production and heat transfer to the environment occur simultaneously. Further study on the reaction control steps shows that when the surface temperature of the semi-char particles is lower than 970 K or higher than 1090 K, the reaction control steps are the oxidative combustion reaction on the semi-char surface and the mass transfer of oxygen from supercritical water to the semi-char particles respectively. In the range of 970 K–1090 K, chemical reactions and diffusion jointly control the combustion reaction. Research results show that increasing the supercritical water temperature, oxygen concentration, volatile content and reducing particle size are beneficial to semi-coke ignition. The critical conditions for semi-coke to ignite are supercritical water temperature of 798 K, oxygen concentration of 7.97 wt.%, particle size of 168 μm, and volatile matter content of 10 wt.%. Bermejo et al.\(^{[75]}\) proposed a coal supercritical water oxidation power generation system. The schematic diagram is shown in Figure 20. After the coal is crushed, it is mixed with air and water at 375 °C and 30 MPa in the supercritical water oxidation reactor. The supercritical water oxidation reaction occurs, and the high-temperature and high-pressure multi-component thermal fluid (components include H\(_2\)O, CO\(_2\), and N\(_2\)) expands in the turbine to do work, and then is reduced to normal temperature and pressure through the condenser and flash tank. Research results show that the net energy efficiency of this system when producing multi-element fluids at 650 °C and 30 MPa parameters is 37%, which can be further increased to 40% when reheat is introduced, which is better than the pressurized fluidized bed constructed by Bermejo et al.\(^{[75]}\) The net energy efficiency of the reheat power generation system with the boiler as the core equipment (bed boiler bed coal content 10%, pressure 1.2 MPa, inlet temperature 300 °C, outlet temperature 830 °C) increased by more than 4% and 8%.
It is worth noting that in order to heat the reactants to a supercritical temperature, a natural gas furnace is installed in the supercritical water oxidation power generation system. Compared with supercritical water oxidation, supercritical hydrothermal combustion has a relatively higher reaction temperature and more reaction heat. Therefore, the coal supercritical hydrothermal combustion power generation system can heat the reactants to the reaction temperature through heat recovery and reheating without consuming additional energy. The schematic diagram of a supercritical hydrothermal combustion power generation system proposed by Shuzhong Wang’s team at Xi’an Jiaotong University is shown in Figure 21[76]. The gas phase and liquid phase components in the multi-element thermal fluid produced by supercritical hydrothermal combustion are separated through a gas-liquid separator. CO₂, N₂ and other gas phase components work through the high-pressure turbine and low-pressure turbine. The high-temperature liquid phase products are mainly responsible for preheating the air and feed water and reheating the high-pressure cylinder exhaust steam.

Converting coal into hydrogen through gasification reactions is another form of clean utilization of coal. Supercritical water gasification technology can not only convert the H element in the material into hydrogen, but also convert part of the H element in the water into hydrogen, so it has high hydrogen production efficiency. For hydrogen production from supercritical water gasification of coal, the hydrogen production rate can reach 180%, even without a catalyst[77]. Due to the principle and process of gasification hydrogen production, general
above-ground coal gasification hydrogen production will inevitably produce and emit a large amount of CO₂. Therefore, Zhang et al.\cite{78} proposed a new supercritical hydrothermal combustion-assisted in-situ coal gasification hydrogen production technology. The schematic diagram is shown in Figure 22. This technology uses renewable energy to generate sub/supercritical water, and further injects it, oxidant, and auxiliary fuel into the ground, causing some coal to undergo supercritical hydrothermal combustion underground. The supercritical water and CO₂ produced by supercritical hydrothermal combustion carry a large amount of heat. On the one hand, they heat the remaining coal and crack it to form coke. On the other hand, they gasify with the coke to produce H₂, CO and other gases. H₂ in the gas phase products can be separated and captured through devices such as H₂ permeable membranes, while CO₂, wastewater, ash, and other substances generated during the gasification process can be directly sequestered in the ground, realizing low-cost carbon sequestration and reducing the risk of environmental pollution on the surface. Based on the energy level and Gibbs free energy minimization theory, Zhang et al.\cite{78} discussed the effects of renewable energy levels, reaction temperatures, auxiliary fuel types, fossil fuel types, combustion coefficients, and sub/supercritical water on system energy level changes and hydrogen production rate. Research results show that blindly increasing the reaction temperature and investing in renewable energy will lead to an increase in system operating costs, a decrease in underground coal mining volume, and an unstable supercritical hydrothermal flame; when the injected supercritical water temperature is 873 K, the combustion coefficient is 0.2 and the moisture content is 90 wt.%.

The CO₂ emissions from coal and petroleum coke hydrogen production reach the lowest, which are 5.7 kgCO₂· kgH₂−1 and 3.9 kgCO₂· kgH₂−1 respectively, which are much lower than those of traditional coal gasification. The hydrogen process’s 19–24 kgCO₂eq·kgH₂−1 complies with the “low carbon hydrogen” (emissions less than 14.51 kgCO₂eq·kgH₂−1) and “clean hydrogen” (emissions less than 4.90 kgCO₂eq·kgH₂−1) standards proposed by the China Hydrogen Energy Alliance\cite{79}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure22.png}
\caption{Schematic diagram of the supercritical hydrothermal combustion-assisted in-situ coal gasification hydrogen production system\cite{78}.}
\end{figure}

4.3. Realize super thermal recovery of deep downhole or submarine heavy oil

According to BP’s “BP World Energy Statistical Yearbook 2022”, world oil consumption will exceed 4.82 billion tons in 2021, an increase of 6.1% compared with 2020 oil consumption. According to forecasts, oil consumption will continue to increase before 2050. The global demand for petroleum resources continues to grow, leading to the gradual depletion of conventional crude oil reserves, and unconventional heavy oil resources have begun to become the focus of petroleum resource development. Heavy oil has the
characteristics of high viscosity and high density. Normally, its viscosity is greater than 50 MPa·s and its density is greater than 0.92 g·cm$^{-3}$. Compared with conventional crude oil, heavy oil has less light fractions and higher colloid and asphaltene content. Heteroatoms such as O, S, and N form complexes with transition metal ions in heavy oil, leading to the aggregation of molecules and further increasing its viscosity, which poses great challenges to its mining. In addition, as heavy oil production expands to deep wells, ultra-deep wells and oceans, gas injection boilers have the disadvantages of large footprint and high heat loss, making it difficult to meet engineering needs. Therefore, the research and development of underground direct steam generation technology that is not limited by well depth, is not restricted by geography, and has high steam generation efficiency is urgent. The principle of applying supercritical hydrothermal combustion multi-element thermal fluid generation technology in the field of heavy oil thermal recovery is shown in Figure 23. Its core equipment is a supercritical hydrothermal combustion reaction device. Its compact structure allows it to be placed either above the well or underground.[81] In the application process, oily wastewater existing in large amounts in oil fields can be used as fuel, air or oxygen is used as oxidant, supercritical hydrothermal combustion reaction occurs in the reaction device, and the generated thermal fluids such as CO$_2$ and H$_2$O are directly injected oil layer. Compared with conventional heavy oil thermal recovery methods, supercritical hydrothermal combustion multi-element thermal fluid generation technology has the following advantages: 1) The reaction device has high thermal efficiency, no exhaust heat loss, and can achieve direct heat exchange between molecules; 2) combustion generates H$_2$O in the multi-element thermal fluid carries a large amount of heat to heat the heavy oil and reduce its viscosity, while CO$_2$ and other gases dissolve in the crude oil, reducing the interfacial tension and further enhancing the fluidity of the heavy oil, thereby increasing heavy oil production; 3) the fuel has strong adaptability and can directly burn a large amount of oily wastewater existing in oil fields, saving fuel costs while eliminating the expenses associated with wastewater treatment; 4) the device has a compact structure and is suitable for environments such as offshore mining platforms. It can even be placed underground, breaking through the application depth limit and realizing increased production of deep heavy oil.

In preliminary research, the team of Shuzhong Wang and Yanhui Li of Xi’an Jiaotong University developed an underground composite thermal fluid reactor combined with supercritical hydrothermal combustion[82,83], as shown in Figure 24(a). Supercritical fuel and oxidant enter the reactor, and a supercritical hydrothermal flame is generated through thermal autoignition and forced ignition, thereby producing the multi-component thermal fluid required for heavy oil extraction. Currently, the team has built a supercritical hydrothermal combustion multi-element thermal fluid generation device with a design pressure of 30 MPa and
a temperature of 650 °C, as shown in Figure 24(b). The device is rated to produce 0.3 tons of a multi-element thermal fluid per hour, at a pressure of 25 MPa and a temperature of 450 °C, which has reached the scale of a pilot device in the field of heavy oil thermal recovery. Geng et al. \cite{84} in this team simplified the reactor into a two-dimensional model and systematically studied the effects of fuel flow rate, fuel concentration, reactor initial temperature, reaction pressure and oxidant temperature on methanol/oxygen supercritical hydrothermal combustion ignition. The fuel mass flow increased from 24 kg·h$^{-1}$ to 1080 kg·h$^{-1}$, and the ignition temperature increased significantly by 398 K. Both oxygen temperature and reaction pressure have optimal values that make the ignition temperature reach the lowest. This study provides an important reference for the scale-up design and ignition operation of hydrothermal burners. Currently, the team is building a comprehensive demonstration research platform supporting the device, and will conduct related research on the ignition characteristics and mechanism, flameout characteristics and mechanism of supercritical hydrothermal combustion multi-element thermal fluid generation technology in the later stage, so as to apply the technology to improve technical and theoretical guidance in engineering.

![Figure 24](image1.png)

**Figure 24.** Supercritical multi-element thermal fluid generator developed by the team of Professor Shuzhong Wang of Xi’an Jiaotong University: (a) Partial generator development plan\cite{82,83}; (b) Representative object.

![Figure 25](image2.png)

**Figure 25.** Numerical simulation results of the relationship between ignition temperature and fuel concentration of a 0.3t·h$^{-1}$ supercritical hydrothermal combustion multi-element thermal fluid generating device\cite{5,84}.

5. Conclusion and outlook

Supercritical hydrothermal combustion technology is a new homogeneous combustion technology that utilizes the excellent reaction and solvent properties of supercritical water to achieve direct heat transfer between molecules. Because supercritical hydrothermal combustion has unique advantages such as strong fuel adaptability, fast reaction rate, and green and pollution-free products, it provides solutions for the clean utilization of traditional fossil energy, efficient mining of heavy oil, and harmless treatment of high-concentration organic pollutants. It has developed a brand-new approach and has received widespread attention from various related fields.

Current experimental research on supercritical hydrothermal combustion mainly focuses on using intermittent and continuous devices to explore the macroscopic characteristics of supercritical hydrothermal combustion, such as ignition temperature, flameout temperature, and flame propagation speed. The commonly used thermal autoignition method usually requires heating the reactants to a supercritical temperature of about 400 °C. When using an ignition device for forced ignition, the fuel can even enter the reactor at 23 °C and generate a supercritical hydrothermal flame. This means that forced ignition technology can significantly reduce the energy consumed in preheating reactants, which is of great significance in promoting the application of supercritical hydrothermal combustion. The flameout temperature is a macroscopic manifestation of the matching relationship between the supercritical hydrothermal flame propagation velocity and the material flow rate. The essence of stable flame combustion lies in selecting the appropriate reactant flow rate to match the supercritical hydrothermal flame propagation velocity.

Establishing a correct numerical model is a necessary condition to further elucidate the microscopic mechanism of supercritical hydrothermal combustion. Compared with the general package reaction, the detailed chemical reaction kinetic model has strong theoretical foundation and good extrapolability, and can explain the reaction mechanism of organic matter in the supercritical hydrothermal combustion process in more detail. In order to reflect the real combustion situation of supercritical hydrothermal flame under high pressure conditions, the real gas state equation needs to be used instead of the ideal gas state equation, and the thermodynamic parameters and transport parameters of the reactants need to be corrected. It is worth noting that supercritical hydrothermal combustion is usually in a turbulent state. Ignition, combustion, and flameout are the results of the interaction between turbulence and chemical reactions. Only considering the impact of turbulent mixing or chemical reactions on combustion alone cannot cover the effects of supercritical hydrothermal flames. Throughout the life cycle, the effects of turbulent mixing and reaction on combustion need to be considered simultaneously.

Currently, the application of supercritical hydrothermal combustion still faces some bottlenecks. First of all, forced ignition technology can effectively reduce ignition energy consumption and reduce the dependence of ignition on preheated fuel. At present, there is still insufficient research on forced ignition of supercritical hydrothermal combustion, and it is impossible to quantitatively explain the density, specific heat capacity, and thermal conductivity of reactants after crossing the critical point. The impact of drastic changes in physical parameters such as viscosity on the ignition mechanism. Secondly, because the structure of the supercritical hydrothermal combustion reactor is very compact, the cross-sectional heat load and volumetric heat load far exceed the recommended values for conventional boilers and other combustion devices. For example, the design power of the cold-wall reactor used in Stathopoulos\textsuperscript{[9]} and Meier et al.\textsuperscript{[37]} is 120 kW, and its cross-sectional heat load and volumetric heat load are 15.2 MW·m\(^{-2}\) and 20.6 MW·m\(^{-3}\) respectively. Currently, there are no clear design guidelines to guide the size design of supercritical hydrothermal combustion reactors. Third, supercritical hydrothermal combustion has the characteristics of high temperature, high pressure, and high oxygen, which puts forward strict requirements for reactor anti-corrosion work. Preventing corrosion in
supercritical hydrothermal combustion reactors is a current research hotspot and is of great significance for advancing the application of supercritical hydrothermal combustion technology.

Author contributions

Writing—original draft preparation, writing and editing, YL and ZL. Both YL and and ZL contributed equally. Conceptualization and methodology, SW and YL; data curation, YD and HL; review and proofread, YL and MR. All authors have read and agreed to the published version of the manuscript.

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Conflict of interest

The authors declare that there are no known competing financial interests or personal relationships between the authors that could have appeared to influence the work reported in this article.

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