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

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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
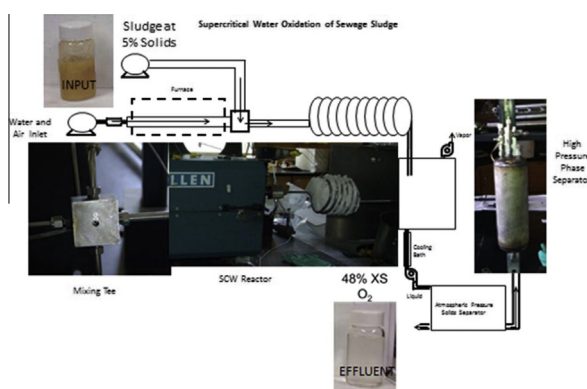
ABSTRACT

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.

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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

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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

pumps (Model 260D). Air and water are fed directly into the system, while the waste stream is delivered via a positive displacement pump that is powered by a syringe pump using the same method demonstrated by Miller et al. (2012). The 316 stainless steel positive displacement pump was custom manufactured by High Pressure (Erie, PA) with a volume of 640 mL. The mixing tee was fabricated in house from 316 stainless steel and threaded with 0.64 cm cone and thread fittings. Eight thermocouples were installed throughout the length of the system; one directly upstream of the mixing tee, one in the mixing tee and the rest throughout the system at 15, 30, 45, 90, 135, and 180 cm from the mixing point.

Downstream of the reactor the temperature of the fluid is reduced to ambient as it travels through a 250 cm long cooling coil of 316 stainless steel (0.64 cm OD, 0.21 cm ID) submerged in an ice/water bath. After the cooling bath, the products enter the first of two separators. Both separators are constructed from 316 stainless steel with volumes of 570 mL each. The first separator is a high-pressure cylinder operating at the pressure of the system from which the liquid effluent is removed from the system. 0.315 cm Swagelok tubing connects the first separator to a metering valve and a pneumatically controlled Equilibar back-pressure regulator (Model EB 1HP1) which allows for continuous removal of liquid and ultra-fine solid particles. The high pressure vapors are metered into the low pressure separator through a Tescom back pressure (Model 26-1722-24) regulator rated for vapor-only streams. Finally, the vapors exit the system through a second Tescom regulator where they are vented out of the system. The effluent gas flow is measured using a dry gas meter (American Meter Company DTM-200A) plumbed downstream of the second separator.

2.2. Continuous reactor operation

The formulation of the simulant was optimized to match both elemental composition and calorific value of actual fecal waste material (Wignarajah et al., 2006). The physiochemical properties and the composition of the simulant can be found in the Supplementary materials. Batches of the simulant were prepared in the lab from a standardized set of ingredients and kept refrigerated at 4 °C until use. Concentration of solids in the mixing tee was calculated using both the water stream pumped into the system as well as the water used in preparation of the simulant. Similar to the process described by Miller et al. (2012) the simulant was manually loaded into the positive displacement pump and fed to the reactor. Oxygen was provided (in the form of compressed air) to the reactor in stoichiometric ratios (determined by TOC) that were equal to, or in excess of, the amount required for full oxidation of the organic fraction of the simulant based on the molecular carbon content of the feed. The (molar) stoichiometric ratio of oxygen was used in the statistical design of the experiments and is referred to as excess oxygen or stoichiometric excess hereafter.

The compressed air and water stream was pumped into the reactor with the simulant feed at set ratios (discussed in Section 2.3) and their combination determined the feed stream concentration. The simulant stream enters the mixing tee at a temperature of approximately 100 °C due to thermal conduction through the tubing and the surrounding insulation from the furnace heat. The supercritical water and air stream enters the mixing tee at the furnace set point temperature. After mixing with the fecal simulant, the temperature of the reaction fluid in the mixing tee varies between 375 and 450 °C indicating that the entire mixture is supercritical. Creating a supercritical fluid instantly has benefits in reaction rate and conversion efficiency (Miller et al., 2012).

To start up the system, the tubing is pressurized with compressed air to between 13 and 15 MPa. Water is then used to increase the system pressure to the operating level (24.1–28.9 MPa). When the operating pressure is reached, the furnace is turned on to achieve and sustain supercritical conditions in the system. Once operating temperature is reached, air and simulant are then delivered to the reactor initiating full operation at SCWO conditions. A TOC analyzer (Shimadzu 5050A) was used to determine the carbon content of the effluent liquid stream. Steady state was determined using two methods, first by the observation of static temperature for longer than 10 min and second, when the equivalent of 2 separator volumes of influent fluid had been processed.
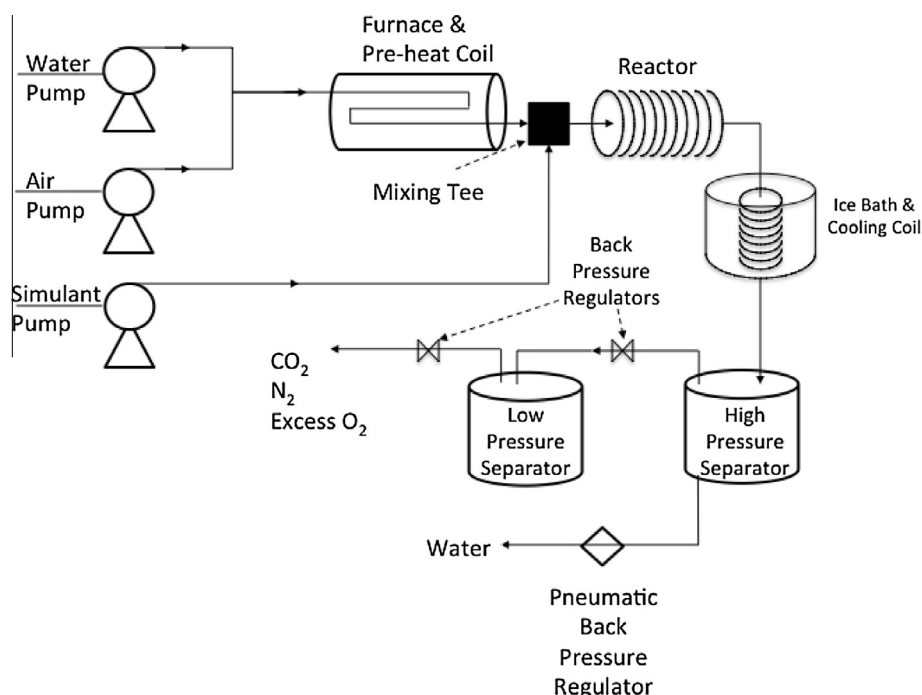

Fig. 1. Schematic of the continuous SCWO reactor apparatus.

When steady state was achieved, fluid temperature and TOC measurements were used to determine performance of the SCWO reaction system. TOC was used directly to determine conversion for the first set of experiments. The effluent was also analyzed with UV absorbance at 546 nm and it was correlated with TOC for determining conversion in the factorial design discussed in Section 3. The maximum fluid temperature in the reactor was measured using thermocouples as discussed in Section 2.1. Again, after achieving steady state, maximum temperature in the reactor was compared with the fluid temperature in the mixing tee. The temperature gain in the reactor is due to the exothermic oxidation reaction and is an important metric indicative of the heat given off by the reaction which correlates to the amount of heat that can be recycled into the preheat stream or used in other process applications.

2.3. Statistical design of experiments

Conversion or conversion efficiency (CE) is a common performance metric associated with chemical reactions, including SCWO. In this study it is defined as one minus the proportion of carbon atoms in the feed that is observed in the liquid effluent (determined by TOC analysis) at steady state, or in other words, the efficiency on a dry, ash-free basis. It is not a sensitive metric in this study due to the length of the reactor and an oxygen supply that is sufficient to achieve full conversion. As a result most measurements displayed statistically full conversion (>98%). In the factorial experiment (discussed in Section 3.1), conversion was determined by UV absorbance as mentioned above. The TOC data from 14 data points was correlated to UV–VIS (Spectronic Instruments, Model 4001/4) absorbance data at a wavelength of 546 nm with a linear correlation with an R^2 value of .954 which allowed to reliably indicate whether or not full oxidation had occurred. Absorbance data were used to confirm complete CE in subsequent experiments reported here.

The second and third metrics studied use direct temperature measurements from the installed thermocouples. The second metric, maximum temperature (T_{max}) observed in the reactor, is straightforward; it is the highest steady state temperature observed in the reactor at each data point. Preliminary SCWO experiments were conducted to determine the distance down the reactor where T_{max} occurred for representative flow rates and concentrations. Thermocouples were installed at those points to ensure accurate observation of T_{max}. The third metric is referred to as fluid temperature increase (ΔT_{fluid}), defined as the temperature difference between the T_{max} and the temperature observed in the mixing tee at steady state. ΔT_{fluid} quantifies the magnitude in temperature gain of due to the exothermic nature of the SCWO reaction. The fourth and final metric measures the efficiency of the heat transfer in the SCWO reaction and is referred to as N_{Ja}. N_{Ja} measures the efficiency of the heat transfer in the SCWO reaction. It is precisely defined as the ratio of two products; in the numerator is the product of the total mass flow rate out of the reactor, the average specific heat of the components of the effluent reacting fluid, and ΔT_{fluid}. In the denominator is the product of mass flow rate of influent solids and the enthalpy of combustion of the product solids. Average specific heat was calculated by using the ideal gas law to calculate enthalpy as a function of temperature. This was combined with the Peng–Robinson equation to estimate the residual properties which was then differentiated to yield the specific heat of the pure species in the reacting fluid as a function of temperature. These specific heats were then combined using the ideal solution assumption. The enthalpy of combustion for the simulant was determined with a bomb calorimeter and has a value 19.88 MJ/kg dry.

$$\text{Conversion Efficiency} = 1 - \left(\frac{\chi_{C,\text{effluent}}}{\chi_{C,\text{solids}}} \right) \times 100\% \tag{1}$$

$$T_{max} = \text{maximum reactor temperature} \tag{2}$$

$$\Delta T_{fluid} = T_{max} - T_{\text{mixing tee}} \tag{3}$$

$$N_{Ja} = \frac{\dot{m}_{\text{total,out}} \overline{C}_P (\Delta T_{fluid})}{\dot{m}_{\text{solids,in}} \Delta H^{\circ}_{\text{combined solids}}} \tag{4}$$

A list of the performance metrics is provided in Eqs. 1–4. Nine experiments were run at a simulant concentration of 4.9% in the mixing tee and using excesses of oxygen between 1% and 68%. Each experiment was repeated, with each repeat being the average of 15–20 independent measurements, to establish reliability of the data. The pre-heat furnace temperature for each experiment was maintained at 600 °C. As the reactor is not located in the furnace (which is the case with most supercritical water gasification studies (Miller et al., 2012; Antal et al., 2000; Hendry et al., 2011), the temperature in the mixing tee was maintained between 400 and 500 °C. This mixing tee temperature is on par with other continuous oxidation studies (Gidner and Stenmark, 2001). It was selected to enable complete conversion and provide a basis for further experimentation. Flow rates were selected in ranges that would achieve turbulent flow in the reactor. The Reynolds numbers for these experiments ranged from 4100 to 4700, ensuring plug flow operation and good radial mixing.

The results of the first set of experiments were used to inform the operating conditions for the second set of experiments. A 2^{4-1}_{IV} factorial experimental design with single replication was performed to evaluate the effect of four variables on ΔT_{fluid} and N_{Ja} (Box et al., 2005). These process variables were selected to provide insight on the optimal operating conditions for continuous SCWO unit operation. The conditions of these runs are described in Section 3.1. The four process variables are: preheat temperature, excess oxygen, operating pressure, and mixing tee concentration.

3. Results and discussion

Fig. 2 shows the results of the first nine experiments designed to inform the levels of the factorial. The figure plots maximum temperature and mixing temperature as a function of oxygen

Table 1
Maximum reactor temperature for increasing concentrations of ethanol and isopropanol data from (Cabeza et al., 2011) compared to the maximum temperature for increasing stoichiometric excess oxygen for the fecal simulant this study.

Feedstock	Concentration (wt.%)	T_{max}
EtOH	0.5	388
EtOH	1	427
IPA	1	440
EtOH	1.5	476
Simulant @ 1% excess	5	495
EtOH	2	511
Simulant @ 5% excess	5	511
IPA	1.5	516
Simulant @ 8% excess	5	537
EtOH	2.5	538
Simulant @ 17% excess	5	539
Simulant @ 28% excess	5	550
IPA	2	566
Simulant @ 38% excess	5	569
EtOH	3	577
Simulant @ 48% excess	5	587
EtOH	3.5	598
IPA	2.5	600
IPA	3.5	631
EtOH	4	634
IPA	4	676
IPA	4.5	708

Table 2a
Operating variables and their levels used in factorial experimental design.

Variable	Symbol	Minus level (−)	Plus level (+)	
Excess O_2	O	30	50	mol%
Concentration	C	5.0%	8%	wt.%, in mixing tee
Pressure	P	24.1	28.9	MPa
Inlet temperature	T_{inlet}	500	600	°C before mixing

excess on the primary vertical axis (left) and conversion based on TOC as a function of oxygen excess on the secondary vertical axis (right). The maximum temperature occurred at the 15 cm thermocouple during each experiment. The experiments in Fig. 2 had a range of residence times between 8.8 and 9.9 s depending on the stoichiometric oxygen excess. At 0% excess (1:1 stoichiometric ratio) conversion of fecal simulant is 94%. It rapidly increases with the stoichiometric ratio reaching conversions between 98% and 100% at 10% O_2 excess and above. Based on standard error calculations, the difference between 98% and 100% conversion is not statistically significant. Therefore, all of these runs achieved effectively full conversion. In terms of the carbon balance the elemental composition of the raw simulant feces contains 44.9% carbon. TOC analysis of the effluents from the experiments in Fig. 2 range from 5.5 to 505 mg/L demonstrating that, for each experiment, almost all of the carbon has been oxidized. Two important conclusions can be drawn from these experiments. First, as air was the selected oxidant for this set of experiments, it can be concluded that air can serve as an effective oxygen source in SCWO processing. Second, low excess oxygen can reliably achieve full feedstock conversion. Both of these conclusions are positive with respect to operating costs and are important in processing applications where destruction of the feedstock is the sole interest (Goto et al., 1998). The results show generally good agreement with literature sources investigating similar applications of SCWO (Bermejo and Cocero, 2006; Garcia-Jarana et al., 2013). It is important to point out that full conversion was not achieved at stoichiometric conditions which deviates from studies using alcohol or other liquid feeds (Marrone, 2013; Bermejo and Cocero, 2006; Quieroz et al., 2013). Mass transport limitations, even under turbulent conditions, may inhibit full conversion at equal stoichiometric ratios for solid and solid slurry feeds indicating a need to operate at stoichiometric excess.

The maximum temperature achieved during each run was used to inform the optimal amount of air to add to the system. Maximum temperature peaks at 49% excess oxygen. This demonstrates that oxygen is the rate limiting species in the SCWO reaction. Consider the data points below 48% excess; it can be seen that while there is sufficient oxygen to achieve statistically full conversion, there is insufficient oxygen to maximize the rate at which heat is generated from the exothermic reaction.

The data points with excess oxygen of greater than 50% show a decrease in maximum temperature. As more air is added to the system, it increases the amount of nitrogen and unreacted oxygen present in the reacting fluid. These species will absorb heat without producing additional energy, effectively reducing the maximum temperature that can be achieved under the specified operating conditions. Optimization of the maximum temperature is a process variable of interest, particularly when implementing heat recycle, which is necessary to achieve autothermal operation. Efficient heat recycle from the high temperature effluent stream to the influent reactants is necessary for a favorable energy balance and scalability of SCWO technology. The reaction system described here, as currently configured, does not incorporate heat recycle. This is discussed in further detail in Sections 3.3 and 3.4.

As mentioned previously, it has been demonstrated that at temperatures above 500 °C, full conversion can be reliably achieved while operating at stoichiometric oxygen conditions for most

feedstocks (Bermejo and Cocero, 2006; Cabeza et al., 2011). In many other studies a co-fuel such as methanol or isopropanol, among others, is used to maximize the temperature when the heat of combustion of a feedstock is too low to generate sufficient temperature for full conversion. In these systems a co-fuel is added to assist with TOC or COD removal and to improve the capacity for heat recycle either through a heat exchanger or a hydrothermal flame regime (discussed in Section 3.1) (Marrone and Hong, 2009; Bermejo et al., 2011; Cabeza et al., 2011). Fig. 2 demonstrates that providing a greater stoichiometric excess of oxygen accelerates the rate of the reaction resulting in a higher value for T_{max}. This suggests that in some cases, excess stoichiometric oxygen can be used in replacement of a co-fuel.

To investigate this concept, experiments were performed to determine T_{max} as a function of ethanol concentration ranging from 0.5 to 4 wt.% at 1:1 stoichiometric excess oxygen ratios. Table 1 compares the maximum reactor temperature for the ethanol experiments including data reported by Cabeza et al. (2011), and the experiments with simulant using increasing stoichiometric excess oxygen. Increasing the stoichiometric excess in the simulant experiments from 1% to 48% resulted in a temperature increase of 92 °C. This is comparable to increasing ethanol concentration from 2 wt.% (511 °C) to 3.5 wt.% (598 °C) and increasing isopropanol concentration from between 1 and 1.5 wt.% to 2.5 wt.%. The Pearson product-moment correlation coefficient (PPMCC) was used to compare the linear correlation between concentration and T_{max} for the alcohol experiments, as well as stoichiometric excess and T_{max} for the simulant data. For ethanol and isopropanol, PPMCC values of 0.996 and 0.975 were observed; a PPMCC value of 0.953 was observed for the fecal simulant showing strong correlation between the two different methods of increasing reaction temperature. This suggests that depending on the feedstock, it may be advantageous to use additional excess oxygen to achieve higher temperatures or faster reactions rather than employing a co-fuel. It is also worth mentioning that using a co-fuel requires supplying oxygen to the system to react with the alcohol in addition to the oxidant for the feedstock, further impacting the process economics.

3.1. Hydrothermal flame regime

The reactor used was not externally heated and the simulant feces was not preheated prior to mixing and entered the system at room temperature and, as mentioned above, is at a maximum of 100 °C when entering the mixing tee. Therefore the temperature increase observed during the reaction was exclusively due to the rapid combustion of the feces in the SCWO reactor. This observation is consistent with the hydrothermal flame reaction mechanism discussed in the literature (Bermejo et al., 2009; Augustine and Tester, 2009; Sobhy et al., 2007). Returning to Fig. 2, it is demonstrated that the difference between the mixing temperature and the maximum temperature exceeded 60 °C in all of the experiments with an average temperature increase of 86.5 °C. As

Table 2b
Detailed standard run order for factorial experiments.

| Standard run order	O	C	T_{inlet}	P
1 & 9	−	−	−	−
2 & 10	+	−	−	+
3 & 11	−	+	−	+
4 & 12	+	+	−	−
5 & 13	−	−	+	+
6 & 14	+	−	+	−
7 & 15	−	+	+	−
8 & 16	+	+	+	+
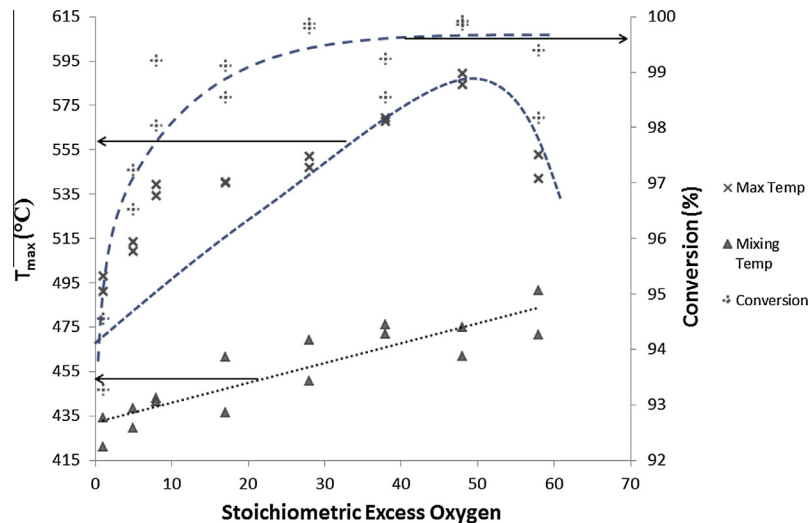
Fig. 2. Maximum reactor temperature, mixing tee temperature and feedstock conversion (conversion was calculated by TOC data) as a function of stoichiometric oxygen excess. The dashed lines are visual aids to distinguish the trends and not regressions or models. The arrows indicate the axis to which the data corresponds.

mentioned above, the maximum temperature occurred 15 cm into the reactor for each experiment, indicating that autoignition took place within 0.43 s and 0.49 s of residence time.

Studies on hydrothermal flames primarily indicate high temperature, short reaction times (50–500 ms), or in limited cases visual observation (Augustine and Tester, 2009) as evidence of flame. A comprehensive criteria for the existence of hydrothermal flame is currently absent from the literature with short reaction time being the primary metric consistent over all relevant studies (Bermejo et al., 2009, 2011; Cabeza et al., 2011; Augustine and Tester, 2009; Serikawa et al., 2002). Despite the lower temperature increase relative to other studies (Bermejo et al., 2011; Cabeza et al., 2011) due to the lower calorific value of the feedstock, the short residence time to the observation of autoignition and the rapid temperature increase likely indicate the presence of a hydrothermal flame.

3.2. Factorial design

Tables 2a and 2b present the process variables, the different levels at which the factorial experimental design was conducted, and the standard order of the runs (not necessarily the order in which they were conducted). The process variables include excess oxygen supplied to the system, concentration in the mixing tee, system pressure and inlet temperature referring to the temperature of the SCF mixture of water and air entering the mixing tee. The 2_{IV}^{4-1} design calls for 8 experiments, (eight sets of conditions, each with replicate runs) which allows quantification of the magnitude of the effects of the four operating variables. This forms the basis for determining which effects are statistically significant to the reaction (Box et al., 2005). The uncertainty calculations are based on standard error, which is estimated by calculating the pooled variance. These values are included in Fig. 3. Effects that are less than the standard error are considered unimportant within the scope of the factor levels provided in Table 2. Figs. 3a and 3b displays magnitude effect plots for the factorial response metrics. These plots show the sign and magnitude of each main effect relative to the overall average for that specific effect in the experimental design. For example, consider the second bar in Fig. 3a which provides the effect of solids concentration (C) on the reactor temperature increase. This figure indicates that the average effect of going from the minus level (4.9% solids in the mixing tee) to the plus level (7.8%) is to increase ΔT_{fluid} by nearly 50 °C.
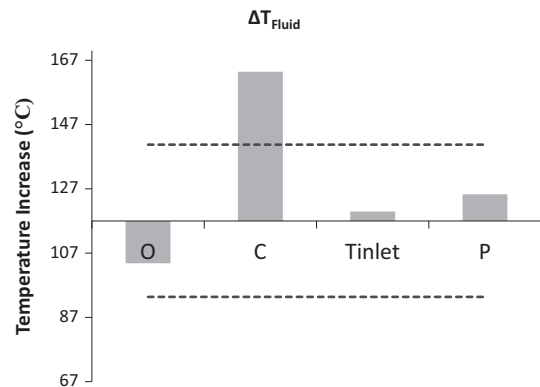
Fig. 3a. Values of the deviation from the mean due to the main effects are shown relative to the standard error (represented by the dashed lines) for fluid temperature increase.
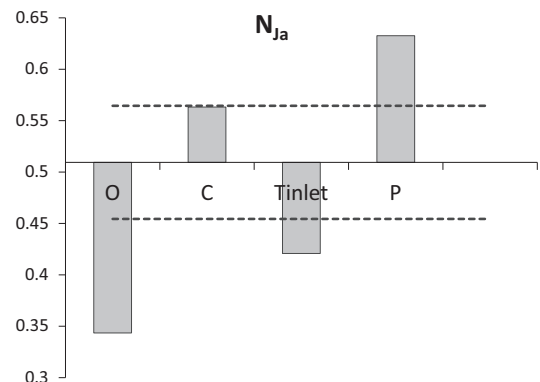
Fig. 3b. Values of the deviation from the mean due to the main effects are shown relative to the standard error (represented by the dashed lines) for N_{Ja}.

3.3. Interpretation of results

As mentioned above, Figs. 3a and 3b plots of the magnitudes of each of the factorial responses. Fig. 3a indicates the effect of the variables on ΔT_{fluid}. Fig. 3b indicates the effect of the variables on the dimensionless number N_{Ja}.

3.3.1. Fluid temperature increase

Fig. 3a demonstrates that increasing the solids content of the waste undergoing treatment is the only variable studied that has a statistically significant impact on the ΔT_{fluid} within the range of the experimental conditions. The magnitude of this impact is worth noting. As shown in Table 2, the difference in the plus and minus levels in concentration is 2.9%. This led to a large temperature increase of 46.4 °C.

Conversely, stoichiometric oxygen excess (O), inlet temperature (T_{inlet}) of the SCF mixture of water and air, and pressure (P) effects were on the level of the noise. Again, the simulant was not preheated. For both inlet temperature and pressure, these were the expected results. As suggested by (Serikawa et al., 2002), above the ignition temperature, the SCWO reaction will proceed spontaneously. By conservation of energy, after nearly complete conversion, no different heat of reaction should be observed. Therefore, inlet temperature was not expected to have an impact on the fluid temperature increase.

Increasing excess oxygen from 29% to 48% stoichiometric excess had a slightly negative, although not significant effect on fluid temperature increase. This is not a surprising result because at these oxygen-loading levels, conversion is complete (>98%). In theory, adding additional oxygen (air) above 29% would diminish the energy balance because of the addition of so much extra nitrogen, which has no positive effect on the exothermic reaction. This is consistent with the results, even though the effect did not appear to be significant.

3.3.2. N_{Ja}

N_{Ja} is a metric that is introduced in this paper in order to provide insight into the magnitude of the efficiency of heat transfer from the reactants into the supercritical reaction fluid. From the definition of N_{Ja} in Eq. (4), we can see that it is theoretically limited at a value of 1 based on the full combustion of the feedstock. In practice, this value is unlikely to be observed due to heat losses to the surroundings. The study presented here shows values of N_{Ja} in the range of .35–.65 indicating moderate to significant heat loss to the reactor walls and insulation. The calculation of N_{Ja} is highly sensitive to the value of the average specific heat of the reacting fluid. Therefore, N_{Ja} is best used as an optimization metric within a SCWO system rather than absolute comparison between separate SCWO systems, which may significantly vary flow, rates, oxidants, and feedstocks.

Studies on supercritical water gasification (SCWG) have determined that pressure variation between 22 MPa and 33 MPa does not have a significant effect on gasification (Hendry et al., 2011). Unlike gasification, pressure was determined to have a statistically significant, positive impact on N_{Ja}. Fig. 3b shows that when increasing pressure from 24.1 MPa to 28.9 MPa, an increase of .123 was observed in N_{Ja}. The reason for this is primarily due to the properties of supercritical water in the temperature and pressure ranges under consideration. At the critical temperature SCW at 24.1 MPa (minus level) and 28.9 (plus level) have approximate densities of 580 kg/m^3 and 600 kg/m^3 respectively. Above the critical point, the density of water decreases rapidly until 410 °C at which point the rate of decrease in density drops off. Above 500 °C, the rate of decrease in density becomes stable for the range of pressures between the critical pressure and 35 MPa (Pioro and Mokry, 2011). Fig. 4 displays the increase in the temperature due to the combustion reaction as the fluid travels down the reactor for a representative number of the factorial experiments. From Fig. 4 it can be seen that the combustion reaction causes an increase in fluid temperature through the range in which the density of water is highly dynamic. Each of the 5 representative temperature profiles passes through 480 °C. At 480 °C, the density of water at 28.9 MPa (plus level) is approximately 30 kg/m^3 higher than at 24.1 MPa (minus level). This difference becomes exponentially greater below 480 °C. As the pressure is increased from the minus level to the plus, the fluid becomes significantly denser at the temperature ranges observed due to the thermophysical properties of supercritical water. As a result, the heat transfer properties of the reaction fluid are correspondingly enhanced. This increases the efficiency with which heat generated in the SCWO reaction is transferred to the supercritical fluid reaction medium resulting in an increase in N_{Ja}.

Stoichiometric oxygen excess and inlet temperature both showed statistically significant, negative effects on N_{Ja}. When increasing the stoichiometric excess from 29% to 48%, N_{Ja} drops by 0.165. Since the selected oxidant was air, when the stoichiometric excess oxygen supply is increased, the amount of nitrogen supplied to the system is similarly increased resulting in greater mass to which heat will be distributed. The heat distributed to the nitrogen and excess oxygen reduces the overall potential for
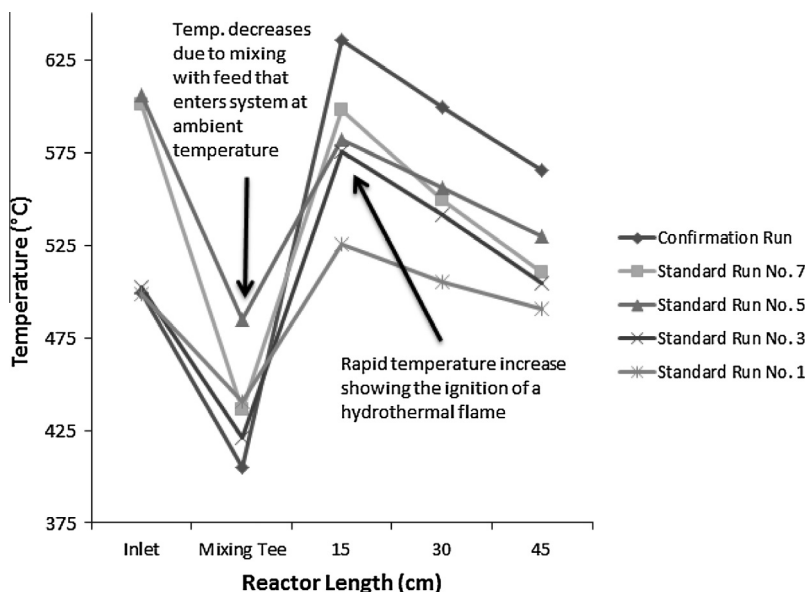

Fig. 4. Temperature profile for representative factorial runs and the confirmation run in the plug flow reactor between T_{inlet} and the thermocouple at 4 cm.

temperature gain, which subsequently limits N_{Ja}. N_{Ja} drops by 0.09 when increasing the inlet temperature from 500 °C to 600 °C. As mentioned above, the density of supercritical water is dynamic in the temperature ranges studied. The difference in density of SCW between 500 °C and 600 °C is decreasing but remains within the same order of magnitude and that can be correspondingly associated with the heat transfer properties of the fluid. As a result, we see a modest, but statistically significant decrease in N_{Ja} when increasing from the minus inlet temperature to the plus inlet temperature.

The main effects of the fourth process variables, concentration (C) was on the level of the noise and therefore did not have a statistically significant impact on N_{Ja} in the experimental space explored.

3.4. Factorial confirmation run

A confirmation experiment was performed at conditions that the factorial design indicated would yield higher values for ΔT_{fluid}, and N_{Ja}. As indicated by the results of the factorial experiment, concentration in the mixing tee was increased to 12% solids, stoichiometric oxygen excess was reduced to 20%, pressure was increased to 30.3 MPa and T_{inlet} was held at the lower factorial level of 500 °C. The observation of T_{max} was among the highest in the entire study and the factorial responses were the highest seen in the study. T_{max} reached 635 °C (Fig. 4) which was more than 40 °C higher than the other experiments with T_{inlet} at 500 °C. The fluid temperature increase was 230 °C, more than 70 °C higher than any other experiment in the entire study. N_{Ja} also showed a significantly increased response of 0.893, 16% higher than the best yield from the original factorial design experiment. This confirmation experiment reinforced the factorial results showing process improvement for all the response metrics.

Acknowledgment

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2015.06.076.

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