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Kinetics study on hydrothermal combustion of methanol in supercritical water

Jie Zhang[a], Shuzhong Wang[b,*], Donghai Xu[b], Yang Guo[b], Mengmeng Ren[b], Jinling Lu[a]

[a] State Key Laboratory Base of Eco-hydraulic Engineering in Arid Area, (Xi'an University of Technology), Xi'an 710048, Shaanxi, China
[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

ARTICLE INFO

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 H_2O_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.

1. Introduction

Within the last decades, supercritical water (SCW, $T > 374\,^{\circ}C$, $P > 22.1\,MPa$) has been extensively applied from both scientific and technological perspectives. Above its critical point, water acts with unique properties that make it be 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

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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_3O^+ 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; Hirosaka 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, alcohols 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; Hirosaka 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_2SO_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 methylamine (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.			
Reference	Rate expression	A	E_a (J/mol)
Rice et al. (1996)	k [a][MeOH]	5.53×10^{12}	179,000
Tester et al. (1993)	k [a][MeOH]	1.585×10^{26}	408,800
Brock et al. (1996)	k [a][MeOH]	1.995×10^{21}	326,570

[a] $k = A \times \exp(-E_a/RT)$.