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RESEARCH ARTICLE

Assessment of carbon recovery from solid organic wastes by supercritical water oxidation for a regenerative life support system

Dongdong Zhang[1,2] • Amanda K. Luther[3] • Peter Clauwaert[3] • Paolo Ciccioli[4] • Frederik Ronsse[2]

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Abstract

The carbon recovery from organic space waste by supercritical water oxidation (SCWO) was studied to support resource recovery in a regenerative life support system. Resource recovery is of utmost importance in such systems which only have a limited total amount of mass. However, the practical waste treatment strategies for solid space wastes employed today are only storing and disposal without further recovery. This work assesses the performance of SCWO at recovering organic wastes as CO_2 and water, to discuss the superiority of SCWO over most present strategies, and to evaluate the different SCWO reactor systems for space application. Experiments were carried out with a batch and a continuous reactor at different reaction conditions. The liquid and gas products distribution were analyzed to understand the conversion of organics in SCWO. Up to 97% and 93% of the feed carbon were recovered as CO_2 in the continuous and the batch reactor, respectively. Residual carbon was mostly found as soluble organics in the effluent. Compared with the batch reactor, the continuous reactor system demonstrated a ten times higher capacity within the same reactor volume, while the batch reactor system was capable of handling feeds that contained particulate matter though suffering from poor heat integration (hence low-energy efficiency) and inter-batch variability. It was concluded that SCWO could be a promising technology to treat solid wastes for space applications. A continuous reactor would be more suitable for a regenerative life support system.

Keywords Supercritical water oxidation · Carbon recovery · Organic space wastes · SCWO reactors performance evaluation

Introduction

Supercritical water oxidation (SCWO) has been studied for decades as a green technology to process organic waste streams (Yao et al. 2018; Zhang et al. 2018, 2019b). Water, as an environmentally friendly solvent, becomes a non-polar solvent in the supercritical phase that enables the dissolution of both organic compounds and oxidants (Bermejo and Cocero 2006). This homogeneous (i.e., supercritical) phase of water together with feedstock and oxidant greatly accelerates the oxidation reaction (Brunner 2014). Meanwhile, the high concentration of active free radicals in supercritical water further enhances organics oxidation (Vadillo et al. 2014). SCWO is capable of fully oxidizing various organic wastes in a few seconds, which is far faster than most conventional waste treatment methods (Al-Duri et al. 2015; Fang 2014). Final products from supercritical water oxidation are carbon dioxide (also minor quantities of carbon monoxide and methane, and negligible quantities ethane are formed in some cases), dissolved and/or suspended inorganics and water, and ideally without additionally formed pollutants (Vadillo et al. 2018). SCWO has been tested out on many organic waste streams, including model compounds (Matsumura et al. 2000), tannery sludge (Zou et al. 2013), and nitrogen-containing organics (Yang et al. 2018).

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✉ Frederik Ronsse
Frederik.Ronsse@UGent.be

[1] Present address: Institute of Urban Agriculture, Chinese Academy of Agricultural Sciences, Chengdu, China

[2] Department of Green Chemistry and Technology, Ghent University, Coupure Links 653, 9000 Ghent, Belgium

[3] Center for Microbial Ecology and Technology (CMET), Ghent University, Coupure Links 653, 9000 Ghent, Belgium

[4] IMC Istituto di Metodologie Chimiche, Area della Ricerca RM 1, 00015 Monterotondo Scalo, Italy

Resources in regenerative life support systems, as those needed for long-term, crew-operated space missions, are limited (Guo et al. 2017). In such settings, resources are impossible to obtain from the outside environment. Waste has to be recycled and maximally reused, and a high turnover of resources is important for the regenerative life support system. Most existing regenerative life support systems are not yet able to completely recycle solid waste, as reported in the literature (Allen et al. 2003; Gitelson et al. 1989; Guo et al. 2014; Yuming et al. 2016). The MELiSSA (Micro-Ecological Life Support System Alternative) project, supported by the European Space Agency, aims to fully recycle all the wastes generated in space (almost all are organic) at a high rate (ESA 2015). The MELiSSA project's aim is to establish a loop that can be used in prospective space travel or outer space colonies, inside which plants and microorganisms generate food and oxygen for the crew and all the waste is fully recycled as CO_2, nutrients and water. Water can be easily recycled and CO_2 is an input for photosynthesis to produce oxygen and edible biomass, typically plant or microbial biomass. Human wastes (i.e., feces, urine, and hygienic products), food wastes, and non-edible parts of plants are the main constituents of solid organic wastes in the MELiSSA project. Prior studies from Chen et al. (2015a) and Takahashi et al. (1989)), Takahashi (1989) have demonstrated that organic wastes could be directly oxidized in supercritical water and near 100% organics were removed as CO_2 and water. However, SCWO would increase energy consumption, increase process risks, and require the use of an oxidant. Therefore, a membrane anaerobic fermentation is applied prior to SCWO to degrade readily biologically available constituents in the waste stream in the MELiSSA loop. This step yields CO_2 and small molecules (volatile fatty acids) that can be recycled or processed in downstream processes and concentrates the solids in a slurry of accumulated undigested plant fibers and microbial biomass. These residues are only slowly decomposed by microorganisms during fermentation processes as reported (Zhang and Li 2019), and thus have to be subjected to SCWO to produce benign final products (carbon dioxide and water) and further approach near 100% of resource recovery at a high rate. As opposed to treating all organic waste directly by SCWO, the preceding fermentation step also reduces the size of the SCWO reactor required, because the sludge represents a small fraction (about 10%) of the total waste mass throughput. A combination of anaerobic fermentation and SCWO, proposed as a possibility for the MELiSSA project, potentially enables a better resource recovery than most regenerative life support systems that have partial or even no solid waste treatment.

Batch and continuous reactors are commonly used to study SCWO (Chen et al. 2015b; Elliott et al. 1994; Vadillo et al. 2012). For using SCWO in the MELiSSA project, a study to compare continuous against batch reactors in SCWO is necessary for safety, maintainability, and energy efficiency issues. To the best of the authors' knowledge, this topic has not been investigated before. Owing to the high working pressure and temperature, batch and continuous reactors differ in many aspects: feeding, discharging, heating-cooling (and heat integration), pressure control, product separation, and even the resulting products' distribution (Council 2001). A high-pressure pump is needed to inject the waste feedstock in continuous reactors (Fang 2014), and the system pressure is usually adjusted by a pressure regulator (at the effluent side). Influent and effluent should preferably be free from dispersed particulates, otherwise blocking of the high-pressure pump and pressure regulator could occur (Chen et al. 2019). These disadvantages are not present in batch reactors: loading feed and oxidant, and unloading reaction products occur before pressurization and after depressurization, respectively; pressurization is effected by the equilibrium pressure upon heating water in a closed vessel. However, batch reactors suffer from long heating and cooling stages (Qian et al. 2015), during which solid products and refractive intermediates could be generated at relatively high oxidant doses compared with continuous reactors (Chen et al. 2017).

This work is to assess the application of SCWO in the MELiSSA project, concerning the resource recovery from solid organic wastes and its feasibility in terms of reactor systems. Carbon recovery is used as the main indicator because the study's goal is to recover carbon in organic compounds as reusable CO_2. Different reaction conditions and reactor types were used to recover carbon from the organic wastes. Both gas and liquid effluents were analyzed. The effects of reaction parameters were investigated to a limited extent. Yet, differences in reactor performances were extensively demonstrated. A comparison between SCWO and present technologies has been given as well.

Materials and methods

Materials

Fermentation sludge was produced by fermentation in an anaerobic bioreactor with crossflow membrane filtration (55 °C, pH 5.3, 10 days hydraulic retention time) of a standardized MELiSSA waste containing red beet, lettuce, wheat straw, fecal material, and toilet paper (Zhang et al. 2018). The fermentation sludge was a liquid suspension with a concentration of 4 wt.% dry matter. The carbon and nitrogen concentrations were 44.5 and 2.2 wt.% dry basis, respectively, and the ash concentration was 6.4 wt.% dry basis. Total organic carbon of the sludge was 17,800 mg/L. Hydrogen peroxide (33 wt.%, bought from VWR) was used as the oxidant. For batch tests, the sludge concentration in the reactor was reduced by dilution to 2 wt.% (dry matter concentration). For the continuous tests, the sludge concentration in the feed mixture was reduced by dilution in water to 1 wt.%. Additionally, 0.25 wt.% of hydrolyzed starch was added to stabilize the feed (sludge and oxidant mixture) and avoid settling in the feed vessel (only in the continuous experiments, details in the "Apparatus and experimental procedures " section). The organic carbon contribution from the added hydrolyzed starch was accounted for in the oxidant dose calculations.

Oxidant equivalence ratio (OER) was used to represent the oxidant dose. OER equal to 1 means oxygen released from the oxidant is theoretically sufficient to fully oxidize the carbon in the waste, as follows:

$$2H_2O_2 + C \rightarrow 2H_2O + CO_2 \qquad (1)$$

Apparatus and experimental procedures

The continuous tests were carried out in a coiled plug-flow reactor, as shown in Fig. 1. The setup was owned and operated by Biomass Technology Group BV (BTG, Enschede, the Netherlands). The coiled reactor was 3.3 m in length with 5.4 mm of inner diameter. The reactor was heated by an electrical oven. The pressure in the system was controlled with a back pressure regulator. A water-cooled heat exchanger was used to cool down the effluent before separation. The feed vessel was filled to obtain a mixture consisting of 1.0 wt.% (dry matter) of sludge and 0.25 wt.% of starch, to which the desired amount of hydrogen peroxide had been added depending on OER value. In order to pump the mixture into the coiled reactor, the feed vessel was pressurized by means of nitrogen gas, supplied by an external gas booster, and the flow rate was regulated by a mass flow controller. The reactor coil was purged with water during the pre-heating. Then, when the temperature and pressure in the system achieved the desired constant values, and the pressure in the feed vessel was equal to the pressure in the system, the valve connecting the feed vessel with the reactor coil was opened, and the water stream was simultaneously turned off. The continuous run stopped when the feed vessel was empty which held a volume of mixture to run for approximately 1 h at a constant flow of 430 mL/h. Both effluent liquid and effluent gas samples were taken every 10 min. At least 4 samples were taken for each condition as repetitions. The reaction pressure was around 25.5 ± 0.5 MPa for every experiment. The batch tests were conducted in a 45-mL autoclave. The description of the setup and the experimental procedural information can be found in our previous study (Zhang et al. 2018).

Different temperatures, residence times, and OER were investigated as shown in Table 1. The batch and continuous systems have different operational conditions because of the inherent working differences of both reactors. Five minutes of residence time was selected in the batch system to minimize the influence of the relatively long heating and cooling periods in the overall obtained results. The temperature range was chosen due to being optimal for carbon recovery while minimizing the nitrogen conversion to toxic products (i.e., NO_x) as indicated in our previous study (Zhang et al. 2018). Sludge oxidation was tested within both batch and continuous reactors under slightly different operational conditions because of the setup variation (i.e., residence and heating time). The OER for the continuous reactor setup was not tested below 1.0 as otherwise the risk of the formation of solid carbonaceous particles would be too high and this could subsequently stop the system from running (especially the back pressure regulator is sensitive to particulates in the effluent) (Zhang et al. 2018).

Product analysis

The gaseous effluent of the batch tests was analyzed using the same methods as in Zhang et al. (2018). The gaseous effluent of continuous tests was analyzed with a GC-2014 Shimadzu Gas Chromatograph equipped with SH-Rxi™-1MS column and FID detector. TOC (total organic carbon) concentration in the aqueous effluent was analyzed with a TOC analyzer (TOC-5000 Shimadzu).

Fig. 1 Diagram of the continuous SCWO setup

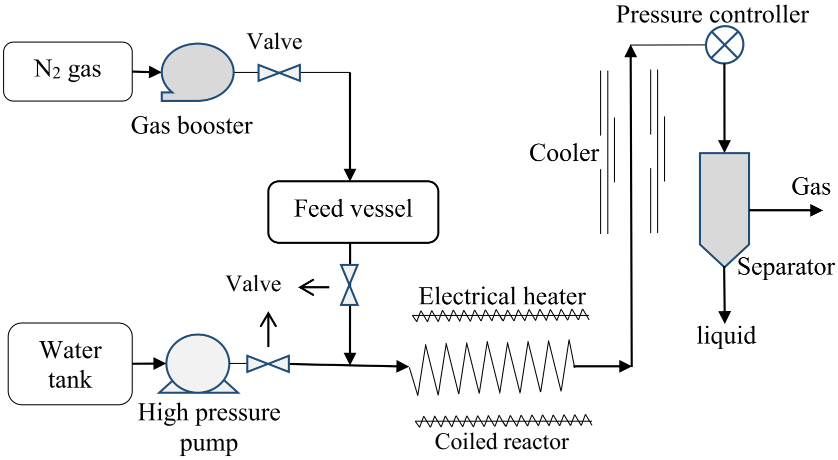

Table 1 Studied parameters in batch and continuous experiments

Continuous reactor (5 experimental conditions)	Batch system (9 experimental conditions)				
450 °C, OER = 2.0, 1 min	400 °C	×	OER = 0.5	×	5 min
500 °C, OER = 1.0, 1 min	450 °C		OER = 1.0		
500 °C, OER = 2.0, 1 min	500 °C		OER = 2.0		
500 °C, OER = 3.0, 1 min					
550 °C, OER = 2.0, 1 min					

The VOC (volatile organic compounds) analysis of the liquid effluent from continuous tests was obtained by headspace technique without any pH adjustment. Aliquots of the liquid solution were put in a tight glass container at 80 °C and flushed with helium at 80 °C. The vapors and gases were transferred into an empty cold trap at − 160 °C, and then injected into a proton transfer time of flight detection mass spectrometer (PTR-TOF-MS 8000 model supplied by Ionicon Analytik) for identification and quantification. The analysis of volatile fatty acids in the aqueous effluent from batch tests was the same as in Zhang et al. (2018).

The elemental analysis on the aqueous effluent from continuous tests was performed with inductively coupled plasma mass spectrometry (ICP-MS), as it is able to detect metals at trace levels. An ICP-MS XSERIES 2 from Thermo Scientific was used for these determinations. The system is equipped with a nebulizer and a spray chamber to produce the plasma; the ion metal content was directly determined by MS through the measure of the intensity of m/z ion peaks produced in the spectra. A nebulizer is used to produce a supersonic expansion of gas to turn the liquid into an aerosol, from which droplets that are too large to be processed in the plasma are removed by a spray chamber. Ions in the plasma are produced by inductively heating the mixture of aerosol with an electromagnetic coil and by mixing it with a flow of argon gas heated at high temperature (ca. 6000–1000 K) in a quartz torch. The use of quartz did not allow to quantify the amount of Si (silicon) in the sample. Before the analysis, all liquid samples were digested and reconstituted in an aqueous matrix to stabilize elements as an ionic solution. Nitric acid was added to the aqueous matrix until a 2% content by volume was reached. The ICP-MS was calibrated by progressive dilution of a 100 ppm multi-element standard solution 6 provided by Sigma-Aldrich. One to 10 mL of each solution was used for sample analysis. To get a quantitative evaluation of P (phosphorus), the ICP-MS system was calibrated by determining the content of P as orthophosphate with the colorimetric method. Ten milliliter aliquots of the solutions were mixed with proper amounts of ammonium molybdate, to form a complex that by reduction with stannous chloride produces a blue colored complex, whose content in the solution can be quantified by spectrophotometry as it strongly absorbs the light at a wavelength of 690 nm. The ICP-MS signal measured in the solutions was fitting quite well with the data provided by the colorimetric method, indicating that the content of polyphosphates and organic phosphates in the solution were negligible with respect to the orthophosphate.

Data processing and evaluation

The efficiency of the oxidation process can be evaluated in several ways. TOC removal efficiency indicates the degradation of organic wastes which is one of the most important values to evaluate the effect of SCWO. The removed carbon mostly goes to CO_2, CO, and maybe other carbon-containing gases. Here, we specifically define carbon recovery as the conversion of carbon from the organic waste stream to carbon dioxide which is the desired end product.

TOC removal efficiency (TRE, in %) is defined as

$$TRE\ (\%) = \frac{[TOC]_{feed} - [\,TOC]_{effl}}{[TOC]_{feed}} \times 100 \tag{2}$$

where $[TOC]_{feed}$ represents the initial TOC concentration in the feed mixture (mg/L). $[TOC]_{effl}$ represents the residual TOC concentration in the liquid effluent (mg/L).

Carbon recovery (CR, in %) is defined to evaluate the carbon conversion efficiency, by calculating the mass fraction (in %) of feedstock carbon (C_{feed} in mg) that is recovered in the CO_2 of the gaseous effluent (C_{CO2} in mg):

$$CR\ (\%) = \frac{C_{CO2}}{C_{feed}} \times 100 \tag{3}$$

Carbon balance closure (CB, in %) is defined as

$$CB\ (\%) = \left(W_{TOC} + W_{CO_2} + W_{CO} + W_{rest-gas-C}\right) \times 100 \tag{4}$$

where W_{TOC}, W_{CO_2}, W_{CO}, and $W_{rest-gas-C}$ represent the mass fraction of carbon in products as TOC, TIC (both in the liquid effluent), CO_2, CO, and other carbon-containing gases to the total organic carbon from the feed, respectively. Specifically for the gas phase, a distinction is made between CO_2, CO, and minor and trace carbon-containing components (CH_4, ethane, ethane, propane, propene, and butane) which are lumped together as $W_{rest-gas-C}$.

Results and discussion

Gas products

The conversion (oxidation) of carbon in the feedstock to carbon dioxide is the primary objective of the study. Carbon recovery as defined in Eq. (3) quantifies the fraction of feed carbon converted to carbon dioxide indicating the efficiency of SCWO, of which the results are shown in Figs. 2 and 3.

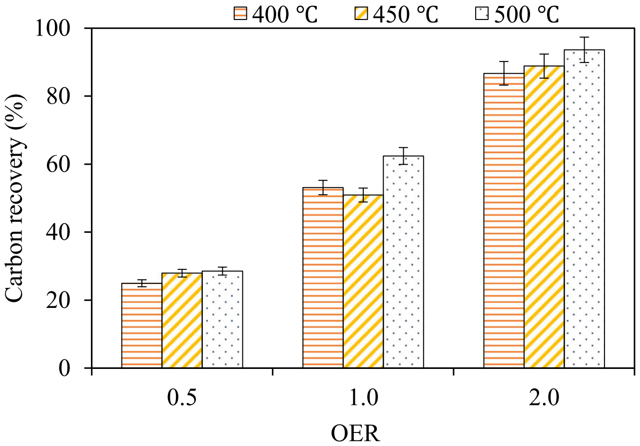

Fig. 2 Carbon recovery (in %) as a function of OER and temperature (in °C) in batch reactor testing at 5 min residence time

From the results, the carbon recovery in both reactors was always higher than 85% at OER ≥ 2.0. Temperature and OER both affected the carbon recovery. The effect of OER on carbon recovery was more substantial than temperatures in the tested ranges, for batch and continuous reactors.

The effect of OER is substantial in batch tests, as shown in Fig. 2. The carbon recovery increased from 28.5% to a maximum of 93.6% with increasing the OER from 0.5 to 2.0 at 500 °C. The observation agrees well with previous studies (Bermejo and Cocero 2006; Savage 1999) in which the OER impacted the carbon oxidation greatly. With more oxidant present in the reactor, sludge is more likely to be oxidized to generate carbon dioxide. In terms of continuous reactor testing, only a minor positive effect from increasing OER on carbon recovery was observed at tested temperatures. The carbon recovery increased from 82.5% to a maximum of 97.6% with increasing OER from 1.0 to 3.0 at 500 °C. The results indicate that high carbon recovery is achievable at OER just above 1.0 and can be further improved at tested temperatures by increasing the OER within the continuous reactor, but less effectively compared with batch reactor systems.

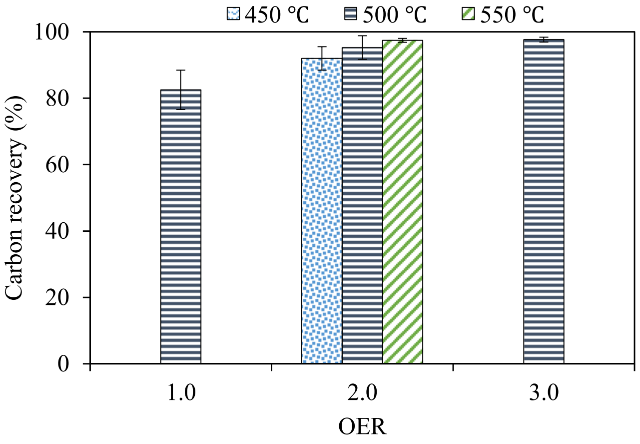

Fig. 3 Carbon recovery (in %) as a function of OER and temperature (in °C) in continuous reactor testing at 1 min residence time

When considering the two reactors under the same conditions (OER = 1.0 and *T* = 500 °C), carbon recovery was lower in the batch reactor (62.5%) than in the continuous reactor (82.5%). The observed difference might result from the different heating strategies used. Batch reactors need a relatively long heating period to bring the reactor and its contents to the desired temperature (e.g., 7 min before reaching 500 °C), during which time sludge components and derived intermediates might undergo significant polymerization reactions along with oxidation and other reactions, specifically in the presence of low OER (e.g., OER ≤ 1.0) (Xu et al. 2015). As a result, carbon probably accumulates in solid products, which are difficult to oxidize, resulting in a lower carbon recovery. In the presence of sufficient oxidant amounts (OER = 2.0) within the batch reactor, polymerization reactions are suppressed during the long heating period, oxidation reactions dominate and oxidize carbon; therefore, the carbon recovery is enhanced. In general, high OER could reduce the formation of solid products and enhance carbon conversion to carbon dioxide even if longer heating trajectories are needed. Nevertheless, the latter phenomenon occurs to a lesser extent within a continuous reactor system.

Temperature was reported to affect carbon recovery greatly (Amrullah and Matsumura 2018; Qian et al. 2015; Xu and Savage 2018). In our study, carbon recovery is found to be less sensitive to temperature in the studied range. In batch tests at OER = 2.0, carbon recovery at 500 °C is 6.9% higher than 86.7% of 400 °C. In continuous tests at OER = 2.0, carbon recovery at 550 °C is 5.4% higher than 92% of 450 °C. It is assumed that the majority of the carbon in the sludge was oxidized at temperatures around 400 °C, resulting in high carbon recovery. However, the residuals were resistant to complete oxidation at tested temperatures. Consequently, a slight improvement from elevated temperatures was observed. Temperatures higher than the tested range might be necessary for complete carbon recovery.

Besides CO_2, carbon can also be converted to other gaseous by-products under SCWO conditions such as carbon monoxide and to a lesser extent, methane and ethene. Gaseous carbon-containing by-products were frequently observed in the batch tests. The continuous tests generated almost only carbon dioxide and also traceable amounts of hydrogen gas. The by-product species and their distribution of the batch tests vary with reaction conditions as is shown in Table 2. Carbon monoxide is one of the most common gaseous by-products within the batch tests but was not detected in the continuous reactor experiments. The concentration of carbon monoxide had a trend from an initial rise to subsequent decline with increasing OER. The maximum CO yield is obtained at OER = 1.0, as shown in Table 2. We assume that polymerization reactions play an important role at OER < 1.0 based on the low carbon balance closure, which suggests the formation of solid products (which were not accounted for

Table 2 Carbon distribution in batch oxidation tests

Experimental conditions		Carbon distribution (mass fraction in %)				CB** (in %)
		Liquid effluent	Gaseous effluent			
Temp (°C)	OER	TOC	CO_2	CO	Rest gas-C*	
500	2.0	6.2	93.6	5.4	0.5	105.7
	1.0	23.6	62.4	5.5	2.9	94.4
	0.5	35.9	28.5	0.7	3.6	68.7
450	2.0	10.0	88.8	6.0	0.8	105.7
	1.0	27.7	50.9	6.6	1.5	86.7
	0.5	41.4	27.9	3.4	1.2	73.9
400	2.0	10.5	86.7	2.3	0.0	99.5
	1.0	27.5	53.1	4.8	0.2	85.7
	0.5	43.4	25.0	2.8	0.2	71.4

*CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, and C_4H_{10}

**Carbon balance is > 100% in some cases, probably resulting from experimental error

in the carbon balance). The oxidation reactions are thus also limited, resulting in low yields of carbon monoxide as well as carbon dioxide. When the OER is 1.0 or above, these presumed polymerization reactions begin to be suppressed because of the abundance of oxidant. Oxidation reactions dominate and lead to the formation of carbon dioxide. With excess oxidant, carbon monoxide is likely to be oxidized to carbon dioxide, resulting in the declining trend of CO yield with OER increasing. However, this decline in the CO yield is less pronounced when process temperatures increased.

Liquid products

Figure 4 demonstrates the effect of temperature and OER on the TOC removal in the liquid effluent. TOC removal increases with increasing OER and temperature as reported by many studies (Ma 2014; Nunoura et al. 2003; Svishchev and Plugatyr 2006). TOC removal indicates the removal of organic carbon from the liquid phase to either solid or gas phases. In the continuous tests, the aqueous effluent was clear with barely visible solid products, and carbon dioxide was found to be the only carbonaceous gas. TOC removal values were close to carbon recovery values indicating that the majority of removed carbon is completely converted into CO_2. To the contrary, TOC removal efficiency values (Fig. 4) were much higher than carbon recovery values (Fig. 2) in the batch tests, especially at low OER (≤ 1.0). The discrepancy between carbon recovery and TOC removal efficiency can be explained by the formation of solid products (which were not collected or quantified), dissolved and incompletely oxidized organic compounds (which are quantified in the effluent TOC) and non-CO_2 gas products as shown in Table 2. These non-CO_2 end products are neither desirable nor easily recoverable in a life support system and hence need further treatment for recovery. With elevated OER, the formation of solid particulates, dissolved organics, and non-CO_2 gaseous species was observed to a lower extent. Therefore, carbon recovery improved and got closer to the TOC removal efficiency.

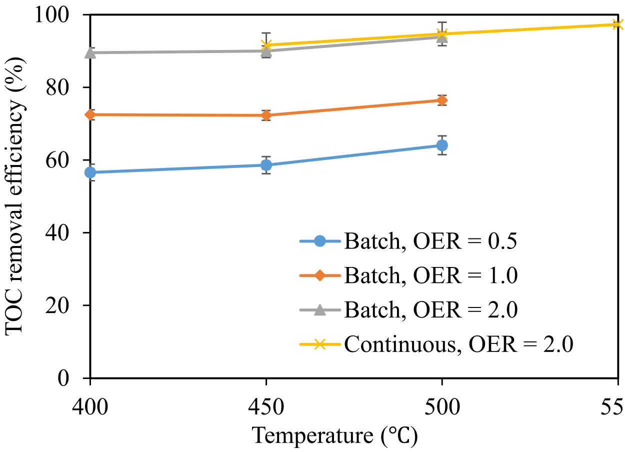

Fig. 4 The effect of temperature and OER on TOC removal efficiency in both batch and continuous tests

TOC removal in all studied cases was below 100%. Volatile organic compounds (VOC) were further analyzed using chromatography for both influent and aqueous effluent of the continuous SCWO experiments. Low molecular weight alcohols and acids were found to be the major compounds in the aqueous phase of influent, as these are typical intermediates formed in anaerobic fermentation, as also studied in the literature (Liu et al. 2019; Xu et al. 2018). After the oxidation process, aldehydes and ketones became the dominant compounds in the VOC fraction of the liquid effluent (Table S.1 in supplementary information). Meanwhile, the VOC content in the liquid effluent was greatly reduced, indicating the oxidation of volatile organics during SCWO. Trace amounts of alcohols and acids were observed in the aqueous effluent suggesting that oxidation was not fully complete (Fig. S.1 in supplementary information). Full recovery (100%) of sludge-C was not achieved at any given conditions.

TOC and volatile fatty acid content in the aqueous effluent from batch tests were analyzed as well. Both component classes decreased greatly after the oxidation process. Volatile fatty acids were one of the major residuals. In the case of OER = 2.0 and 500 °C, 621 mg C/L of total organic carbon is observed in the liquid effluent, of which 179 mg C/L were volatile fatty acids (details in Table S.2 in supplementary information). This residual carbon in the aqueous effluent is hard to dispose of and needs further study.

Supercritical water oxidation is conducted under severe process conditions which can result in corrosion and salt precipitation problems. As a result of corrosion, the effluent from SCWO might contain residuals from the reactor wall (i.e., metals leaching from the alloys out of which the reactor is constructed). Besides, dissolved inorganic compounds in the influent might precipitate during the oxidation process because of the dramatically decreased solubility of salts in supercritical water (Voisin et al. 2017). Sludge contains both organic and inorganic compounds (Dai et al. 2017). The research objective is to recover resources from waste streams, which is to degrade organics in the waste stream to CO_2 while retaining nutrients (i.e., inorganic compounds) in the aqueous effluent, as the latter nutrients are required for further compartments of the MELiSSA (e.g., photosynthetic compartment). We evaluated the inorganic (nutrient) compounds that survived SCWO as well as elements that may have leached from the reactor wall, as shown in Table 3. Batch samples were not analyzed as no sufficient effluent quantities were available.

Table 3 demonstrates that most dissolved nutrient species (i.e., Na, K, P) survived the SCWO process but suffered great losses in quantity in the effluent (especially Mg, Ca). Additionally, the effluent got contaminated by Cr and Mo, which are most probably from the reactor alloy material and released to the aqueous phase due to corrosion and leaching during the SCWO process. The loss of nutrients is assumed to result from salt precipitation in the reactor due to the significantly low solubility of salts in supercritical water. Interestingly, it is surprising to observe that the concentration of most nutrients and heavy metals decrease with reaction conditions getting harsher (i.e., higher OER and/or higher T). Harsher conditions should be capable of leaching more metals (e.g., Cr) from reactor alloys; however, this is counteracted by the lower solubility of inorganic compounds. We suspect that nutrients as well as leached heavy metals are more likely to precipitate inside the reactor under harsher conditions. The recovery of all elements has to be further investigated.

Feasibility of batch versus continuous reactor discussion

High sludge oxidation efficiency is reached by applying SCWO. A maximum TOC removal of 93.8% and 97.6% were achieved for batch and continuous reactors, respectively, of which their corresponding effluents are both clear without visible solids. Carbon dioxide was the major end product. The sludge oxidation behavior (including its optimum) was slightly and differently influenced by process conditions in batch compared with continuous reactors. Higher temperatures and higher OER both have positive influences on organic compound oxidation but to a different extent. The effect of varying temperature upon oxidation for both reactor systems is minor resulting from the already high working temperature. Though less economic, sludge oxidation could likely still be improved by further increasing process temperature.

In comparison, the effect of altering OER had a substantial effect on sludge oxidation in both batch and continuous tests. For SCWO in batch tests, visible solids were formed in tests with OER ≤ 1.0 and these disappeared with OER increasing above 1.0. A multitude of reactions could have occurred during the inherent long pre-heating period of the batch tests to generate recalcitrant intermediates and side products that cannot be fully oxidized at low OER that remain in the final effluent, including tar and char-like compounds. With increasing OER, less to no solids were observed in batch tests as well. In comparison with batch, sludge oxidation carried out in the continuous reactor is less sensitive to variation in OER. Negligible solid products were observed in the effluent only at OER = 1.0 and completely disappeared in tests with higher OER. However, the continuous tests also demonstrated that the formation of solids needs to be avoided to guarantee the proper functioning. Most continuous reactors have a back-pressure valve to control the system pressure which typically cannot tolerate solid particles in the effluent. Alternatively, filter elements may be needed for safeguarding the back pressure regulator against potential carbonaceous solid particles (but this further complicates the setup).

Gas effluents in batch and continuous reactor tests also turned out to have a different composition. Carbon dioxide was the only carbon-containing gas in all continuous tests while carbon monoxide, methane, and other carbon-containing gases were detected in the batch tests. These incompletely oxidized gases need further downstream oxidation to achieve full carbon recovery.

In terms of operational procedures, the amount of water inside the batch reactor will yield the desired equilibrium pressure at a given temperature, and so reactant mass loading needs to be precisely controlled to avoid an undesired pressure value. The feed volume added to the batch reactor is always less than the reactor volume. For instance, the 45-mL batch reactor used in this study needed only 5.18 g of water to yield 30 MPa at 500 °C. Consequently, this further reduces the feed processing capacity of a batch reactor (see below).

Pressure in the continuous reactor was controlled by a back pressure regulator. The residence time is inversely proportional to the feed flow at a fixed temperature and pressure. SCWO

Table 3 Elemental analysis by the ICP-MS (µg/g) of reactor liquid effluents from continuous reactor experiments

	Influent mixture	500 °C, OER = 1.0	500 °C, OER = 2.0	550 °C, OER = 2.0
Li	0.002	< 0.001	< 0.001	< 0.001
Be	0.000	0.000	0.000	0.000
Na	98.511	13.675	9.8985	8.56
Mg	7.993	0.084	0.068	0.0505
Al	1.675	0.007	0.007	0.003
P	1.510	0.735	0.870	0.565
K	140.054	18.326	20.511	24.156
Ca	34.833	0.2575	0.741	0.5125
V	0.006	0.0015	0.0015	0.001
Cr	0.194	7.423	2.1375	0.7985
Mn	0.179	< 0.001	0.001	< 0.001
Fe	1.204	0.000	0.000	0.000
Co	0.002	< 0.001	< 0.001	< 0.001
Ni	0.070	0.004	0.0055	0.009
Cu	0.106	0.0495	0.0455	0.0385
Zn	1.686	0.006	0.005	0.011
Ga	0.006	0.001	< 0.001	0.000
As	0.000	0.000	0.000	0.000
Rb	0.036	0.0055	0.0065	0.008
Sr	0.089	0.001	0.0025	0.001
Mo	0.010	0.217	0.037	0.058
Ag	0.001	< 0.001	< 0.001	< 0.001
Cd	0.004	0.001	< 0.001	< 0.001
Cs	0.000	0.000	< 0.001	< 0.001
Ba	0.089	0.0205	0.0025	0.002
Pb	0.037	< 0.001	0.000	< 0.001

processes commonly include pre-heating, reaction, and cooling stages. The pre-heating and cooling stages are much longer than the fast SCWO reactions, and is especially true for batch reactors. During the batch tests at 500 °C, 7 and 2 min are required for heating and cooling stages, respectively, while reaction time was short (≤ 5 min). Continuous setups do not need separate stages of heating and cooling, as these stages can be performed in-line upstream and downstream of the reactor, respectively—and additionally providing the possibility to recover the heat released upon cooling of the effluent to heat up fresh influent by means of a heat exchanger, further increasing the thermal efficiency of the process. Notwithstanding the above-mentioned advantages, continuous setups suffer from feeding problems. The fermentation sludge consisted of unreacted plant fibers, up to 2 mm long. The particles induce clogging in high-pressure pumps. Due to the small scale of this study, a pressurized vessel was used to feed the system. This is consistent with other alternative methods (Chen et al. 2016; Li et al. 2018) to bypass the issue with particles in the feedstock in continuous setups. However, a pressurized feeding vessel is not suitable for long-term operations in scaled-up setups. On the contrary, batch setups have the advantage of being flexible enough to handle a wide variety of feed types including dispersions and sludges.

The theoretical scale-up to a 1-L reactor is given in Table 4. A 1-L continuous reactor is capable of dealing with 124.2 L influent (1 wt.% dry matter content) in 24 h running at given conditions, while a 1-L batch reactor can only handle 12.96 L influent (2 wt.% dry matter content) in the same time period (in a perfect situation without considering the time lost for loading and unloading of the reactor). The capacity of a scaled-up 1-L continuous reactor can handle wastes corresponding to that generated by nearly 20 crew members per day (each person can generate 1 L of ~ 6.3 wt.% sludge every day in the MELiSSA study), recovering at least 553 g carbon per day. In a more real application, the working concentration of the influent sludge could be higher (e.g., > 4 wt.%) for better efficiency and energy self-sustenance (Veriansyah and Kim 2007). For the batch reactor to meet the working capacity of the theoretical 1-L continuous reactor, the capacity has to be scaled up multiple times (far above 1 L), which poses additional safety issues in terms of expansion volume (in case of leak/rupture).

Table 4 Comparison of SCWO capacity between continuous and batch reactor (24 h (1 day) running at 500 °C, 25 MPa and OER = 2.0)

	Tested reactor scale		Theoretical scale-up	
	Continuous	Batch	Continuous	Batch
Reactor volume (mL)	100	45	1000	1000
Influent concentration (wt.% dry matter)	1.0	2.0	1.0	2.0
Oxidant	H_2O_2	H_2O_2	H_2O_2	H_2O_2
Residence time (s)	60	60	60	60
Heating and cooling time (per run[a], in s)	/	540	/	540
Total heating and cooling time (s)	3600[b]	540 × 6 × 24[c]	3600	540 × 6 × 24
CO2 recovery (%)	> 97.6	> 93.8	> 90	> 90
Major end product	CO_2	CO_2	CO_2	CO_2
Throughput (L)	/	/	124.2	12.96

[a] Batch reactor needs heating and cooling for each load

[b] Continuous reactor needs only one heating stage at the very start and one cooling at the end

[c] Total heating and cooling time include 540 s per run, 6 runs per hour and 24 h per day

[d] $\left(\frac{90\ \text{mL}}{60\ \text{s}}\right) \times (24–1)$ h, a 1-L reactor would only load 90 mL influent at given conditions

[e] 90 mL/run × 6 run/h × 24 h

In comparison with other waste treatment methods (being hydrothermal liquefaction, only anaerobic fermentation), supercritical water oxidation is superior in its high oxidation efficiency within short residence time while only needing a small setup. One of the previous studies (combining aerobic fermentation with worm conversion) was operated for 93 days to reach the cellulose and lignin degradation of 98.6% and 93.1%, respectively, and a carbon recovery of only 65% (He et al. 2010). With the combination of anaerobic fermentation and SCWO, the organic load in the waste can be recovered up to a maximum of 98%. Nevertheless, the recovery of inorganic compounds is not efficient in SCWO. Inorganic components are mainly deposited inside the setup, as stated in Table 3 and the literature (Zhang et al. 2019a). The leaching of toxic heavy metals from the reactor alloys is likely to be problematic if the aqueous effluent is reused in a closed system (i.e., for plant growth). Further study of reactor materials in combination with reactor design is required to suppress the leaching of reactor alloy materials into the effluent. Additionally, effective strategies to avoid precipitation of inorganics but recover them instead are of utmost importance.

Conclusion

SCWO proves to be suitable for carbon recovery from organic wastes for its high efficiency and capacity. Organic components can be near completely oxidized and recycled which is more superior than most present treatments in life support systems. With regard to the practical application of different reactor systems, the continuous reactor generates carbon dioxide as the only carbonaceous gas and has an almost 10 times higher throughput capacity than a similar-sized batch reactor. Besides, solid products are less likely to be formed in the continuous reactor. As a result, the continuous SCWO reactor is recommended for application in a regenerative life support system.

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