Review on an Advanced Combustion Technology: Supercritical Hydrothermal Combustion

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Abstract: Supercritical hydrothermal combustion, a new and promising homogeneous combustion technology with a wide range of application scenarios and broad development prospects, provides creative ideas and means for the enhanced degradation of organic wastes, hydrothermal spallation drilling, thermal recovery of heavy oil, etc. This technology is elaborated upon in five parts: (1) introducing the main devices including semi-batch reactor and continuous reactor to study the hydrothermal flame in accordance with research institutions, (2) presenting the research status of related numerical simulation from the angles of reaction kinetics and flow-reaction, (3) summarizing the characteristics of hydrothermal flame and combustion by five key parameters, (4) dividing up ignition process and explaining ignition mechanism from the perspectives of critical physical properties of water and heat transfer and mixing conditions, (5) discussing and forecasting its industrial applications including hydrothermal spallation drilling, the thermal recovery of heavy oil, the clean conversion and utilization of coal-based fuel, and the harmless treatment of pollutants.

By and large, this paper analyzed in detail everything from experimental equipment to industrial applications, from combustion characteristics to ignition mechanisms, and from summary conclusions to prospect prediction. In the end, herein is summarized a couple of existing paramount scientific and technical obstacles in hydrothermal combustion. Further significant studies in the future should include excellent reactors, advanced monitoring techniques, and powerful computational fluid dynamics.

Keywords: hydrothermal combustion; reactor; combustion characteristics; ignition mechanism; applications

1. Introduction

Supercritical water (SCW) refers to the water at the conditions above the critical point (Tc = 374.15 °C, Pc = 22.12 MPa). Phase change leads to the variations in physical and chemical properties, thus profoundly affecting chemical reactions. Due to SCW’s special properties, like low viscosity, low dielectric constant and high diffusivity, the reactions between organic matters and oxidants in SCW, called supercritical water oxidation (SCWO), are thoroughly homogeneous and rapid. In this process,
carbon elements in the organic matters are converted into carbon dioxide, elements such as chlorine, sulfur and phosphorus are converted into corresponding inorganic salts, and most of the nitrogen elements are converted into nitrogen gas, thereby realizing an efficient and harmless treatment of organic wastes. Because of its cleanability, efficiency and thoroughness, SCWO has been viewed as the most promising organic waste treatment technology in the 21st century [1]. In 1982, Massachusetts Institute of Technology (MIT) scholar Modell first proposed the SCWO based on the phenomenon that organic matters and oxygen could completely mix and rapidly reacted with each other in supercritical water. In the next three or four decades, this technology has achieved fruitful results in the harmless treatment of organic wastewater and sludge [2], and several research institutes and commercial companies have promoted the commercialization of SCWO in waste treatment [3–5].

With the advancement of theoretical and experimental research on SCWO, its limitations begin to emerge. There are generally three major obstacles restricting the low-cost and reliable industrial implementation of SCWO technology: salt-deposition [6,7], corrosion [8–10] and high energy consumption. For traditional SCWO, raw materials need to be preheated to supercritical temperature. With the gradual increase of the temperature from subcritical to supercritical, the dielectric constant and the number of water’s hydrogen bonds decrease, and inorganic salts in the raw materials deposit on the inner surface of the preheating equipment or conveying pipeline. Besides, the inorganic salts produced in the process of SCWO may also precipitate and form salt deposit, leading to the blockage of pipelines and equipment and the malfunction of the system. Bermejo et al. designed a transpiring wall reactor (TWR) and evaluated its ability to counter corrosion and salt-deposition [11]. Under the condition of SCWO with flame, Príkopský et al. tested the performance of two TWRs with different transpiration intensities in anti-corrosion and anti-salt deposition [12]. The region near the critical point of subcritical-to-supercritical transition is a high-density area (300–420 °C). The dielectric constant of water and the solubility of inorganic salts are enormous, and it is easy to entice severe corrosion damage of tubes and equipment [13]. Moreover, the highly energy-consuming preheating process of realizing the supercritical state, especially adopting tubular reactors with a simple plug-flow, restricts the popularization of SCWO technology.

The hydrothermal flame is defined as the flame produced in water above the critical point [14], which is essentially a more intense oxidation reaction. In the 1980s, Franck et al. first used “hydrothermal flame” to describe the flame produced in the experiment when studying the reaction of methane and oxygen in supercritical water at 500 °C and 200 MPa [15]. Because of its potential to overcome the limitations of SCWO, this flame began to attract the attentions of researchers (see Table 1). Compared with the moderate temperature of SCWO (450–650 °C), the local temperature (>1000 °C) reached by the flame improves the removal efficiency of organic matters (10–100 ms needed for completion) and recalcitrant organic matters, making it possible to design smaller and more effective reactors. Furthermore, the heat it releases can be used as the internal heat source of SCWO, reducing its dependence on preheating and avoiding corrosion and salt-deposition in the process towards the supercritical state. Additionally, supercritical hydrothermal combustion (SCHC) can even be regarded as a means of obtaining energy [16–18]. For example, the SCHC of coal is a new combustion technology that can realize the efficient utilization of clean energy [19–21]. The formation of pollutants like NOx, SOx and dust can be restricted without desulphurization, denitrification and dust-collecting equipment, not to mention the low-cost capture of CO2. In addition, by taking advantage of the high-pressure water environment and a tremendous amount of heat released in the customized reactor, hydrothermal combustion is also applied in flame-jet drilling for geothermal energy exploitation [22,23]. With the flame heating the rock surface, thermal stresses generate and gradually strengthen, thus making rocks crack inside and then break up. In addition, the SCHC could directly happen in strata among fuel, oxidant and water, and then releases large amounts of heat to gasify the cooling water, heating up the heavy oil and reducing its viscosity. Therefore, this potential application in the field of the thermal recovery of heavy oil has recently aroused extensive attention among researchers. Moreover, due to these characteristics, it can be applied in heavy oil recovery in the deep reservoirs and even offshore ones as well.
Augustine pointed out that the study of hydrothermal combustion was still in its infancy [14]. Ten years since then, however, the experimental and numerical simulation studies on the characteristics and applications of hydrothermal flame have been further improved. Some studies have even begun to investigate the interpretation of the transcritical ignition mechanism and the magnification criterion for SCHC reactors. As the main experimental apparatus to study the generation and the characteristics of hydrothermal flame, hydrothermal flame reactor (HFR) is designed to confine the flame in a certain space. For example, to explore the hydrothermal spallation drilling of methanol [24,25] and ethanol [26], the ETH water-cooled hydrothermal burner (WCHB) has been upgraded to the fourth generation [23,27], and equipped with advanced measuring [22] and ignition devices [23]. Taking methanol [28,29] and isopropanol [17,30–37] as the auxiliary fuels, the University of Valladolid has optimized their TWRs [33,37] to study the characteristics and effects of hydrothermal flame enhanced SCWO treatment for recalcitrant pollutants. Xi’an Jiaotong University has been gradually expanding its research from coal [20] to high-concentration textile wastewater [38] to methanol [39,40], sludge [38] and quinoline [41] and a series of other fuels in its self-designed reactor [42].

Among the characteristics of hydrothermal flame, two key features, i.e., the operating pressure (supercritical pressure) and the presence of supercritical water (as reactant and reaction environment), can distinguish hydrothermal combustion from gas-phase combustion at atmospheric pressure. Generally speaking, the current research on the characteristics of hydrothermal flame and combustion are mainly focused on five aspects, namely ignition temperature, extinction temperature, ignition delay time, flame temperature distribution, and flame propagation speed. As a supplement to experiments, the numerical simulation is of great significance in helping to explain experimental results, summarize reaction laws, and better understand the hydrothermal combustion [29,37,43].

Ignition, a process of a sudden increase in reaction rate in a non-reactive system, includes spontaneous ignition and forced ignition, caused by both physical and chemical factors. In terms of the ignition process and ignition mechanism, it can be divided into supercritical ignition and transcritical ignition based on existing research results of hydrothermal combustion ignition, based on the supercritical or subcritical state of reactants. Transcritical ignition is a key stage in the process of achieving hydrothermal combustion by feeding cold materials. The ignition mechanism of supercritical ignition and transcritical ignition are slightly different due to the drastic changes of physical properties of the transcritical process, but ignition is generally the result of the interaction of critical physical properties, heat transfer and mixing. Reddy et al. studied the difference in the effect of oxidant flow rate (0.5–3 mL/s) on ignition delay time under subcritical (380 °C, 20.5 MPa) and supercritical (400 °C, 22.5 MPa) conditions [44]. The disappearance of phase interface and the change of reaction mechanism caused by supercritical pressure and the alterations of reaction mechanism and component transport caused by supercritical water have profoundly changed the ignition mechanism and the ignition process. In practical application, we hope to inject raw materials at room temperature to overcome salt-deposition-caused blockage and preheating-caused high-energy consumption in the SCWO treatment of recalcitrant pollutants. Therefore, it is necessary to study the mechanism of transcritical ignition.

Currently, there are only few reviews [14,36,45–47] on the characteristics and improvements of experimental apparatus, the numerical simulation progress, the characteristics of flame and combustion, and especially the ignition process and mechanism, which is not enough for relevant scholars to learn about current research status within limited time. To sort out research outcomes and deficiencies in the existing literature, and to provide useful information for follow-up research, this review was divided into five parts to summarize the literature related to hydrothermal combustion, especially the articles published in the past ten years: (1) Introduction to critical experimental devices (semi-batch reactor and continuous reactor) in different categories according to their institutions. (2) Introduction to the applications of numerical simulation in the field of hydrothermal combustion from the angles of reaction kinetics and flowreaction. (3) Summary of research results of supercritical hydrothermal flame and its combustion characteristics by five key factors. (4) Division of the ignition process and explanation of the ignition mechanism from the perspectives of critical physical
properties, heat transfer and mixing. (5) Discussion and forecast of the industrial applications from aspects of hydrothermal spallation drilling, thermal recovery of heavy oil, clean conversion and utilization of coal-based fuel and harmless treatment of pollutants. Its skeleton is arranged from experimental equipment to industrial applications, from combustion characteristics to ignition mechanism, and from summary conclusions to prospect prediction. Generally speaking, this review is beneficial for readers to understand the ignition mechanism and the factors affecting flame stability, as well as the design and optimization of HFR, thus promoting its industrial application.
Table 1. Reactors and main objectives of worldwide research institutes.

| Institute                                | Rector Type                        | Objective                                                                 | Ref.  |
|------------------------------------------|------------------------------------|---------------------------------------------------------------------------|-------|
| Karlsruhe Institute of Technology, Germany | Semi-batch reactor                 | The visual observation and temperature measurement of hydrothermal flame | [15]  |
| Sandia National Laboratories, USA        | Semi-batch reactor                 | Threshold concentrations for ignition and their relations with temperature | [48]  |
| Ebara Research Company, Japan             | Continuous reactors                | SCWO strengthened by hydrothermal flame to deal with recalcitrant reactants| [49]  |
| McGill University, Canada                | Semi-batch reactor                 | The observation, description and environmental evaluation of hydrothermal flame as a tool to destruct complex organic wastes | [50]  |
|                                           | Semi-batch reactor                 | The effects of hydrothermal flame on the destruction of naphthalene       | [51]  |
| MIT, USA                                 | Continuous reactors                | Verified the generation and the stability of hydrothermal flame and, its application in thermal spallation drilling | [52]  |
| ETH Zurich, Switzerland                  | Continuous reactors (WCHB-1)        | SCWO strengthened by hydrothermal flame to deal with organic components    | [53]  |
|                                           | Continuous reactors (WCHB-2)        | Evaluation on the newly-designed HFR reactor                             | [54]  |
|                                           | Continuous reactors (Transpiring wall) | The influence of mass flux and temperature of the transpiration on the reactor performance | [11]  |
| ETH Zurich, Switzerland                  | Continuous reactors (Transpiring wall) | The performance of the transpiring wall reactor in anti-corrosion and anti-deposition | [12]  |
|                                           | Continuous reactors (WCHB-3)        | Combined experiments with numerical simulation to investigate the ignition process | [43]  |
|                                           | Continuous reactors (Transpiring wall) | The ignition, extinction and stability of hydrothermal flame              | [24]  |
|                                           | Continuous reactors (WCHB-4)        | The forced ignition of methanol-oxygen and its influencing factors        | [55]  |
|                                           | Continuous reactors (WCHB-4)        | The forced ignition of turbulent diffusion flame and the drawing of its ignition map | [23]  |
|                                           | Continuous reactors (WCHB-4)        | The new type of ignition device and the performance of different nozzles  | [22]  |
| Shandong University, China               | Continuous reactors (Transpiring wall) | The effects of operation parameters on the performance of the reactor and the determination of optimal parameters from the angles of energy consumption and investment cost | [56]  |
| University of Valladolid, Spain          | Continuous reactors (Transpiring wall) | The status of SCWO with hydrothermal flame in different mixers            | [30]  |
|                                           | Continuous reactors (Tubular reactor) | The formation and the stability of premixed hydrothermal flame and its influencing factors, including feed rate, temperature and concentration | [33]  |
| Institution | Reactor Type | Description |
|-------------|--------------|-------------|
| Continuous reactors (Tubular reactor) | SCWO strengthened by hydrothermal flame to deal with recalcitrant compounds | [32] |
| Continuous reactors (Transpiring wall) | The impact of operation parameters including flow rate, temperature and concentration on the characteristics of hydrothermal flame | [31] |
| Continuous reactors (Transpiring wall) | Analysis on the new reactor and its energy recovery performance by test and numerical simulation | [37] |
| NASA Glenn Research Center, USA | Continuous reactors | Transition to the turbulence of buoyant near-critical water jets and the role of buoyancy | [57] |
| | | The characteristics of laminar and turbulent diffusion flame and the formation of soot | [58] |
| | | The auto-ignition and stability of ethanol hydrothermal flame | [59] |
| Indian Institute of Technology Roorkee, India | Semi-batch reactor | The impact of the temperature of semi-batch reactor and oxidant on the ignition of hydrothermal flame | [60] |
| | | The impact of oxidant characteristics like flow rate on the ignition of the hydrothermal flame at near-critical temperature and supercritical temperature | [44] |
| No (numerical simulation) | Built and validated the detailed chemical kinetics model for methanol SCHC | [39] |
| No (numerical simulation) | Investigated the effects of operation parameters like methanol concentration on the characteristics of the hydrothermal flame | [61] |
| No (numerical simulation) | Built and validated the detailed chemical kinetics model coupled with a simple flow model for methanol SCHC | [40] |
| No (numerical simulation) | Verified that quinoline solutions could be ignited without co-fuels like methanol and isopropanol | [41] |
| Semi-batch reactor | Used counterflow diffusion flames to deeply understand hydrothermal flames and developed a Flamelet Generated Manifold table for advanced turbulent flame simulations | [62] |
| No (numerical simulation) | Developed a real-fluid flameless/progress variable model for laminar hydrothermal flames | [63] |
| No (numerical simulation) | Investigated the real-fluid effects on both laminar diffusion and premixed laminar hydrothermal flames | [64] |
| No (numerical simulation) | Directly used numerical simulation to investigate auto-ignition characteristics of turbulent diffusion hydrothermal flames | [65] |
| No (numerical simulation) | Use high-fidelity numerical simulation and homogeneous auto-ignition to study the flame structure and stabilization mechanism of laminar diffusion hydrothermal flames | [66] |
2. Characteristics and Improvements of Experimental Apparatus

Supercritical HFR, the main device to verify the generation of hydrothermal flame and study its characteristics, can withstand the designated high pressure and high temperature, confine hydrothermal flame in a certain space, and significantly alleviate corrosion and salt-deposition. According to the feeding modes of reactants, reactors can be sorted out into semi-batch reactors and continuous reactors. The former is mainly used to explore the ignition feasibility and characteristics of simple organic compounds, such as methane and methanol. Unlike semi-batch reactors’ one-off feeding, continuous reactors can constantly feed fuels and oxidants into the chamber to sustain the flame. Additionally, almost all of the different continuous reaction systems share the similar flow diagram, which means the designing concepts are nearly identical (Figure 1). The effects of their different structures and operating parameters (fuel concentration and flow rate, etc.) on the characteristics of flame ignition and extinction and the efficiency of removing pollutants are the primary concerns. Moreover, continuous reactors consist of tubular and volumetric structures, such as TWR and WCHB. With diverse research purposes, the reactors used by relevant groups have different appearances. If the hydrothermal flames are not properly controlled in the reactor, this will lead to the acceleration of thermal wear and corrosion and the production of nitrogen oxides [49].

The increasing development and improvement of reactors determine the study of combustion characteristics of different reactants under different operating conditions and the verification and perfection of numerical simulations. Therefore, taking research institutions as the main body to comb its development vein from the two major classifications of the reactor, this part aims to point out the inadequacies of reactor structures and to give valuable suggestions.

Figure 1. Flow diagram of the facility.
2.1. Semi-Batch Reactors

Although developed by different institutions, semi-batch reactors, the first kind of reactor to observe the hydrothermal flame, basically have the same system [45]. Its operation flow is relatively simple: First, water and fuel with specific parameters are fed into a semi-batch reactor before the reactor is pressurized and preheated to the designated state (subcritical or supercritical), and then oxidant is injected into the reactor at a specific temperature and flow rate. The generation of hydrothermal flames is judged by a visualization window or measuring thermocouple temperature. But due to the limitations of the reactor structure, several key subjects fail to be investigated: (1) in the ignition process of the turbulent diffusion hydrothermal flame, diffusion mainly controls chemical reactions due to its larger timescale [44], while the weak turbulence in the reactor fails to reflect accurate ignition delay time; (2) the blurry boundary between flame ignition and flame extinction due to unstable combustion fails to study the extinction characteristics; (3) the effects of some key operating parameters such as fuel flow rate on the stability of hydrothermal flame fail to be evaluated; (4) the influences of fluctuant operating parameters on the process of continuous combustion fail to be probed. All of these have inspired the development and application of continuous reactors.

Franck et al. [15,67] from Karlsruhe Institute of Technology (KIT) observed laminar reverse diffusion flames in a semi-batch reactor for the first time (Figure 2a). The apparatus they used, mainly made by cylindrical nickel-based superalloy with 80 mm o.d. and 30 mm i.d., was a reaction cell of about 30 mL sample volume, which could hold a sample pressure of up to 200 MPa at 500 °C and above for hours. Two openings at the opposite ends were equipped with sapphire windows of 15mm diameter and 10mm thickness, to directly observe the hydrothermal flame. In addition, there were another four openings, one for the burner, one for a sheathed chromel-alumel thermocouple, and two for the stainless steel capillaries to extract samples and connect the reaction cell with the feed autoclaves, respectively. During the feeding, the bellows were compressed slowly and steadily by special gears, high-torque electric motors and electronic controls. In the meantime, the equivalent number of products was driven out of the cell and entered the gap between bellows and autoclaves, thus forming a circular motion with stable pressure. This reactor was designed to prove the existence of hydrothermal flame. Though product analysis could be carried out by sampling, it was hard to quantitatively understand the laminar reverse diffusion flame with only one thermocouple. Compared with Franck, Sandia National Laboratory designed a semi-batch reactor with its visualization window, measurement methods, feeding mode and safety improved (Figure 2b) [48,68]. To clarify the generation progress of diffusion hydrothermal flame and obtain information on its composition and temperature, three sapphire windows were installed to realize optical diagnostics, recording visible emission with a video camera and shadowgraph images on the videotape, and acquiring composition values and HFR temperatures from spontaneous Raman spectroscopic measurements. During the experiment, reactants including water, fuel and oxidizer were injected through high-pressure liquid chromatography (HPLC). Besides a cylinder fitted with a floating piston that was indispensable in dealing with gas-phase oxidizer, the materials and connections of pipeline system were also designed to minimize potential risks. In addition, the reactor and all the oxygen pipelines were enclosed by secondary shields. Owing to the introduction of in-situ online diagnostic apparatuses, one giant leap has been taken in better understanding the hydrothermal flame.

The visual flame cell with a relatively simple structure, designed by Sobhy et al. of McGill University, is mainly composed of ignition nozzle, sapphire window viewport, reaction chamber and external heater (Figure 2c) [50,51]. This bench-scale reactor system with a traditional reaction chamber structure could observe the flame with a charge coupled device (CCD) and a near infrared (NIR) camera and analyze reaction products with two novel gas analyzers. The obtained information about CO and NOx could help explain reaction paths. This paper mainly centered on ignition mechanism, the influence of different fuel concentrations on the characteristics of hydrothermal flame, and reaction products, especially NOx. Therefore, the detailed pros and cons of the reactor structure would not be given here. The semi-batch reactor from NASA John H. Glenn Research Center was to
explore the role the SCWO played in destroying the metabolic wastes of human [69](Figure 2d). Reddy studied the ignition mechanism of n-propanol air hydrothermal flame [60] and the impacts of oxidant characteristics on ignition with this reactor [44]. Its 480 mL chamber capacity, which was dozens of times larger than that for those mentioned before, mitigated the impacts of flow characteristics on the ignition mechanism. Additionally, its whole system that could run in a gravity-free environment could be used to investigate how both buoyancy and mechanical mixing affected flame morphology and reaction rate.

Figure 2. Four kinds of semi-batch reactors (a) Karlsruhe Institute of Technology (adapted from [15,67]); (b1, b2) Sandia National Laboratory (adapted from [48,68]); (c) McGill University (adapted from [50,51]); (d) NASA John H. Glenn Research Center (adapted from [60]).

2.2. Continuous Reactors

Continuous reactors, which ensure the consecutive inflow of reactants and the outflow of products for the realization of an uninterrupted operation, can overcome the defects of semi-batch reactors and make up the insufficient researches on the ignition mechanism and the stability of turbulent diffusion flame. The fast reaction flow rate and the short residence time in the tubular reactor lead to poor flame stability, and salts produced during oxidation are easy to deposit on the inner wall surface and even cause a blockage. While in a volumetric reactor that can be further upgraded by the addition of visualization and measurement device, enough circulating room could ensure the accumulation and collision of free radicals. The reactor design of SCWO is extremely similar to that of HFR, and more valuable information regarding SCWO reactors was in Xu’s review [70].
2.2.1. ETH Zurich

In 1992, ETH started to study hydrothermal flame and design continuous reactors [27]. For the characteristics of hydrothermal flame, reactors need to meet a few requirements: (1) powerful performance and high space-time yield, (2) exceptional stability and low extinction temperature, (3) excellent endurance and anti-corrosion. La Roche et al. pointed out that there were three feasible ways to overcome the problems of salt-deposition and corrosion in wall boundary layer control: convective cooling, transpiration cooling and film cooling [71]. Based on them, TWR and WCHB, therefore, were finished. By applying the knowledge in hydrodynamics, TWR could prevent products from contacting with the inner wall surface and precipitating, and WCHB could restrict its reaction area by a cold-water layer. In the early stage, the influence factors of hydrothermal flame and its effects on destroying organic pollutants were studied [25]. Since 2010, ETH has begun to shift the research focus to supercritical hydrothermal spallation drilling (HSD), and the experiments have been mainly involving the characteristics of alcohol hydrothermal flame and its rock-breaking effect. So the WCHB, which is more suitable for downhole conditions, has attracted more attention and been upgraded to the fourth generation.

The amelioration for WCHB was thorough and comprehensive. The first generation of WHCB (WCHB-1) was used to prove the possibility of SCWO with continuous hydrothermal flame (Figure 3d) [27]. After the injection of artificial wastewater from the feed tube and the ensuing mixing with oxygen, a high-temperature mixture was formed. Cold water in the outer annulus protected the wall from high-temperature damage. During the reaction, the tip of the hydrothermal flame could be observed through a sapphire window. The second generation WCHB (WCHB-2) was developed on the basis of WCHB-1 (Figure 3e) [27]. The whole flame length, even the part within the stabilization zone near the tip of the core tube, was thus optically accessible. It adopted a new burner, to improve the blockage and other problems caused by treating actual wastewater containing solid particles. Then the third generation (WCHB-3) made it possible to deeply understand hydrothermal flame (Figure 3f) [27]. It improved the visualization and measurement of flame by increasing the window numbers from 2 to 4. Simultaneously, the new material chosen for the reactor not only satisfied the needs of optical diagnosis and measurement technology, but prevented the damage of pulsating laser. Moreover, to enhance the research on hydrothermal spallation drilling, ETH has built the latest WCHB (WCHB-4) [22,23], whose volume was 5.83 L, design pressure was 650 bar, and design temperature was 500 °C (Figure 3g). A telescopic K-type thermocouple with a diameter of 3 mm was installed at the outlet of two concentric tubes to measure the temperature of the nozzle exit. The fuel injection nozzle, another key component of the burner, was mainly used to mix reactants and observe the effect of its structure on the cross-section temperature of hydrothermal flame in subsequent experiments.

In the process of designing TWR, researchers, based on both WCHB-1 and WCHB-2, made corresponding changes: (1) abandoned the sapphire window and injected reactants from the top of the reactor; (2) considered the factors of economy and thermodynamics in determining the radius and length of reactor and extended the transpiring wall as far as possible to make sure all effluent parameters were within the set range, (3) determined an appropriate injector length to balance both smooth reactant flow and weak heat exchange among reactants. The first version of TWR (Figure 3a) that was finished after the inspection on the structural strength was further optimized, thus generating its second version (Figure 3b) [72]. First of all, due to the serious flaws in the screw-connection concept of the WCHB reactors caused by unknown spring constants and uncertain behaviors of screw connections during installation, the screw connections were replaced by enhanced self-blocking variants with bushings, to make sure most energy could be absorbed by the braced parts and the spring constants of these parts could be precisely determined. Besides, the accessibility of the oxygen 1 connection was improved, and the shape of the transpiring wall was revised. In order to reduce the difficulty of manufacturing, the second version of the reactor was fine-tuned during the processing (Figure 3c).

In general, from WCHB-1 and TWR to WCHB-4, the reactors designed by ETH have more and more complex structure and diversified functions. With the increase of the window numbers from
one to four, the ability to obtain information continuously improves, which the whole flame structure instead of just the tip of the flame can be observed at the same time. Moreover, the addition of a forced ignition device enables the investigation of a new ignition method, and the variation of nozzle inspires innovative ways to enhance the effect of hydrothermal flame.

Figure 3. TWR and WCHB from ETH (a) The first version of TWR (adapted from [72]); (b) The modified version of TWR (adapted from [72]); (c) The final version of TWR (adapted from [72]); (d) WCHB-1 (adapted from [27]); (e) WCHB-2 (adapted from [27]); (f) WCHB-3 (adapted from [27]); (g) WCHB-4 (adapted from [22,23]).

2.2.2. University of Valladolid

As one of the main institutes, the High Pressure Process Group in the University of Valladolid (UVa), Spanish, has been carrying out investigations from the effects of SCWO on recalcitrant organic matters to the enhancement of degradation efficiency with hydrothermal flame even to the performance of new cooled wall reactor (CWR, which resembles the WCHB of ETH, so the WCHB is used to represent CWR) in energy production. According to the corresponding research content, it has designed various types of reactors, including tubular reactors (Figure 4e–g) [30,32], TWR [33,73,74] and WCHB, with the scale of experimental system expanded from the laboratory level to the pilot level. In terms of the hydrothermal combustor, its new structure upgraded based on the SCWO reactor consisted of the inlet, outlet, and heat-resistant walls (water-cooled wall and transpiring wall) among other parts. In 2006, Bermejo et.al tested the performance and the reliability of three kinds of transpiring walls (Figure 4a) [73]. Wall 1 was completely made by porous materials; Wall 2 was made of nonporous materials for the top and porous materials for the left; Wall 3 was made out of nonporous materials for its upper and lower sections and porous materials for the left. The results showed that Wall 3 was the best. This was because (1) the upper section not only kept the wall from high-temperature damage for a long time, but prolonged the residence time before the
mixture with the transpiring flow, and alleviated excessive cooling of the reaction chamber under a high reaction flow rate and a high cooling water rate; (2) the lower section could remain even under subcritical conditions, and the nonporous materials were safe and economical. Therefore, Wall 3 was adopted in subsequent TWRs [33,74]. On the basis of the previous TWR scheme, the innovative WCHB with excellent cooling performance and durability for hydrothermal combustion has been proposed (Figure 4b) [31,75,76]. In addition, its simplicity made it easy to instruct the design of the reactor and the study of hydrothermal flame by comparison between experimental results and numerical simulation results. In order to explore the possibility of using the hydrothermal flame as the way of energy production, the structure and the whole operation system of the reactor were perfected (Figure 4c) [37,77]. The first modification was its inlet and outlet. The reactants flowed into the chamber from the bottom, and the cooling water flowed from the top to the bottom through the annulus between the outer wall and the reaction chamber, dissolving the deposited salt, and thus overcoming the blockage caused by salt-deposition. Furthermore, the other great change was its upper section. Some of the products could be collected from the upper outlet to avoid mixing with cooling water, which was beneficial for the subsequent product analysis and energy generation.

![Figure 4. TWR and Mixers from the University of Valladolid (a) adapted from [74], (b) adapted from [75], (c) adapted from [37], (d–g) adapted from [30]).](image)

2.2.3. Xi’an Jiaotong University

Since 2005, Xi’an Jiaotong University has been committed to the research on the SCHC theories and applications, such as the mechanism and process development of clean conversion and utilization of coal-based fuels [20,21], the mechanism and kinetics of hydrothermal combustion of methanol and other alcohol fuels [39,40,78], the development of high-efficiency HFR [70] and multi-
component thermal fluid generator [79]. Its laboratory now has one multi-functional SCHC bench, whose main reactor is shown as below (Figure 5a). With the inlets of fuel and oxidant made of radial concentric tube, the reactor is composed of an outer cylinder bearing wall and an inner cylinder combustion chamber. The annular gap between the both cylinders acts as the cooling water channel. The wall of the inner cylinder can be switched into a water-cooled wall or a transpiring wall depending on different research purposes. When it is used as a water-cooled wall, the cooling water flows through the annular gap from the lower inlet to the upper outlet, and the characteristics of hydrothermal flame and the wall’s cooling performance can be examined. When it is used as a transpiring wall, the cooling water enters the annular gap from the inlet at the top of the bearing wall and seeps into the reaction chamber through the inner porous transpiring wall. Thus, the characteristics of hydrothermal flame and the formation of water film on the inner surface of the transpiring wall can be investigated. However, there are still some problems coming out during the operation: (1) the long delivery line results in a large amount of heat loss, and the temperature would be lower than expected even with certain thermal insulation measures; (2) when the unstable hydrogen peroxide is used as the oxidant, different degrees of decomposition will occur after it was pumped into the reactor, thus affecting the accuracy of the experimental results.

Moreover, by combining the design experience of the previous experimental platform and current research requirements, this team now is devising an innovative platform. With its key features of replaceable nozzles and staged combustion, this reactor (Figure 5b) can be used to investigate ignition and flame stability, wall cooling performance at a large flow rate, and even the potentiality and evaluation of integrating hydrothermal flame with a direct-fired downhole steam generator [80].

Figure 5. High-efficiency HFR from Xi’an Jiaotong University (a) first version; (b) second version

2.2.4. Others

Unlike the above stated three institutions, NASA John H. Glenn Research Center, Serikawa’s team from Ebara Research Company, Fengming Zhang’s team from Shandong University, and Augustine from MIT are mainly concentrated on the study of hydrothermal combustion. In addition to using a semi-batch reactor to explore the effects of buoyancy and gravity on temperature and concentration in subcritical and supercritical fluids, the NASA John H. Glenn Research Center has also designed a continuous hydrothermal combustion reactor to investigate the spontaneous ignition and the stability of ethanol hydrothermal flame. Consisting of two orthogonal window bores with 3.75 cm in diameter and 5.3 cm in length, this reactor is made from Inconel 625 and can hold a sample
pressure up to 340 atm at 538 °C, with its total liquid test cell volume of 57 cm³ (Figure 6a) [58]. Each of the four thermowells installed on one side accommodates a thermistor and is used for determining the local fluid temperature. However, because of the thin flame zone, the extremely steep temperature gradients, and the thermal inertia of the thermowells, thermistors fail to provide flame temperature. Moreover, considering the analysis of the cell volume and the flow rate of reactants, it is supposed that the reactor is unable to carry out hydrothermal combustion experiment at a high flow rate. Serikawa et al. and Zhang et al. paid more attention to enhancing the treatment effect of SCWO with hydrothermal flame on recalcitrant chemicals. The pilot-scale reactor from Serikawa’s team (Figure 6d) has a large volume of 0.8 L to assure a successful operation at a high flow rate [49]. Figure 6b shows the schematic illustration of the reactor with coaxial nozzles from Zhang Fengming’s team [56]. This reactor has a main body with an effective reaction volume of 1.8 L and is made by 301 stainless steel, with its inner transpiring wall made of 316 L. While Augustine focused on the use of hydrothermal flame for HSD and designed the reactor structure based on that from the ETH [52], this reactor (Figure 6c) was mainly used to explore combustion characteristics, such as the ignition temperature and extinction temperature of methanol and hydrogen hydrothermal flames under different concentrations, and the effects of different nozzles on flame stability, so as to provide data support for HSD. Fuel, oxygen and cooling water enter from the bottom of the reactor and the products get out from the top.
3. Research Status of Numerical Simulation

Due to the harsh reaction condition (supercritical state) of hydrothermal combustion, it is excessively difficult to carry out experiments. At present, the experimental results are deficient and need to be improved: the explanation of transcritical ignition mechanism, guidelines for scale-up reactor design and the stability improvement of hydrothermal flame under the condition of a large flow rate in a confined space. As the functions of the computational fluid dynamics (CFD) are gradually enhanced, numerical simulation is becoming more and more significant in supplementing and even guiding experiments. The combination of experiment and numerical simulation is beneficial to the multi-dimensional interpretation of experimental results, the quantitative analysis of a certain factor and the determination of the microscopic mechanism. Because of the particularity of the supercritical environment, an accurate simulation needs to be done to solve the great variation of physical properties, whilst the influence of supercritical water and high pressure on the reaction process should be considered. The numerical simulation of hydrothermal combustion, especially in recent years, has achieved fruitful outcomes. The chemical kinetic model has gradually developed from the overall reaction kinetic model obtained by experimental fitting to the more theoretical detailed chemical kinetic model (DCKM). The flow model starts with a zero-dimensional flow-reaction model and evolves to a more realistic turbulent flow through laminar flow. The simulated reactor developments from semi-batch to volumetric, and the effects of nozzle structure on the reaction are further studied. Based on this, this part attempts to summarize the existing results of numerical simulation in reaction kinetics and flow-reaction, in order to provide a reference for the subsequent, more complex simulation.

3.1. Reaction Kinetics

In the study of SCWO and SCHC, the chemical reaction network theory [11], the overall reaction kinetic model and the DCKM are generally used to describe the reaction laws. The first holds that the initial organic reactants can be generally converted in three ways: direct oxidation to final products, indirect oxidation from unstable intermediate products to final products, and indirect oxidation from stable intermediate products to final products. The determination of intermediate products is the key. For an overall reaction kinetic model, the rate constant is obtained by determining the reactant concentration variation along with reaction time at different temperatures. Then, the activation energy and pre-exponential factor of the reaction are fitted according to Arrhenius law. With the generally low concentration of organic matter and less heat release in this kind of experiment, the temperature is basically stable during the reaction. By comparing and analyzing the reaction rate constants obtained from different experimental data, Vogel et al. found that the reaction rate constants were highly dispersed [81]. They held that the kinetic parameters of the reaction acquired by fitting were affected by the initial concentration of the material, the oxidation coefficient and the non-ideal flow mixing. Moreover, from the angle of the mechanism of free radical chain reaction, they also pointed out the deviations of the overall reaction kinetic model in the induction stage and the chain termination stage. Despite the poor extrapolation of the overall reaction kinetic model obtained by experimental fitting, its related researches and rich experimental data provide the basis for the verification of higher-order mechanisms. Compared with the first two methods, the more accurate DCKM includes all the reaction-related free radicals and intermediates, among which the elementary reactions may occur and thus lead to an accurate description of the induction stage, chain branching stage and chain termination stage. The kinetic data of these elementary reactions are generally derived from quantum chemistry and transition state theoretical calculations, and verified by standardized experiments.

In 1991, Webley et al. established the DCKM of C-1 based on the kinetic data of NIST, which has been used to simulate the SCWO of methane, methanol and formaldehyde [82]. Although the effect of pressure on the reaction kinetics was considered, the simulation results still underestimated the...
experimental reaction rate by nearly 10 times. Webley assumed that the limitation of the model was due to the unobvious role of water in the conventional gas-phase combustion elementary reaction and the failure of the modified model to reflect the water’s effects in the supercritical environment. Holgate et al. adopted the kinetic data of Professor Dryer from Princeton University, considered the role of water as the third body of collision, and refined the sub-mechanism of H2/O2 [83]. These efforts assured a better prediction of the conversion of H2, but still underestimated the conversion rate of CO under lean-burn conditions. Dagaut et al. [84] and Alkam et al. [85] modified the rate constants of sensitive reactions in the existing model, so that the model was empirically in good agreement with the experimental data. Brock et al. [86] established the DCKM of C-1 for SCWO using the kinetic parameters recommended by Baulch et al. [87,88], and supplemented the kinetic data of single-molecule reactions and pressure-dependent bimolecular reactions under the high-pressure limit. Without any adjustment of experiment-based parameters, the predicted accuracy of the model was encouraging. On the basis of the detailed gas-phase combustion mechanism of benzene, Dinaro et al. realized the accurate prediction of the concentration distribution of benzene and phenol under the condition at 813 K and 24.6 MPa by supplementing the new reaction pathway of C6H5OO [89]. Queiroz et al. modified the kinetic parameters of the overall reaction kinetic model of isopropanol combustion by comparing the axial temperature curves obtained from previous experiments of isopropanol hydrothermal combustion, and thus well reproduced experimental results [34]. Based on methanol DCKM of gas-phase combustion [90], Ren et al. optimized nine pressure-dependent reactions and four sensitive reactions, and proposed a DCKM for methanol SCHC by synthesizing the literature data and calculating the high-pressure limits [40]. This model improved the prediction accuracy of CO and CO2 concentration distribution and deepened the understanding of the ignition mechanism, ignition temperature and extinction temperature. In essence, both SCWO and SCHC have higher reaction pressure and lower reaction temperature than gas-phase combustion, and water as the reaction environment and reactant have a profound influence on the reaction path. Therefore, for the modification of gas phase elementary reaction kinetics, it is often necessary to add some intermediate products and the reaction paths of these products.

In addition to the reaction kinetic parameters and reaction paths of DCKM, the thermodynamic parameters such as specific heat capacity and enthalpy also need to be modified. Because of the drastic changes of thermodynamic properties near the critical point, the theoretical calculation is difficult. Queiroz et al. summed up the thermodynamic models used to calculate the density and heat capacity of SCWO mixtures [36], and found that most of the work available estimated mixture properties by using conventional cubic equations of state (EoS) or averaging tabulated reference properties of the pure components. Brock et al. increased the reaction pressure in the calculation, so that the density calculated by the ideal gas EoS could be consistent with that of supercritical water under the actual pressure [86]. The Chemkin-real gas software package used in the research of Alkam et al. [85] and Steeper et al. [48] could replace the ideal gas EoS with the real gas equation of state. Qian et al. modified the thermodynamic data of ethanol and isopropanol in the process of exploring the co-oxidation mechanisms of sludge and alcohol in supercritical water, so that the calculated results were closer to the experimental values [78].

3.2. Flow-Reaction

In the field of SCWO, plug flow reactor (PFR) and continuous stirred tank reactor (CSTR, or perfectly stirred reactor, PSR) are used to represent the flow in tubular and volumetric reactors. In essence, both PFR and PSR belong to zero-dimensional flow-reaction model. Queiroz et al. respectively simulated the flow of the core tube, the upper volume of the reactor and the cooling part of the reactor by using PFR, PSR, PFR flow models, and then incorporated the overall reaction kinetic model obtained by experimental fitting and the Peng–Robinson EoS describing the variation of density and enthalpy with temperature, to accurately predict the temperature distribution of premixed flame [34]. Koido et al. numerically studied the laminar premixed hydrothermal flame of ethanol in one-dimensional tube flow [91]. After weighing the pros and cons of some EoS and overall reaction kinetic
models, they selected the EoS of Lee-Kesler et al. and the ethanol overall reaction kinetic model of Schanzenbacher et al. [92] based on experimental fitting data. Moreover, equations obtained by Chung et al. [93] and Wilke et al. [94,95] were used to estimate transport properties such as viscosity, thermal conductivity and diffusion coefficient. For 4.3 wt% ethanol, they investigated the effects of preheating temperature (350 °C, 400 °C), flow velocity (1.0 m/s, 2.0 m/s, 3.0 m/s) and wall heat dissipation coefficient (0.0 W/m²/K, 2500 W/m²/K, 25,000 W/m²/K) on the flame temperature distribution in the tube. The results showed that the temperature rise at the preheating temperature of 350 °C (ΔT = 80 °C) was about 200 °C lower than that at preheating temperature of 400 °C (ΔT = 280 °C) because of the significant specific heat capacity in the transcritical region, and that the increase in flow velocity led to the thickening of the reaction zone.

Narayanan et al. [43] and Sierra-Pallares et al. [29] have respectively carried out two-dimensional axisymmetric numerical simulation for the WCHB-3. They all adopted the Peng–Robinson EoS to calculate the density, specific heat capacity and enthalpy of the components in the supercritical state. The Peng–Robinson EoS is written as:

\[
P = \frac{RT}{v' - b_c} - \frac{a_c}{v'(v' + b_c) + b_c(v' - b_c)}
\]

where \(v' = v + VT\),

\[
a_c = 0.45724 \frac{R^2T^2}{P_c^2}
\]

\[
b_c = 0.077796 \frac{RT_c}{P_c}
\]

\[
\alpha = \left[1 + \kappa \left(1 - \sqrt{T_c}\right)^2\right]
\]

where \(VT\) is the constant volume translation, \(T_c\) is the critical temperature, \(P_c\) is the critical pressure. \(a_c\) and \(b_c\) represent the intermolecular attractive and repulsive forces, respectively. In order to remain brevity, the introduction of other coefficients like \(b_1\) would not be given here.

While Narayanan adopted Chung’s model [93] to get the viscosity and thermal conductivity and He’s model [96] to obtain the mass diffusion coefficient, Sierra-Pallares adopted Lucas’s model to calculate the viscosity and thermal conductivity and Mathur’s model [97] to get the mass diffusion coefficient. In terms of Chung’s model, the formula of dynamic viscosity is written as:

\[
\eta = \eta_0 \eta^d = 1.0 \times 10^{-7} \left(\frac{1}{G_2} + E_{y}y + \frac{\Omega_{y}}{F_{m}v}T^{*}r\eta^d\right)\frac{40.785\sqrt{M_{m}T}}{V_{m}^{2/3}\Omega_{v}}
\]

where \(\eta^d\) is low-pressure viscosity, \(k_{m}\) is a correction factor for polar substance and \(\Omega_{y}\) is the collision integral as a function of temperature. For the sake of brevity, the introduction of other coefficients would not be repeated here.

Additionally, the formula of thermal conductivity in Chung’s model is written as:

\[
\lambda = \frac{31.2\eta^{d}v}{M_{m}} \left(G_{2}^{-1} + B_{b}y\right) + qB_{y}y^{2} \sqrt{TrG_{2}}
\]

where \(\eta^{d}\), \(B_{b}\) and so on are parameters appeared in the process of getting dynamic viscosity. Similarly, due to the need of brevity, the introduction of other coefficients would not be given here.

In addition, Narayanan calculated the turbulent reaction rate with a standard eddy-dissipation model under the assumption that the chemical reaction rate was much higher than the turbulent
mixing rate in turbulent diffusion flame and the reaction rate depended on the mixing rate. Sierra-Pallares also assumed that turbulent mixing limited the rate of reaction, but the Schmidt number \((\text{Sc} = \mu/\rho D)\) of much greater than 1 in the supercritical fluid made it hard to directly express the turbulent mixing rate by the momentum dissipation rate (vortex dissipation). Therefore, the transfer equations of variance components were solved \([96,98]\). Both teams achieved reasonable prediction outcomes over the temperature distribution in supercritical hydrothermal flame in turbulent diffusion. Moreover, the results showed that because the fuel flow rate was about 50 times than that of oxidant, a large reflux zone formed in the downstream of the oxidant outlet. However, because the DCKM was not involved, both of them could not effectively predict the critical ignition or extinction process where the chemical reaction rate played a major role and could only reproduce the flame temperature distribution in the stable combustion condition with high inlet temperature. On the contrary, in the simulation of the volumetric premixed reactor, Queiroz et al. considered that the time scale for chemical reaction was large than that for turbulent mixing at lower inlet temperature, so they adopted an overall reaction kinetic model and ignored the effects of turbulent pulsation on the reaction rate \([35]\).

Neither the assumption of turbulent mixing rate limit nor the chemical reaction rate limit could guarantee that the stated simulations exactly cover the whole process of ignition, stable combustion and extinction. In order to overcome these defects, it is necessary to introduce the DCKM and establish a higher-order turbulence-reaction model to accurately describe the interaction between turbulence and chemical reactions in the whole process. That is also the basis for deeply understanding SCHC and analyzing the influence of the burner structure on flow-field and combustion characteristics, structural optimization design and scale-up design. In view of the corresponding inadequate research, Ren compared three turbulence-reaction models, namely the finite-rate/eddy dissipation model, dckm/eddy-dissipation concept model (edc), and the flamelet generated manifold model (FGM)/presumed probability density function (PDF), in her doctoral thesis \([99]\). Especially, as an important model of studying diffusion flame, counter-flow diffusion flames could describe the effects of chemical reaction, reactant flow and component diffusion on the flame structure in detail. In addition, Ren et al. improved the CHEM1D software by modifying the equation of state, specific heat capacity, thermal conductivity and viscosity, and established a counter-flow diffusion flame model suitable for supercritical hydrothermal combustion. With that model, they analyzed the effects of the unique thermodynamic properties and transport characteristics of supercritical fluid on the characteristics of diffusion flame, and explored the mechanism of inlet conditions' effects on flame characteristics and stability. In the end, a FGM table generated could provide good closure of the non-equilibrium chemical source term in further turbulent flame simulations \([62]\).

4. Characteristics of Flame and Its Combustion

As a new type of homogeneous combustion, SCHC, which is different from atmospheric gas-phase combustion, has two main features: supercritical reaction temperature, and water acting either as the reactant or as the reaction environment. Therefore, it has many other unique combustion characteristics, such as ignition temperature, extinction temperature, ignition delay time and flame propagation speed. Taking the supercritical pressure turbulent combustion in the aerospace field as an example \([100]\), the supercritical pressure mainly has the following effects: (1) the disappearance of the phase interface determines the key role of the turbulent mixing process in the whole turbulent combustion; (2) the general strong changes in thermophysical properties during the combustion lead to a large error by using the calculation method of physical properties at low pressure to calculate high-pressure combustion; (3) the supercritical pressure has an impact on the reaction process because of the pressure-dependent reactions in DCKM. In addition, the changes of physical properties of water as the reactant and environment and its participation in reaction have profound impacts on the ignition mechanism and combustion characteristics \([101]\). First, the strong buoyancy effect caused by sudden drop in water density in the transcritical process affects the diffusion and mixing of fuel and oxidant. Second, Henrikson et al. believed that water affected the oxidation of fuel
by increasing the generation rate of OH free radical, and that the key elementary reactions included
\[ \text{CH}_3 + \text{H}_2\text{O} = \text{CH}_4 + \text{OH} \] and \[ \text{H} + \text{H}_2\text{O} = \text{H}_2 + \text{OH} \] [102]. But Holgate et al. thought that the change of
water density affected the two branched chain reactions: \[ \text{HO}_2 + \text{H}_2\text{O} = \text{H}_2\text{O}_2 + \text{OH} \] and \[ \text{H}_2\text{O} + \text{H} = \text{H}_2 + \text{OH} \] [103]. Tatsuya Fujii speculated that the supercritical water promoted the production of OH free
radical through \[ \text{HO}_2 + \text{H}_2\text{O} = \text{H}_2\text{O}_2 + \text{OH} \], thus promoting the decomposition of methanol [101]. At
present, most literature have been focusing on the description of macroscopic combustion
characteristics of hydrothermal flame (see Table 2). The difference between hydrothermal flame and
atmospheric flame and the uniqueness of hydrothermal flame itself are rarely explained from the
perspective of microscopic reaction mechanism. Based on the importance of combustion
characteristics in the design of reactors and the determination of operating parameters in industrial
applications, this part will focus on the summary of existing research works on hydrothermal
combustion characteristics.
Table 2. Summary of experimental investigations of SCHC.

| Reactants             | Operation Parameters | Oxidant Temp. (°C) | Oxidant Flow Rate |
|-----------------------|----------------------|--------------------|-------------------|
|                       | Fuel Conc. | Fuel Temp. (°C) | Fuel Flow Rate |                       |                      |
| Methane               | Oxygen      | 30 mol%         |                | 1.6 mL/s | [15]                |
| Methanol, methane     | Oxygen      | 1–50 mol%       |                | 16.7-50 mL/s | [48]           |
| Isopropanol           | Air        | 2–6 vol%        | 470            | 3 mL/min 377 | 1.3–2.4 fold of stoichiometric | [49] |
| Methanol              | Air        | 18.3–45.9 wt%   |                | /          | 0.5–1.5 ml/s | [50] |
| Methanol, Hydrogen    | Oxygen      | Methanol 25 wt%; Hydrogen 3–6 wt% | Methanol 500–550; Hydrogen 600–300 | Methanol 0.2–0.5 g/s; Hydrogen 0.04–0.06 g/s | 400–450 | 1.5 fold of stoichiometric | [52] |
| Methanol              | Oxygen      | 4–25 wt%        | /              | 2.1 g/s / | 1.1 g/s | [53] |
| Methanol              | Oxygen      | 16.5–30 wt%     | /              | 3.2 g/s / | 1.5 g/s | [54] |
| Methanol              | Oxygen      | 6–28 wt%        | /              | 1.5–1.6 g/s / | 1.2 fold of stoichiometric | [72] |
| Methanol              | Oxygen      | 16–22 wt%       | 200–350        | 1.5 g/s 300–400 | 1.2 fold of stoichiometric | [11] |
| Methanol              | Oxygen      | 16–22 wt%       | 345–370        | 1.6 g/s 395–430 | 1.2 fold of stoichiometric | [12] |
| Methanol              | Oxygen      | 12–16 wt%       | 698–675        | 1.8–2.0 g/s 675,656 | 0.64–0.62 g/s | [43] |
| Methanol              | Oxygen      | 6–28 wt%        | Varied         | 1.5 g/s 400 | 1.2 fold of stoichiometric | [24] |
| Ethanol               | Oxygen      | 7.5–20 wt%      | Ethanol 370–420; Ignitor 450–800 | 20 and 30 kg/h 390 | 45–119 Nl/min | [55] |
| Ethanol               | Oxygen      | 20–32.5 wt%     | Ethanol 23–83; Ignitor 360 ± 40 | / / | / | [23] |
| Ethanol               | Oxygen      | 32.5 wt%        | 300–400        | 20 and 50 kg/h / | 0.8,1.0,1.2 fold of stoichiometric | [22] |
| Methanol              | Oxygen      | 35 wt%          | Water 400–600  | 2–5 kg/h / | 1.4–1.8 fold of stoichiometric | [56] |
| Fuel             | Oxidizer    | Concentration | Flow Rate | Temperature | Reaction Rate |
|------------------|-------------|---------------|-----------|-------------|---------------|
| Isopropanol      | Air         | 4 and 5 wt%   | >400      | 5.6–18 kg/h | >400          |
| Isopropanol      | Air         | 8–9.5 wt%     | >400      | 13, 20 and 25 kg/h | >400 |
| Isopropanol      | Oxygen      | 1–4.5 wt%; Ammonia 2–8% | >400 | 9 kg/h | >400 |
| Isopropanol      | Oxygen      | 8 wt%         | >400      | 20 and 40 kg/h | >400 |
| Isopropanol      | Air         | Isopropanol 13.5 wt%; Ammonia 25 wt% | 200–25 | / | 20 |
| Ethanol          | Air         | 2.3 wt%       | 425       | 1.0–3.0 mL/min | 425 |
| Ethanol          | Air         | 30–50 vol%    | Water 425 | 2.0 mL/min | Close to reactor temperature | 1.0 and 7.0 mL/min |
| N-Propanol       | Oxygen      | 1.2–6 wt%     | 380 and 420 | / | 450 and 400 |
| N-Propanol       | Oxygen      | 2.4 wt%       | 380 and 400 | / | 400 °C and 450 °C |

[30] [31] [32] [33] [34] [35] [36] [37] [38] [39] [40] [41] [42] [43] [44] [45] [46] [47] [48] [49] [50] [51] [52] [53] [54] [55] [56] [57] [58] [59] [60]
4.1. Ignition Temperature

Generally, spontaneous ignition and forced ignition are two ignition ways in hydrothermal combustion. Spontaneous ignition temperature (SIT) refers to the minimum fuel inlet temperature that ensures spontaneous ignition, which means it is actually material temperature. To avoid confusion, the temperature of the heating wire that arouses the flame is defined as the forced ignition temperature (FIT). Based on the preheated reactants, ignition temperature can determine the power consumption of a system and whether the salt-deposition blockage can be overcome or not. The operating and geometric parameters of the reactor are two kinds of factors that affect the ignition temperature. Lower incident velocity, longer residence time and the use of volumetric reactors have been proved to be feasible measures to lower the ignition temperature.

The correlation between SIT and fuel concentration is unobvious. Príkopský studied the relationship between methanol concentration and SIT, and found that the SIT was insensitive to the change of mass fraction. Similarly, with other operation conditions keeping the same, although the mass fraction of methanol increased from 0.14 to 0.22, the SIT was stable at about 480 °C [24]. Augustine et al. measured the SIT of the methanol hydrothermal flame under different operation conditions, and drew an ignition map regarding the relation between SIT and mass fraction [52]. From the map, we can tell that the SIT varies from 500 to 550 °C and the increase of fuel concentration has no significant effect on the decrease of SIT, which is inconsistent with Steeper’s works [48]. Comparing the conditions of two experiments, Augustine thought that the SIT was sensitive to the structure of the reactor as well.

The specially designed structure of the reactor could tremendously reduce SIT. The ignition experiments of 16 wt% methanol conducted in WCHB-3 [27] sharing the same nozzle as the TWR showed that SIT in WCHB-3 was in the range of 410–430 °C, while SIT in TWR fluctuated between 470 and 490 °C, and that there was a gap in heat dissipation between WCHB-3 and TWR due to different ways and distances of entering the reaction chamber for fuel and oxidant, and the cooling water in WCHB-3 also affected the temperature field. Bermejo et al. found that the TWR with a tubular mixer and a post-mixing zone could start the combustion when the reactant temperature was as low as 150 °C [74]. Then they further studied the effects of four diverse tubular mixers on ignition by measuring the axial temperature of cross-sections and the TOC of effluent products [30], and found out that it was the Mixer-1 that first generated the flame, followed by the Mixer-3, while the Mixer-2 and Mixer-4 failed to produce the hydrothermal flame. From the perspective of free radicals, they considered that there was a connection between the reaction rate and the dissipation of free radicals. The two key factors affecting flame formation were high temperature and high velocity. High temperature promoted the production of free radicals, then reflux and post circulation enhanced the collision between newly generated free radicals, thereby reducing the ignition delay time. Mixer-3 and Mixer-4’s failures were due to a shorter residence time led by high flow velocity, insufficient accumulation of free radicals, and the recirculation and back-mixing.

Besides SIT, in order to ignite relatively cold materials, some institutions have also begun to study forced ignition with heating wire to determine the relationship between FIT and fuel temperature. Meier tested a new type of hot surface ignition device on WCHB-4 for the ignition of ethanol-oxygen turbulent diffusion hydrothermal flame at room temperature [23]. The experimental results showed that the ethanol with concentration of 20–32.5 wt% and temperature of 23–83 °C could be ignited at the FIT of 360 ± 40 °C, and the ethanol’s FIT was close to its SIT under atmospheric condition (368.8 ± 7.4 °C) because of their insensitivity to fuel concentration. Therefore, forced ignition is practical and promising in industrial applications. The relationship between FIT and fuel concentration is also worth noticing. With the increase of concentration, FIT was basically stable at 360 ± 40 °C, and 22.5 wt% seemed to be the limit. Below this limit, no flame could be produced in this reactor. Thus, inspired by this experiment, it is necessary to determine the feasible range of fuel concentration and find ways to reduce the minimum required fuel concentration for the future applications of forced ignition.
4.2. Extinction Temperature

Extinction temperature refers to the lowest fuel inlet temperature of avoiding extinction, and it is also an important index to measure the stability of hydrothermal flame. The lower the extinction temperature is, the better the stability of the hydrothermal flame becomes and the lower the demand for fuel preheating achieves. Thus, it is necessary to maintain hydrothermal combustion at room temperature to reduce energy consumption and realize the miniaturization and high efficiency of the reactor. Operating parameters and geometric parameters of the reactor can affect the extinction temperature, and both higher fuel concentration and lower injection velocity can decrease extinction temperature according to some works.

Different from the ignition temperature, the effect of fuel mass concentration on extinction temperature is extremely significant. The experiments done by Príkopský showed that with the rise of mass fraction, the extinction temperature obviously decreased from 380 °C for 12 wt% to 340 °C for 20 wt% [27]. Wellig et al. observed an analogous phenomenon [72]. When the mass fraction was less than 11 wt%, the extinction temperature was still above the critical temperature, and once the mass fraction exceeded 27 wt%, the extinction temperature would be less than 100 °C, which meant that the injection of cold fluid could also maintain hydrothermal combustion. In the experiments of testing the effects of different tube mixers on the hydrothermal flame in TWR, Bermejo et al. realized stable flame with injection temperature in the range of 390 °C to 50 °C, which referred to extinction temperature [31]. Moreover, according to the isopropanol extinction experiment in the semi-batch reactor, Reddy et al. pointed out that the extinction temperature was almost inversely proportional to the fuel concentration [60].

The flow rate and the type of oxidants also affect the extinction temperature. Bermejo et al. studied the factors influencing extinction temperature in the tubular reactor and TWR at the same time, and found out that in the tubular reactor, the flow rate of the reactants determined the minimum injection temperature maintaining the flame (extinction temperature) [33]. Slower flow velocity in the tube corresponded to lower extinction temperature, which was always close to the critical temperature of the water. Meanwhile, in the TWR, the stability of the hydrothermal flame could be realized when the injection temperature of reactants was as low as 170 °C. Through analysis, researchers considered that compared to 3–24 m/s in the tubular mixer (reactor), the flow velocity in the main reaction chamber of TWR was basically between 0.1–0.01 m/s. Additionally, by comparing the effects of oxygen and air on hydrothermal flame, they found out that air could achieve lower extinction temperature with the same fuel flow rate. The air took up more space under the condition of the same oxygen content. This might promote the mixing between oxidants and isopropanol during the flow process, resulting in lower extinction temperature.

The mixing degree of reactants and the flow-field are the key conditions to determine extinction temperature. Príkopský pointed out that the size of the nozzle would impact the flow-field in the reactor and the flame stability [27]. Combined with the re-circulation zone near the nozzle obtained by Narayanan et al. [43] and Sierra-Pallares et al. [29] in the calculation of two-dimensional axisymmetric flow-reaction, we speculate that the backflow of high-temperature reactants can transfer heats and free radicals back to the fuel and oxidant at the inlet, so as to reduce the extinction temperature. Though coupling DCKM and PSR, Ren calculated the minimum extinction temperature of methanol with different concentrations, and found out that there was a negative correlation between concentration and minimum extinction temperature, and that the temperature was lower than the experimental extinction temperature at the same concentration. Significantly, for 6 mol% methanol, both of them were extremely close to the critical temperature of water [40]. Ren thought that it might be due to the drastic change of water’s physical properties near the critical temperature, which strengthened the back-mixing effect and improved flame stability.

4.3. Ignition Delay Time

The ignition delay time is defined as the time required for the transition from the initial state to sudden temperature rise when the combustible material has reached the ignition condition. In the field of gas-phase combustion, controlling the relative magnitude of ignition delay time and residence
time determines whether the flame can be produced and whether the combustion is thorough or not. Shorter ignition delay time means that the reactor is more portable, and the start-up process is safer. According to Gordon [104], the ignition delay time as a very important function of all experimental parameters reflected the interactions among the factors of reactant diffusion, heat production and heat dissipation. In fact, there is no difference between SCWO and SCHC, so the free radical chain mechanism used for explaining the SCWO reaction process is also suitable for the delay analysis in the ignition process. Such an autocatalytic mechanism will yield an S-shaped conversion-time curve as opposed to the exponential curve observed first-order kinetics [81]. In hydrothermal combustion, the ignition delay stage corresponds to the induction stage of the chain mechanism.

Sobhy et al. observed the ignition delay of hydrothermal flame in a semi-batch reactor, and pointed out it was the consequence of the combination of component mixing and chemical reaction delay [50]. However, the ignition delay time under specific conditions was not clearly stated in this literature, and only the delay of 10–15 s was observed. Moreover, for every 50 °C increase in air temperature, the delay time will be shortened by 1~2 s. Ren et al. supplemented the calculation of ignition delay time of methanol with a specific range of concentrations (2–15 mol%) at a preheating temperature (350–550 °C), with an oxidant coefficient of 1 [40]. The results showed that as the preheating temperature increased, the ignition delay time decreased exponentially, which was similar to the variation trend of the ignition delay time in conventional gas phase combustion. At the same time, by comparing with the experimental results of Sobhy, Ren also found that their calculated value (4–11 s) was smaller than the experimental value (10–15 s). Ren believed that the reason for this difference was that the reactants were assumed to be completely mixed in the calculation process, while the experimental values included the effects of the component mixing process.

Reddy et al. studied the ignition characteristics of the n-propanol laminar reverse diffusion flame in a semi-batch reactor with experimental parameters including reactor temperature, oxidant temperature and n-propanol concentration [60]. Results showed that with the other parameters keeping the same, the ignition delay time significantly reduced with the increase of temperature in the reactor. In addition, it was worth noting that the ignition of laminar diverse diffusion flame proved that strong buoyancy caused by density difference had positive effects on ignition. More information about the influence of buoyancy on hydrothermal flame was in NASA’s experiments in Section 4.5. Subsequently, Reddy et al. further studied the effects of oxidant flow rate (0.5–3 mL/s) on ignition delay time under subcritical (380 °C, 20.5 MPa) and supercritical (400 °C, 22.5 MPa) conditions, while comparing their differences [44]. In the first case, the oxidizer flow rate of 1.5 mL/s corresponded to the shortest ignition delay time and was extremely beneficial to spontaneous ignition. While in the second case, the ignition delay time decreased monotonously with the growth of oxidant flow rate. Combined with numerical simulations, the researchers found that the generation of hydrothermal flame under subcritical conditions mainly depended on thermal diffusion and buoyancy, which promoted the mixing of n-propanol and oxygen. Yet for supercritical conditions, the large Froude number meant that the mixing effect of buoyancy was not as intense as that in the subcritical state, and the mixing of fuel and oxidant mainly depended on the flow mixing (mechanical mixing). Restricted by the type of reactor, Reddy’s research still needs to be improved, which means: (1) The weakened effect of turbulent mixing in the reactor affected the reference value of comparison between subcritical and supercritical ignition delay times; (2) the missing stable combustion stage led to an unclear boundary between extinction and ignition, and the extinction characteristics failed to be studied; (3) the ignition mechanism was still vague, the division of ignition stage was worse, and the phenomena of ignition core generation and edge flame diffusion were not described.

In comparison with a semi-batch reactor, the study of ignition delay time in a continuous reactor is of great significance in industrial applications. By comparing the residence time of fuel and oxidant in the reactor (0.155 s) obtained by Wellig et al. [24] under experimental conditions with the minimum ignition delay time (0.37 s) calculated by using DCKM in a closed homogeneous reactor, Ren et al. found that the results were contrary to their anticipation, and that if the residence time was shorter than the ignition delay time, the flame could not generate [99]. Ren believed that the structural characteristics of the volumetric reactor led to the production of the reflux zone and the accumulation
of free radicals, thus accelerating the chain reaction and reducing the ignition delay time. Therefore, more attention should be paid to the influence of the structural design of the continuous reactor on the ignition delay time because it was practical and potential to realize SCHC while minimizing the size of the reactor as far as possible.

4.4. Flame Temperature Distribution

Flame temperature distribution, which refers to the temperature distribution in the reaction chamber after ignition, is often used to verify the accuracy of numerical simulation, guide the structural design of the reactor, and select the material for the reactor. It is affected by many operating factors including but not limited to fuel concentration, fuel flow rate and incident temperature. The reactor structures, especially the nozzle, also impact the temperature field by changing the flow-field [22]. At present, the contact measurement method (thermocouple) used in most experimental platforms affects the accuracy of the results, because of its insensitivity to intense temperature variation and interference to the flow-field. Therefore, this phenomenon should be taken into account in verifying numerical simulation. Príkopský measured the axial temperature distribution at different reactant temperatures, and found out that the reactants’ temperature rise of 50 °C or so could bring about the increment of about 100 °C at each point in the axial direction [27]. This showed that a relatively higher injection temperature could promote the reaction and exothermic process. When exploring the effects of hydrothermal flame enhanced treatment on recalcitrant organic compounds such as acetic acid, Cabeza studied the role of isopropanol concentration by measuring the maximum temperature in the reactor [32]. They found out that, with the increase of the isopropanol mass fraction, the maximum temperature rose, and the time for its appearance moved up.

Air ratio shoulders important responsibility for flame strength, namely flame temperature distribution. In Serikawa’s experiments, the flame could be barely seen at a low air ratio (m=1.1) [49]. With the increase in air ratio, the weaker flame became more intense and a red luminous flame was clearly observed at the air ratio higher than 1.8. On the contrary, through the measurement of OH and CH free radicals’ distribution by chemical fluorescence spectrum, Príkopský found different results that excess oxygen had no effect on the determined flame position but only slightly strengthened the flame intensity [27]. Therefore, determining the effect of excess oxygen should be further studied in the future.

4.5. Flame Propagation Speed

In gas-phase combustion, the flame propagation speed featuring the moving velocity of the flame front in space during the combustion is an important parameter for the evaluation of flame stability. It depends on many factors, including the nature of the combustible material itself, pressure, temperature, oxygen excess, flow state and heat dissipation. If it is larger than the fluid flow velocity, the front end of the flame will move to the nozzle, while if it is smaller, the hydrothermal flame will be blown out. Only when both items are equal to each other can stable flames be obtained. Comparing with gas-phase combustion, many scholars have found that the propagation speed of hydrothermal flame is one order of magnitude lower than that of gas-phase combustion. Therefore, special attention should be paid to this difference in the design of reactors and the determination of operating parameters.

The stability of the hydrothermal flame depends on the deceleration of reaction flow and the acceleration of flame propagation speed. The reason why the flame stability in the volumetric reactor is better than that in the tubular reactor is that the flow rate of reactants can be significantly reduced in the large flow area. As to how to improve the flame propagation speed, Bermejo believed that strengthening the injection temperature of reactants was a practical measure to maintain flame at a high velocity. In order to get a clear picture, it is necessary to determine the flame propagation speed. In describing the relationship between temperature and flame propagation speed, Bermejo [33] adopted the expression deduced by Semenov. The results showed that the speed increased with injection temperature. In comparison with a higher flame propagation velocity (0.4–3 m/s) in gas phase combustion, the hydrothermal flame propagation velocity varied from 0.01 to 0.1 m/s in the
volumetric reactor, which was also consistent with the experimental results by M.C. Hicks [59]. However, it should be noted that due to the fact that the properties of the mixture in the supercritical state cannot be calculated accurately, there is still a deviation for the calculated value. Based on the above conclusions, Bermejo gave some suggestions to guide the scale-up design of the reactor. For example, the fluid velocity in a volumetric reaction chamber must be between 0.1–0.01 m/s. In addition, it was also found that the flame propagation velocity changed little at a low fuel concentration, but whether a high concentration fuel had an effect on the flame propagation velocity was not clear.

With visualization apparatus, Hicks obtained the propagation velocity of axial laminar diffusion of hydrothermal flame at both low air velocity condition (50 vol% ethanol of 2 mL/min, air of 2 mL/min) and high air velocity condition (50 vol% ethanol of 2 mL/min, air of 7 mL/min) [59]. At a low air velocity, the flame propagation velocity was basically stable, with average value about 4.6 cm/s. While at a high air velocity, the variation of flame propagation velocity along the axis was not monotonous with a minimum value of 5 cm/s. By comparing the generation process of the flame kernel, Hicks believed that the minimum value appeared near the extinction point of the flame kernel on the nozzle side, because of insufficient combustible reactants. Due to the supplementation of reactants by mixing and the heat released by reaction, the speed of the flame away from the nozzle continued to increase. This study revealed that the complete mixing of fuel and oxidant help improve the flame propagation speed and the stability of the hydrothermal flame.

5. Ignition Process and Mechanisms

Due to supercritical pressure and supercritical water, the ignition of the transcritical hydrothermal flame, including spontaneous ignition and forced ignition, is different from that of gas-phase combustion in both process and mechanism. Based on the research outcomes of hydrothermal combustion, ignition can be divided into supercritical ignition and transcritical ignition according to the state of reactants. Reddy et al. studied the differences in the effects of oxidant flow rate (0.5–3 mL/s) on ignition delay time under subcritical (380 °C, 20.5 MPa) and supercritical (400 °C, 22.5 MPa) conditions [44]. They found out that even if the transcritical process involves drastic changes in the physical properties of the reactants, the ignition mechanisms of both ignition forms are slightly different. But on the whole, ignition is the consequence of the interactions among critical physical properties, heat transfer and mixing. In practical industrial applications, problems of blockage and high-energy consumption caused by salt-deposition and preheating are expected to be solved by injecting materials at room temperature. Therefore, it is necessary to study the ignition mechanism of transcritical ignition. Based on the works of supercritical pressure combustion of liquid rocket engine and existing ignition-related literature, this part attempts to explain the ignition mechanisms from the perspectives of critical physical properties, heat transfer and mixing, so as to provide a reference and guidance for further theoretical research and industrial application.

5.1. Ignition Process

Agarwal [105] divided the process of spontaneous ignition of non-premixed flame into four stages—“no ignition”, “random spot”, “flash-back” and “lifted flame”. Reddy et al. also included the critical ignition stage in the division of the life cycle of turbulent diffusion hydrothermal flame [45]. After reactants were pressurized and heated in the pretreatment stage, they (fuel, oxidant and water) were injected into the reaction chamber at the same time. Due to the high flow rate of fuel and oxidant, they contacted with each other through convection and diffusion. Then through mixing and reacting, the flame front continued to develop until it caught fire successfully. Ignition was the fourth stage in the whole process. Hicks observed the spontaneous ignition of the ethanol-water-air system injected by laminar flow had three stages: random spots, flash-back, and stabilization (see Figure 7) [59]. The results showed that the formation and disappearance of random hot spots might occur more than once before the stable flame was finally established. The initial flame did not propagate to the nozzle to form a stable flame, mainly because the flame propagation speed was limited by temperature, fuel concentration and turbulent mixing intensity. However, the initial process of flame formation and
extinction meant that there was still an exothermic oxidative reaction that increased the density and temperature gradients and induced the buoyant mixing between fuel and oxidant, which in turn continued to promote flame formation. After a series of random spots, the flame approached to the nozzle, while the flow in the area behind the nozzle gradually changed into the laminar flow, partly because of the intensification of local viscosity caused by the local temperature rise beyond the critical point. Once the flame stabilized at the burner, the area for the flame tip became more disordered. At the same time, the flame color became yellower due to the presence of soot. Compared with the airflow of 2 mL/min, the turbulence of the flow-field with a higher flow rate (7 mL/min) was stronger, so the time to reach the stabilization was shorter and the flame was brighter. The above experimental results are of great significance for the investigation of spontaneous ignition behaviors in the microgravity environment that NASA is interested in. The lack of buoyancy mixing in microgravity is not conducive to laminar spontaneous ignition, so it is necessary to generate a certain degree of turbulence by increasing injection speed or manmade fluctuations to ensure the complete mixing between fuel and air.

Gordon proposed a thermal spontaneous ignition model to simulate the laminar diffusion flame generated by injecting fuel into a static oxidation environment [104]. With this model combining the main physical and geometric parameters in the ignition process, they found that spontaneous ignition would occur when the jet height was high enough, and that the jet temperature rose along the axial direction to the ignition point and a stable flame would form with enough energy released from the ignition core. On the one hand, this model could be used to evaluate the designated experimental parameters (such as flow velocity, fluid temperature, and reactant concentration). On the other hand, it was considered as the first step to understand the interactions among the main basic physical processes. Based on this, a more complex first-order analysis model and thermal spontaneous ignition model suitable for coaxial burners might be developed. Subsequently, by modeling the process of forced ignition on the hot surface, Stathopoulos predicted the heat surface temperature and heat flux required to ignite the mixture flowing through the hot surface [106]. All these works provided a theoretical basis of the follow-up research on hot surface ignition devices for his team.

Furthermore, by using hydrogen and oxygen as reactants, Song et al. carried out a two-dimensional direct numerical simulation (DNS) of the ignition process of the turbulent diffusion hydrothermal flame, to try to understand the generation process of hydrothermal flame from the microscopic mechanism [65]. The whole combustion process was divided into pre-ignition stage, ignition stage and post-ignition stage, in which the first two stages were their main concerns. In the pre-ignition stage, the reaction heat was scarcely released, and HO2 and H2O2 radicals with relatively higher concentration appeared in the region with a lower mixing degree. At the beginning of the ignition stage, two ignition cores appeared in the region with relatively high heat release and OH free radicals, and in the region that was far away from the lower mixing area. After formation, each ignition core rapidly expanded, and then a pair of edge flames emerged, which propagated in the opposite direction with a speed of 1.286 m/s until colliding with others. The collision continued and a continuous flame surface eventually formed in a certain area. The results showed that spontaneous ignition always occurred in the mixing degree from 0.8 to 0.85 (the mixing degree of the equivalent ratio equals 0.911).
5.2. Ignition Mechanism

At present, there are few systematical researches on ignition mechanism. Through the summary of these scarce literature, this section will introduce the works regarding three types of factors that determine the ignition mechanism, in order to assist scholars in collecting information and filling up research gaps.

5.2.1. Critical Physical Properties

Pseudo critical temperature refers to the temperature under the maximum isobaric special heat capacity of the working medium, and this temperature value increases along with pressure. The point with max specific volume change does not coincide with the point with max constant pressure specific heat change, resulting in a transition region changing from pseudo-liquid to pseudo-vapor state, namely the critical region of supercritical water [107]. In the transcritical process, the physical parameters of water change drastically, which can be considered from two aspects: flow characteristics and heat transfer characteristics (Figure 8). In the flow characteristics, dynamic viscosity characterizes the internal friction coefficient of fluid viscosity. The dynamic viscosity of water decreases sharply near the critical point, approaching gas. The characterization parameters of heat transfer features include thermal conductivity, thermal diffusion coefficient, and constant pressure specific heat capacity. The thermal conductivity peaks around the critical point and grows with the pressure in the proximity of critical pressure. The thermal diffusion coefficient describes the thermal inertia of fluid, indicating the ability to react to the heat distribution change decreases to the bottom. Near the critical point, the response of the fluid to the surrounding heat diffusion becomes retarded, then the temperature gradient begins to develop, providing a strong driving potential for buoyant flow. The promoting effect of critical physical properties on ignition is illustrated by taking hot surface forced ignition as an example. After the subcritical reactants around the hot surface accept heat, the heat spreads rapidly to the surrounding local area due to the high thermal conductivity. However, because of the low thermal diffusion coefficient of the reactants near the critical point and strong thermal inertia, the heats are still mainly concentrated in the local area, resulting in temperature rise. This lays a foundation for subsequent ignition. The experiments by Stathopoulos showed that the rise in mass flow rate barely impact the FIT but only caused the variation of ignition power [55]. These facts revealed that the FIT depended on the change of the physical properties of reactants rather than flow intensity.

Generally, because of the values incompletely consistent with the real critical properties of mixture, the critical properties of the mixture calculated by the critical properties of each component
according to certain criteria are called pseudo-critical properties [108], which include pseudo-critical temperature (distinguished from the pseudo-critical temperature of pure matter) and pseudo-critical pressure. The determination of pseudo-critical temperature has important reference value for ignition, especially for the determination of FIT. By the linear interpolation of data on the pseudo-critical properties of ethanol-water mixture, T. Meier determined that the pseudo-critical temperature and pseudo-critical pressure of 32.5 wt% ethanol were 333.5 °C and 166.3 bar, respectively, and found that the addition of oxygen further reduced the pseudo-critical temperature and pressure of the mixture [22]. Therefore, in response to the fluctuation of local temperature, pressure, and mixing degree, the position of the pseudo-phase transition changes dynamically along the axial direction of the nozzle, thus affecting the ignition and combustion characteristics.

Figure 8. Density, enthalpy, thermal conductivity, viscosity, thermal diffusion and capacity at constant pressure (Cp) normalization as a function of temperature at 22.13 MPa.

5.2.2. Heat Transfer

Heat transfer mainly includes heat conduction and convective heat transfer. As above mentioned, heat conduction is mainly determined by the thermal conductivity of reactants. So, this section will focus on convective heat transfer. Significantly, this coefficient as an engineering concept rather than a physical parameter changes with complex external conditions, such as different flow patterns and hot surface properties. The experimental studies on the convective heat transfer coefficient of supercritical fluid are generally carried out in a simple tubular or annular geometric structure, to guide the design of supercritical water reactor (SCWR). In the experiments of forced ignition, the role of the hot surface is partly similar to that of the bluff body, which promotes the mixing of reactants. So, it is impossible to draw lessons from existing results obtained by the flow in the tubular geometry. Right now, there are few studies regarding the convective heat transfer coefficient of supercritical mixtures, and the pseudo-critical point of the mixture influencing the coefficient cannot be determined accurately. Therefore, it is necessary to experimentally quantize this coefficient to help determine the size, power, and geometry of the hot surface ignition device.

Supercritical heat transfer can avoid the local instability of heat transfer caused by phase transition [109]. In most circumstances, the convective heat transfer of the fluid will be enhanced near the critical point and the convective heat transfer coefficient reaches the highest point. Stathopoulos et al. found that when the heat flux was low, the convective heat transfer coefficient increased obviously near the pseudo-critical point of the mixture, and the convective heat transfer was
extremely strong (Figure 9a) [26]. As a supplement, Stathopoulos further verifies the heat transfer enhancement [55]. Adopting the WCHB-4 reactor with a forced ignition device, they experimentally analyzed the effects of reactant temperature and composition on the ignition power required for forced ignition. With the same reactants, the ignition power was almost constant for the lower reactant temperature. Once the reactant temperature approached a certain value, the ignition power decreased sharply, especially when the mass fraction was 12.5%. As the temperature continued to rise, more ignition energy was needed. The researchers believed that the relationship between ignition power and reactant temperature was related to pseudo-critical point. Below the pseudo-critical temperature, the reactants did not become homogeneous, and the power was mainly consumed in the phase transition of reactants around the hot surface. When the reactant temperature exceeded the pseudo-critical temperature, most power was exploited in the ignition of homogeneous combustible reactants. From the perspective of heat transfer enhancement, the temperature corresponding to the minimum ignition power was about 326 °C, which would be slightly less than the pseudo-critical temperature of the mixture according reasonable guess.

However, sometimes heat transfer deteriorates and the convective heat coefficient plunges sharply [110]. Heat transfer deterioration is probably due to the interactions among these factors including low mass flow rate, high heat flux, and special relations in different temperatures (fluid temperature < pseudo-critical point < wall temperature). In Stathopoulos’s experiments [26], when the heat flux increased to 0.7 MW/m², there was almost no improvement of convective heat transfer near the pseudo-critical point, compared to other temperatures (Figure 9b). We believe that the reason for this phenomenon is the same as that causing heat transfer deterioration, but to a different extent.

Figure 9. (a) Influence of the used heat flux for a water–nitrogen mixture (mf = 40 kg/h, mN₂ = 130 Nl/min); (b) Influence of the used heat flux for a mixture of water-ethanol–nitrogen (mf = 25 kg/h, mN₂ = 220 Nl/min, ). (adapted from [26]).

5.2.3. Mixing

Buoyancy Mixing

As mentioned earlier, buoyancy mixing is mainly due to the spatial difference in fluid density and the variation extent of the density with temperature. The effect of density is usually expressed by the thermal expansion coefficient and Froude number. The peak of the thermal expansion coefficient near the critical point theoretically reflects the important contribution of density to the buoyancy mixing that occurs during transcritical processes. M.C. Hicks pointed out that the transcritical process was a sign of the emergence of a large scale of buoyancy convections, and even small temperature differences (~1 °C) was to cause strong buoyancy effects [59]. They observed that the strong buoyancy convection started at 370 °C and disappeared at the temperature exceeding 400
°C, reflecting the strong temperature-dependent nature of density during the transcritical process. Serikawa investigated the variation of the water state with the temperature at supercritical pressure, and found that before 374 °C, it was still clearly liquid and the same as the water at normal temperature and pressure; once the temperature reached the critical point, water suddenly lost its transparency and turned black, which presented the characteristic of critical water; as the temperature continued to rise, the black became gray; when it reached 400 °C, the water became completely transparent again, and there was no visible phase separation after 400 °C. The above results also support the dramatic physical changes in the transcritical process (Figure 10a) [49].

To evaluate the effects of buoyancy on the flow and temperature fields [69,111], U.Hegde et al. removed the exothermic chemical reaction and obtained a temperature map by simulation under both normal gravity and zero gravity. With gravity, entrainment and high velocity could be clearly seen near the central axis, and the zone of temperature spread was obviously narrower due to the buoyancy. With zero gravity, the mixing away from the nozzle was insufficient, and the inertia force was dominant only in the position near the nozzle, the normal gravity and zero gravity were similar (Figure 10b). By controlling the existence of gravity, the results showed the influence of the buoyancy caused by the density gradient on the mixing. Furthermore, based on existing simulation works, U.Hegde experimentally observed the effect of buoyancy on the mixing process in three scenarios, which were subcritical jet injected into subcritical water, supercritical jet injected into supercritical water, and supercritical jet injected into subcritical water [57]. They found that the first two scenarios had similar results, and that with the increase of Reynolds number (Re), the position where the flow transferred to the turbulent flow was getting closer and closer to the nozzle. However, in the third scenario, the buoyancy mixing induced by the density difference was very strong, and even if the jet’s Re was low, the distance required for the transition to turbulence was short. Therefore, by combining the definition of the intrinsic characteristic vorticity and the Froude number of turbulence, the author proposed the effective Froude number $F_{eff}$. In case of $1/F_{eff} >> 1$ and small Reynolds number, the jet exhibited a turbulent plume behavior, which also corresponded to the third scenario. In case of $1/F_{eff} \sim O(1)$, the Re determined the behavior of the jet, that was, the flow was laminar with small Re and would change into turbulent flow when the Re was greater than 2000. Utilizing $F_{eff}$ and Re, U.Hegde theoretically explained the anomalies of the third scenario. These works provide an important reference for numerical simulation to be as close as possible to the actual working conditions.

**Figure 10.** (a) Influence of temperature on the water flow at 25 MPa (50 mL min$^{-1}$ water and 1 nL min$^{-1}$ air) (adapted from [49]); (b) Illustration of buoyancy effects showing non-reacting axisymmetric jet of heated fluid injected into the body of cooler fluid (adapted from [59]).
Mechanical Mixing

In addition to buoyant mixing, mechanical mixing as another important way of mixing, has not been clearly defined in the previous literature. In this paper, the mixing caused by the high flow rate of the reactants, nozzle structure, flow shearing, and diffusion is collectively regarded as mechanical mixing. Due to the aforementioned advantages of the volumetric reactor that are in contrast to those of the tubular reactor, the influence of the structure of a volumetric reactor on the hydrothermal flame is of paramount concern. In the existing volumetric reactors from ETH and NASA, reactants are injected into the chamber through a free jet. Compared with the flow in the tube, the interactions between the wall and jet are weak, and the shear layers between jet and fluid in the reactor and the presence of the nozzle greatly enhance the mixing, thereby affecting the entire ignition process. A high flow rate facilitates the transition from laminar flow to turbulent flow. By controlling the flow rate of the oxidant, Hicks et al. identified the difference in reaction paths at different mechanical mixing intensities by means of luminescence spectroscopy [58,59]. And they found by measuring the results that at the wavelength of 310 nm corresponding to OH radicals, the flame B with a low airflow rate was lack of OH radicals, while there was a peak on the curve of flame A with a high airflow rate.

Generally speaking, the generation of the flame is the result of the joint effort of physical and chemical factors. The ignition mechanism of hydrothermal flame can be attributed to a certain degree of mixture of reactants undergoing intense oxidation reaction after a certain residence time (ignition delay time), and the reactant temperature determines the ignition delay time. The buoyancy mixing of the reactants (especially the water near the critical point) and the mechanical mixing caused by the nozzle structure, coupled with the self-diffusion, synergistically realize a proper mixing degree of the reactants. At the same time, the heats from the oxidation reaction or external heating device are transferred rapidly through heat conduction and convective heat transfer among the reactants with high thermal conductivity and thermal diffusion coefficient, resulting in the rise of local temperature and the appearance of flame. Through the division of the ignition process, it can be found that when the reactants with appropriate mixing degree reach the appropriate temperature, hot spots will be randomly produced, and then gradually develop into a continuous flame surface, and finally achieve stable flames.

6. Existing and Potential Industrial Applications

As an advanced combustion mode, SCHC, which has promising prospects in industrial applications, includes hydrothermal spallation drilling, the thermal recovery of heavy oil, clean conversion and utilization of coal-based fuel, and harmless treatment of pollutants. In view of the above four aspects, this section will introduce the current progress of hydrothermal combustion in relevant fields.

6.1. Hydrothermal Spallation Drilling

Exploration shows that 99% of the earth body is higher than 1000 °C and the geothermal energy reserves are abundant. As a sustainable energy source, geothermal energy is becoming more and more significant [112]. At present, one of the problems of developing geothermal energy is the drilling of thermal wells. For the traditional rotary drilling, the drilling equipment wear quickly, the operation on the hard rock is slow, and the drilling cost exponentially increases with the drilling depth. The thermal spallation drilling technology is a potential alternative to rotary drilling. It aims to produce thermal stress inside the rock surface by rapidly heating the rock surface. With the increase of thermal stress, the internal defects of the rock (such as cracks) propagate, resulting in the fracture of the rock into fragments. When the target well depth is large (2–10 km), the water-based drilling fluid can be used to balance the pressure during drilling. SCHC is exactly in line with the downhole high-pressure liquid environment, and the formed flame can be used as a potential heat source for cracking. This technology is called hydrothermal spallation drilling (HSD) [113]. In addition to drilling, the hydrothermal flame is also used to expand holes around the well in order to
enhance the relations between geothermal reservoirs and lay a foundation for subsequent fracturing. Recently, ETH has taken the lead to develop a complete set of dedicated devices, and confirm the feasibility and great potential of the technology by field tests [114].

In his doctoral thesis [115], Stathopoulos summarized a number of challenges in practical applications of HSD, including forced ignition, convective heat transfer and water entrainment. According to research needs, ETH has built a pilot platform with a complete measurement and control system, to test the technical solutions against some key problems, explore the scientific issues like the characteristics of HSD, and help verify the simulation results of the actual downhole working conditions. Stathopoulos et al. customized a heat flow sensor for the process, and developed a set of excellent correction methods to accurately measure the convective heat transfer coefficient [116]. Their test results showed that the standard deviation of the sensor relative to the reference heat flux was less than 2%, and the total uncertainty was less than 5.5%. Subsequently, Stathopoulos et al. tested the hot surface forced ignition of the ethanol-oxygen hydrothermal flame on the pilot platform, to evaluate the self-developed ignition device and understand the effects of the changes of transcritical fluid properties on the ignition mechanism [55]. The study on the convective heat transfer coefficient was a further advance of the research results in reference [26]. It pointed out that ignition temperature was passively related to the fluid temperature, and specific fluid temperature corresponded to specific minimum ignition temperature (see Section 5 for more details). Later, T. Meier et al. improved Stathopoulos’s ignition device and increased the length of resistance wire by winding, thus further promoting the ignition power [22,23].

In addition, due to the axial heat loss caused by the convolution of ambient cold water in the hydrothermal flame jet, heat concentration on the rock surface and rock-breaking effects changed. Therefore, it is necessary to have a comprehensive understanding of the flow field and the temperature field between the HSD head and the rock surface in the whole process, so as to determine appropriate operating parameters for efficient rock-breaking. By combining with experiments and numerical simulation, Martin J explored two kinds of heat transfer processes in supercritical water jets, entrainment and stagnation flow in the real downhole environment, thus providing a valuable reference for subsequent practical applications [113]. Kant et al. used a high-speed pyrometer and a heat flow sensor in the experiment to creatively determine the minimum boundary conditions for cracking rock, such as the lowest rock surface temperature and convective heat transfer coefficient [117]. Subsequently, in order to further determine the distribution of heat flux on the whole rock surface, Kant proposed a technique for measuring instantaneous heat flux for three-dimensional heat conduction, to solve practical problems caused by complex multi-dimensional heat transfer [118].

6.2. Thermal Recovery of Heavy Oil

With the increasing demand for oil and the irreversible reduction of light crude oil reserves, the development and utilization of heavy oil accounting for a large proportion of oil and gas resources in the world has become an important way to improve the energy structure. The high viscosity and the low freezing point of heavy oil lead to many difficulties including its flow in the reservoir, wellbore lifting, surface gathering, and pipeline transportation. Most commonly used visbreaking methods involve thin-oil blending visbreaking, heating visbreaking, upgrading visbreaking, and chemical visbreaking. The heating visbreaking consists of steam drive, steam soaking and steam-assisted gravity drainage (SAGD). Steam produced in a steam injection boiler on the ground is injected into the formation. Yet the whole operation process generally has some shortcomings, such as low efficiency, high pollution, and need for quality water and sewage treatment. In addition, with the exploitation of heavy oil expanding to deep wells, ultra-deep wells and ocean, the disadvantages like large footprint and high heat loss of gas injection boiler are more obvious, which make it difficult to meet the needs of the project.

Combining the above requirements combine with the research results of HSD, the “hydrothermal combustion steam-gas generation technology” was proposed by Xi’an Jiaotong University to produce heat carriers needed in the process of heavy oil recovery. The fuel and oxidant enter the compound thermal fluid generator in the downhole and carry out hydrothermal
combustion in the supercritical water environment. Then, the composite thermal fluids produced (steam, CO₂, N₂, etc.) are adjusted to the required parameters needed for thermal recovery before being injected into the stratum. CO₂ and other gases dissolve in crude oil, to reduce viscosity and increase fluidity. At present, the team has developed a complete system and multiple burners, and is building a laboratory-scale platform for feasibility verification. Generally speaking, the main challenges this technology are facing include: (1) ignition and flame stability under large flow conditions, (2) reactants’ transport and signal feedback, (3) structure design of the reactor, (4) how to prevent explosion induced by overpressure caused by hard start-up, and (5) how to avoid backflow and blockage after cessation.

6.3. Clean Conversion and Utilization of Coal-Based Fuel

The SCHC for coal is a new combustion technology that can realize efficient and clean utilization of coal without pollutants terminal control [20]. Compared with conventional coal combustion technologies, it can restrict the formation of pollutants like NOx, Sox, and dust without desulphurization, denitrification, and dust collecting equipment, and easily realize the low-cost capture of CO₂. Therefore, it has an extremely superior environmental protection performance. At present, there are three main ways for its implementation: (1) coal-based fuel goes directly into HFR in the form of coal water slurry [21], (2) coal-based fuel first enters the supercritical water gasification (SCWG) reactor in the form of coal water slurry. After solid residues (mainly consisting of inorganic salts, oxides, and gravel) are removed, the products with abundant syngas and methane are injected into HFR [19], as (3) coal-based fuel first enters the SCWG reactor in the form of coal water slurry. After partial gasification and full separation for obtaining the required synthesis gas, the remaining fluid with semi-coke as the main organic matter enters HFR. The high-temperature and high-pressure products (including steam, CO₂, N₂ and other gases) directly push the steam turbine to generate electricity [119] or supply heats to the outside (Figure 11) [20].

So far, research on SCHC mainly focuses on liquid fuels rather than solid fuels such as coal. Ma studied the hydrothermal combustion characteristics of semi-coke obtained from coal gasification, and observed the SCHC process of semi-coke, included accumulating heats through heterogeneous chemical reactions and exchanging heats with the surrounding fluids [20]. Because the reaction rate was still subject to the mass transfer rate of oxygen in supercritical water, for millimeter-sized semi-coke particles, the complete burnout time was about 5 to 7 min, and for micron-sized semi-coke particles, it took about 4 to 7 s to burn out. The simulation results showed that the increase of supercritical water temperature and volatile content and the decrease of the particle-size were beneficial to the ignition of semi-coke. The critical conditions for the semi-coke ignition include 798 K of water, 7.97 wt% of oxygen concentration, 168 μm of particle size and 10 wt% of volatile content. Generally speaking, influence mechanisms about the effects of the characteristics of supercritical water and pulverized coal on the ignition of coal, and the SCHC kinetics of pulverized coal may be the major concerns.
Figure 11. Schematic diagram of SCHC coupled power generation system (adapted from [21]) 1—Coal mill; 2—Pump; 3—SCHC system; 4—Ash bucket; 5—Valve; 6—Gas-liquid separator; 7—High-pressure turbine; 8—Generator; 9—Preheater; 10—Medium-pressure turbine; 11—Low-pressure turbine; 12—Condenser; 13—CO2 recovery unit; 14—Water preheater; 15—Reprocessing device; 16—Circulating pump; 17—Air compressor; 18—Air preheater; 19—Steam extraction and heat recovery device.

6.4. Harmless Treatment of Pollutants

The advantages like efficient and thorough removal of high-concentration pollutants are a paramount driving force for the development of SCHC technology. Many scholars found that this flame can remove nearly 99% pollutants within shorter residence time (a few seconds). Up to now, recalcitrant compounds or intermediates controlling reaction rate include sludge [38], quinoline [41], naphthalene [51], toluene [67], acetic acid [32], and ammonia nitrogen [32]. Their research status can be found in stated contents, so no detailed introduction is given here.

The reactor is still the core for the harmless treatment of pollutants, but there are few relevant criterions for its structure design and scale-up design. At present, these treatments have been carried out with a relatively small flow rate. The experimental results of ETH showed that the ignition temperature and extinction temperature were strongly affected by the size of the nozzle. The experiment and simulation results of the University of Valladolid showed that the propagation speed of the flame was smaller than that of gas-phase flame. In the scale-up design of the reactor, controlling the flow velocity of reactants in the reactor can ensure an excellent flame stability. In the future, the internal structure design of HFR with a vast flow that can ensure reliable ignition and stable flame will largely determine the successful commercial applications of hydrothermal combustion in the field of pollutant treatment.

7. Research Needs and Challenges

Based on current research status, a couple of critical scientific and technical issues need to be dealt with to realize successful industrial applications of SCHC (Figure 12). Scientific issues involve ignition mechanisms and combustion characteristics. Hydrothermal flame has proved to be different from the aforementioned gas-phase combustion, and it depends on the interactions among critical properties, heat transfer, and mixing. Ren [62] and Gao [63] et al. were committed to building and improving numerical models for hydrothermal combustion, such as the real-fluid flamelet/progress variable (FPV) model, to make a preliminary but paramount explanation of ignition process from the angles of free radical reactions and flame structure. However, there are few studies constructing an overall perspective of the ignition process and involving interactions among different parameters, the dominated position between chemical limitation and diffusional limitation, and the migration
and transformation of elements such as C/N. Concerning the characteristics of flame, many papers have given a rough picture of the uniqueness of hydrothermal flame, but failed to give sufficient more accurate quantitative measurements like the propagation speed of flame (the team of the University of Valladolid only acquired a rough value [33]). The solutions to the aforementioned challenges count on advanced measurement technologies including Raman spectra.

The introduction to technical issues starts from ignition technology, to device durability technology, to wall cooling technology and to flame stability technology. In practical applications, HSD, the harmless treatment of pollutants and the generation and stabilization of flame need to be guaranteed under the condition of large flow in a confined space. With regard to ignition, the reactor structure could further decrease ignition temperature compared with fuel concentration [27]. In the meantime, a forced ignition device could ensure the generation of the flames in ambient reactants, resulting in the need for preheating [23]. Thus, it is important to improve the design of nozzle and forced ignition device. Regarding the device durability, the anti-corrosion and explosion-proof of the reactors in both HSD and thermal recovery of heavy oil should be paid attention due to its installation in strata. The wall cooling technology involving the selection of cooling wall materials and the control of cooling water flux is also a crucial part. It is necessary not only to ensure no damage on the wall under the condition of intense heat release, but also to prevent the super-cooling inside the reactor from affecting the flame stability. When it comes to flame stability, the formation of recirculation zone is non-negligible. In SCHC, however, there are few researches on the impacts of its formation conditions and size on flame characteristics. In addition, because of the partial gas phase and liquid phase properties of the supercritical fluid, the features of the recirculation zone are far from those of gas phase combustion in a mature gas turbine combustor, so the related conclusions fail to be directly applied to guide the design of HFR.

**Figure 12.** Scientific and technical challenges and applications of SCHC.

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