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Review

Transpiring wall reactor in supercritical water oxidation

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ABSTRACT

Reactor corrosion and plugging problems have hindered the commercialization of supercritical water oxidation (SCWO) for wastewater purification. The use of transpiring wall reactor (TWR) is an effective means to overcome the above two problems by forming a protective water film on the internal surface of the reactor to aviod contacting corrosive species and precipitated organic salts. This work mainly aims to objectively review experimental investigations and numerical simulation results concerning TWR. Subsequent investigations for parameters optimizations of TWR are also proposed in order to ultimately build effective regulation methods of obtaining excellent water film properties. All this information is very important in guiding the structure design and operation parameters optimization of TWR.

Keywords: Supercritical water oxidation; Transpiring wall reactor; Corrosion; Plugging; Salt deposition

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1. Introduction

Supercritical water ($T > 374.15\,^{\circ}\mathrm{C}$, $P > 22.12\,\mathrm{MPa}$) has some unique properties such as high diffusion coefficiency, very low dielectric constant and viscosity, and small amounts of hydrogen bonds. Supercritical water can be regarded as a benign non-polar organic solvent, which is completely miscible with organic matter and oxygen, leading to no limitation of interfacial mass transfer resistance (Bermejo and Cocero, 2006b; Cabeza et al., 2011). Physicochemical properties of supercritical water have been objectively introduced in detail (Galkin and Lunin, 2005; Kruse and Dinjus, 2007). SCWO is a promising technology to deal with organic wastes, with this technology, organic wastes can be thoroughly oxidized and decomposed into harmlessly small molecular compounds such as CO_2, N_2, water under excess oxidant condition in single-phase supercritical water. Hetero-atoms in oragnic matters are mineralized into corresponding acids or inorganic salts, and the formation of nitrous oxides is inhibited owing to the low reaction temperatute. SCWO is particularly suitable for disposing organic wastewaters with high toxicity, high concentration and bio-refractory components. It can also recover energy and achieve heat self-sufficiency to ensure an economic advangtage (Veriansyah and Kim, 2007; Vadillo et al., 2011). When mass concentration of organic matters in feedstock is in the range of 3–4%, maintaining the whole reaction process commonly does not require an extra energy input process (Gidner and Stenmark, 2001; Griffith and Raymond, 2002). Furthermore, compared with incineration, SCWO does not have the problems of high cost, public resentment and secondary pollutants (Veriansyah and Kim, 2007) like dioxins formation (Kikuchi et al., 2011). Hence, SCWO has attracted much attention in the past three decades. To date, some pilot-scale plants and commercial plants have been employed to deal with different varieties of oragnic pollutants such as wastewaters and sewage sludge (Ma et al., 2003; Marrone et al., 2005; Bermejo and Cocero, 2006b; Marrone, 2013). However, harsh reaction conditions (high temperature, high pressure, excessive oxygen and corrosive ions, etc.) easily induce severe reactor corrosion problems, meaning a shorter reactor life and a poorer treatment result due to the formation of corrosion products. On the other hand, inorganic salts will precipitate in supercritical water due to its extremely low dielectric constant, which will result in reactor plugging owing to their deposition and further causes expensive and frequent shutdowns of the whole SCWO plant. These two key problems are still not effectively solved and seriously hinder the extensive commercialization of SCWO. Thus, pilot-scale and industrial-scale SCWO plants for real wastewater treatments are now still scarce (Marrone, 2013).

Wellig et al. (2009) think that reactor corrosion and plugging problems have to be solved by fluid dynamics and process engineering means utilizing a sophisticated apparatus and a processing. Hodes et al. (2004) also point out that the above problems can be accommodated by system designs and/or operational procedures. Kritzer (2004) reports that corrosion in supercritical water depended on solution properties (like density, temperature, pH value, electrochemical potential) and material characteristics (such as alloy composition, surface condition, material purity, heat treatment). It is difficult to find one material or design which can withstand all feed types under all operation conditions in SCWO (Kritzer et al., 1999a,b, 2000; Brunner, 2009). However, it has been proved that SCWO can be continuously operated for an acceptable period of time via several effective methods to reduce the reactor corrosion rate. These corrosion control approaches include the use of high corrosion resistance material, liner, coating, employing transpiring wall/film-cooled wall reactor, adsorption/reaction on the fluidized solid phase, adopting vortex/circulating flow reactor, pre-neutralization, cold feed injection, feed dilution with non-corrosive wastes, effluent dilution/cooling, and optimization of operation conditions (Marrone and Hong, 2009). It is better to fix reaction conditions such as heteroatom types in feedstock, reaction temperature and pressure in order to select an appropriate reactor material. Generally speaking, nickel-base alloys show a benign corrosion resistance performance under supercritical conditions while titanium is good at subcritical conditions (Kritzer and Dinjus, 2001).

Hodes et al. (2004) have reviewed fundamental principles and studies on salt deposition and control in supercritical water. The options of avoiding reactor plugging include using specific reactor configurations and selecting suitable operation conditions, involving reverse flow tank reactor with a brine pool, transpiring wall reactor, reverse flow tubular reactor, centrifuge reactor, downflow type reactor, fluidized bed reactor, double wall stirred reactor, deep shaft reactor, and transpiring wall reverse-flow tank reactor, adsorption/reaction on a fluidized solid phase, high velocity flow, mechanical brushing, rotating scraper, reactor flushing, additives, low turbulence/homogeneous precipitation, crossflow filtration, density separation, and extreme pressure operation, etc. (Marrone et al., 2004; Brunner, 2009; Bermejo et al., 2006b; Obuse et al., 2006; Xu et al., 2010, 2012). Furthermore, Calzavara et al. (2004) set a moving surface and a stirrer in their reactor for salt deposition on it. Príkopský et al. (2007) install a protective metal sleeve replaced easily to prevent salts from depositing on the internal surface of their axial reactor. However, no one reactor design or operation mean has been proved to be obviously superior to the others in all aspects.

Nowadays, it seems that the most effective approach to overcoming reactor corrosion and plugging is to design an appropriate reactor. Reactor configuration design is considered as the key problem of SCWO commercialization (Brunner, 2009). Although tubular reactor is most widely used due to its simplicity and reliability properties, it is not fit to dispose high salt-containing feedstock or highly corrosive feedstock (Vadillo et al., 2011). Moreover, rapid exothermic reactions may result in uncontrolled hot spots. It is very expensive to coat the high-temperature and high corrosion resistant material on the inner surface of the tubular reactor. Corrosion and plugging problems are still big risks in the real operation, and even make commercial SCWO plants inactive (Marrone, 2013).

Herein, TWR has become a very important selection in SCWO (Kawasaki et al., 2006; Bermejo et al., 2006b; Bermejo and Cocero, 2006a; Gong et al., 2009; Gong and Duan, 2010; Zhang et al., 2011b), which is even regarded as the most promising reactor construction (Kritzer and Dinjus, 2001; Bermejo and Cocero, 2006b). As elucidated in Fig. 1. TWR is mainly composed of a pressure-bearing wall and a porous transpiring wall (a non-load-bearing reaction chamber). It perfectly solves the corrosion and plugging problems by forming a protective transpiration water film on the inner surface of the porous transpiring wall to prevent corrosive species and precipitated salts from contacting the reactor inner surface (Wellig et al., 2005; Zhang et al., 2010; Xu et al., 2010). TWR has a promising future so that many researchers have paid much

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