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Sub- and supercritical water oxidation of anaerobic fermentation sludge for carbon and nitrogen recovery in a regenerative life support system

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ABSTRACT

Sub- and supercritical water oxidation was applied to recover carbon as CO_2, while maintaining nitrogen as NH_4^+ or NO_3^-, from sludge obtained from an anaerobic fermenter running on a model waste composed of plant residues and human fecal matter. The objective was to fully convert carbon in the organic waste to CO_2 while maintaining nutrients (specifically N) in the liquid effluent. In regenerative life support systems, CO_2 and nutrients could then be further used in plant production; thus creating a closed carbon and nutrient cycle. The effect of the operational parameters in water oxidation on carbon recovery (C-to-CO_2) and nitrogen conversion (to NH_4^+, NO_3^-) was investigated. A batch micro-autoclave reactor was used, at pressures ranging between 110 and 300 bar and at temperatures of 300–500 °C using hydrogen peroxide as oxidizer. Residence times of 1, 5 and 10 min were tested. Oxidation efficiency increased as temperature increased, with marginal improvements beyond the critical temperature of water. Prolonging the residence time improved only slightly the carbon oxidation efficiency. Adequate oxygen supply, i.e., exceeding the stoichiometrically required amount, resulted in high carbon conversion efficiencies (>85%) and an odorless, clear liquid effluent. However, the corresponding oxidizer use efficiency was low, up to 50.2% of the supplied oxygen was recovered as O_2 in the effluent gas and did not take part in the oxidation. Volatile fatty acids (VFAs) were found as the major soluble organic compounds remaining in the effluent liquid. Nitrogen recovery was high at 1 min residence time (>94.5%) and decreased for longer residence times (down to 36.4% at 10 min). Nitrogen in the liquid effluent was mostly in the form of ammonium.

1. Introduction

For future long-term crew-operated space missions, such as travel to and the colonization of neighboring planets, the crew cannot rely on food, water and O_2 being resupplied from earth in a sustainable way. As space ships only have limited supplies of food and other resources, and extraction of useable resources in the direct vicinity of the space ship/colony is either challenging or not always possible, a combination of different technologies to completely recycle all waste streams to food, water and O_2 is mandatory. Organic waste streams to be recycled include human feces and urine, toilet paper, food waste and other organic wastes (including plant waste). A combination of recycling technologies to generate food, water and air is often termed a 'regenerative life support system' (Clauwaert et al., 2017). These regenerative systems attempt to close the cycles for carbon, hydrogen, nitrogen, phosphorus, sulfur and other inorganic nutrients. In the waste treatment compartment of the 'MELiSSA' loop, the regenerative life support system of the European Space Agency (ESA), organic waste is thermophilically fermented at 55 °C and a pH of 5.3 to maximize the conversion of organic waste into volatile fatty acids, ammonia and other (micro) nutrients. However, since a fraction of the organic waste is not rapidly biodegradable (e.g. cellulose and lignin from plant fibers), a dedicated 'fiber degradation unit' (FDU) is foreseen for the oxidation of fibrous, recalcitrant biomass. One potential FDU technology to process organic waste (including difficult-to-degrade constituents) is supercritical water oxidation (SCWO). Using water above its critical point, i.e. $T = 374$ °C and $P = 22.1$ MPa (Bermejo and Cocero, 2006; Brunner et al., 1994), in the

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presence of an oxidizer (i.e., air, pure O_2 or hydrogen peroxide), the carbon and hydrogen in the waste can be converted, to a high extent, into CO_2 and H_2O, respectively. Nitrogen is ideally converted into ammonium or nitrate and recovered from the liquid effluent for further use as a fertilizer in the MELiSSA loop. Combining biological degradation processes like fermention with SCWO is beneficial, as the TOC (total organic carbon) load of the incoming waste stream (to the SCWO unit) is already reduced in the preceding fermentation process, thus limiting the equipment size and oxidizer demand of the subsequent SCWO process.

Supercritical water has been studied for many years for its unique properties. As water reaches supercritical conditions, the hydrogen bonds between individual water molecules are largely broken and consequently, the dielectric constant is reduced by at least one order of magnitude compared to ambient conditions (ε_r = 80.1 at 20 °C) (Kruse and Dahmen, 2015). As a result, supercritical water behaves as a non-polar solvent, able to dissolve organic compounds and being perfectly miscible with oxygen (O_2) which all together results in the oxidation of organics in a single phase. Supercritical water oxidation is considered a promising method to rapidly and completely destroy organic matter, especially hazardous wastes and hard-to-decompose organic wastes, such as anaerobic fermentation sludge. Several process parameters, such as temperature, residence time and oxygen concentration have been demonstrated to affect the oxidation efficiency (Krajnc and Levec, 1996; Rice and Steeper, 1998). SCWO to process organic waste streams has been studied by several research groups (Al-Duri et al., 2015; Helling and Tester, 1988; Lee et al., 1990; Li et al., 2013; Portela et al., 2001; Savage, 1999; Schmieder and Abeln, 1999; Wang et al., 2011). Chen et al. (2015) studied the destruction of submarine food waste using supercritical water oxidation. Conversion of TOC and TN (total nitrogen) at 500 °C, 240 bar, an oxidizer equivalence ratio (OER) of 2 and 60 s residence time was 99.7% and 94.5%, respectively. Li et al. (2013) studied the TOC removal of municipal sewage sludge using SCWO and obtained a 97.9% COD (chemical oxygen demand) removal at 500 °C, 300 bar, an OER of 2 and 10 min residence time. The use of model compounds has also attracted some attention (Schmieder and Abeln, 1999). The results of these model compound studies indicate that temperature, OER and residence time are proportional to the oxidation efficiency.

The possibility of controlled and complete destruction of organic (solid and liquid) wastes, with the ability to reclaim water, nutrients and CO_2 and without the drawbacks associated to incineration, has led to the evaluation of SCWO technology as a suitable candidate in regenerative life support systems for long-term space missions (Bubenheim and Wydeven, 1994; Drysdale et al., 2003; Kudenko et al., 2000; Takahashi and Tanaka, 1992). Most researchers applied model mixtures of wastes mimicking waste that is produced during crew-operated space missions. Takahashi (Takahashi et al., 1989) studied a mixture of human urine, feces and wipes in a batch reactor with 60 and 120 min residence time. The study focused on removal of COD rather than conversion to carbon dioxide. It was found that carbon was converted to CO, CH_4, C_2H_6 and minor concentrations of other gas products. Few researchers had clear results aiming specifically at the complete conversion to CO_2. In the present work, complete decomposition of the organic waste and conversion to carbon dioxide are set as the main goals. The idea is to reuse the carbon (as CO_2) for growing plants, as part of the regenerative life support system. A secondary goal was to keep the nitrogen originating from the waste dissolved (NO_3^- or NH_4^+) in the liquid effluent for potential further re-use as fertilizer.

In this study, both sub- and supercritical water oxidation of sludge from a fermented model waste stream was investigated in a batch reactor. Although similar conversion rates as SCWO will not be attained with subcritical water oxidation, being a milder process, it is less energy intensive and less prone to salt precipitation (being one of the main problems in SCWO technology). Hence the inclusion of subcritical water oxidation in this study. The effect of reaction parameters including OER, temperature and residence time on the oxidation degree of the fermentation sludge was investigated. The process performance was evaluated by means of carbon-to-CO2 conversion efficiency, the nitrogen retention and the oxidizer use efficiency. The overall objective was to identify the oxidation in hot, compressed water as a feasible zero-waste technique in which carbon and nitrogen can be fully reclaimed, and furthermore, to find the optimal conditions for this process.

2. Materials and methods

2.1. Materials

Fermentation sludge was collected from a thermophilic membrane bioreactor fermenting a mixture of red beet, lettuce, wheat straw, toilet paper, and human feces. It was operated under anaerobic conditions, with slight overpressure (0.1 bar) and pH controlled at 5.3 to inhibit methanogenesis. Ultra-thurax was applied to homogenize the fermentation sludge and to reduce the size of dispersed solids in the fermentation sludge. A homogeneous dispersion with a dry matter content of 4 wt% was obtained. The characterization of the sludge can be seen in Table 1. For the oxidation experiments, the final sludge concentration in the micro-autoclave was set to be 2 wt%. The oxidizer was a 33 wt% H_2O_2 solution, obtained from Sigma-Aldrich. Additional deionized water was introduced to the micro-autoclave reactor for both reaching desired sludge concentration and adjusting the pressure in the sealed reactor at set-point temperature – see Section 2.2.

2.2. Apparatus and experimental procedure

All experiments were performed in a 45 mL batch cylindrical autoclave with top and bottom covers, which was made of INCOLOY 825. Typically, fermentation sludge (further diluted to 2 wt% DM in reactor) and H_2O_2 solution were introduced in the reactor (prior to heating) according to the desired oxidizer equivalence ratio. Deionized water was added to have a total amount of water in the autoclave, which upon heating to set point temperature, will yield the desired equilibrium pressure. Total amount of water was calculated by multiplying the reactor volume with the water density at the desired (set point) temperature according to the compressed water and superheated steam tables (Harvey, 1998). The reaction pressure at 300 °C was set at 110 bar (requiring a total of 16.08 g water), while pressures at 400 °C (16.08 g water), 450 °C (6.18 g water) and 500 °C (5.18 g water) were all set at 300 bar for supercritical conditions. The experimental pressure obtained during the experiments was slightly higher than the equilibrium pressure of water, as gaseous products were formed from the oxidation reaction.

After sample and reactant introduction, the reactor was sealed and a leakage test with 100 bar N_2 was performed, which also served to purge any air in the reactor's headspace. Following this, the reactor was pressurized using 3 bar N_2 after which the reactor was immersed into a hot sand bed fluidized by hot air. The reactor temperature was measured with an in-line thermocouple and pressure was measured by an in-line pressure transmitter. After the set-point temperature was reached (heating at an average rate of 0.9 °C/s), the autoclave was kept at this constant temperature for a pre-set time and then retracted from the sand bed and immersed into cold water for cooling down. The time at set-point temperature will be further referenced as 'residence time' throughout this study. Cooling down from 500 °C to 200 °C was at rate of 10 °C/s.

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