Hydrothermal oxidation of fermentation filtrate for use in a regenerative life support system

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Abstract:

A regenerative life support system is required in long-term human space missions to recycle carbon, nutrients and water from waste streams generated by the crew and food production system. The European Space Agency's life support system, envisioned by the MELiSSA project, utilizes anaerobic thermophilic fermentation as a first step to degrade organic waste. 'Hydrothermal oxidation was studied to potentially further decompose the fiber rich sludge drained from the anaerobic bioreactor. As volatile fatty acids are the main residuals with respect to soluble organic carbon in the membrane filtered permeate of the anaerobic bioreactor, the possibility to independently oxidize the residuals with hydrothermal oxidation was investigated.

Temperature (300 to 380℃), residence time (t_R) (28-60s) and the oxidizer equivalent ratio (OER) (1 to 4) were the experimental variables in the oxidation tests using a continuous tubular reactor and hydrogen peroxide as the oxidizer. A filtrate from the effluent obtained from the anaerobic fermentation of a model feed (wheat straw, red beet, lettuce, faeces, and toilet paper) was used as input to these experiments, and contained 0.5 wt% dry matter. The purpose of this study was to optimize the process conditions for oxidation of organic carbon to CO_2, while retaining the nitrogen in the liquid effluent. Non-condensable gases were analysed by gas chromatography and the liquid effluent was analysed by means of total organic carbon (TOC), and total nitrogen content.

CO_2 was the major carbon-containing gas product as expected, and nitrogen was partly converted into nitrate. The highest oxidation efficiency (of the feedstock TOC) achieved in our tests was 68.2%, and with 16.7% of the total nitrogen being converted to nitrate at 380℃, t_R=48s and OER=4. To conclude, the carbon conversion was far from complete at the conditions tested. Hereafter a first-order reaction rate was regressed to estimate the TOC removal rates.

1. Introduction

Mass recovery is a primary requirement for a closed system. A long term manned space mission is a typically closed system, which requires recycling of carbon, nutrients and water from waste streams generated by the crew and food production system[1]. The European Space Agency's life support system, envisioned by the MELiSSA project, utilizes anaerobic thermophilic fermentation as the first step to degrade MELiSSA waste. However, this process can never fully degrade all organics, which consists of large number of unaffected recalcitrant fibers in sludge and volatile fatty acids (VFAs) dissolved in membrane permeate[2]. It is important to further degrade undecomposed organic waste as well as maintain the environment for microorganism grows in anaerobic fermenter. The fiber rich sludge and VFAs rich filtrate are frequently drained from the anaerobic fermenter for further decomposition. Hydrothermal oxidation is an ideal method to decompose sludge and VFAs at a high efficiency. Nitrogen is simultaneously oxidized during process. The filtrate obtained from anaerobic fermenter contains water soluble organics and micro organic particles, while most unaffected TOC were in form of fibers and other insoluble organics in sludge. VFAs and sludge oxidation are assumed to have different TOC capacities and optimized reaction conditions. Sludge oxidation has been studied in a batch reactor. The filtrate, with less TOC content, is considered to be conducted in a continuous reactor with largely excess oxygen at around critical temperature to maximize carbon recovery. Nitrogen distribution is also studied.

2. Materials and methods

2.1. Materials

Filtrate was obtained from anaerobic fermenter from CMET (Ghent University). The mixture of wheat straw, red beet, lettuce, faeces, and toilet paper (MELiSSA waste)was thermophilically fermented. Filtrates was collected through a 45 μm membrane from anaerobic fermenter. Table 1 illustrates the properties of the filtrate. Hydrogen peroxide was obtained as oxidizer and diluted with distilled water to desired concentration.

Table 1 Chemical characteristics of undiluted filtrate (wet mass)

Parameters	Value
Total organic carbon (TOC) (mg/L)	3300
Total inorganic carbon (TIC) (mg/L)	25
Dry matter (wt.%)	0.77
Total nitrogen (TN) (mg/ L)	246.46
Total nitrate (mg/ L)	0.45
Total organic N (mg/ L)	101.17

2.2. Apparatus and experimental procedure

All experiments were performed in a coiled tubular reactor system. Feed and oxidizer stream were separately pumped into system by high pressure diaphragm metering pumps and preheated before mixed in a mixing tee. After exiting the reactor, the effluent was cooled by a heater exchanger to below 30°C. Solid was removed by the separator. Following, effluent passed through a filter in case smaller particles. After depressurized by a back-pressure regulator, gas and liquid products were separated and collected. Gas flow was recorded by gas flow meter. An electromagnetic stirrer was used to homogenize filtrates. An assembly unit was applied to get rid of the gas from H_2O_2 stream before accessing the pump. Temperatures ranged from 300 to 380°C. Filtrate concentration in mixture was 0.44wt% at all experiments after mixing filtrate stream with oxidizer stream. Hydrogen peroxide concentration in oxidizer stream was decided by OER.

2.4. Data expression and interpretation

Carbon recovery (CR) is defined as:

$$CR = \frac{[C]_{co_2}}{[TOC]_{feed}} \times 100\%$$

Where $[C]_{co_2}$ represents the carbon concentration in form of carbon dioxide in gas phase (mg/s), $[TOC]_{feed}$ represents the TOC concentration from feed (mg/s).
TOC removal efficiency (TRE) is defined as:

$$TRE = \frac{[TOC]_{feed} - [TOC]_{effl}}{[TOC]_{feed}} \times 100\%$$

Where $[TOC]_{feed}$ represents the initial TOC concentration in mixture (mg/L). $[TOC]_{effl}$ represents the residual TOC concentration in the liquid effluent (mg/L).
Carbon balance (CB) is defined as:

$$CB = W_{TOC} + W_{TIC} + W_{CO_2}$$

Where W_i represents the mass fraction of carbon in product i to total carbon from feed.
Hydrogen yield is defined as :

$$H_2 \text{ yield} = \frac{[H_2]_{gas}}{[weight]_{filtrate}} \times 100\%$$

Where $[H_2]_{gas}$ represents the weight of hydrogen gas in gas effluent (mg/s). $[weight]_{filtrate}$ represents the dry weight of filtrate running for experiments (mg/s).
Nitrate conversion (NC) is defined as:

$$NC = \frac{[Nitrate]_{effi}}{[N]_{feed}} \times 100\%$$

Where $[Nitrate]_{effi}$ represents the concentration of nitrate in the liquid effluent

(mg/L).

Organic nitrogen decomposition (OND) is defined as:

$$OND = \frac{[ON]_{effi}}{[ON]_{feed}} \times 100\%$$

Where $[ON]_{effi}$ represents the concentration of organic nitrogen in the liquid effluent (mg/L). $[ON]_{feed}$ represents the concentration of organic nitrogen from feed (mg/L).

Nitrogen recovery (NR) is defined as:

$$NR = \frac{\text{Sum } [N]_i}{[N]_{feed}} \times 100\%$$

Where $[N]_i$ represents the ammonia, nitrate or nitrite concentration in the liquid effluent (mg/L), $[N]_{feed}$ represents the total nitrogen in feed mixture (mg/L).

3. Results and discussion

3.1 Effect of operation parameters on carbon recovery

The effect of residence time on hydrothermal oxidation of filtrate is illustrated in Figure 1. Experiments under different temperatures were conducted in diverse residence times to satisfy the setup limits. Filtrate is not fully oxidized as shown in Figure 1. Only up to 46.9% carbon from feed filtrate can be converted into carbon dioxide at given reaction conditions. Carbon recovery can be enhanced by prolonging residence time at all temperatures. The effect of residence time under high temperature is more obvious than low temperature which can be explained by free radical reaction mechanism that higher temperature generates more free radicals to boost reaction [3].
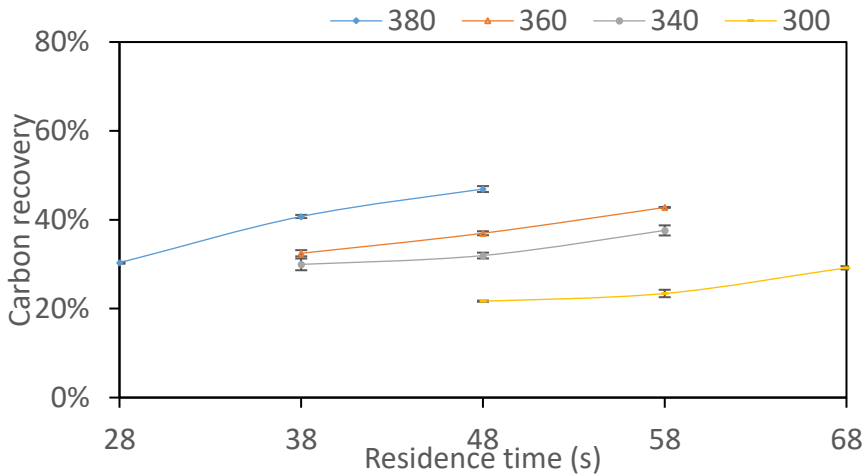

Figure 1 Effect of residence time on CR under 300, 340, 360 and 380℃ at OER=2.

Figure 2 shows the effect of OER on carbon recovery at t_R =48s under various temperatures. It can be observed from Figure 2.a that OER has significant impact on

carbon recovery. There is a positive correlation between OER and carbon recovery. The influence of OER can be enhanced by applying higher temperature. Comparatively, carbon recovery at 380℃ benefits more than at 300℃ from increasing OER.
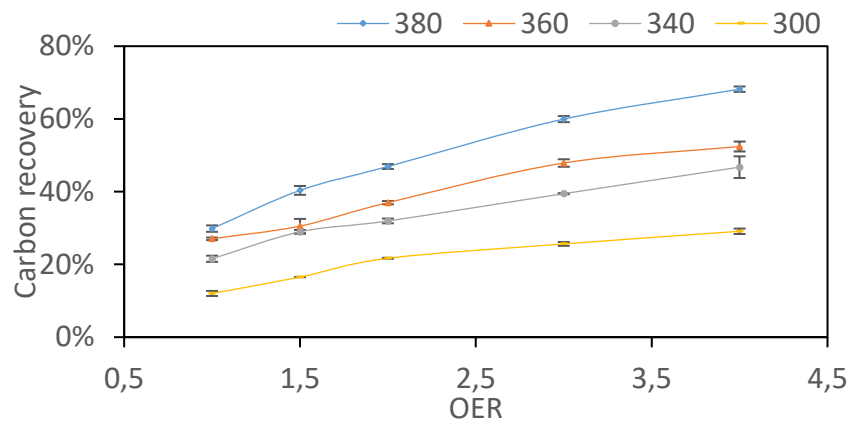
Figure 2 Effect of OER on CR under 300, 340, 360 and 380℃ at t_R = 48s.

3.2 Effect of operation parameters on nitrogen recovery

Nitrogen in MELiSSA waste was partly converted after anaerobic fermentation. Filtrate contains 58.8wt% nitrogen as ammonium and 41.0% nitrogen as organics. This work was to decompose the 41.0% organic nitrogen by means of oxidation. Nitrogen recovery efficiency of hydrothermal oxidation is evaluated by means of organic nitrogen decomposition. A maximum of 80.1% nitrogen recovery was obtained, resulting in total of 91.8% nitrogen recovery by combining fermentation and oxidation process. Final nitrogen products are nitrate, ammonium, few nitrogen in organics in liquid effluent and ammonia escaped in gas.

Figure 3.a demonstrates the results of organic nitrogen decomposition at OER=2 under different temperatures. The big lead of organic nitrogen decomposition under supercritical phase over subcritical phase indicates the positive effect of temperature. Decomposition of organic nitrogen increases slightly as prolonging residence time. The effect of residence time is not as effective as stated by previous studies[4, 5]. The effect of residence time is enhanced in higher temperature as shown from tests at 380℃ in Figure 3.

The effect of OER on organic nitrogen decomposition is shown in Figure 3.b. Organic nitrogen decomposition increase significantly when increasing OER from 1 to 2.

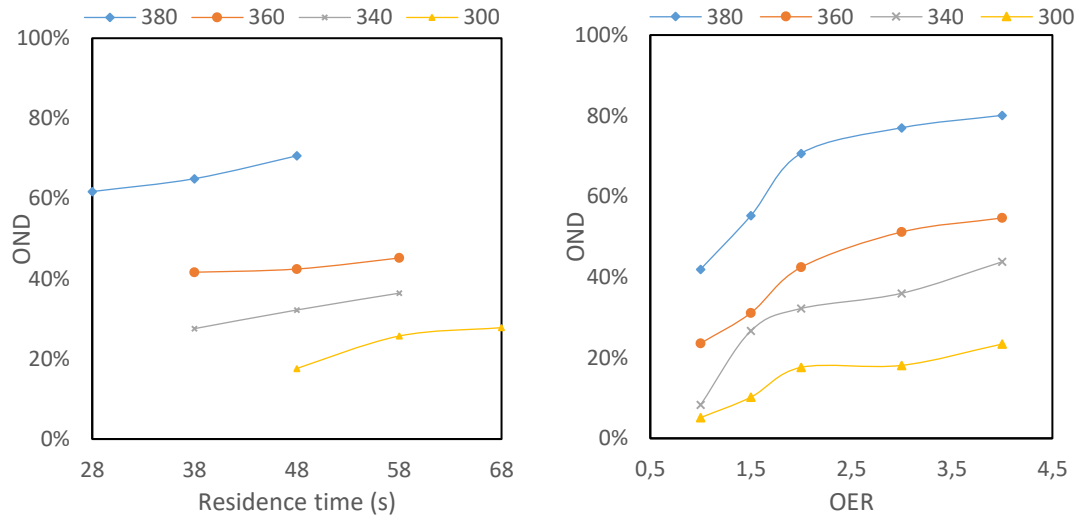(a)   (b)

Figure 3 Effect of (a) residence time at OER=2 and (b) OER at t_R =48s on organic nitrogen decomposition

Nitrogen oxidation occurs simultaneously with nitrogen decomposition. Ammonia is partly oxidized to nitrate. Ammonia could be from filtrate as well as decomposition product of organic nitrogen. N_2 and NO_x are not found in gas product probably due to low working temperature as studied[6-8]. Nitrite concentration is insignificant. Nitrate can be directly reused by plants and more favorable than ammonia for a regenerative life support system. The conversion from ammonia to nitrate is low(<20%) and greatly affected by temperature and OER. Nitrate conversion at 380℃ is obviously higher than subcritical phase. It consists with previous reports that conversion from ammonium to nitrate at subcritical phase is restrained and enhanced at supercritical phase[4, 6].

4. Conclusion

Fully recycling of filtrate has not been achieved in given conditions. Carbon recovery and nitrogen recovery are diverse in operational conditions. Carbon dioxide is almost the only gas products from hydrothermal oxidation of filtrate. A maximum of 68.2% carbon recovery is obtained. Higher temperature and OER will increase the carbon conversion to carbon dioxide. Nitrogen is slightly converted into nitrate with most remaining as ammonium. Total nitrogen recovery could reach 91.8%. Both temperature and OER have positive influence on nitrogen recovery and formation of nitrate.

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