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Supercritical water oxidation of a model fecal sludge without the use of a co-fuel

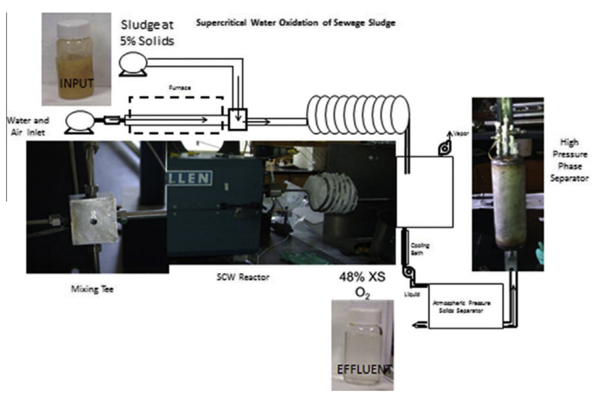
A. Miller [a], R. Espanani [b], A. Junker [d], D. Hendry [c], N. Wilkinson [b], D. Bollinger [c], J.M. Abelleira-Pereira [c], M.A. Deshusses [c], E. Inniss [d], W. Jacoby [a,b,*]

[a] *Chemical Engineering, University of Missouri, United States*
[b] *Bioengineering, University of Missouri, United States*
[c] *Civil and Environmental Engineering, Duke University, United States*
[d] *Civil and Environmental Engineering, University of Missouri, United States*

HIGHLIGHTS

- A new supercritical water oxidation reactor was designed and constructed.
- A factorial design was used to evaluate the effect process variables on oxidation.
- The non-dimensional number N_{Ja} is introduced to evaluate heat transfer efficiency.
- Model feces compounds were fully oxidized by hydrothermal flame.

GRAPHICAL ABSTRACT



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ABSTRACT

A continuous supercritical water oxidation reactor was designed and constructed to investigate the conversion of a feces simulant without the use of a co-fuel. The maximum reactor temperature and waste conversion was determined as a function of stoichiometric excess of oxygen in order to determine factor levels for subsequent investigation. 48% oxygen excess showed the highest temperature with full conversion. Factorial analysis was then used to determine the effects of feed concentration, oxygen excess, inlet temperature, and operating pressure on the increase in the temperature of the reacting fluid as well as a newly defined non-dimensional number, N_{Ja} representing heat transfer efficiency. Operating pressure and stoichiometric excess oxygen were found to have the most significant impacts on N_{Ja}. Feed concentration had a significant impact on fluid temperature increase showing an average difference of 46.4 °C between the factorial levels.

1. Introduction

The conversion of carbon residues into smaller molecules through hydrothermal treatment processes is well documented and numerous review articles have been published noting the accomplishments in the different aspects of processing in this field

* Corresponding author at: 234 Agricultural Engineering Building, University of Missouri, Columbia, MO 65211, United States.
E-mail address: jacoby@missouri.edu (W. Jacoby).

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(Kruse, 2008; Marrone, 2013; Vadillo et al., 2013). The use of supercritical water for processing of these carbon residues has shown promising developments in recent years prompting an increased focus on supercritical water oxidation as a potential wastewater, sludge, or sewage treatment method. Demonstrating this focus is the number of companies who have, or are currently attempting to operate this process at a commercial scale including the Aquacritox process, General Atomics, Hanwha, and SRI International (Marrone, 2013). While interest in the field has spiked, there still remain numerous challenges that require further development. Principal among those are solids feeding, corrosion, salt precipitation, reactor plugging, and, from a commercial standpoint, high upfront capital cost (Marrone and Hong, 2009). The work presented here focuses on development and optimization of solids feeding.

As a basic overview, the development of supercritical water oxidation (SCWO) as a technology has mainly been focused on the destruction of organic wastes. Beyond the critical point of water (374 °C, 22.1 MPa), most organic compounds become soluble; similarly, oxygen is infinitely miscible in water at these conditions. Conversely, many salts that are soluble in liquid water become insoluble at supercritical conditions. The solubilized organic compounds in supercritical water creates a homogeneous reacting fluid, significantly reducing the mass transport limitations, making it an ideal medium for processing. In the absence of oxygen, carbon compounds gasify in supercritical water. In the presence of oxygen, the compounds rapidly oxidize to CO_2 and H_2O. Most of the commercial systems currently in operation generally have a residence times on the order of minutes or less (Marrone, 2013; Tester et al., 1993). The short residence time is due to the conditions that supercritical water provides. Indeed, the high temperature causes the reaction to occur extremely rapidly (Svanström et al., 2004). Furthermore, recent studies into the behavior of hydrothermal flames in SCWO have also demonstrated the capacity to operate at near complete conversion with very short residence times (Bermejo and Cocero, 2006).

Recent work has vastly enhanced the current understanding of hydrothermal flame kinetics through the use of tubular and transpiring wall reactors (Bermejo et al., 2009, 2011). These studies showed autoignition temperatures, corresponding to the existence of a hydrothermal flame, of isopropyl alcohol (IPA) in the range of 450–505 °C resulting in >99% TOC removal at residence times under 2 s. It has also been demonstrated that the hydrothermal flame reaction can be initiated with near-ambient feed injection temperatures with can reduce the occurrence of plugging in the upstream process (Bermejo et al., 2011). Cabeza et al. (2011) extended this work to study the destruction of recalcitrant compounds, acetic acid and ammonia, under hydrothermal flame conditions using isopropyl alcohol as a co-fuel demonstrating that a minimum of a 2% IPA solution must be added to achieve ignition. The hydrothermal flame kinetic regime for IPA feeds has also been described using a modeling process to determine the absence or existence of the flame regime based on inlet conditions and IPA concentration (Quieroz et al., 2013). The model indicates that total destruction of the IPA can be achieved at feed injections as low as 246 °C. The work presented in the current study expands on the knowledge developed by the University of Valladolid by potentially operating under the hydrothermal flame regime without the need of an alcohol co-fuel which is a significant limitation of their work.

In current practice, both commercially and at the bench top scale, a variety of both organics and some inorganics are being processed using SCWO. Of particular interest is the effluent vapor, which consists of CO_2, N_2 and excess O_2, with the NO_x and SO_x going directly to the liquid effluent (Pirkanniemi and Sillanpaa, 2002). Therefore the vapor stream is compliant with most conventional environmental regulations (Kim et al., 2010). SCWO effectively provides a fast, single step conversion process with fast reaction rates. Despite the numerous advantages, it is troubled with several notable challenges. Among those are corrosion and salt deposition (Vadillo et al., 2011). These issues are the focus of various studies (Takahashi et al., 2012; Xu et al., 2010; Stark et al., 2006) and solutions to these challenges are generally in the form of improved materials and pre-treatment methods. These solutions are presented with the caveat that higher strength materials and enhanced pre-treatment significantly add to the cost and footprint of a technology with an already high capital requirement (Griffith and Raymond, 2002). For this reason, abundant feedstocks that require zero or minimal pretreatment, such as feces, are ideal for SCWO.

Rapid conversion of municipal solids waste and similar solid waste streams have become one of the primary areas for focus for supercritical water (SCW) processing technology (Wilkinson et al., 2012). Xu et al. (2012) described the application of this technology to sewage sludge in China demonstrating high rate of conversion (~99%) and at moderate residence times. Li et al. (2013) demonstrated the use of H_2O_2 as an oxidant in treating municipal sludge, identifying effectively full chemical oxygen demand (COD) removal at low oxidant dose. It is well documented that conversion of the organic material in human waste streams is easily accomplished (Vadillo et al., 2013) at supercritical conditions. Significant destruction (>90%) of total nitrogen requires a minimum operating temperature of 540 °C (Gidner and Stenmark, 2001; Augustine and Tester, 2009). The economics of SCWO are less clear. Griffith and Raymond (Griffith and Raymond, 2002) suggest that SCWO technology is economically advantageous relative to other waste treatment processes and that operating at a large scale (9.8 dry tons/day) is important for viability. Conversely, Xu et al. (2012) provide an economic analysis suggesting that per ton treatment, operating at a much smaller scale with correspondingly smaller capital investment can significantly reduce cost.

The number of large-scale SCWO units that are no longer in operation may suggest that operating at a smaller scale could be advantageous (Sobhy et al., 2007). This study seeks to explore smaller scale SCWO (1 kg/h) from an experimental standpoint by using a bench top SCWO unit to destroy simulated feces. These experiments served to define the optimal operating conditions for process variables that will later be used to design and operate a SCWO unit that has a capacity on the order of 100 kg/day of dry solids.

2. Experimental

2.1. Continuous reactor apparatus

A continuous reaction system was designed and fabricated. It has been operated in over 50 experimental runs totaling more than 200 h. A schematic of the system is provided in Fig. 1. The reactor is built from 305 cm of 316 stainless steel tubing with 0.953 cm outer diameter and a 0.515 cm inner diameter. In order to minimize heat loss, the reactor was coiled into rings (12 cm diameter) and covered with fiberglass insulation. The system is plumbed with 316 stainless steel tubing (0.64 cm OD, 0.21 cm ID) directly upstream and downstream of the reactor. Stainless steel was selected for this unit because of its cost effective economics at the lab scale. Corrosion resistant metals will be necessary for commercial applications. Heat is delivered to a stream of compressed air and water by a 60 cm Mellen three-zone split furnace (Model SC12-2). Downstream of the furnace, the now supercritical water and air mixture meets with the waste slurry stream in the mixing tee where the reaction begins. Air, water and waste streams are delivered to the mixing tee using a series of Teledyne Isco syringe