Kinetics study on hydrothermal combustion of methanol in supercritical water

Jie Zhang\textsuperscript{a}, Shuzhong Wang\textsuperscript{b,\ast}, Donghai Xu\textsuperscript{b}, Yang Guo\textsuperscript{b}, Mengmeng Ren\textsuperscript{b}, Jinling Lu\textsuperscript{a}

\textsuperscript{a} State Key Laboratory of Eco-hydraulic Engineering in Arid Area, (Xi’an University of Technology), Xi’an 710048, Shaanxi, China
\textsuperscript{b} Key Laboratory of Thermo-Fluid Science and Engineering of MOE, School of Energy and Power Engineering (Xi’an Jiaotong University), Xi’an 710049, Shaanxi, China

**Abstract**

Supercritical hydrothermal combustion has received a great deal of attention as an innovative and potential treatment technology wherein the corrosion and salt deposition problems during supercritical water oxidation processes can be avoided effectively. A detailed chemical kinetics model for methanol was employed and validated to understand the hydrothermal combustion process mechanism in supercritical water. Based on this elementary reaction model, how the two key indicators (ignition and extinction temperatures) worked during combustion reaction was studied. Moreover, the influences of operational parameters (fuel concentration, oxidation coefficient and reactor type) and corresponding reaction mechanism were investigated. It reveals that \( \text{H}_2\text{O}_2 \) was identified as one key intermediate product in the combustion kinetics of methanol. Initial concentration and injection flow rate of aqueous fuel were two significant factors that determined the extinction temperature, which decreased as the concentration increased or the injection flow rate reduced. Moreover, a minimum limit for the initial fuel concentration existed above which a stable hydrothermal flame could form. The oxidation coefficient affected combustion temperature in a manner that depended on the coefficient range. The combustion temperature elevated with the oxidation coefficient in the fuel-rich area while dropped in the oxidant-rich area. This phenomenon was interpreted from the point of view of thermodynamics and mechanism. In order to maintain stable flames at as a low injection temperature as possible, vessel reactors were more desirable to be applied for hydrothermal combustion reaction, deriving from the discrepancy in order of magnitude for flow velocity between tubular and vessel reactors. Finally, it is found that the enhancement of auxiliary fuel methanol in decomposition of organic pollutants stemmed from two reasons: high reaction heat release and co-oxidative effect, whereas the refractory compounds could suppress the ignition of methanol in supercritical water.

© 2015 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

Within the last decades, supercritical water (SCW, \( T > 374 \degree \text{C}, \ P > 22.1 \text{MPa} \)) has been extensively applied from both scientific and technological perspectives. Above its critical point, water acts with unique properties that make it an excellent medium for oxidation of hazardous organic waste (Bermejo et al., 2008; Gopalan and Savage, 1994; Lee et al., 2002; Rice and Steeper, 1998; Savage and Smith, 1995; Vera Pérez et al., 2004; Yu and Savage, 2000). Supercritical water presents a non-polar...
solvent and complete miscibility with almost all organics as well as permanent gases such as nitrogen, oxygen, and carbon dioxide (Hayashi et al., 2007; Lee et al., 2006; Onwudili and Williams, 2007; Sánchez-Oneto et al., 2007; Veriansyah et al., 2005, 2007). Therefore, supercritical water oxidation (SCWO) proceeds in a single phase without limitation of interfacial transfer resistance. Together with the considerably high reaction temperature (400–700 °C), it leads to fast reaction kinetics and complete mineralization of organic wastes through oxidation in SCW. Although a number of studies have confirmed the favorable effects of SCWO on purification of a variety of hazardous waste streams, two major inevitable technical problems, i.e., corrosion and salt deposition, remained to inhibit the industrial applications of this process (Asselin et al., 2010; Marrone and Hong, 2009; Príkopský et al., 2007; Schubert et al., 2010a,b). First, the combination of supercritical water and active ions such as Cl\(^{-}\), F\(^{-}\), H\(_2\)O\(^{+}\) and oxygen could make a corrosive environment, leading to the corrosion of process equipments in the system. Moreover, vessel fouling and blockage due to the precipitation of salt particles in SCW were the most notable problems during SCWO processes. The second problem emerged due to the poor solubility of salts in SCW (Kritzer and Dinjus, 2001). When salty waste water was heated up above the critical temperature, the salts would precipitate and adhere to vessel surfaces as agglomeration or salt scar, which obviously hindered heat transfer. Several approaches involving optimization of construction material and structure designs or modification of processes have been proposed to solve the dual problems. Hydrothermal flames were realized as oxidation of fuel species in SCW when temperature of reagent was higher than the autoignition temperature. It has been identified as a promising alternative to conventional SCWO technology for coping with the challenges of corrosion and plugging.

The hydrothermal flame was a new combustion method, which was discovered by Schilling and Franck (1988). With a high enough concentration of organic aqueous solution as well as the temperature above the autoignition temperature, it is possible to generate hydrothermal flames in SCWO processes. This phenomenon occurred due to the autoignition temperature of organic compound reduced under high pressure conditions (Cabeza et al., 2011, 2013; Hirotsuka et al., 2007; Narayanan et al., 2008; Queiroz et al., 2013, 2015; Sierra-Pallares et al., 2009). Ignition can happen easily as the organic feeds were gaseous fuels, solvents or other flammable organic compounds, while auxiliary fuel was required to form hydrothermal flames as with recalcitrant compounds. Serikawa et al. (2002) achieved the isopropyl alcohol hydrothermal flames in a SCWO reactor and recorded by a CCD camera from the sapphire window. They observed that hydrothermal flames behaved the similar morphology to conventional flames, and rapid combustion of organic fuel produced the local high temperature and thus generated bright light. Hydrothermal flames have been reported in several SCWO reactors and showed substantial advantages over flameless processes (Bermejo et al., 2006b, 2011a,b; Cabeza et al., 2011; Cocero et al., 2002; Hirotsuka et al., 2007; Serikawa et al., 2002; Wellig et al., 2005, 2009). First, it is possible to initiate combustion even when the feed inlet temperature was below 100 °C, which could successfully overcome the two challenges of corrosion and plugging during the preheating system. In the ETH Zurich (Wellig et al., 2009), the transpiring wall reactor with a diffusion hydrothermal flame was investigated, it is found that the flame burned steadily even at the injection temperature as low as 92 °C for 28.1wt% methanol aqueous fuel. Bermejo et al. (2011b) examined the formation and stabilization of premixed hydrothermal flame in a cooled-wall reactor with isopropyl alcohol as fuel. Experimental results show that a stable hydrothermal flame can be obtained at the feed injection temperature of 100 °C with the fuel concentration of 9 wt%.

Príkopský et al. (2007) injected a feed containing 3 wt% Na\(_2\)SO\(_4\) into the transpiring wall reactor with hydrothermal flames as internal heat source. No plugging in the reactor and other equipments was observed during the experiments, but only 65% of the salt was detected in the effluent. Second, organic pollution can be completely destructed within residence time in the order of magnitude of 100ms during hydrothermal flames (Bermejo et al., 2011b; Príkopský et al., 2007; Serikawa et al., 2002; Wellig et al., 2009). The superiority in reaction processes approved the construction of smaller reactors, which was economically favorable. Finally, in hydrothermal flame reactors, rapid oxidation of fuel aqueous feed enabled the flame temperature to reach a high level (700–1200 °C), which facilitated energy recovery. The research for hydrothermal combustion in both tubular reactors (Bermejo et al., 2011a; Cabeza et al., 2011) and vessel reactors (Bermejo et al., 2011b; Serikawa et al., 2002; Wellig et al., 2009) indicated that the maximum temperature in a SCWO reactor in the presence of flames can reach above 700 °C. Thus, the high quality of aqueous effluent from the hydrothermal flame reactor can be employed as the heat or power sources during industrial processes.

The detailed chemical kinetics model (DCKM) has been reported in several SCWO reaction studies for various species regarding H\(_2\), CO (Brock and Savage, 1995; Holgate and Tester, 1994), methane (Webley and Tester, 1991), methanol (Brock et al., 1998; Castello and Fiori, 2012), benzene (Dinaro et al., 2000), methylphosphonic acid (Sullivan et al., 2004) and methylene (Benjamin and Savage, 2005; Li and Oshima, 2005), which takes the similarity between SCWO chemistry and gas-combustion chemistry in the same temperature range as foundation. Moreover, several investigators have successfully employed the detailed chemical kinetics model to analyze the co-oxidation mechanism for binary mixture reactants during SCWO processes (Hayashi et al., 2007; Ploeger et al., 2006b; Savage et al., 2000). It is further confirmed that the SCWO chemistry is analogous to that of gas-phase combustion proceeding via radical reaction mechanism. We postulated that whether the mechanism-based model can be available for simulating the combustion reaction in supercritical water. Once validated, this method can be used to understand and model processes with supercritical hydrothermal flames.

In this study, the DCKM model for combustion of methanol was adopted in order to reproduce the hydrothermal combustion reaction of methanol in SCW. Detailed information on ignition and extinction limits and influences of operation parameters such as the fuel concentration, the fuel inlet

Table 1 – List of references for the compared first-order reaction kinetics of methanol.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Rate expression</th>
<th>A</th>
<th>E(_a) (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice et al. (1996)</td>
<td>k [MeOH]</td>
<td>5.53 × 10(^{12})</td>
<td>179,000</td>
</tr>
<tr>
<td>Tester et al. (1993)</td>
<td>k [MeOH]</td>
<td>1.585 × 10(^{15})</td>
<td>408,800</td>
</tr>
<tr>
<td>Brock et al. (1996)</td>
<td>k [MeOH]</td>
<td>1.995 × 10(^{15})</td>
<td>326,570</td>
</tr>
</tbody>
</table>

\(^{a}\) k = A \times \exp(-E_a/RT).
rate, the oxidation coefficient and the reactor configuration were reported. Further, the decomposition characteristics of organic involving fuel and refractory pollutants with the interaction effect during hydrothermal combustion processes were studied. The research results would offer an effective evidence and guidance for achieving stable hydrothermal flames in SCWO reactors.

2. Establishing and validating the kinetics model

Skodje et al. (2010) have proposed an elementary reaction model for combustion of methanol in their investigation, which involves 93 elementary reaction steps and 18 chemical species. It has been reported that SCWO chemistry is analogous to that of gas-phase combustion proceeding via radical reaction mechanisms. Therefore, in this study, Skodje’s combustion kinetics model for methanol was adopted to develop the mechanism model for methanol combustion in SCW. We calculated temporal conversion profiles for SCWO of methanol according to kinetics equations from Rice et al. (1996), Tester et al. (1999) and Brock et al. (1996) listed in Table 1 for the purpose of evaluating the validity of the mechanism model, as shown in Fig. 1. The comparison of predicted results of the detailed chemical kinetics model and three kinetics equations, revealed slight differences between the patterns for the calculated methanol conversion temporal profiles obtained by means of these two sources. It can be seen from the DCKM curve that the oxidation of methanol in SCW involved the induction phase, the propagation phase and the termination phase. The DCKM model described the reaction process from the perspective of mechanism, while the first-order kinetics model didn’t work well, due to the limitation of this model. However, it shows that the residence times at which methanol conversions reached 1.0 were very close (0.05–0.08 s). Moreover, this mechanism-based model has been successfully applied in our previous study for SCWO of methanol (Zhang et al., 2013). Accordingly, it leads us to speculate whether this model can reproduce satisfactorily the behavior of SCWO reactions for methanol with hydrothermal flames inside, which would be evaluated in the later discussion.

3. Results and discussion

3.1. Ignition and extinction temperature

The ignition temperature and the extinction temperature are two critical key parameters for operation of hydrothermal flame reactors. The ignition temperature is defined as the lowest injection temperature of fuel stream immediately before the event of ignition, while the extinction temperature is defined as the lowest fuel injection temperature into the combustion chamber immediately before the event of extinction (Wellig et al., 2009).

3.1.1. Ignition temperature

The ignition of the hydrothermal flame takes place after the fuel and oxidant were heated up to the autoignition temperature. The ignition temperature was the injection temperature of reactants as soon as ignition occurred. It is a key parameter during the startup process of hydrothermal combustion. Researchers always regarded the appearance of sharp increase in the temperature at the nozzle exit as the ignition of hydrothermal flames (Bermejo et al., 2011a; Cabeza et al., 2011; Wellig et al., 2009). Serikawa et al. (2002) found that for 5 vol% isopropyl alcohol solution, the injection temperature of 470 °C ensured the spontaneous ignition of hydrothermal flames, while flames didn’t ignite immediately at the injection temperature of 380 °C. But the following flameless and exothermic oxidation increased the reactor temperature, and as the reactor temperature achieved 470 °C the flame suddenly ignited. Furthermore, Sobby et al. (2007, 2009) reported the ignition delay for the methanol-air and naphthalene-methanol-air hydrothermal flames. Within the seconds of the delay process, the flameless oxidation provided sufficient energy to heat reactants to the autoignition temperature. It indicates that before the ignition of hydrothermal flames, the energy accumulation for achieving the autoignition temperature was not only from the external heat source at preheating step, but also from release of reaction heat during the oxidation of reactants. Correspondingly, the ignition temperature differed from the autoignition temperature, and the former generally was lowered than the latter.

Ignition temperature was an indicator of difficulty for the hydrothermal flame igniting. Bermejo et al. (2006b) reported that the isopropyl alcohol aqueous solution with a concentration of 6.5 wt% required the injection temperature above 420 °C for ignition of the flame in a SCWO transpiring wall reactor. Serikawa et al. (2002) also recognized that a fuel temperature higher than 470 °C was necessary for the formation of hydrothermal flames. It is suggested that the ignition of aqueous fuel always took place in supercritical region in which fuel compounds were oxidized in a single-phase environment. We speculated the possible explanation that the injection temperature above the critical temperature not only ensured larger energy supply, but also provided the homogeneous atmosphere, leading to fast oxidation and thus quick release of energy to heat up fuel steams to the autoignition temperature. Therefore, the existence of a single-phase mixture of aqueous fuel and oxidant was a requisite condition for ignition of aqueous fuel in SCW. Moreover, it is reported that several initial parameters could affect the ignition temperature. Wellig et al. (2009) employed methanol as an internal heat source for combustion of hydrothermal flames. They found that the dependence of the ignition temperature on the methanol

![Fig. 1 – Calculated methanol conversion in supercritical water oxidation at 873 K, 25 MPa.](image-url)
concentration was weak, and the ignition temperature ranged between 466 °C and 490 °C as the concentration ranged from 15 wt% to 22 wt%. Conversely, the flow rate of the initial steam largely influenced ignition which occurred at relatively high temperatures in the case of high flow rates. Moreover, several researchers (Bermejo et al., 2011b; Cabeza et al., 2011; Serikawa et al., 2002; Wellig et al., 2009) have pointed out that there existed the minimum fuel concentration below which ignition of the hydrothermal flame was not available and flameless oxidation proceeded even at supercritical injection temperatures.

3.1.2. Extinction temperature

Extinction temperature was an important parameter guaranteeing stabilization operation of the hydrothermal flame, which was the lowest inlet temperature of aqueous fuel that prevented flameout during the hydrothermal combustion process. That is, after the hydrothermal flame ignited in a SCWO reactor, the flame would maintain combustion as long as the fuel injection temperature was higher than the extinction temperature.

The calculated results based on the detailed chemical kinetics model for hydrothermal combustion of methanol are presented in Figs. 2 and 3, which separately demonstrate the reaction temperature and temporal variations of reactants as a function of the preheat temperature, T0, at the constant initial methanol concentration (\(w_f\)) of 15 wt% and the oxidation coefficient (\(\phi\)) of 2.0. In Fig. 2, the discrete points are calculated results, while the lines are obtained by fitting these results. For the preheat temperature lowered than 573 K, the reaction temperature was still the preheat temperature at both residence times (\(t_0\)) of 0.001 s and 0.01 s. As the preheat temperature increased to 573 K, sharp increase in temperature profiles occurred. The reaction temperature was 1000 K at 0.001 s, while elevated to the equilibrium temperature of 1653 K at 0.01 s. It is supposed that the hydrothermal flame can’t ignited until the preheat temperature achieved 573 K for the 15 wt% methanol solution. Accordingly, there appeared to be a threshold for the preheat temperature of fuel steam triggering the hydrothermal combustion reaction, which is defined as “extinction temperature”.

In the above calculation, the substantial increment in the reaction temperature at 0.01 s was employed as the criterion for production of the hydrothermal flame. This is because 0.01 s was supposed to be the largest induction time for methanol supercritical hydrothermal combustion reactions. In Vogel’s et al. (2005) research about the kinetics for methanol oxidation in SCW, they reported that the increase in the methanol concentration or the reaction temperature will significantly shorten the induction time. An Arrhenius-type model for the induction time has been fitted based on previous studies, as shown in Eq. (1). It is calculated that the induction time for methanol SCWO was 0.06 s at 600 °C, while 0.007 s at 700 °C. The concentration of the methanol solution introduced into supercritical hydrothermal combustion reactions was several orders of magnitude higher than that in SCWO reactions. Moreover, it has been revealed that the combustion temperature in supercritical hydrothermal flames ranged between 700 °C and 1200 °C (Bermejo et al., 2006a,b, 2011a; Serikawa et al., 2002; Sobhy et al., 2009; Wellig et al., 2009), which further confirmed that the induction time for supercritical hydrothermal combustion of methanol was less than 0.007 s (the induction time for SCWO reaction of methanol at 700 °C). Therefore, it is reasonable to select 0.01 s at which the reaction temperature presented significant rise as the boundary for ignition of the hydrothermal flame.

Fig. 3 demonstrates the temporal variations of molar concentration for CH3OH, CO and CO2 with variable preheat temperatures ranging from 533 K to 613 K. It can be observed that methanol began to react at 1.0 × 10⁻⁴ s in flames (\(T_0 ≥ 573\) K), while the intermediate product CO and the final product CO2 were generated. Moreover, as \(T_0\) increased from 573 K to 613 K, the methanol concentration varied synchronously, and peak heights in CO temporal profiles were approximately equal. When \(T_0\) was lower than the extinction temperature of 573 K, there were no hydrothermal flames. It appeared in reactant concentration variations that initial reaction prominently lagged behind that with flames, and the methanol concentration began to decline until 0.01 s.

\[
\tau_{ind} = (7.58E + 09)^{-1} \exp \left( \frac{144,000}{RT} \right)
\]

Wellig et al. (2009) suggested that the higher methanol concentration permitted the lower inlet fuel temperature. 6 wt% concentration of methanol steam corresponded to the inlet temperature of 444 °C, while 28 wt% to a lower temperature of
92 °C. They noted that at least 11 wt% methanol allowed the desired subcritical injection temperature. The stable flame can be sustained even with a non-preheated 30–32 wt% methanol steam. In Bermejo’s et al. (2011a) research, it was observed that the isopropyl-alcohol concentration was necessary to increase up to 10 wt% in order to maintain the steady hydrothermal flame with the injection temperature as low as 170 °C. Cabeza et al. (2011) conducted an investigation for hydrothermal flames in a tubular reactor and obtained the consistent variation trend of the extinction temperature with the aqueous fuel concentration. Another operation parameter regarded as prominently impacting on the extinction temperature was the injection flow rate of the feed steam. The experimental results obtained by Bermejo et al. (2011a) showed that the extinction temperature changed as the function of the fluid injection velocity in a SCWO tubular reactor, which increased with the fluid velocity. Therefore, the extinction temperature with oxygen as oxidant lowered than that with air for the same aqueous fuel, because the total flow rate of the former was less than that of later. Experiments performed in a continuous vessel reactor also achieved the identical conclusion that the more injection flow rate, the higher injection temperature of fuel steam was required for the stable flame (Bermejo et al., 2011b). Considering the above discussions, it is demonstrated that regardless of tubular reactors and vessel reactors, the aqueous fuel concentration and the feed injection flow rate were two significant operation parameters that affected the extinction temperature of hydrothermal flames in SCW. The extinction temperature increased with the feed injection flow rate, while reduced with the fuel concentration. We will introduce the conception of the flame front velocity to account for the above conclusions.

Flame is defined as the surface where the combustion reaction proceeds. In the case of a premixed flame, this surface separates the cold reagent from the hot combustion product. This surface propagates toward the inlet reagent at the velocity of the flame front (Bermejo et al., 2011a). The flame keeps stable if the flame front velocity is equal to the steam flow velocity, while the flame will be extinguished if the flame front velocity is lower than the steam flow velocity, and the flame will move until fuel and oxidant mix if the flame front velocity is higher than the steam flow velocity. Serikawa et al. (2002) proposed that the maximum fuel flow rate for the 785 mL inner volume reactor was 3 mL/min, and the larger reactor diameter was required for the higher fuel flow rate. This phenomenon can be explained by the comparison between the flame and flow velocity in the reactor. When with a constant flame velocity, increasing the steam flow rate but keeping the diameter of the reactor constant would lead to an increment of the flow velocity in the reactor. And the flow velocity can be greater than the invariable flame velocity, which would cause undesired flameout. Consequently, in order to ensure stable hydrothermal combustion, the reactor diameter needed to be increased with the fuel flow rate to avoid the situation that the flow velocity was superior over the flame velocity. The velocity of flame front is estimated and developed by Glassman and Yetter (2008), which has been applied to Bermejo’s investigation for calculating the hydrothermal flame velocity in a transpiring wall reactor (Bermejo et al., 2011a), as expressed in Eq. (2),

\[ S_c = \sqrt{\frac{2 lc^2 \alpha_0 \overline{w_0}}{(\overline{c_p})^3} \left( \frac{T_0}{T_f} \right)^2 \left( \frac{n_1}{n_p} \right)^2 L_c^2 \left( \frac{RT_f}{E_a} \right)^3 e^{-\frac{E_a}{RT_f}} (T_f - T_0)^2} \]

where \( T_0 \) is the temperature of unburned mixture into the combustion chamber; \( T_f \) specifies the flame temperature; \( \lambda \) represents the thermal conductivity; \( \overline{c_p} \) is the specific heat evaluated at \( T_f \); \( \overline{c_p} \) is the average specific heat between \( T_0 \) and \( T_f \); \( \alpha_0 \) is Arrhenius pre-exponential factor; \( w_0 \) is the mass fraction of fuel; \( n_1/n_p \) is the ratio between mole number of reactant and product; \( E_a \) is the energy of activation; \( R \) is the gas constant; and \( Le \) represents the Lewis number of unburned mixture which is the ratio of thermal to mass diffusivities, as shown in the following equation:

\[ Le = \frac{\lambda}{\rho D} \]

In the above description, \( \rho \) is the mixture’s density, and \( D \) is the mass diffusivity of fuel in the mixture, which was calculated by the correlation proposed by He (1997).

\[ D_21 = \left[ 0.61614 + 3.0902 \exp \left( -0.87756 \sqrt{M_1 Vc_1 r_1} \right) \right] \times 10^{-10} (V_1^k - 23) \sqrt{T/M_2} \]

where \( M_1 \) and \( M_2 \) are the molecular masses for solvent and solute, respectively, in g/mol; \( V_1 \) and \( V_2 \) are the molar volume and critical molar volume of solvent in cm\(^3\)/mol; \( \rho_1 \) and \( \rho_{cr} \) are the density and critical density of solvent; \( T \) is the temperature. The parameter \( k \) is approximately 1 if the reduced solvent density \( \rho_1 / \rho_{cr} = V_1/V_2 \) is greater than 1.2, but became low while \( \rho_1 \) is less, and can be represented by the following expressions.

\[ \begin{cases} k = 1 & \rho_1 \geq 1.2 \\ k = 1 + (\rho_1 - 1.2) / M_1 & \rho_1 \geq 1.2 \end{cases} \]

The mixture density and transport properties such as thermal conductivity, specific heat are calculated as mass-fraction weighted average \( \bar{Y} = \sum_{i=1}^{nc} x_i Y_i \).

We will calculate the velocity for hydrothermal flames of methanol solution. For the hydrothermal flame of methanol, Wellig et al. (2009) reported that different concentrations of methanol 8.1, 16.0 and 22.1 wt% corresponded to the extinction temperatures of 678, 559 and 498 K, as well as the flame temperatures of 874, 953 and 1071 K, respectively. The reaction kinetics parameters for methanol SCWO were obtained from Rice’s et al. (1996) research, in which the pre-exponential factor \( A_0 = 5.53 \times 10^{12} \text{s}^{-1} \), and the activation energy \( E_a = 179 \text{kJ/mol} \). According to the above description, we calculated the velocity for hydrothermal flames of methanol in SCW at concentrations of 8.1, 16.0 and 22.1 wt%, respectively, as illustrated in Fig. 4.

Fig. 4 represents the hydrothermal flame velocity at incremental temperature of the unburned mixture \( T_0 \), which shows that the supercritical hydrothermal flame velocity varied between 0.01 m/s and 0.1 m/s. Two prominent features are revealed from the flame velocity profiles. The first one is that at a constant methanol concentration, the velocity of hydrothermal flames increased with the fuel injection temperature \( T_0 \) and facilitated the ignition of aqueous methanol fuel. The second feature for the flame velocity profiles at different methanol concentrations is that the flame velocity showed an increment with the initial methanol concentration at the identical temperature of the unburned mixture. Based on the
above findings, it explains the fact that at a lower fuel concentration, a higher temperature of \( T_0 \) is required to ensure the flame velocity exceed the flow velocity in the reactor. Accordingly, the extinction temperature reduced with the initial fuel concentration during normal operation of hydrothermal combustion processes. In addition, it is noted that both two profiles for methanol concentrations of 16.0 wt% and 22.1 wt% obviously concaved down at the initial temperature \( T_0 \) of 660 K. This is because at the quasi critical point of water, there existed the maximum peak of specific heat capacity, and thus the calculated flame front velocity variation didn’t smoothly rise with the initial temperature \( T_0 \).

Overall, ignition temperature and extinction temperature were two important indicators for inlet temperature of fuel and oxidant steams. It was not a injection temperature of mixture that was higher than the extinction temperature can guarantee aqueous fuel ignition, but the injection temperature above the extinction temperature ensured that the flame didn’t be extinguished after ignition.

### 3.2. Influences of process parameters on the hydrothermal flame combustion

#### 3.2.1. Initial fuel concentration

The flame temperature was defined as the highest fluid temperature in hydrothermal combustion reactors. It is reported that several operation parameters could influence the hydrothermal flame stability and temperature, such as the initial concentration of the aqueous fuel, the injection temperature of the feed steam, the oxidation coefficient and the nozzle geometric structure, etc. First, we simulated the supercritical hydrodynamic combustion reaction of methanol at different fuel concentrations to determine the influence of the fuel concentration on the hydrothermal flame temperature, as shown in Fig. 5. It demonstrates the calculated reaction and equilibrium temperature variations as a function of the methanol concentration ranged from 3 wt% to 20 wt%. Obvious linear increase of 1141 K at the equilibrium temperature can be seen with the methanol concentration increasing from 3 wt% to 20 wt%. It seems that the more the fuel concentration, the more reaction energy released, leading to the more significant temperature enhancement of the reaction system. Cabeza et al. (2011) conducted the investigation of hydrothermal flames in a tubular reactor. They found that increasing the initial fuel concentration led to the increment in the flame temperature and the organic removal efficiency, while the reduction of the fuel concentration caused the delay for the highest temperature point in the tubular reactor. Bermejo et al. (2011b) studied the influence of operation parameters on the hydrothermal flame in a cold-wall reactor. The experimental results show that the fuel concentration, the feed injection temperature and the flow rate were the main factors that affected the flame temperature. In order to have flame temperature between 600 °C and 700 °C, the fuel concentration was requested to increase as the feed injection temperature decreased, while the injection temperature was requested to increase as the injection flow rate increased. The conclusions mentioned above for supercritical hydrothermal combustion were consistent with our calculation results. It once again validated the feasibility of the mechanism-based model for supercritical hydrothermal combustion of methanol.

Moreover, conspicuous discrepancy was observed by comparing the reaction temperature at \( t_0 = 0.01 \)s with the equilibrium temperature profile, as presented in Fig. 5. For \([\text{CH}_3\text{OH}]_0 \leq 12 \text{ wt}\%\), the reaction temperature at \( t_0 = 0.01 \)s was still equal to the initial preheat temperature (573 K), while the reaction temperature at \( t_0 = 0.01 \)s rapidly elevated up to the equilibrium temperature as the methanol concentration increased to 15 wt%, where hydrothermal flames were produced in the system. It reveals that there appeared to be a threshold \([\text{CH}_3\text{OH}]_0\) concentration below which there were no hydrothermal flames generated at the corresponding preheat temperature. The hydrothermal flame has been defined as “When the organic waste concentrations are high enough and the temperature is above the autoignition temperature of fuel, it is possible to form flames called hydrothermal flames”, in which there presented the minimum restriction for the initial fuel concentration. Moreover, Serikawa et al. (2002) reported that the sporadic and luminous red flame was observed as the inlet isopropyl alcohol concentration was higher than the volume concentration of 2 vol% (TOC = 9600 mg/L). No flames were observed as the isopropyl alcohol concentration was lower than this value. It is speculated that under the threshold of the fuel concentration, the energy released from the

---

**Fig. 4** – Influences of the fuel injection temperature on the hydrothermal flame velocity at different methanol concentrations of 8.1, 16.0 and 22.1 wt%.

**Fig. 5** – Calculated equilibrium temperatures and reaction temperatures at \( t_0 = 0.01 \)s as a function of the initial fuel concentration at \( T_0 = 573 \text{ K}, P = 25 \text{ MPa } \phi = 2.0 \).
oxidation of fuel organic was not enough for combustion of flames.

3.2.2. Oxidation coefficient
It has been reported that oxidation coefficient was an important factor which significantly affected the hydrothermal flame formation and the flame morphology (Serikawa et al., 2002). In order to explore the effect of oxidation coefficient on hydrothermal combustion reaction, we simulated the combustion of methanol in SCW by the elementary reaction model. Fig. 6 depicts the influence of oxidation coefficient $\phi$ on the equilibrium temperature and the products concentration, in which the mole fraction of $H_2O$ was that generated from reactions. As shown in Fig. 6, the reaction products included $H_2$, $CO$, $CO_2$ and $H_2O$ in the fuel-rich area, while $CO_2$ and $H_2O$ in the oxidant-rich area. Moreover, a substantial peak in the equilibrium temperature profile appeared at the oxidation coefficient $\phi = 1$, as did the $CO_2$ and $H_2O$ mole fractions.

Thermodynamically, as $\phi < 1.0$, the oxidant in the reaction system was insufficient, leading to incomplete combustion of fuel and reduction of reaction heat release. Thus, the temperature rise reduced as oxidation coefficient decreased in the fuel-rich area. However, the temperature also dropped with the greater oxidation coefficient in the oxidant-rich area ($\phi > 1.0$). First, the oxygen mole fraction increased with the higher oxidation coefficient, while the methanol mole fraction reduced, and thus the combustion heat of the reaction system decreased. Moreover, the mean specific heat dropped with the oxidation coefficient on account of the increment in the gas proportion. Compared with combustion heat, the mean specific heat decreased more slowly with $\phi$. It is interpreted that oxygen was consumed along with the production of $CO_2$ and $H_2O$, whose specific heats were higher than that of oxygen. At the same time, the fuel fraction decreased almost linearly with the oxidation coefficient, leading to the direct reduction of the combustion heat. Overall, the equilibrium temperature fell off as $\phi$ increased with excessive oxidant.

Free radical reaction is reported to dominate reactions in supercritical water (Anitescu et al., 2005; Hayashi et al., 2007; Henrikson et al., 2003; Ploeger et al., 2006a,b), which is because supercritical water is highly aprotic and nonpolar with a low dielectric constant. Fig. 7(a) displays the calculated temporal variations of intermediates concentrations at $T_0 = 573 K$, $\omega_f = 15$ wt% and $\phi = 2.0$. Substantial peaks appearing in $H_2O_2^*$ and $H_2O_2$ profiles in Fig. 7(a) indicate that $H_2O_2^*$ and $H_2O_2$ accumulated at first and then were consumed by intermediate organics. Furthermore, regardless of the residence time, profiles of the $H_2O_2^*$ concentration were always several orders of magnitude lower than those of $H_2O_2$, suggesting that $H_2O_2$ should be one of key components during combustion of methanol in supercritical water, which was consistent with the kinetics analysis for methanol oxidation in the previous study (Hayashi et al., 2007). Nevertheless, the $OH^*$ mole fraction always kept zero until combustion reaction was completed, and then showed a sharp rise to $2.0 \times 10^{-4}$ after the equilibrium time of 0.01 s. It reveals that $OH^*$ radical was insufficient during combustion reaction, which was produced and consumed immediately, and thus was unable to be retained until the end of reaction. Accordingly, we calculated the temporal variation of $H_2O_2$ with varying oxidation coefficients, as displayed in Fig. 7(b). There was neglected effect of oxidation coefficient on the maximum value of the $H_2O_2$ concentration with sufficient oxidant ($\phi > 1$), but the $H_2O_2$ profile peak appeared at the later time as the oxidation coefficient increased from 1.0 to 2.5. It is supposed that $O_2$ restrained the accumulation of $H_2O_2$, and thus postponed the oxidation reaction, as shown in Reactions (R1) and (R2). Additionally, at $\phi = 0.8$, insufficient oxidant not only delayed the $H_2O_2$ profile from reaching the peak but also led to the obvious decrease of the maximum value of the $H_2O_2$ mole fraction, thereby hindering overall reactions. As mentioned above, we interpreted the effect of oxidant on combustion reactions from the reaction mechanism perspective.

\[
\begin{align*}
H_2O_2^* + HO_2^- & \leftrightarrow O_2 + H_2O_2 & \text{(R1)} \\
H_2O_2 + O & \leftrightarrow OH^* + HO_2^* & \text{(R2)}
\end{align*}
\]

3.3. The distinction between tubular and vessel hydrothermal combustion reactors
The literature reviews with regard to the research of hydrothermal flames in different types of reactors are listed in Table 2, which summarizes the employed fuel compound, the aqueous fuel concentration, the ignition temperature for the hydrothermal flame, etc.

As shown in Table 2, the stable hydrothermal flame can be obtained even with a subcritical injection temperature for the vessel reactor (Bermejo et al., 2011a,b; Serikawa et al., 2002; Welig et al., 2009). It has been demonstrated that the hydrothermal flame burned steadily as injecting methanol solution and oxygen at 200–300 °C after ignition in the transpiring wall reactor, and the inlet temperature of fuel steam at 100 °C can also achieve the desired results with 27 wt% methanol (Welig et al., 2009). Bermejo et al. (2011b) found that the initial temperature of 110 °C enabled the stable combustion of isopropyl alcohol in a transpiring wall reactor once the flame was ignited. On the contrary, the performance of tubular reactors was relatively poor. Cabeza et al. (2011) conducted investigations on hydrothermal flames in a tubular reactor with the isopropyl alcohol aqueous solution as fuel. They found that the injection temperature for the reaction steam was required to exceed 370 °C during the flame combustion to ensure a steady hydrothermal flame, which was detrimental to salt-containing steam due to salt precipitation in the preheating system.
Based on the above conclusions, it has been proved that injection of subcritical fuel feed over the hydrothermal flame was only possible in vessel reactors. But in the case of tubular reactors, the injection temperature above the critical temperature of water was required to keep the stable hydrothermal flame. Therefore, vessel reactors seemed to be more favorable for the formation and stabilization of hydrothermal flames, especially at a low injection temperature. Next, we will compare the flame velocity with the flow velocity in different types of reactors to demonstrate the above distinction.

We calculated the flame velocity ($S_f$) and the flow velocity ($V_f$) according to the experimental operation data obtained from Cabeza et al. (2011), Bermejo et al. (2011b) and Wellig et al. (2009) investigations for the hydrothermal flame in different reactors, as illustrated in Fig. 8. Cabeza employed a tubular reactor, while the other three sets of profiles in Fig. 8 present velocities of $S_f$ and $V_f$ in vessel reactors, wherein Bermejo-1 and Bermejo-2 show the results with two different injectors but the same reaction chamber. As it can be seen, for the vessel reactors, the flow velocity in the reaction chamber was low, generally less than 0.01 m/s. The flame front velocity ranged between 0.01 m/s and 0.1 m/s, which tended to be larger than the flow velocity. Therefore, in vessel reactors, it is possible to heat the unburned fuel by combustion products in the reactor. Thus, even though the injection temperature of aqueous fuel was lower than the critical temperature, the hydrothermal flame can keep stable. However, for the tubular reactor, the flow velocity was high ranging between 1 m/s and 2 m/s, which was far greater than the flame front velocity. Consequently, the most energy that preheated reactants to the autoignition temperature was from the external heat source in the tubular reactor. It is necessary for the aqueous fuel to be injected into the tubular reactor at a supercritical temperature, which was adverse for salt-containing feeds. Overall, vessel reactors were advantageous over the tubular reactors in maintaining steady hydrothermal flames with subcritical injection temperatures.

### 3.4. Decomposition of organics in the hydrothermal flame

The higher flame temperature (700–1200 °C) promoted organic compounds to be oxidized completely. Many studies on the hydrothermal flame have suggested that organic compounds can achieve complete degradation during combustion of the

---

**Fig. 7** – Active intermediates mole fractions predicted for hydrothermal combustion of methanol in supercritical water.

**Fig. 8** – The comparison between the hydrothermal flame velocity and the flow velocity in different types of reactors: solid, flame velocity $S_f$; hollow, flow velocity $V_f$.

---

**Table 2** – Summary of the investigation for hydrothermal flames in different types of reactors.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Reactor type</th>
<th>Fuel</th>
<th>Fuel concentration</th>
<th>Ignition temperature (°C)</th>
<th>Extinction temperature (°C)</th>
<th>Flame temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cabeza et al. (2011)</td>
<td>Tubular reactor</td>
<td>Isopropyl alcohol</td>
<td>1.0–4.5 wt%</td>
<td>400–425</td>
<td>390–406</td>
<td>440–708</td>
</tr>
<tr>
<td></td>
<td>Tubular reactor</td>
<td>Isopropyl alcohol</td>
<td>4 wt%</td>
<td>354–425</td>
<td>354–425</td>
<td>620–685</td>
</tr>
<tr>
<td></td>
<td>Transpiring wall reactor</td>
<td>Isopropyl alcohol</td>
<td>6.5–10.1 wt%</td>
<td>–</td>
<td>169–364</td>
<td>611–749</td>
</tr>
<tr>
<td>Bermejo et al. (2011b)</td>
<td>Cold-wall reactor</td>
<td>Isopropyl alcohol</td>
<td>8–9.5 wt%</td>
<td>400</td>
<td>30–300</td>
<td>600–700</td>
</tr>
<tr>
<td>Serikawa et al. (2002)</td>
<td>Vessel reactor</td>
<td>Isopropyl alcohol</td>
<td>2.08–5.83 vol%</td>
<td>–</td>
<td>375–405</td>
<td>800–1100</td>
</tr>
<tr>
<td>Wellig et al. (2009)</td>
<td>Transpiring wall reactor</td>
<td>Methanol</td>
<td>6–28 wt%</td>
<td>490–466</td>
<td>92–444</td>
<td>539–976</td>
</tr>
</tbody>
</table>
hydrothermal flame. Wellig et al. (2009) reported that the methanol conversion of all hydrothermal flame experiments were higher than 99.9%. And the residual methanol mass fraction increased and the methanol conversion dropped with decreasing the inlet temperature of the reaction feed. This was due to the decrease in the reaction temperature and the more significant role played by multi-phase effects at subcritical inlet temperature. In the investigation on the hydrothermal flame of isopropyl alcohol, Bermejo et al. (2011b) revealed that TOC removals higher than 99% were possible with the presence of hydrothermal flames at the temperature of 650–700 °C and the residence time of 0.3–1.2 s. Moreover, refractory pollutants could also decompose effectively in the presence of hydrothermal flames in SCW. Incomplete oxidation of nitrogenous organic compounds in supercritical water generally led to the formation of ammonia, whose destruction was the limiting step in the overall reaction (Cabeza et al., 2014). It is reported that ammonia can’t be decomposed until the temperature reached up to 640–700 °C in the absence of catalyst. Besides, acetic acid has been identified as one of the most refractory intermediates for the oxidation of more complex organics in SCW and is considered to be a key rate-controlling compound during the overall SCWO process (Krajnc and Levec, 1997; Lee, 1996; Maharrey and Miller, 2001; Savage and Smith, 1995; Takahashi et al., 2012; Yu and Savage, 2000). Cabeza et al. (2011) used the isopropyl alcohol/acetate and the isopropyl alcohol/ammonia as auxiliary fuels, respectively, and confirmed that complete TOC and TN removals were both obtained. Serikawa et al. (2002) also realized that effective decomposition of dioxins could be achieved in the presence of hydrothermal flames. Therefore, SCWO with the hydrothermal flame allowed organic pollutants to decompose completely in a less residence time compared with the flameless process.

On the other hand, auxiliary fuels were generally labile organic compounds, such as methanol, ethanol and isopropyl alcohol. Several investigators have reported that the oxidation of reactive species in mixtures accelerates the rate of refractory, stable species oxidation decomposition in SCW, which is defined as SCWO co-oxidation reaction (Anitescu et al., 2005; Hayashi et al., 2007; Savage et al., 2000). It is assumed that auxiliary fuels oxidize much more rapidly and that the oxidation would produce a concentration of reactive intermediates at a shorter reaction time, a portion of which would then attack other stable species during the SCWO process. Methanol has attracted special attention from many researchers as co-oxidative species in studies, which confirmed the co-oxidation enhancement for methanol on several refractory compounds decomposition during the SCWO process. Accordingly, we speculate that during the supercritical hydrothermal combustion process, auxiliary fuel oxidation not only provided the high-temperature environment for effective degradation of pollutants, but also co-oxidized stable species in mixtures, thus accelerating the rate of pollutants disappearance kinetics further. It is another significant advantage of the supercritical hydrothermal combustion technology.

Nevertheless, while enhancing the refractory species destruction rate, the oxidation of auxiliary fuels could be suppressed for the plunder of reactive intermediates, thereby inhibiting the combustion process in SCW. Accordingly, we examined the temporal reaction temperature as a function of the phenol concentration ranging from 0.0 to 10.5 wt% at T₀ = 573 K and φ = 2.0, as demonstrated in Fig. 9. It can be seen that concentrations of methanol and phenol were determined by abiding the criterion that the sum of the reaction heat for the two compounds was equal to that for the 15 wt% methanol aqueous solution. Hence, the concentration of phenol increased while that of methanol reduced correspondingly. The concentration of methanol was 0.0 until the phenol concentration reached up to 10.5 wt%, which is for the reaction with pure phenol. It is obvious that the fuel aqueous solution ignited at 1.0 × 10⁻⁴ s and reached equilibrium at 1.0 × 10⁻³ s in the absence of phenol. Moreover, temperature profiles in Fig. 9 showed a notable dependence on the initial phenol concentration, that is, not only the ignition was postponed as the phenol concentration increased from 0.0 to 6.1 wt%, but also the equilibrium temperature shifted to a lower value and appeared at a later residence time. An increment in the ignition time can be observed with the phenol concentration increasing from 0.0 to 1.65 wt%, while with phenol further increasing to 4.2 wt% and 6.1 wt%, the ignition was delayed to 0.1 s and 1 s, respectively. The ignition was not registered since the phenol concentration achieved 6.7 wt% or more. Obviously, the presence of phenol inhibited the combustion of methanol in SCW, which was reflected in the postponing of ignition and the reduction of the equilibrium temperature. Furthermore, there appeared to be no flames generated when the phenol proportion increased to a specified value. It is supposed that in the methanol/phenol reaction system, reactive intermediates H₂O₂ and HO₂⁻ produced by methanol oxidation were consumed by phenol during the mixture reaction process, leading to less reactive intermediates available for methanol reaction. Consequently, the rate of methanol combustion was suppressed by the addition of phenol. If the supercritical hydrothermal combustion was applied for treatment of organic wastes, the inhibition effect of pollutants on combustion characteristics should be paid special attention.

4. Conclusion

In this work, the kinetics study for hydrothermal combustion of methanol in SCWO reactors was carried out, using a previously developed model for combustion of methanol in order to describe the formation and combustion characteristics of methanol in supercritical water. Two important indicators
ignition and extinction temperatures, which correspondingly are the minimum temperatures associated with start-up and operation processes, were interpreted from the reaction kinetics perspective. It was in favor of reducing the extinction temperature with the higher fuel inlet concentration or the lower injection flow, which could be accounted for by flame front velocities at different conditions. The influence of the initial fuel concentration confirmed that there appeared to be a threshold value for the methanol concentration below which the hydrothermal flame was not available. The variation of oxidation coefficient can’t be ignored, attributing to the fact that oxygen participated in the accumulation of H₂O₂ that played a substantial role during hydrothermal combustion of methanol. The vessel reactor was recommended relative to the tubular reactor for the purpose of obtaining the stable hydrothermal flame with a subcritical inlet fuel temperature. Finally, the auxiliary fuel methanol represents conspicuous enhancement in decomposition of refractory pollutants from two effects: high oxidation heat release and co-oxidative advantage in SCW. Conversely, the reaction of refractory pollutants could suppress the oxidation rate of methanol in SCW, especially for phenol. Even when the phenol concentration was increased to 6.7 wt% with 6 wt% methanol, no flames generated in SCW. Therefore, the presence of refractory organics should be paid particular attention during supercritical hydrothermal combustion of the mixture fuel.

Acknowledgments

This work was supported by the Projects from National Natural Science Foundation (nos. 51406146, 21206132) and Shaanxi Province Natural Science Foundation of China (2014Q2081).

References

