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Supercritical Water Oxidation: Testing of Ersatz Wastewater

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Supercritical Water Oxidation (SCWO) technology is under consideration by NASA for treatment of wastewater and other wet waste streams. The dramatic changes in water's thermophysical properties near its critical point (374°C and 22 MPa) result in nearly complete solubility of organics and gases. The absence of inter–phase transport processes and phase separation results in dramatically reduced reaction timescales and the elimination of complications of two–phase transport and processing in reduced gravity. Other advantages are that the product streams are microbially inert,benign, amenable to resource recovery and organic waste

This paper first described the design and construction of tubular SCWO reactor built at NASA Glenn. It consists of separate wastewater and oxidizer inlets, which are independently heated and pressurized to conditions approaching the critical point of water. These flows enter a reactor chamber having a volume of 62 ml. The reactor section is heated to the desired temperature in the range of 450 °C – 650 °C. A pressure regulator maintains the operating pressure nominally between 27.6 MPa and 28.3 MPa. The reacted fluid is captured downstream of the pressure regulator during an experiment run. A separate vent line may also be used for collection of the effluent. Next, the results of SCWO experiments using both a representative organic (ethanol) as well as a wastewater simulant provided by NASA Ames are presented. Raman analysis of the pre–reacted and post–reacted solutions are presented. Finally, initial efforts on supplementary chemical kinetics modeling of ethanol oxidation with and without inclusion of a nitrogenous compounds (ammonia) are presented.

Keywords: supercritical water oxidation, wastewater, Raman, high pressure, water reclamation

I Introduction

THE drive toward effective closure of life support systems for extended duration space missions will be enabled by technologies that allow resource reclamation from the air, water, and waste streams. Regenerative systems such as those designed to grow plants for food will require extensive resource reclamation (e.g., carbon dioxide, water and plant nutrients) from bio-waste streams in order to be practicable. Supercritical Water Oxidation (SCWO) is a

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process where organic compounds can be efficiently oxidized in water above its critical point at 647.3 K (374.1°C) and 22.1 MPa. Under these conditions, organic compounds and gases become completely soluble in water leading to extremely high reaction rates between dissolved oxygen and organic materials. SCWO is considered a "green" technology because of its ability to recover energy and reclaim water from wet waste streams without producing pollutants such as NO_x or SO_x, which require further scrubbing. The primary products of oxidation are carbon dioxide and water with the inorganic material precipitated out of solution as salt or converted into oxides which can readily be separated from the effluent stream.

The primary objectives of the work described in this paper were: to (i) design and construct a tubular SCWO reactor for the oxidation of an ersatz waste water sample provided by NASA Ames, (ii) perform the necessary operational checkouts of the reactor using a representative organic constituent (ethanol), (iii) perform SCWO of ersatz waste water representative of waste streams from the International Space Station and (iv) obtain an understanding of the chemical kinetics of SCWO oxidation of organic streams containing nitrogen compounds.

II Motivation for Work

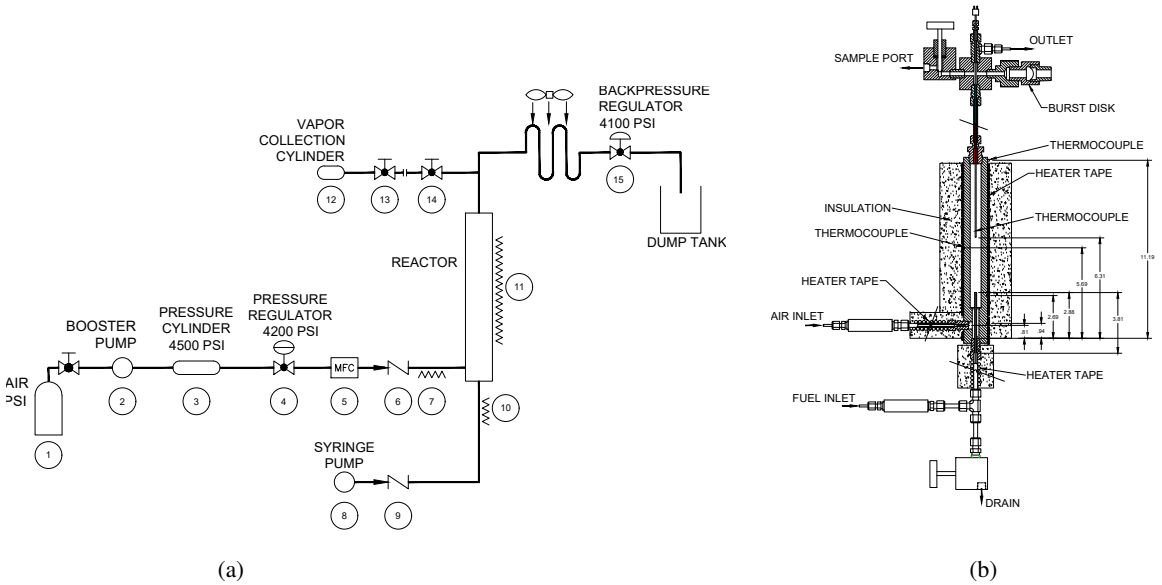
SCWO is a technology in which wastewater or a "slurry processed" waste stream, with entrained solid contaminants, is introduced into a reactor vessel at temperatures and pressures above the critical values of water (i.e., 374 °C and 22.1 MPa). At levels above water's critical point, distinctions between liquid and solid phases no longer exist and gases (e.g., O_2 , N_2 , CO_2) and organic material become highly soluble in water. In typical SCWO operating conditions (e.g., from 450 °C to 550 °C and at pressures of 25.3 MPa) oxidation of carbonaceous waste consistently exceeds 99.99% with reactor residence times often well under one minute. High destruction efficiencies for a wide range of compounds at relatively low temperatures (400 °C to 550 °C) have been demonstrated with reactor residence times on the order of seconds. This is largely due to the dramatic changes in the thermophysical properties of water, when transitioning from sub-critical to supercritical, resulting in reductions in diffusive time scales governing thermal, mass and momentum transport within the reactor. At supercritical conditions these diffusive time scales are similar to that of a dense gas. Additionally, because of the depolarization of the water molecule at supercritical conditions inorganic salts (e.g., NaCl , $MgCl_2$, $CaCl_2$) become insoluble and begin to precipitate out as solids.[1,?] For example, NaCl at ambient conditions (i.e., 25 °C and 1.0 atm) has a solubility of approximately 30% by weight, whereas at supercritical conditions (i.e., 600 °C and 250 atm) the solubility reduces to less than 0.003% by weight. This technology, when operated in the appropriate regime, has the potential to separate inorganic material, oxidize essentially all organics, and eliminate all microbial contamination. The product stream, depending on the constituents of the feed stream and operating regime, will typically consist of CO_2, N_2, water, inorganic precipitate, and mineral acids (from organic sulfur, phosphorous, halogens).[3,5]

The primary advantage of SCWO is the ability to carry out oxidative reactions at very high reaction rates on organic contaminants in *wet waste streams*. This includes waste streams ranging from gray water to slurries heavily loaded with mixtures of organic and inorganic solids. SCWO is an attractive candidate technology for processing solid and liquid wastes for long duration space and extra-terrestrial planetary missions because (i) pre-drying of waste is not required, (ii) product streams are benign, microbially inert, and easily reclaimed, (iii) waste conversion is complete and relatively fast, and (iv) with proper design and operation, reactions can be self-sustaining. In addition, because of the absence of inter-phase reactant transport due to the single phase nature of SCWO reactions, reaction timescales are greatly reduced and many of the complications associated with two-phase transport and processing in reduced gravity environments are eliminated.

III Experimental Setup A. Hardware Description

The design of the SCWO reactor used for the experiments described in this work, referred to as the Advanced Exploration Systems (AES) SCWO Reactor, was based on the design heritage of a number of laboratory scale SCWO reactors built by NASA Glenn Research Center.[2] A schematic of the AES SCWO Reactor infrastructure is shown in Figure 1a and Table 1 along with details of each of the significant components. The infrastructure can be thought of as comprising four main sub-systems; these being, (i) the oxidant (in this case, air) supply sub-system, (ii) the a fuel injection subsystem, (iii) the reactor sub-system and the (iv) collection sub-system. Air (21% O_2 with balance N_2) is used as the oxidant for all the tests reported in this work. However, there is nothing that prevents a variety of oxidants from being used in this system, such as gas mixtures with diluents other than N_2 containing *lean* to *rich* concentrations of O_2 or even liquid oxidants, such as solutions of hydrogen peroxide. The air supply sub-system relies on a booster pump to increase the pressure of the air from the supply tank (typically a K-Bottle) to the required operating pressure

of the reactor. Based on the current operating limits of the burst disk and the temperature limit controls, the Maximum Design Pressure is 34.5 MPa (5,000 psia) with a Maximum Design Temperature of 593 °C. Based on the burst disk and temperature controls, the Maximum Operating Pressure is 28.3 MPa (4100 psia) and the Maximum Operating Temperature is 575°C (1,067 °F). The air supply sub-system uses a Mass Flow Controller that is capable of delivering steady flow rates from 0.5 slplm to 5.0 slplm at pressures up to 34.5 MPa (5,000 psia).



(a) (b)

Figure 1: The Advanced Exploration (AES) SCWO Reactor used for water reclamation studies, (a) the support infrastructure with a desription of the system hardware and (b) a sketch of the AES SCWO reactor showing orientation of reactor feed lines, reactor test section, thermocouple placements, heating elements and thermal insulation.

Hardware Description	
1.	K bottle, compressed air
2.	Booster Pump , 3/8” NPT inlet, 1/4” NPT outlet, 55.1 MPa (8000 psi) rating
3.	Storage Cylinder, 1/4" NPT inlet and outlet, 34.5 MPa (5000 psi) 5000 psi rating
4.	Pressure Regulator, 1/4" NPT inlet and outlet, 0-41.3 MPa (0-6000 psi) range
5.	Mass Flow Controller, 1/4" tube inlet and outlet, 34.5 MPa (5000 psi) rating, 0.5 to 5.0 slpm range
6.	Check Valve, ¼" NPT inlet and outlet, 96.2 MPa (13950 psi) rating
7.	Heater Rope, 3 ft. long, 125 W, 120 VAC, 482 °C (900 °F) rating
8.	Syringe Pump, 500 HP, 1/8" tube outlet, 507 ml capacity, 34.5 MPa (5000 psi) rating
9.	Check Valve, ¼" NPT inlet and outlet, 96.2 MPa (13950 psi) rating
10.	Heater Rope, 3 ft. long, 125 W, 120 VAC, 482 °C (900 °F) rating
11.	Heater Tape, 8 ft. long, 624 W, 120 VAC, 760 °C (1400°F) rating
12.	Sample Cylinder, ¼" NPT inlet, 50 cc capacity, 12.4 MPa (1800 psi) rating
13.	Needle Valve, ¼" NPT inlet and outlet, 20.7 MPa (3000 psi) rating
14.	Needle Valve, ¼" NPT inlet and outlet, 51.5 MPa (7465 psi) rating
15.	Backpressure Regulator, 1/8" NPT inlet and outlet, 0 to 5000 psi range

Table 1: Hardware components for the AES SCWO Reactor.

The fuel injection sub-system relies on a large 507 ml “syringe pump" (i.e., a high pressure Teledyne piston pump) to supply the liquid “fuel", or for purposes of these tests, the contaminated water, to the reactor and is capable of delivering very precise flows ranging from 0.01 ml/min to 10.0 ml/min. Each of the injection lines is heated with separate controllers so that both the air and fuel injection streams are separately heated up to near critical temperatures. The air enters through the side port, at the bottom of the reactor and the “fuel" (i.e., the alcohol solution or ersatz waste water) enters through the bottom fitting. The fuel does not enter the reactor core until 3.0 in. above the base of the reactor.

With the relative positioning of the two inlet ports, an annular axisymmetric flow configuration is established at the exit plane of the fuel line. Figure 2 illustrates this configuration showing the entrance into the reactor of the two separate reactant streams. The oxidizer stream (air) enters the reactor from the side port and the fuel enters the reactor from the bottom port. Reactant mixing does not begin until approximately 7.3 cm (2.8 in.) from the base of the reactor. A mixing region will precede the reaction region for a certain distance downstream of the fuel's exit plane, depending on the reactant temperatures, injection velocities, reactivity of the waste stream and degree of turbulent and/or diffusive mixing.

This particular injection configuration would greatly benefit from optimization based on a number of factors such as injection velocities, injection temperatures, reactor temperature and pressures, fuel type and possibly a host of other parameters. However, the focus of this work was not the development of an optimized injection and/or ignition system for a SCWO reactor but rather the determination of the SCWO conversion efficacy of typical waste water contaminants as a function of the aforementioned parameters.

The SCWO Test Cell is a *tube reactor*, comprising the *reactor sub-system* Figure 1b, and was machined from an Inconel rod, with a total reactor volume of 62 ml. A thermocouple extends through an adapted fitting at the top of the reactor and registers temperatures in the predominant reaction region. This thermocouple provides the best real-time indication of the presence and extent of the oxidative reactions.

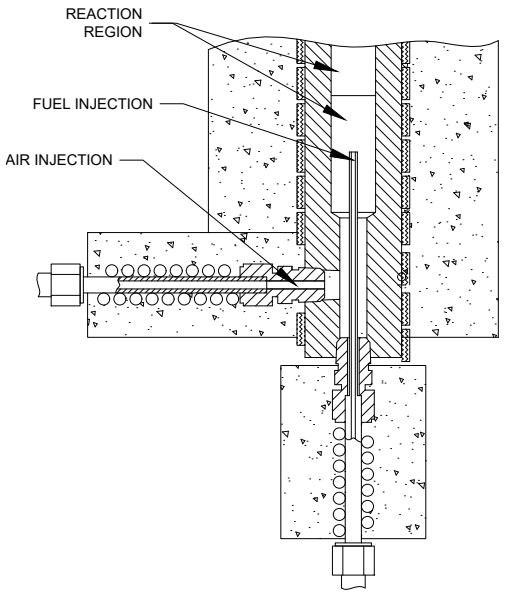


Figure 2: Illustration of the injection configuration of the two reactant streams; oxidizer (air) entering from the side port and the “fuel" solution entering the reactor from the bottom port. Each injection line is equipped with separately controlled heating elements.

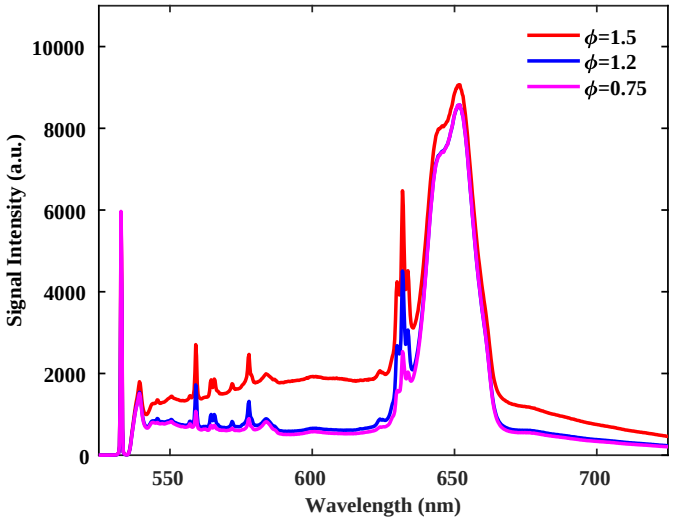
Finally, the *sample collection sub-system* consists of two methods for sample collection, depending on whether the sample is liquid or vapor. Liquid samples are collected by allowing the product stream to completely depressurize and cool to ambient conditions. The cooling occurs through a coiled heat exchanger prior to passing through the back pressure regulator at which point the product stream is depressurized and the condensibles are collected in a dump tank. The vapor sample is collected upstream of the cooling coil and back pressure regulator by attaching an evacuated 50 ml sample cylinder to the outlet valve.

To date, no buildup of salt precipitate has been observed in the reactor. The concentration of salts in the diluted wastewater is small (<0.5% total). It is therefore likely that any salt precipitating in the supercritical fluid region is not agglomerating, and thus not depositing in any noticeable amount on the walls of the reactor. Most of the salt is presumably exiting with the fluid stream and redissolving downstream of the depressurization point.

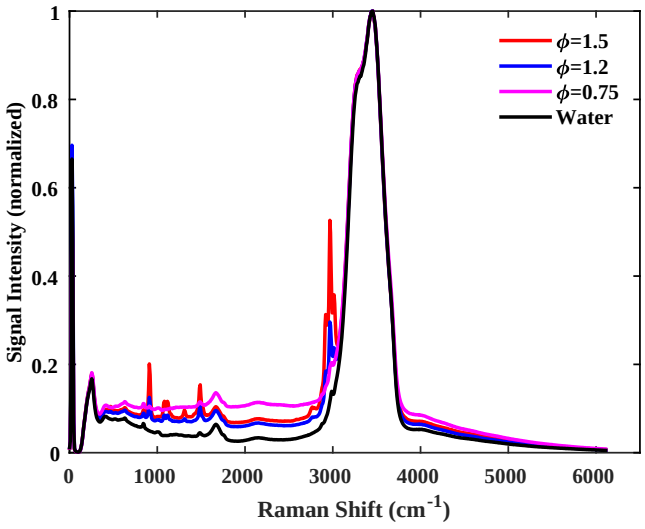
A Experiment Procedures

Prior to the start of each test the reactor is heated and filled with air to the appropriate target pressure, nominally 27.6 MPa (4,000 psia). Once the reactor has been pressurized with air, the temperature set point used by the Labview logic for controlling the cell temperature, is increased in increments of ∼100 °C. This staged heating continues until the "bulk fluid" temperature (T_B), as measured by the inserted thermocouple aligned with the center of the reactor, Figure 1b, reaches the target test temperature. The target test temperature for initial tests was ∼450 °C but for subsequent tests with ethanol and wastewater simulant was typically around 525 °C.

The line heaters for the air and the "fuel" (aqueous ethanol solutions or ersatz wastewater) are then activated by setting the appropriate temperatures (typically near the critical point of water, between 350 °C and 375 °C) for the injected reactant streams. Once temperatures and pressures in the reactor reach the operating conditions, the air stream flow, from the side inlet port, is initiated by entering the desired flow rate, nominally from 0.5 slpm to 5 slpm.



(a)



(b)

Figure 3: Raman shift following SCWO conversion (a) without "min/max" normalization and (b) with "min/max" normalization for a fixed flow rate of fuel (C_2H_5OH(aq)50%) at 2.0 ml/min and varying fuel equivalence ratios, ϕ = 0.75, ϕ = 1.2 and ϕ = 1.5 based on different air flow rates.

After air flow has been initiated the fuel flow rate is specified on the piston pump and the fuel flow is initiated. The test commences once fuel flow is initiated and sample collection typically begins once near “steady conditions" are achieved in the reactor. Adjustments are made to the reactor heater, as needed, in order to maintain cell temperatures at the target test temperature. Depending on the rates of flow for the two reactant streams and the concentration of the fuel, the heating power to the reactor is adjusted downward. It is of interest to note, that under some test conditions, heating power to the reactor was completely shut off and heating power to the inlet lines had to be decreased in order to maintain temperatures at the target reactor temperature due to the energetics of the SCWO reactions. This is discussed in greater detail in Section IV.

IV Results and Discussions

The following discussion is separated into three sections, the first two of which discuss the actual experiments performed. The last section is devoted to a discussion of the results of preliminary efforts on developing the chemical kinetics of a limited class of SCWO reactions relevant in the conversion of ISS wastewater. Detailed chemical kinetics are only available for a few of the various contaminants that are listed in Table 2, which is an ISS wastewater model developed at Marshall Space Flight Center.

At present, chemistry modeling has been limited to ethanol solutions (the key organic contaminant in ersatz wastewater), and ammonia, the decomposition product of hydrolyzed urea and ammonium bicarbonate. To date, chemical kinetic calculations using ethanol solutions have been completed and are briefly presented in Section

A SCWO Conversion of Ethanol Solution

A series of SCWO experiments were initially conducted using only ethanol-water solutions at three different ethanol concentrations; i.e., 10, 30 and 50 %. The purpose of these tests was twofold, (i) to verify the performance of and operating procedure for the new AES reactor design and (ii) to measure the extent of oxidation occurring as a function of temperature and pressure. Evidence of a sensible temperature rise due to the heat-of-reaction from oxidation was obtained.

Raman signals for three cases, with the fuel (C_2H_5OH (aq) 50%) flow rate held constant at 2.0 ml/min and the air flow ranging from 2.0 slpm, 2.5 slpm and 4.0 slpm are shown in Figure 3 for the raw data (a) before applying a “min/max" normalization and (b) after applying a “min/max" normalization. In this normalization, each Raman spectrum is normalized between 0 and 1. As a comparison, the Raman shift is shown for pure water overlaid on the normalized Raman shift for each of the ethanol solutions that were oxidized at supercritical water conditions. As one would expect, the lower the equivalence ratio (amount of “excess" fuel relative to the stoichiometric oxygen) the weaker the intensity of the observed Raman shift for ethanol, suggesting that a higher percentage of the alcohol is oxidized due to increased availability of oxygen per unit of fuel. This trend is displayed by observing a consistent decrease in Raman signal intensity for the dominant Raman shift of ethanol, as seen at the wavenumber of 3,000 cm^{-1}.

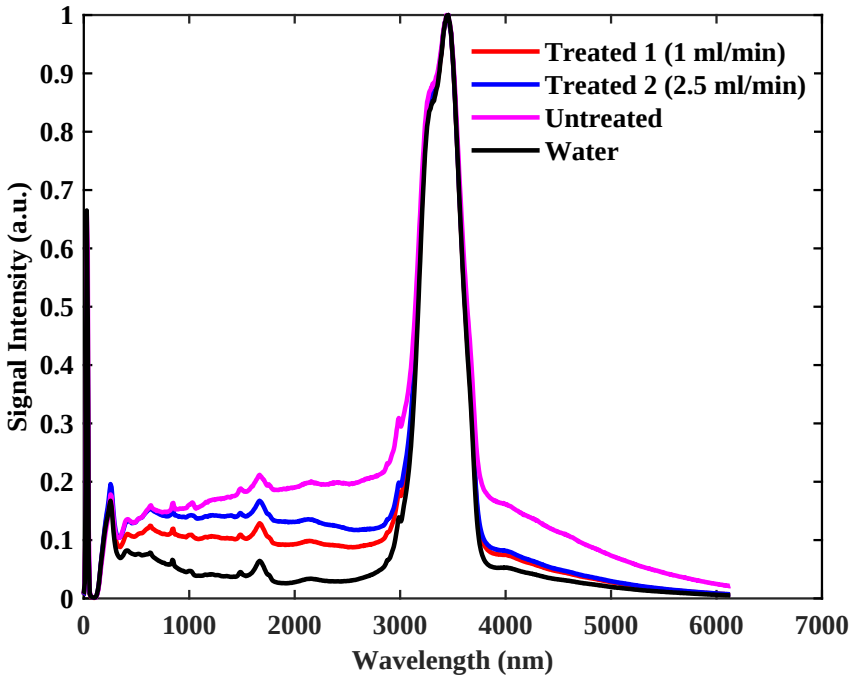


Figure 4: Plot of Raman shift from two treated samples with different fuel flow rates (1 ml/min) and (2.5 ml/min) compared with the Raman shift of pure water and untreated ersatz wastewater.

For the case where the air flow rate relative to the fuel flow rate results in an equivalence ratio less than one, the Raman shift at 3,000 cm^{-1}essentially disappears, indicating that all of the ethanol has been oxidized. It can be concluded that for this particular reactor configuration (i.e., temperature, pressure, reactor residence time and reactant mixing) the oxidation of ethanol in supercritical water is complete.

It is interesting to note that for wave numbers less than 3,000 cm^{-1} the spectral profile shows a reversal in the Raman shift profile. That is, in this lower wave number region, the test with a 4.0 slpm air flow (equivalence ratio of 0.75) shows a higher Raman shift intensity profile than that for the lower air flows, at 2.0 slpm and 2.5 slpm (equivalence ratios of 1.5 and 1.2, respectively). One explanation may be that because of the different levels of ethanol in the Raman samples both the energy from the excitation laser, incident on the probe volume, as well as the energy from the excitation laser that is scattered into the detector may be different. That this occurs is clear from the relative intensities of the excitation laser line (532 nm).

B SCWO Conversion of Ersatz Waste Water

The contaminants and their relative concentrations in the ersatz wastewater are listed in Table 2. Ethanol, as previously noted, is the organic compound with the highest concentration. Of the listed compounds, alcohols, siloxanes and urea are of particular interest because of the difficulty of removal with other technologies under consideration, e.g., reverse osmosis and distillation.

For the experiments described, the wastewater concentrate was partially diluted with two parts of distilled water to one part of the concentrate (i.e., 1 liter of the concentrate was diluted to 3 liters). This still results in a much higher concentration of contaminants compared to the expected concentrations, which are achieved by diluting 1liter of the concentrate to 15 liters. The reason for doing so, at least for the initial tests, was to see if the oxidation of the organics yielded a sensible temperature rise in the reacting stream due to their exothermic oxidation reaction. This may have some implications in making the system more energy efficient.

The min-max normalized Raman spectra for the untreated and SCWO treated water are shown in Fig. 4. The two treated cases were for water flow rates of 1 ml/min and 2.5 ml/min and for an air flow rate of 0.5 slpm. As with the ethanol cases, the main water peak at 3200 cm^{-1} is reproduced equally for all cases. At the higher wavenumbers beyond approximately 3700 cm^{-1} both of the treated waste water spectra follow the pure water spectrum closely whereas the untreated wastewater spectrum falls off more gradually. A similar behavior is observed at the lower

wavenumbers below approximately 3100 cm^{-1}. It is interesting to note that, similar to the well oxidized ethanol-water case, the background spectral levels of the treated wastewater are higher than that of the pure water.

Liquid Chemicals	**Solid Chemicals**	
	Organic Concentrate	Inorganic Concentrate
Propylene Glycol	Benzoic Acid	Potassium Chloride
Ethanol	Caprolactam	Ammonium Bicarbonate
Acetone	Urea	Sodium Fluoride
2-(2-butoxyethoxy) Ethanol (DGME)		Potassium Iodide
N,N-Dymethylformide		
2-Ethoxyethanol		
1-Methyl-2-Pyrrolidinone		
2-Propanol		
1-Propanol		
4-Ethylmorpholine		
Formic Acid		
Lactic Acid		

Solid Chemicals	**Amt. Req. in 4 L(g)**
Zinc (II) Acetate dihydrate	0.57
Nickel (III) Acetate tetrahydrate	0.2114
Liquid Chemicals in Acetate Concentrate	**Amt. Req. in 4 L(mL)**
Acetic Acid	12.875
Liquid in Direct Addition Concentrate	**Amt. Req. in 4 L(mL)**
Benzyl Alcohol	0.368
Diethylphthalate	0.121
Trimethyl Silianol	0.038
Benzothiazole	0.013
2-Ethyl-1-Hexanol	0.029
Decamethylcyclopentasiloxane (d5)	0.062
Dodecamethylcyclohexasiloxane (d6)	0.060
Octamethylcyclotetrasiloxane (d4)	0.061
Dimethoxydimethylsilane	2.106
Solid Chemicals in Direct Addition Concentrate	**Amt. Req. in 4 L(g)**
Calcium Sulfate	0.11551
Dimethyl Sulfone	0.01224
Hexamethylcyclotrisiloxane (d3)	0.06122
Phosphate Addition	**Amt. Req. in 60 L tank(g)**
Monobasic Potassium phosphate	0.05

Table 2: Ersatz wastewater used for SCWO testing.

This aspect will be studied further in future studies by considering: (i) the behavior of the wastewater when it is taken to supercritical conditions in the presence of a neutral fluid (e.g., nitrogen), (ii) the oxidation of a single component of interest in the water, e.g., urea and (iii) the oxidation of a mixture of two components, such as urea and ethanol, in water. At the same time, laboratory chemical analysis of the oxidized wastewater will be conducted to ascertain its composition and compare with the Raman spectra.

Visual inspection of the treated water and the untreated water showed a clear difference in the clarity before and after treatment as shown in Fig. 5 for the 2.5 ml/min flow rate of the untreated water. In addition, it was noted

that shaking a vial of the diluted wastewater concentrate resulted in bubbles or foam near the meniscus which lasted for several seconds. For the treated wastewater, on the other hand, no foaming was observed. This presumably indicated that chemicals that cause foaming (e.g., surfactants, such as the siloxane compounds) had been removed by the treatment.

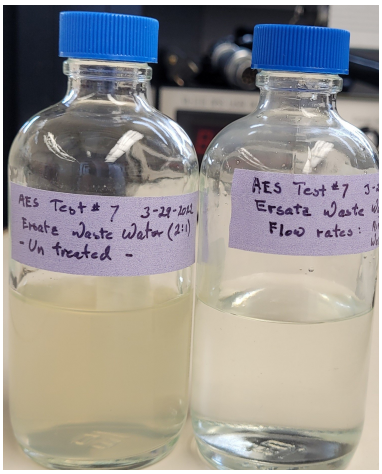


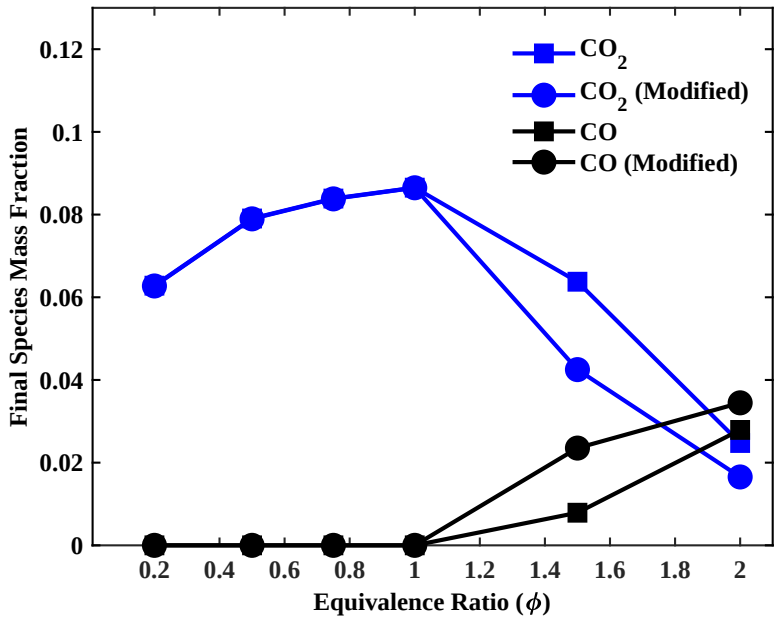
Figure 5: Image of untreated (left) and SCWO treated (right) wastewater showing the difference in clarity.

C SCWO Chemistry Modeling - Aqueous Ethanol Solutions

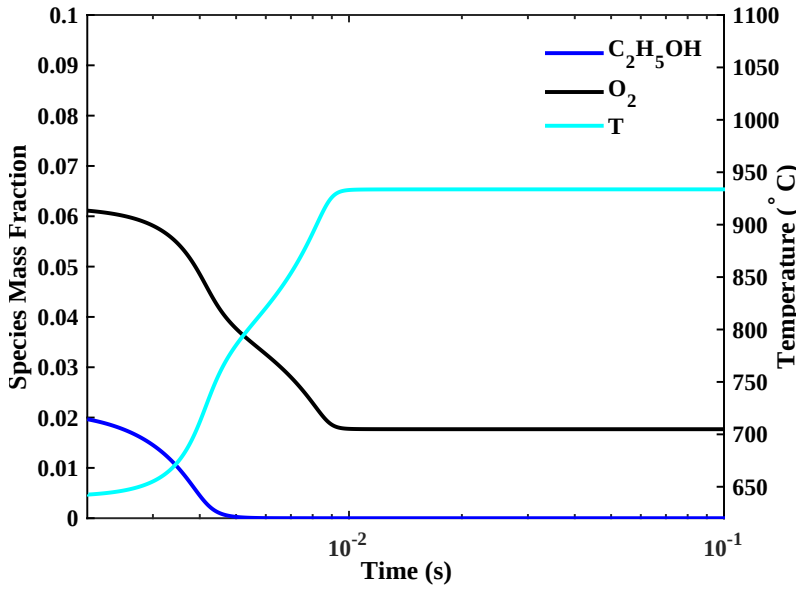
Detailed chemical kinetics are available for only a few of the various contaminants listed in Table 2. At present, for chemistry modeling purposes only ethanol (the organic contaminant with the highest concentration) and ammonia (expected decomposition product of urea and ammonium bicarbonate) have been studied. To date, chemical kinetic calculations with ethanol water solutions have been completed and are briefly described The modeling efforts in this study are conducted using Cantera, an open source software for chemical kinetics studies using a zero-dimensional "perfectly stirred" reactor. This configuration implies a well mixed homogeneous system that is not limited by diffusive transport and is suitable for studying the chemistry in the experimental flow-through reactor once the wastewater and air streams have mixed together. The model does not include details of the mixing process.

Conditions of constant pressure and a fixed volume are imposed. The fuel (wastewater) stream and oxidizer stream flow rates and compositions are specified at the inlet to the reactor. The starting temperature is also an input and adiabatic conditions are assumed as is appropriate for a well insulated reactor. The pressure ($\sim$ 27.3 MPa) and initial temperature (450 °C–550 °C) range of the experiment suggests that conditions are well to the right of the Widom pseudocritical line for water which enables the approximation of using the ideal gas equation of state. Detailed chemical kinetics can be included depending upon availability.

At present, two mechanisms for ethanol have been incorporated; the high temperature mechanism of Marinov[4] and the Marinov mechanism modified for low temperature reactions,[6] as suggested by Sandia. The high temperature mechanism is suitable for flaming oxidation as in hydrothermal flames. Incorporation of the low temperature mechanism enables better predictions at low organic concentrations in the wastewater feed when the associated heat release is not sufficient to significantly raise the temperature of the flow.



(a)



(b)

Figure 6: Plots from numerical analysis showing (a) the extent of incomplete oxidation of ethanol with the original Marinov ethanol mechanism (only high temperature chemistry) and the modified mechanism (including low temperature chemistry) and (b) the reactor residence time required for complete oxidation with the modified mechanism.

Urea, which is a component of the ersatz wastewater undergoes hydrolysis to form ammonium carbamate:

$$H_2O + CO(NH_2)_2 \rightarrow [NH_4][H_2NCO_2] \tag{1}$$

this then undergoes a decomposition reaction to form carbon dioxide and ammonia:

$$[NH_4][H_2NCO_2] \rightarrow CO_2 + 2NH_3 \tag{2}$$

Ammonium bicarbonate, which is a major component of the ersatz wastewater, also produces ammonia according to

$$[NH_4HCO_3] \rightarrow NH_3 + H_2O + CO_2 \quad (3)$$

An ammonia oxidation mechanism for high pressure conditions has been identified. This mechanism is currently being incorporated into the Cantera model. Various computations with oxidation of ethanol-water mixtures have been carried out. It is important to have sufficient oxygen available for complete oxidation. Insufficient oxygen leads to incomplete oxidation of the carbon to carbon dioxide resulting in the presence of carbon monoxide. This is shown in Fig. 6a where in both the original and modified ethanol mechanisms, carbon monoxide is present for equivalence ratios greater than one. The cases are for a C_2H_5OH 5%-v (aq) solution.

A second quantity of interest is the time it takes to complete the oxidation once the reactants are mixed. The residence time of the wastewater/air flow in the reactor varies with their flow rates but is computed to be on the order of tens of seconds for the flow rates used. Computations indicate that peak temperatures in the flow are obtained within milliseconds once the reactions commence. This is shown in Fig. 6b, where using the modified mechanism the peak temperature occurs in about 3 ms after the start of oxidation. This case used a C_2H_5OH 3%-v (aq) solution and a stoichiometric ratio of 0.714 (i.e. 40% excess oxygen).

Axial temperature distribution within the reactor flow stream is not being measured in the experiment. However, some of the experimental runs with the ethanol oxidation released enough heat to increase the temperature of the reactor walls above their initial values as will be described in a follow-on paper. The peak temperature here occurs about half-way along the reactor length. This is consistent with the model results, suggesting that mixing of the fuel and air stream is complete within the first half of the reactor. It should be possible to decrease the length of the reactor, particularly if a suitable passive mixing mechanism is introduced. This mechanism could, for example, be a direct impingement of the wastewater and air streams.

V Conclusion

A tubular flow supercritical water oxidation reactor has been built and is operational at NASA Glenn. The reactor section has a volume of 62 ml and is equipped with separate heated inlets for the wastewater and air streams. The initial temperature of the reactor, at start of testing, is typically in the range of 450 °C to 550 °C with working pressures in the range of 27.6 MPa and 28.3 MPa (4,000 psia - 4,100 psia). Tests with different concentrations ethanol-water were first carried out both to check out the system and also to exercise the Raman diagnostic. These tests showed that, in the presence of sufficient oxygen, the ethanol may be completely oxidized in supercritical water. Additionally, tests were conducted with partially diluted ersatz wastewater concentrate. Visual observations of the treated water and corresponding Raman spectra indicated that the organic contaminants in the wastewater were likely destroyed. Future work will correlate Raman spectra with chemical lab measurements of the constituents of the treated wastewater as well as supercritical water oxidation of single and dual contaminant mixtures.

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