行百里者半九十
——战国策
On reaching the last leg of a journey, you are only half way there
-- Strategies of the Warring States

Promotor: Prof. dr. ir. Frederik Ronsse

Department of Green Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, Ghent, Belgium

Dean: Prof. dr. ir. Marc Van Meirvenne

Rector: Prof. dr. ir. Rik Van de Walle

Hydrothermal oxidation for carbon and nitrogen recovery from organic wastes in a closed ecologic life support system

Dongdong Zhang

Thesis submitted in fulfillment of the requirements for the degree
of Doctor (PhD) in Applied Biological Sciences

Dutch translation of the title:
Hydrothermale oxidatie voor koolstof- en stikstofwinning uit organisch afval in een gesloten ecologisch levensondersteunend systeem

Cover illustration: by Dongdong zhang. Space picture from © ESA.

This work was supported by the financial support of the Belgian Science Policy (BELSPO) in the FDU project of MELiSSA project (ESA's life support system research program), the scholarship support from the China scholarship Council (CSC) and the Special Research Fund (BOF) in Ghent University

For citation: Zhang, D. (2018). Hydrothermal oxidation for carbon and nitrogen recovery from organic wastes in a closed ecologic life support system (Doctoral dissertation). Ghent University, Ghent, Belgium.

ISBN: 978-9-4635715-8-6

Acknowledgements

It’s really a pleasant experience to finish my *Journey to the West*. I would like to express great gratitude to all those who provided me with help and support during my doctoral studies.

First of all, I would like to express my sincere gratitude to my promoter Prof. Frederik Ronsse. His priceless and untiring support have helped me overcome the inevitable difficulties that I have encountered during my PhD. I have benefited from his expertise and knowledge in the fields of biomass conversion, thermal chemical, and chemical engineering. He provided guidance and advice, but also constructive criticism and encouragement that helped this thesis to assume its present form. Also, I would like to give my special thanks to Prof. Wolter Prins and Dr. Diego López Barreiro for their guidance and support at the beginning of my hydrothermal oxidation research.

I would also like to acknowledge the financial support of the Belgian Science Policy (BELSPO) in this FDU project (ESA contract number 4000113452/15/NL/AT), the BOF funding from Ugent and funding from China Scholarship Council. Their financial support make my research possible and my stay in Ugent well. The kind help from Dr. Amanda K Luther and Dr. Peter Clauwaert are also greatly acknowledged. Being working in a same project, they helped me a lot in data analysis and results discussion.

I am proud to say that I am a member of the *Thermochemical Conversion of Biomass* (TCCB) research group. It has been wonderful experience working with all the members – Mehmet Pala, Stef Ghysels, Dilani Rathnayake Mudiyanselage, Ligia da Silva Lima, Przemyslaw Maziarka, Jonas De Smedt, Adriana Estrada Leon, Prof. Jan G Pieters, Lut De Wit, Dieter Iemants, Eddy Philips, my tutor students Litse Huyghe and Matthias Vandemoortele, and those who have left the department. It is also important to acknowledge the people from another group – Prof. Eveline Volcke, Luis Corbala Robles, Hong Quan Le, Kimberly Tumlos

Solon, Stijn Decru, Janis Baeten and Annelies Van den Hove. It was an enjoyable experience to share the office and work together with them during the past years. I would like to also thank Huaming He, Xiaogang Shi, Zuoyi Yan, Junfeng Gao, Xinyu Wan, Qi Niu and Nannan Wu for their help in both study and live in Belgium. Special thanks to Mingsheng Jia and Lingshan Ma being kind friends to work and enjoy life together. Many thinks also go to those I cannot give a detailed list here.

And also many thanks to my badminton friends who made my life here at Belgium even more enjoyable – Zongcheng Lin, Tiantian, Lei Wang, Xin Tong, Xu Zhang, Way Cern Khor, Yayun Chen, Junwen Zhai, Weidong Li, Tingting Cui Yu Xue, Zhoujian Diao, Yang Li and all other friends who played together. Together with you, we participated in numerous badminton tournaments around Belgium and won some prizes. I miss the time we played together and I would like to play with you again in the future!

Finally, I would like to appreciate my upmost love to my parent, Yong Zhang and Mingyu Wu, my brother Xiaodong Zhang, and my grandparents Yuyang Zhang and Dengying Ding. I attribute much of my achievements to them. Without their support, I will never be able to reach where I am now. Also, I want to thank my most pretty and intelligent (秀外慧中) girlfriend Lin Ouyang for accompanying me and support each other during our PhD periods.

Time to hug the world!

Dongdong Zhang
Ghent, December 05, 2018

Notation index

Abbreviations

CELSS	Closed ecological life support system
CWAO	Catalytic wet air oxidation
ESA	European Space Agency
FDU	Fiber degradation unit
MELiSSA	Micro-Ecological Life Support System Alternative
OER	Oxidant equivalent ratio
SCWO	Supercritical water oxidation

Nomenclature

ANR	Ammonium nitrogen recovery	%
CB	Carbon balance closure	%
COD	Chemical oxygen demand	g O_2/L
CR	Carbon recovery	%
ID	Inner diameter	mm
NNR	Nitrate nitrogen recovery	%
NR	Total nitrogen recovery	%
OD	Outer diameter	mm
OE	Oxidation efficiency	%
ON	Organic nitrogen	mg/g
OND	Organic nitrogen decomposition	%
OUE	Oxidizer use efficiency	%
TIC	Total inorganic carbon	mg/g or mg/L
TN	Total nitrogen	mg/g or mg/L
TOC	Total organic carbon	mg/g or mg/L
TRE	TOC removal efficiency	%
VFA	Volatile fatty acid	mg C/L
VOC	Volatile organic compounds	mg/L

Latin symbols

A	Arrhenius pre-exponential constant	$(mol/L)^x/s$
a	Reaction orders of TOC	s^{-1}
b	Reaction orders of O_2	s^{-1}
c	Reaction orders of H_2O	s^{-1}
df	Column film thickness	μm
E_a	Activation energy	J/mol
L	Length	m
$Log\ R_o$	Severity factor	-
M	Mass	g
NO_3^--N	Nitrate nitrogen	mg/g
NH_4^+-N	Ammonium nitrogen	mg/g
NO_2^--N	Nitrite nitrogen	mg/g
P	Pressure	MPa
r	Global reaction rate	-
R	Universal gas constant	8.314 J/(mol K)
S	Stroke length	mm
T	Temperature,	°C or K
V	Volume,	cm^3
W	Mass fraction of carbon	%
X	TOC removal efficiency, equal to TRE	%
Y	Yield	mg/g

Greek symbols

τ	Residence time	min or s
ρ	Density	g/cm^3
ϕ	Flow rate	g/s
κ	Reaction rate constant	$(mol/L)^x/s$

Subscripts

$_0$	The initial state	-
$_{effl}$	Liquid effluent	-
$_{feed}$	Feedstock	-
$_{gas}$	Gas effluent	-
$_i$	A single component in a group of components	-
$_{rest\text{-}gas\text{-}C}$	Components of CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8 and C_4H_{10}	-

Abstract....VII
Abstract (Dutch)....XI
Aim and Outline of the thesis.... 1
Chapter 1 Introduction 5
1.1 Closed ecological life support system (CELSS).... 6
1.2 Hydrothermal oxidation 12
1.3 Conclusion.... 25
Chapter 2 Introduction to the experimental reactors 27
2.1 Continuous tubular reactor.... 28
2.2 Batch reactor 34
2.3 Continuous plug-flow reactor.... 39
Chapter 3 Hydrothermal oxidation of five model compounds.... 41
3.1 Introduction.... 42
3.2 method and materials.... 44
3.3 Results and discussion.... 48
3.4 Conclusion.... 57
Chapter 4 Sub- and supercritical water oxidation of anaerobic fermentation sludge for carbon and nitrogen recovery in a regenerative life support system 59
4.1 Introduction.... 61
4.2 Materials and methods 63
4.3 Results and discussion.... 68
4.4 Conclusion.... 81
Chapter 5 Feasibility of carbon recovery from fermentation sludge via supercritical water oxidation in either batch or continuous reactor 83
5.1 Introduction.... 84
5.2 Materials and methods 86
5.3 Results and discussion.... 89
5.4 Conclusion.... 99
Chapter 6 Mild temperature hydrothermal oxidation of anaerobic fermentation filtrate for carbon and nitrogen recovery in a regenerative life support system 101
6.1 Introduction.... 102
6.2 Materials and methods 105
6.3 Results and discussion.... 108
6.4 Conclusion.... 121
Chapter 7 Effluent recirculation during mild supercritical water oxidation dramatically improves oxidation efficiencies techno-economic viability.... 123
7.1 Introduction.... 124
7.2 Methods and materials.... 126
7.3 Results and discussion.... 131
7.4 Conclusion and perspectives 136
7.5 Transformation to CELSS.... 138

Chapter 8 Summary and perspective 139
  8.1 Summary 139
  8.2 Perspective of hydrothermal oxidation in closed life support systems .. 141
  8.3 Perspectives of hydrothermal oxidation 144
Appendix 147
Reference 159
Curriculum Vitae 181

Abstract

Extraterrestrial exploration and colonization is one of the first steps for humanity to discover the mysteries of the Universe and to ensure long-term survival of humanity. To make this dream come true, we have to meet basic requirements, including energy and resources for people to live away from Earth. Food, water and breathable air are the utmost basic requirements. Humans have studied the possibility to support life with a man-made ecosystem, or also called a closed ecological life support system (CELSS). There is no CELSS that has “unlimited resources” like Earth. Therefore, a CELSS for use in space exploration has to recycle all wastes. The study of solid waste recycling in life support systems only got minor attention and is not implemented thus far.

This study aims to fully recycle the resources from wastes, avoiding the depletion of resources because of storage and disposal of solid waste which is the current practice. The research in this doctoral thesis is financially supported by the European Space Agency (ESA). In the concept of ESA’s MELiSSA (Micro-Ecological Life Support System Alternative) loop, organic wastes are firstly treated in a thermophilic bioreactor to mainly generate volatile fatty acids (VFAs), ammonium and carbon dioxide. These products can be further used in recycling of resources. However, the thermophilic bioreactor is not able to fully decompose all the organic waste. Plant fibers, as the main constituent of solid MELiSSA waste, greatly resist the anaerobic bioreactor and they end up in the digestate. The material loss represented by the undigested plant fibers in the waste is one of the main bottlenecks in the MELiSSA loop. Hydrothermal oxidation was proposed to decompose (residual) fibers and recover carbon and nitrogen. The research in this doctoral thesis composes the use of hydrothermal oxidation technology to maximize the carbon conversion to carbon dioxide and the nitrogen conversion to soluble nitrogen compounds because these can be easily recycled in the MELiSSA loop.

Hydrothermal oxidation is a chemical reaction that oxidizes dissolved or suspended organics in water using either air, oxygen, hydrogen peroxide or other oxidants as oxidizer. Carbon contained in the waste feed after hydrothermal oxidation can be oxidized into carbon dioxide. Nitrogen can be oxidized to nitrite, nitrate, and other nitrogen compounds depending on reaction conditions. Temperature, residence time and oxidizer to carbon ratio are commonly studied parameters that affect hydrothermal oxidation greatly.

Five model compounds were subjected to hydrothermal oxidation to study the performance of hydrothermal oxidation technology on organics conversion to carbon dioxide. From these results, complete conversion of model compounds was not achieved at 380 °C which was the highest attainable temperature in the given setup. The general trend observed was that higher carbon conversion was obtained at longer residence time and higher amounts of oxidizer injection.

The hydrothermal oxidation of fermentation sludge in both subcritical and supercritical water was investigated. The effect of above mentioned process parameters on hydrothermal oxidation of fermentation sludge were studied in a micro-autoclave. A maximum of 97.1 % carbon conversion to carbon dioxide was achieved. As a general trend, with harsher reaction conditions, carbon conversion was higher. The recovery of nitrogen was greatly affected by temperature. Higher temperatures improve the conversion of organic nitrogen to ammonium as well as ammonium to N_2 or NO_x. 400 °C was found to be the optimal temperature for nitrogen recovery. Next, both continuous and batch hydrothermal oxidation reactors were compared to evaluate the feasibility to recover carbon and nitrogen from the fermentation sludge which was obtained from a thermophilic fermenter running on simulated MELiSSA waste. The continuous reactor was found to have a higher capacity than batch reactors in decompose organic wastes but the latter reactor was more versatile to lots of feedstock types.

Fermentation permeate – also obtained from the thermophilic fermenter running on a simulated MELiSSA waste and mainly consisting of VFAs (volatile fatty acids) - was also tested in hydrothermal oxidation to recover carbon and nitrogen. The effect of different process parameters was investigated. The maximum TOC (i.e. total organic carbon) removal during permeate oxidation was only 68.2% with a maximum of 91.8% nitrogen found in either NH_4^+ or NO_3^- at the same reaction conditions. The low carbon oxidation in the permeate resulted from the fact that a great part of the carbon in this waste stream is in the form of acetic acid, which is specifically difficult to degrade in hydrothermal oxidation. Moreover, a reaction kinetic was proposed to describe the carbon conversion in the permeate. The activation energy for filtrate oxidation was found to be 95.7 kJ/mol. Reaction order of filtrate and oxygen were 1 and 0.42, respectively.

Due to the high risks (high pressure and temperature, corrosion issue, salt plugging problems,…) of hydrothermal oxidation technology, an effluent recirculation method was proposed to keep the oxidation setup to a small size while being able to decompose organics completely owing to prolonged residence times. A smaller sized reactor is more suitable for use in a closed life support system with the intention to be used in space. The recirculation method can be further extended to decrease the risks during performing the hydrothermal oxidation in other aspects. What’s more, the recirculation method enables one setup to be versatile to oxidize different organics with different degrees of recalcitrance without adjustment of operational conditions.

In summary, the objective to recover carbon and nitrogen from MELiSSA waste based fermentation sludge were successfully obtained. Resource recovery from fermentation permeate was partly accomplished but a kinetic analysis was performed to guide future study. In the end, a process method was proposed to decrease the technological risks of hydrothermal oxidation for application in a closed life support system.

Abstract (Dutch)

Buitenaardse verkenning en kolonisatie is één van de eerste stappen van de mensheid om de mysteries van het Universum te ontsluiten alsook het bestaan van de mensheid te garanderen over langere termijn. Om deze droom mogelijk te maken, moeten we de basisbehoeften voorzien, inclusief energie en grondstoffen om te kunnen overleven buiten de planeet Aarde. Water, voedsel en zuurstof zijn de primordiale basisbehoeften. De mogelijkheid om leven te ondersteunen in een kunstmatig ecosysteem, ook wel gesloten bioregeneratief levensondersteunend systeem genaamd (*closed ecological life support system, CELSS*), werd reeds bestudeerd. Echter, geen enkel *CELSS* beschikt over "ongelimiteerde" grondstoffen zoals planeet Aarde. Het is daarom noodzakelijk dat een *CELSS* voor ruimteverkenning alle gegenereerde afvalstromen volledig recycleert. Het recycleren van vast afval daarentegen, kreeg tot op heden weinig aandacht in het onderzoek en werd nog niet geïmplementeerd.

Het onderzoek in dit doctoraal proefschrift heeft tot doel alle grondstoffen uit organisch ruimte-afval terug te winnen, hierbij de uitputting van grondstoffen te vermijden doordat het opslaan en lozen van vast afval (zoals nu nog gebeurt) niet meer nodig is. Het onderzoek in deze thesis werd financieel gesteund door de Europese Ruimtevaartorganisatie ESA. In het concept van ESA's MELiSSA kringloop (*Micro-Ecological Life Support System Alternative*), wordt organisch afval eerst verwerkt in een thermofiele bioreactor om dit voornamelijk om te zetten tot vluchtige vetzuren, ammonium en koolzuurgas. Deze producten kunnen verder gebruikt worden als grondstof in het gesloten levensondersteunend systeem. Echter, de thermofiele bioreactor is niet in staat om alle bestanddelen in organisch afval af te breken. Plantenvezels, als voornaamste bestanddeel van organisch ruimte-afval, zijn grotendeels bestand tegen de microbiële afbraak en aldus eindigen deze in het digestaat. Het permanente verlies aan grondstoffen door de niet-afbraak van plantenvezels vormt één van de belangrijke obstakels in de MELiSSA kringloop. Hydrothermale oxidatie werd aldus voorgesteld om de residuele plantenvezels af te breken en koolstof en stikstof terug te winnen. Het onderzoek in dit doctoraal proefschrift bestaat uit het ontwikkelen van hydrothermale oxidatietechnologie om de

omzetting van koolstof naar koolzuurgas en de omzetting van organische stikstof naar oplosbare stikstofcomponenten te maximaliseren, gezien beide eindproducten kunnen hergebruikt worden als secondaire grondstof in de MELiSSA kringloop.

Hydrothermale oxidatie is een chemische reactie die opgeloste of gesuspendeerde organische bestanddelen kan oxideren door gebruik te maken van lucht, zuurstof, waterstofperoxide of een andere oxidantia. Koolstof gebonden in de bestanddelen van de organische afvalstroom kan aldus geoxideerd worden tot CO_2 en stikstof wordt omgezet tot nitriet, nitraat en overige oplosbare stikstofcomponenten afhankelijk van de reactie-omstandigheden. Temperatuur, verblijftijd en de verhouding oxidans/koolstof zijn vaak bestudeerde procesparameters gezien hun grote invloed op de oxidatiereactie.

Vijf modelcomponenten werden onderworpen aan hydrothermale oxidatie om de performantie van de technologie te bestuderen in termen van omzetting van koolstof naar CO_2. Uit de resultaten bleek dat geen volledige oxidatie kon worden bereikt bij een temperatuur van 380°C, dewelke de hoogste bereikbare temperatuur was in de gebruikte experimentele opstelling. Een algemene trend die werd waargenomen was dat langere verblijftijden in de reactor, alsook grotere hoeveelheden oxidans die werden toegevoegd leiden tot een hogere oxidatie van koolstof tot CO_2. De hydrothermale oxidatie in zowel subkritisch als superkritisch water werd bestudeerd. Het effect van de eerder vermelde procesparameters op de omzettingsefficiëntie werd nagegaan. Een maximum omzetting van 97.1% van koolstof naar CO_2 werd behaald. Een algemene trend was dat hoe intenser de procesomstandigheden, hoe efficiënter de oxidatie verliep. De terugwinning van stikstof was grotendeels afhankelijk van de gebruikte temperatuur. Hogere temperaturen bevorderen de omzetting van organische stikstof naar ammonium, en verder de omzetting naar N_2 en NO_x. Een temperatuur van 400°C werd bevonden als zijnde de optimale temperatuur om stikstof terug te winnen. Vervolgens werden batch en continue reactoren gebruikt om de haalbaarheid van oxidatie van koolstof en stikstof in fermentatieslib (dat werd bekomen uit een anaerobe fermentor die gevoed werd met een gesimuleerd ruimte-afval), bestudeerd. Hier werd geconcludeerd dat de continue reactor een hogere doorvoercapaciteit heeft dan een batch reactor

Het permeaat van de bioreactor die gevoed werd met een gesimuleerd ruimte-afval werd eveneens onderworpen aan hydrothermale oxidatie. Dit permeaat bestaat voornamelijk uit een oplossing van vluchtige vetzuren. De maximum TOC-verwijdering (TOC = totale opgeloste koolstof) bedroeg slechts 68.2 % terwijl 91.8 % van de oorspronkelijke stikstofhoeveelheid teruggevonden werd in het effluent onder de vorm van NH_4^+ of NO_3^- bij dezelfde reactie-omstandigheden. De lagere omzetting van koolstof kan worden verklaard doordat het permeaat rijk is aan azijnzuur, een component die gekend staat voor zijn hoge stabiliteit onder omstandigheden van hydrothermale oxidatie. Tenslotte werd ook een reactiekinetiek afgeleid, om de omzetting van koolstof in het permeaat te beschrijven. Voor de activatie-energie van de oxidatie van het permeaat werd een waarde bekomen van 95.7 kJ/mol. De reactie-orde van het permeaat en zuurstof waren respectievelijk 1 en 0,42.

Omwille van de hoge risico's geassocieerd met hydrothermale oxidatie (hoge temperatuur, hoge druk, snelle corrosie, zoutafzetting,...) werd een recirculatiemethode voorgesteld met als doel de reactor voor hydrothermale oxidatie in grootte te beperken terwijl volledige afbraak gegarandeerd wordt door de lange verblijftijd. Een kleinere reactor is eveneens beter geschikt om te worden ingezet in een gesloten levensonderhoudend systeem in ruimtevaartmissies. De recirculatiemethode kan worden uitgebouwd om de risico's in hydrothermale oxidatie te beperken. Bovendien, recirculatie staat toe het verwerken van verschillende organische afvalstromen met verschillende gevoeligheid tot oxidatieve afbraak, zonder dat de operationele omstandigheden in de reactor telkens moeten worden gewijzigd.

Om samen te vatten, het doel om koolstof en stikstof uit slib afkomstig uit de fermentatie van organisch ruimte-afval terug te winnen, werd succesvol gehaald. Grondstoffenterugwinning uit het permeaat daarentegen, werd echter gedeeltelijk behaald en een reactiekinetiek werd afgeleid om zo toekomstig onderzoek te

ondersteunen. Tenslotte werd een proces voorgesteld om de risico's geassocieerd met hydrothermale oxidatie te beperken.

Aim and Outline of the thesis

The development of this thesis is driven by the MELiSSA project aiming to achieve complete decomposition of MELiSSA wastes in a closed system for recovery of carbon and nitrogen. Previous research on the oxidation of solid CELSS waste were typically conducted with the raw waste which required a large amount of oxidizer. As a means of potential improvement, in this doctoral research the sludge from anaerobic fermentation of raw CELSS waste is subjected to hydrothermal oxidation. During anaerobic fermentation, part of the waste is converted into volatile fatty acids, ammonium and gases (including CO_2), while some unconverted constituents are left in the sludge (major ingredients of this sludge are undecomposed fibers and insoluble organics). As a consequence, the organic load for the subsequent hydrothermal oxidation process is greatly reduced. Additionally, the hydrothermal oxidation has also been tested to decompose the remaining organics in the filtrate following the anaerobic fermentation in compartment I to evaluate potential advantages (including feedstock flexibility) of this technique over biological downstream conversion. What's more, the main objective of this research is to convert carbon to carbon dioxide and nitrogen to soluble (reusable) nitrogen while previous studies only focused on organics decomposition. Finally, a novel and improved process is proposed to nearly fully decompose organics under constant mild conditions. The improved SCWO process is based upon effluent recycling and may be further implemented in a CELSS. Meanwhile, the effluent recycling process has several advantages that can serve as a potential solution to some hydrothermal oxidation problems.

The thesis is organized into 8 chapters.

Chapter 1 generally introduces the background of the CELSS and MELiSSA research project. It states the recent researches and major requirements of a closed life support system. The advantages and risks of the hydrothermal oxidation technology are discussed and the potential of hydrothermal oxidation to treat wastes originating in a CELSS is demonstrated.

Chapter 2 states the structure and detailed operational procedures of one batch and two continuous reactors that were used to carry out hydrothermal oxidation experiments to treat wastes from the MELiSSA project within this doctoral thesis. The continuous reactor was used in chapters 3 and 6 to oxidize model compounds and filtrate, respectively. The batch reactor was used in both chapter 4 and 5 to deal with sludge.

Chapter 3 studies the oxidation of 5 model compounds of which, cellulose and lignin were selected as they are the typical plant fiber constituents found in the MELiSSA sludge obtained after fermentation of the raw waste in compartment I. Furfural and phenol were chosen as model compounds to represent intermediates from cellulose and lignin decomposition, and acetic acid was selection as it is known to be the most resistant intermediate in hydrothermal oxidation. Oxidation studies of acetic acid and phenol were easy to found. Cellulose, lignin and furfural had hardly any studies before. Besides, it is important to know reaction phenomena and product distributions in hydrothermal oxidation process which was omitted by many researches. Oxidation of the 5 model compounds was conducted in both subcritical and supercritical water. Product distribution and reaction phenomena under different reaction conditions were observed and analyzed.

Anaerobic fermentation sludge oxidation was performed in **Chapter 4** within a batch reactor. Carbon and nitrogen recovery results were investigated under all reaction conditions. The effect of different parameters (i.e. temperature, residence time and OER) were discussed and evaluated. Gas and liquid products and their distribution were analyzed to understand the sludge oxidation mechanism in order to obtain the optimized carbon or/and nitrogen recovery.

To study the feasibility of hydrothermal oxidation for specific application in a CELSS, **Chapter 5** studied the performance of different reactors at recovering carbon from fermentation sludge. The operational procedures, carbon recovery, products distribution and processing capacity were compared. Besides, the fate of inorganic compounds after hydrothermal oxidation were investigated to evaluate the function of hydrothermal oxidation at resources recovery..

Being encouraged by the results from chapter 4 and 5, fermentation filtrate oxidation was studied in **Chapter 6** to understand the feedstock flexibility of hydrothermal oxidation over biological downstream conversion. The study was carried out in both subcritical and supercritical water to recover carbon and nitrogen by using the continuous reactor described in chapter 2. The influence of different parameters on carbon and nitrogen recovery were discussed. A kinetic modelling was further established to understand filtrate oxidation.

It was proved in above chapters that hydrothermal oxidation of organic wastes could achieve high carbon and nitrogen recovery. However, it is important to notice that optimized conditions varies with feedstock types. Harsher reaction conditions benefits carbon recovery but leads to more corrosion and costs. To take advantage of hydrothermal oxidation technology resulting in application in a closed environment, **Chapter 7** is proposed. It states a new recirculation process for hydrothermal oxidation that can greatly improve oxidation efficiency at mild reaction conditions while keep the reactor at a smaller dimension. The process was tested with 3 model compounds.

Chapter 8 concludes the overall process of the MELiSSA waste recovery and prospected applications of hydrothermal oxidation. Supporting data can be found in **Appendix**.

Chapter 1 Introduction

In this introductory chapter, the background of establishing the closed ecological life support systems is given, followed by a brief introduction to the current research of closed ecological life support systems and technologies used. It also provides further detail of the MELiSSA closed life support system, in which the research in this dissertation is situated. In closed life support systems, solid waste management, including recovery, is one of the major problems. The application and development of hydrothermal oxidation technology in waste treatment is discussed in detail. The risks and advantages of hydrothermal oxidation technology are provided.

1.1 Closed ecological life support system (CELSS)

1.1.1 What is CELSS?

With the development of human society, limited space and resources on Earth have forced people to find more habitable space, energy and resources. The development of underground spaces and high-rise buildings are stratagems to increase the living and working spaces for people. Renewable energy is also being studied and introduced on a massive scale in order to reduce dependence on fossil fuels while meeting society's ever increasing demand for energy. However, these measures might not be enough for the long-term development and sustenance of humanity. Though the present situation is not pressing, the development of potential solutions is necessary to allow the human society to thrive in the far future. Meanwhile, the measureless mysteries of the Cosmos need to be uncovered. Consequently, humans have to explore and move beyond planet Earth one day. The development of deep-space exploration (i.e. beyond earth's orbit like the current space missions, including the International Space Station) has to be considered. Potentially unlimited space and resources are out there. For example, the moon, the nearest astronomical object to our Earth, has vast quantities of rare earth elements and valuable resources like helium-3 that can be used in the development of renewable energy sources on Earth (Crawford 2015). A moon or Mars colony are also being considered and have been depicted in many movies and science fiction novels (Zhao 2007).

Table 1-1 Basic requirements to support a person in space (Takahashi 1989, Nelson et al. 2010).

Basic requirements	1 day (g/person)	1 year (kg/person)
Food (dry)	624	219
Oxygen	835	329
Water in food	500	183
Drinking water	1850	657

For deep space exploration and habitation, we have to satisfy the basic living needs consisting of breathable air, food and water. In deep space, these resources cannot be satisfied by the supply from Earth given the long distances and the high costs of supply spacecraft (Gustan et al. 1982). Table 1-1 shows the basic requirements to support a person in space. A man-made closed ecological life support system that has a similar function to Earth's biosphere is an option to recycle all waste generated during a space mission and to regenerate air, food and water for the crew. Lots of names have been given to such systems varying in size, complexity and the degree of material closure. Bioregenerative Technology (Nelson et al. 1994), Biospheric Systems (Allen et al. 1987, Allen 2002), Controlled Environmental Life Support Systems (Tibbits et al. 1982, Hill et al. 1989),Closed Ecological Systems for Life Support (Oswald et al. 1965, Nelson et al. 1992) and Regenerative Life Support Systems (ESA 2018) are names given to these typical self-sustaining life support systems. These concepts were developed to work independently without in and outgoing resources.

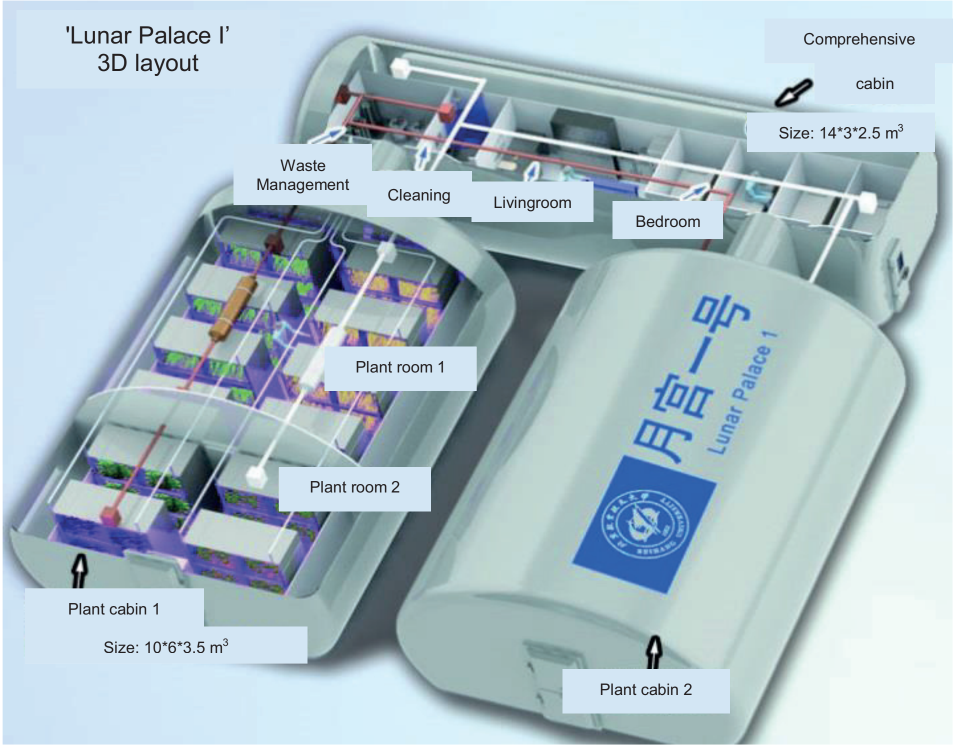


Figure 1-1 Lunar Palace 1 © (CNSA)

Europe, Japan, Russia, the United States, the People's Republic of China, and even private companies all have studied CELSS within the past 50 years (Oleson et al. 1986, Takahashi et al. 1989, Wheeler 2003, Nelson et al. 2010). The largest CELSS ever built was Biosphere 2, located in Oracle, Arizona. Two experiments for the purpose as CELSS were carried out by Biosphere 2 during 1991-1994, and both failed. The environment was hard to control due to limited knowledge back in the time (Marino et al. 1999). However, the Biosphere 2 experiments improved human's understanding of complex systems and was a brave attempt towards the life support of humans in a closed and artificial ecosystem. BIOS-3 was a closed ecosystem designed by Russia. BIOS-3 was smaller than Biosphere 2 and was more designed to the practical applicability in a long-term space mission. The objective was to create a small, self-sustaining system (Guo et al. 2017). Biosphere 2, on the other hand, was larger in scale and complexity (Nelson et al. 1993). China also studied the CELSS. Lunar Palace 1 was successful in carrying out a 105 days experiment with a multi-crew (Fu et al. 2016). The experiments have been carried on since then and lasted for 370 days, the system is displayed in Figure 1-2. The MELiSSA (Micro Ecological Life Support System Alternative) program of the European Space Agency is another typical project working on closed ecological life support systems (Clauwaert et al. 2017), as shown in Figure 1-2. More details on MELiSSA are provided in section 1.1.3.

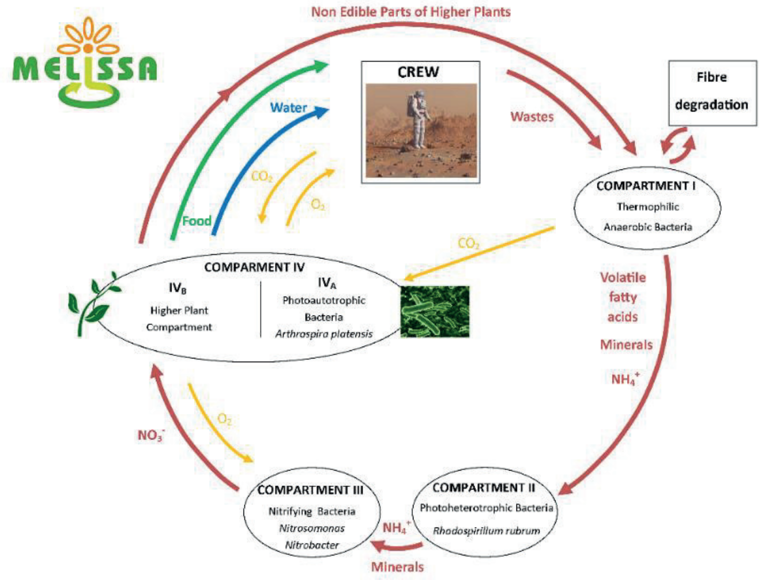


Figure 1-2 MELiSSA Loop © MELiSSA (ESA 2015 e), fiber degradation was the unit where the work in this dissertation was situated.

1.1.2 Challenges in CELSS

The primary motivation of CELSS is the regeneration of food, water and air. As the CELSS are far smaller than Earth's natural ecosystem, CELSS have to accelerate the recovery of carbon, nitrogen and other nutrients from waste which otherwise would take years on Earth in an ecosphere with vast quantities (buffers) of carbon, nitrogen, oxygen and nutrients. On the other hand, the CELSS are characterized by a low level biodiversity and a complex surrounding environment, making the stability and long-term operation a challenge (Gitelson et al. 2003).

Biological processes are important components of CELSS to provide water, air and food. What's more, the stabilization of the closed ecosystem relies on the use of green plants (Nelson et al. 2003) which are commonly used as a source of food and oxygen through photosynthesis (Blüm 2003). One of the six modular units of the *Mars on Earth research* was used for growing crops (Silverstone et al. 2003). *Bios-3* had 4 compartments, 2 of which were accommodated by higher plants and one was occupied by algae. All the gas and water purification needs (for people and animals) were satisfied by the higher plants and algae in *Bios-3* (Gitelson et al. 2003). Microbes and algae can also be applied to purify wastewater (Nelson et al. 1992, Marino et al. 1999). However, biological processes are not the only single option in regenerative life support systems. Physicochemical processes (i.e. electrolysis and membrane separation), can serve in the post-treatment (i.e. removing inorganic salts) of wastewater (Holtzapple et al. 1989, Smith et al. 2006). Non-edible biomass and other organic wastes are not easily nor rapidly treated by biological processes. Integrated systems combining physicochemical and biological processes have thus been considered. In the *Phase 3 of Lunar-Mars Life Support Test project*, only approximately 25% of the oxygen regeneration was provided by green plants while the rest was provided by physicochemical processes. Solely using physicochemical processes was also studied for some wastes. For instance, the crew's fecal matter was treated by an incineration system in the *Lunar-Mars Life Support Test* project (Pickering et al. 1998). Incineration is capable of eliminating dry wastes but leads to the production of ashes and secondary pollutants (Al-Duri et al. 2015). Besides, the water content in many organic waste streams may be too high for considering their processing by means of incineration.

In general, the regeneration of atmosphere and water was around 100% in CELSS as demonstrated in most studies (Guo et al. 2014). However, solid wastes in most cases were not fully recycled but stored (Guo et al. 2017). The stored solid wastes didn't participate in the recycling and represented a permanent loss of resources. In order to fully recover all wastes, hydrothermal liquefaction has been applied in the MELiSSA project as a post-treatment to the residuals after mechanical grinding, anaerobic fermentation and filtration (Lissens et al. 2004). Some independent researches on full recovery from solid wastes have been conducted.

In the 1980s, Takahashi et al., (Takahashi et al. 1987) studied the catalytic wet oxidation of model wastes (mainly urine and feces) at a temperature of 120 to 374 °C with a residence time of several minutes to hours. Au, Pd, Pt, Rh and Ru were the used catalysts. Most nitrogen in the waste was converted to N_2, however, COD reduction was low and unstable. Wet oxidation of CELSS model wastes with temperatures from 250 to 500 °C has also been studied (Takahashi et al. 1989). Oxidation of model wastes was low at subcritical conditions with 2 hours residence time and increased to 100 % at supercritical conditions. Ammonium oxidation was constantly lower than 50 % at the given conditions. Turc et al., (Turc et al. 1999) studied the SCWO (supercritical water oxidation) of model wastes at 450 °C. Air was directly used as oxidizer without the formation of CO or NO_x. Timberlake et al., (Timberlake et al. 1982) oxidized human urea at 650 °C and got full decomposition of urea to nitrogen gas, water and carbon dioxide. Hong et al., (Hong et al. 1987) applied the SCWO for near complete conversion of urine and feces in a lab scale reactor dimensioned for a 8-person crew. Carbon was converted into carbon dioxide or char. Nitrogen was converted to nitrogen gas while the other major heteroatoms were removed as ash. Miller et al., (Miller et al. 2015) investigated the conversion of a feces simulant without using a co-fuel. Many other studies have been conducted on supercritical water oxidation of human wastes and all achieved near complete oxidation (Price 1982, Hübner et al. 2016). Hydrothermal oxidation of cellulose, lignin and hemicellulose, which are the main compounds of inedible parts of higher plants, have also been studied (Hao et al. 2003, Suzuki et al. 2006, Wahyudiono. et al. 2007).

In summary, the decomposition of solid wastes for CELSS were studied as the major purpose by some people. However, there were few to none studies forced on the purpose to recover carbon, nitrogen and other resources from solid wastes. The MELiSSA project is one of those who aims at the latter purpose.

1.1.3 The MELiSSA project

The MELiSSA research program is to develop an artificial ecosystem for long-term space missions, for instance to lunar bases or to Mars. It started 25 years ago and is managed by the ESA, aiming at the recovery of food, oxygen and water from organic wastes and carbon dioxide (Nelson et al. 1994, Lissens et al. 2004, Nelson et al. 2010). The MELiSSA loop has 5 compartments combined to do the work. As shown in Figure 1-2, these compartments are referred to as compartments I-IV, while the crew is considered the fifth compartment in which the waste streams originate. The loop starts in compartment I by transforming all organic wastes (named as MELiSSA wastes, including human feces and urine, toilet paper, food waste and inedible plant waste) to ammonium, CO_2, volatile fatty acids and minerals by anaerobic fermentation (ESA 2015 a). Ammonium, volatile fatty acids and minerals are further introduced into the photoheterotrophic compartment (II) to remove carbon (ESA 2015 b). Residuals with minerals and ammonium as main components are converted into nitrate and minerals in the nitrifying compartment (III) (ESA 2015 c) followed by the photoautotrophic compartment (IV) (ESA 2015 d) to generate oxygen and food. In the first compartment, only 70 % of the protein in the waste undergoes proteolysis and only 44 % of the fibers are degraded (ESA 2015 a). These low numbers pose a recovery-limiting step in the first compartment. As a result, a supplementary physicochemical process to achieve complete degradation of these residual proteins and fibers is necessary. Hydrothermal oxidation has been proposed as being a potential unit operation to degrade these residuals that cannot decomposed by the anaerobic fermentation in the first MELiSSA compartment (ESA 2015 a).

1.2 Hydrothermal oxidation

Hydrothermal oxidation is a general term to describe the oxidation of organic compounds in hot, compressed water. Further classification is made based on temperature and pressure (Naoko et al. 2002). Wet oxidation, subcritical water oxidation and supercritical water oxidation are 3 main studied types of hydrothermal oxidation (Nitta 1987, Takahashi 1989). Wet oxidation is a hydrothermal oxidation process running at temperatures below 300 °C while the residence time is in the order of hours (Dietrich et al. 1985). Subcritical water oxidation is the oxidation at temperatures between 300-374 °C (Brunner 2014). Supercritical water oxidation (SCWO) is defined as oxidation at temperatures above the critical point of water (T = 374 °C, P = 22.1 MPa) (Bermejo et al. 2006). Complete oxidation of waste in supercritical water could be achieved in seconds in some extreme conditions (Rice et al. 1998, Brennecke et al. 1999).

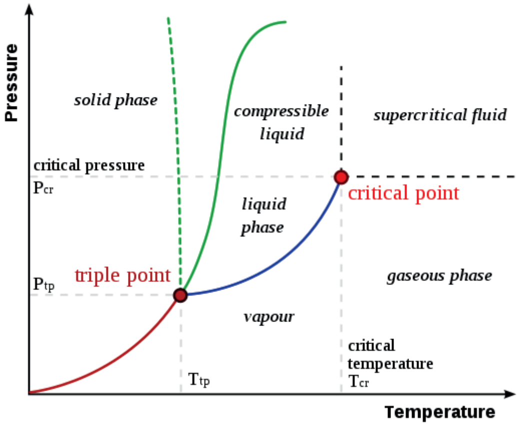


Figure 1-3 Pressure – temperature phase diagram of water

Water is normally considered as a polar solvent, thus being a good solvent to salts but a poor one for most organic compounds. Water is considered to be neither acid nor base. Pure water is thought to have zero electrical conductivity.

However, the above-mentioned properties could be dramatically altered by heating water under pressure (Tester et al. 1993, Mishra et al. 1995, Luck 1999, Bermejo et al. 2006). Water remains in the liquid form even if the temperature is increased as long as the pressure is higher than equilibrium vapor pressure, as shown in Figure 1-3. Nevertheless, the properties of the water change dramatically upon heating under pressure (Barner et al. 1992), as shown in Figure 1-4. The dielectric constant of water decreases from about 80 at 25 °C to less than 2 at 450 °C (Peterson et al. 2008). When surpassing the critical point, water thus becomes a poor solvent to salts but a good solvent for various organic compounds and nonpolar gases (Timberlake et al. 1982). Meanwhile, hydrogen bonding of the water molecules becomes weak resulting in near-critical water having both acidic and basic characteristics; the ionic product of water ($[H^+]*[OH^-]$) evolves from 10^{-14} at room temperature toward 10^{-11} at near-critical conditions (Jin et al. 2011). When temperature and pressure both surpass the critical point (T = 374 °C, P = 22.1 MPa), water is no longer considered a liquid nor a gas (Cocero et al. 2000), its state is termed a supercritical phase. Changes in physical properties (e.g. density in Figure 1-4) in supercritical water goes even dramatically (Mitton et al. 2001). Because of the dramatic changes in solubility of organics, supercritical water can provide a homogeneous phase for reactions with (otherwise insoluble in regular water) organic compounds (Brunner 2009).

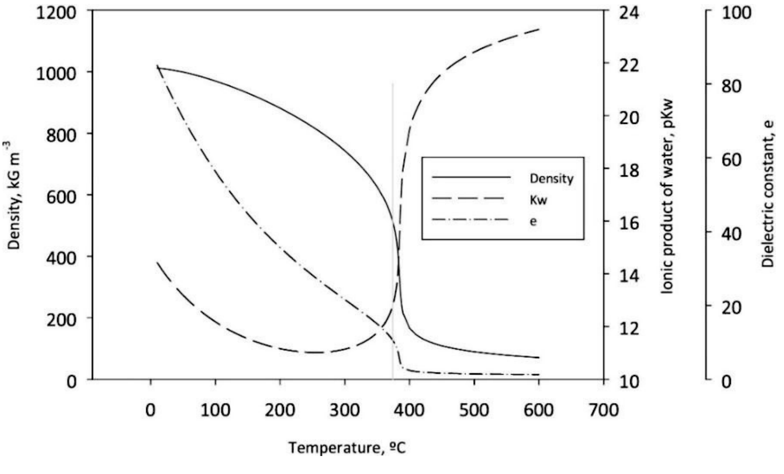


Figure 1-4 Water properties (density, ionic product and dielectric constant) of subcritical and supercritical water (Cocero et al. 2018).

Organics can be oxidized in hot, compressed water in the presence of an oxidizer, a process termed hydrothermal oxidation (Svishchev et al. 2006). Hot pressurized water, especially supercritical water, can enhance hydrothermal oxidation by dissolving organics and forming a homogeneous phase of the solvent-reactant-oxidizer mixture (Dietrich et al. 1985). The oxidation reaction is completed in minutes or even seconds. Under the proper conditions, feedstock carbon is converted into carbon dioxide with sometimes traces of carbon monoxide, methane or ethane. Hydrogen is converted to water. Feedstock nitrogen is converted to nitrogen gas, NO_x or soluble nitrogen species (i.e. ammonium, nitrite and nitrate) depending on the working conditions (Shin et al. 2012, Yang et al. 2017, Yang et al. 2018). Heteroatoms and metals are converted to the corresponding stabilized oxides (Fang et al. 2000, Kudenko et al. 2000, Wellig et al. 2005). Hydrothermal oxidation is an exothermic reaction, some studies state that if the organics concentration in the feedstock is higher than 4 *wt.%*, hydrothermal oxidation can be self-sustaining without the need of an external heat source (Vadillo et al. 2012).

Besides hydrothermal oxidation, hot pressurized water also has many other applications. Hydrolysis reactions are easy to perform due to the high reactivity of hot pressurized water (Shi et al. 2013, Capanema et al. 2017). Subcritical water extraction can be applied because of the high solubility of nonpolar compounds (Sahena et al. 2009).

Though hot pressurized water can create a homogeneous phase for oxidation, reduced solubility of salts could lead to their precipitation. The deposition of salts is considered one of the main problems in supercritical water oxidation. Transfer pipes and reactors can be blocked by the rapid precipitation of salts. Meanwhile, corrosion of reactor materials by hot pressurized water in combination with the oxidative environment is another major problem. No corrosion-resistant materials can withstand the harsh conditions of hydrothermal oxidation. Many studies (see section 1.2.5 and 1.2.6) have been done to resolve these problems but improved reactor materials and reactor configurations are still needed to be researched in order to come up with system designs that ensure long-term, corrosion-free performance (Marrone et al. 2009, Xu et al. 2010, Dong et al. 2012, Xu et al. 2012, Vadillo et al. 2013).

1.2.1 Hydrothermal oxidation of organics

Hydrothermal oxidation has been extensively studied in the last decades for the decomposition of organics. The mechanisms of hydrothermal oxidation (typically SCWO) were investigated by studying many model compounds (Rice et al. 1998, Schmieder et al. 1999, Brunner 2009). Acetic acid has been studied for its appearance as a major intermediate while demonstrating refractory properties (i.e. being highly stable). Phenol has been studied being a common toxic material in wastewater (Portela Miguélez et al. 1997, Matsumura et al. 2000, Kruse et al. 2003, Nunoura et al. 2003). Cellulose, as the most abundant natural polymer, has also been studied (Brunner 2009, Brunner 2014, Cantero et al. 2015). Acetic acid and ammonium are common intermediates. The conversion efficiency of acetic acid is low at low temperature. Goto et al. (Goto et al. 1998) studied the decomposition of acetic acid at process conditions consisting of a temperature of 385 °C, a residence time of 30 min and excess oxidizer addition to reach complete conversion. Helling and Tester (Helling et al. 1988) observed no decomposition of ammonium below 525 °C. Apart from model compounds, a lot of real wastes have been studied to solve real world problems, like textile wastewater (Söğüt et al. 2007), cutting oil waste (Portela et al. 2001), wastes from life support systems (Takahashi et al. 1989) and food wastes (Jin et al. 2001). Table 1-2 shows more details of some hydrothermal oxidation experiments that have been document in the scientific literature. From these studies, more than 99 % organic carbon conversion can be achieved under optimized conditions for many organic compounds in several seconds which proves that hydrothermal oxidation is a promising waste treatment technology (Chang et al. 2007). Operational conditions should be optimized depending on the feedstock and economic considerations. Typically, the optimal temperature can range from 300 to 800 °C, pressure can range from lower than the critical point up to 40 MPa, and residence time can range from seconds to minutes (Gloyna et al. 1993, Gloyna et al. 1995, Brunner 2014). Oxidation of polymers were found to be greatly temperature and residence time dependent (Park et al. 2001, Zhang et al. 2007, Onwudili et al. 2009).

Table 1-2 Examples of hydrothermal oxidation experiments from literature

Temperature (°C)	Residence time (s)	OER	Feed types	Setup types	Results	ref
400 - 550	60 - 300	< 10.0	dioxin	Batch	Dioxin Decomposition up to 98 %	(Zhao et al. 2014)
350 - 500	150 - 300	1.0 -3.0	tannery sludge	Batch	COD removal up to 96 %	(Zou et al. 2013)
400 - 600	0 - 400	0 – 4.0	quinazoline	Batch	TOC removal up to 97 %.	(Gong et al. 2016)
400 - 500	30 - 600	1.5 -3.5	oil-based drill cuttings	Batch	TOC removal up to 89.2 %	(Chen et al. 2017)
200 - 500	0 - 3600	/	wastewater containing amoxicillin and ciprofloxacin	Batch	TOC removal up to 63%	(Stavbar et al. 2017)
450 - 550	0 - 600	0 – 4.0	textile sludge	Batch	TOC removal up to 98.6	(Zhang et al. 2017)
400 - 600	60 - 240	1.0 -3.0	pesticide wastewater	Continuous	COD removal up to 99%, TN removal up to 87 %	(Xu et al. 2015)
400 - 600	4 -12	0 – 4.0	nylon 6/6	Continuous	COD removal up to 98.52%	(Söğüt et al. 2007)

Temperature is one of the most important process variables in hydrothermal oxidation. For most organic compounds, the higher the temperature at which the reaction is carried out, the more organic compounds are decomposed. Goto (Goto et al. 1998) studied hydrothermal oxidation of municipal sludge in the temperature range 200 – 600 °C and found faster and better TOC removal at higher temperature. Jin (Jin et al. 2001) carried out hydrothermal oxidation of kitchen waste at temperatures between 400 and 450 °C, and stated that higher temperature gave higher TOC removal efficiency. Chen (Chen et al. 2015) investigated the decomposition of rice from 300 to 500 °C. TOC conversion increased from 87 % at 300 °C to 99.98 % at 500 °C, while the concentrations of TN (total nitrogen) and NH_3-N decreased with an increase in temperature. Tan (Tan et al. 2014) reported the temperature sensitivity of organic compound destruction in hydrothermal oxidation processes. For the 12 kinds of organic compounds they studied, their conversion efficiency increased with an increase in temperature. There are some organic compounds (e.g. ammonium (Goto et al. 1999) and pyridine (Schmieder et al. 1999)) that decompose very slowly at low temperature but extremely quick when temperature is increased above a certain level.

Oxidizer equivalence ratio (OER) is another important parameter. Pérez (Pérez et al. 2004) operated SCWO of phenol with excess oxygen between 1.1 and 1.39 (being OER of 2.1 and 2.39 respectively) and achieved up to 99.9 % phenol removal. Oxygen and hydrogen peroxide are commonly used as oxidizer. Normally, the reaction order of the oxidizer is considered to be 0.3-0.5 (Portela et al. 2001). Oshima (Oshima et al. 1998) conducted SCWO of phenol using oxygen as oxidizer and the phenol removal was proportional to the power n = 0.48 of the O_2 concentration. Söğüt (Söğüt et al. 2007) operated SCWO of textile wastewater with different levels of hydrogen peroxide, assuming a zero order for oxygen concentration when oxygen is in excess. Portela (Portela et al. 2001) also studied the reaction order with respect to oxygen, and concluded that the reaction order was almost zero due to the large oxygen excess used (i.e. the molar ratio of oxygen to phenol was > 21).

Residence time in all hydrothermal oxidation processes is important to achieve higher compound removal and processing capacity of the process. Residence time for most hydrothermal oxidation processes is less than 1 min, but varies with feedstock type and reaction temperature. Complete conversion can be slowly achieved at low temperature and vice versa (Du et al. 2013). Thus, the balance between reaction time and temperature should be considered.

Pressure is not as important as temperature in affecting the SCWO process (Cantero et al. 2015). Increased pressure increases the density of water as well as the dielectric constant resulting in an improvement of the oxidation reaction rate (Chen et al. 2015). Sato (Sato et al. 2004) demonstrated the density effect on partial oxidation of methane in supercritical water and found that pressure affected methane conversion positively. Pressure in most researches were at similar level, from 22 MPa to 40 MPa, few studied SCWO at pressures higher than 40 MPa (Rice et al. 1998, Matsumura et al. 2000, R. L et al. 2000, Williams et al. 2005). Fixed pressure at different process temperatures was commonly conducted (Güngören et al. 2013, Zou et al. 2013).

1.2.2 Hydrothermal oxidation of nitrogen products

Nitrogen-containing organic compounds in industrial and municipal waste is getting more attention in recent years for their environmental threat by the accumulation of nitrogen species, resulting in pollution of the environment. Catalytic wet air oxidation (CWAO) and supercritical water oxidation are two promising chemical oxidation techniques that have been studied in the last decades to remove nitrogen from waste feedstocks (Benjamin et al. 2005, Yang et al. 2018). CWAO process operates at temperature typically between 120 °C and 310 °C with catalyst, using air as the oxidizer to oxidize organic and some inorganic components. The process normally has a residence time from hours to days (Takahashi et al. 1987). Nitrogen can be removed to some extent in the order of seconds by SCWO. Despite the disadvantage of longer residence times, the process conditions in the CWAO are milder, and thus more easily manageable, when compared to SCWO. Phuong (Phuong Thu et al. 2016) and Osibo (Osibo 2011) studied nitrogen removal using CWAO by means of applying different reaction conditions such as temperature, residence time, pressure and catalyst type (Ding et al. 1996, Curtin et al. 2000). Temperature is the primary parameter for determining nitrogen removal efficiency. Higher temperature always boosts nitrogen removal in CWAO. More feedstock nitrogen was converted into ammonium with increasing temperature and more nitrogen gas was produced at the same time. Ammonium was the primary product and could be further oxidized to N_2 as the main final product in the CWAO process. Pressure was thought to be the least affective parameter (Al-Duri et al. 2017). The presence of a catalyst is very important to CWAO (Lee et al. 2002). Non-catalytic wet air oxidation demonstrated quite low nitrogen removal efficiency. Catalysts can largely improve nitrogen recovery. For example, in Phuong's report (Phuong Thu et al. 2016), Ru/TiO_2 achieved a selectivity to N_2 and nitrate of 85% and 15%, respectively after 22 h while in the presence of Pt/TiO_2 the selectivity to N_2 was 89 % after 8 h.

SCWO works under more severe conditions than CWAO. Nitrogen removal in SCWO is faster and more efficient. Ammonium, nitrate, nitrite, N_2, N_2O and NO_x

were common end products from SCWO using N-containing waste feedstock. Nitrate and nitrite in most reports showed low concentrations in the effluent. Ammonium is a major SCWO intermediate and hard to decompose. N_2 and N_2O are both products from ammonium oxidation (Osibo 2011, Shimoda et al. 2016). N_2 formation is favored over N_2O at higher temperature. Pure chemicals, like 1,8-diazabicyclo[5.4.0]undec-7-ene($C_9H_{16}N_2$) (Osibo 2011) and acrylonitrile (Shin et al. 2012), and real wastes, like high strength coking wastewater (Du et al. 2013) and dyeing wastewater (Wang et al. 2013), as well as other materials have been studied for nitrogen removal by means of SCWO. Most researchers (Osibo 2011, Du et al. 2013, Cabeza et al. 2014, Al-Duri et al. 2015, Chen et al. 2015, Al-Duri et al. 2016) found that the conversion to ammonium and N_2 were enhanced with increasing temperature. As ammonium is a recalcitrant intermediate, oxidation of ammonium is usually considered as the rate-controlling step. Ammonium can still be detected above 650 °C in the effluent (Killilea et al. 1992). However, its degradation becomes more obvious when temperature is higher than 500 °C according to Wang (Wang et al. 2013). A high oxidizer equivalence ratio is also important to achieve ammonium oxidation. Increasing the temperature in the absence of an oxidizer results in higher ammonium concentration (Wang et al. 2013). In the presence of excess oxidizer, ammonium concentration decreased and ammonium conversion to N_2 increased (Garcia-Jarana et al. 2013, Gong et al. 2016). It can be concluded that excess oxygen is needed for complete ammonium conversion to N_2. Prolonging the residence time without excess oxygen has little effect on ammonium oxidation and N_2 formation (Wang et al. 2013). Initial concentration was also found to affect nitrogen removal (Osibo 2011, Garcia-Jarana et al. 2013, Wang et al. 2013). It was found that nitrogen and ammonium removal, and N_2 formation can be enhanced by increasing the initial concentration. To improve nitrogen removal, co-oxidation was introduced to SCWO. Methanol was added by Shimoda (Shimoda et al. 2016) to oxidize ammonium. Isopropanol (Cabeza et al. 2014, Al-Duri et al. 2015, Al-Duri et al. 2016) was also introduced to remove N-containing wastes. Both methanol and isopropanol can supply extra free radicals, specifically HO•, which help in the ammonium oxidation to gaseous nitrogen. Shin (Shin et al. 2012) also introduced $Ca(NO_3)_2$ and $Ca(OH)_2$ to convert 95 % reactive nitrogen from acrylonitrile to nitrogen gas which was only 14 % without the introduction of $Ca(NO_3)_2$. Nitrate from $Ca(NO_3)_2$ reacted with ammonium to produce nitrogen gas and to reduce total nitrogen in the effluent.

Nitrogen removal still needs to be studied further. The usage of catalysts in SCWO needs more research. Nitrogen removal of different feedstock might need different reaction parameters and only few feeds have been studied thus far. Ways to reduce oxidizer usage and energy consumption are future study points.

1.2.3 Hydrothermal oxidation of other inorganic substances

The behavior of heteroatoms like sulfur and phosphorus were also studied in hydrothermal oxidation. They are typically converted to the corresponding mineral acids (H_2SO_4 and H_3PO_4) (Fedyaeva et al. 2012). Chlorinated waste was studied by (Muthukumaran et al. 2000), hydrochloric acid was one of the reaction products and caused corrosion problems. With the addition of Na_2CO_3, significant reduction of corrosion was achieved. Saline feedstocks and corrosive solvents were oxidized by (Fauvel et al. 2005) with a porous reactor. Phosphorus was totally converted to phosphoric acid in the aqueous effluent. SCWO of sulfur was carried out by Wang (Wang et al. 2003), thiosulfate and sulfate were predominant sulfur containing products in the effluent.

Metal ions in the waste feedstock should be preferably removed before entering the SCWO system because of the low solubility in hot pressurized water. Metal ions (in salts) would precipitate in the reactor and lead to plugging and corrosion (Bo et al. 2009, Yao et al. 2018). Metal ions can also be converted into stabilized metal oxides after hydrothermal oxidation. Because of the low solubility of salts in hot pressurized water, this technique can also be applied with the specific aim to recover heavy metals from liquid feedstock (Fang 2014).

1.2.4 Subcritical water oxidation

There is no clear definition of the subcritical phase. Most publications tends to take hot pressurized liquid water in a temperature range between 300 and 374 °C as subcritical water (Yesodharan 2002, Marcus 2012, Villegas et al. 2016, Zhang et al. 2017). Subcritical water provides milder conditions compared to water at the supercritical phase (Vadillo et al. 2014). Full oxidation of organics needs longer residence times in subcritical water or may even be incomplete regardless of the applied residence time (Portela et al. 2001). Therefore, subcritical water oxidation is less well studied. However, the milder process conditions typical of subcritical water oxidation may also provide a benefit in terms of demanding less strict requirements of the reactor materials with respect to mechanical strength and temperature resistance (Vadillo et al. 2013). Also, subcritical water oxidation may be more suitable for some temperature sensitive products. Nitrogen, for example, is sensitive to temperature (Al-Duri et al. 2008). Process temperature can greatly shift the nitrogen oxidation products distribution. Nitrogen is more likely to be retained in the form of ammonium, nitrate and nitrite by subcritical water oxidation – whereas N_2 or N_2O are more common when using supercritical water in the oxidation process (Vadillo et al. 2011).

1.2.5 Challenges of hydrothermal oxidation

Corrosion and salt precipitation are two well-known problems of hydrothermal oxidation (especially SCWO) processes. Corrosion is caused by many reasons such as extreme pH values and high pressure. No materials have been found to be stable under all conditions. Stainless steel, titanium and nickel-based alloys are common materials used to construct SCWO setups (Brunner 2009). Many ideas (e.g. corrosion resistant layer (Marrone et al. 2009) and reactor redesign in section 1.2.6) have been proposed to control the corrosion. Salt precipitation is inevitable in supercritical water where salt solubility decreases to almost zero. Precipitated solids attach to the reactor inner walls leading to plugging problem (Bermejo et al. 2006). Heat recovery is another issue when designing reactor systems. Being an exothermic reaction, feeds with a heating value of 930 kJ/kg or higher are capable of generating enough energy for preheating the incoming feed from room temperature to 400 °C and equivalent energy for running the pump (Cocero et al. 2002). Proper heat integration is of great interest in industrial-scale application. Continuous flow reactors are preferred by most researchers to investigate SCWO processes for their continuous operation, faster heating and safety. Meanwhile, batch reactors are considered useful (Takahashi et al. 1989, Onwudili et al. 2007) because one of the major benefits of batch reactors is the autogenous pressure build-up (steam pressure provided by the water) whereas continuous reactors need to rely on high-pressure pumps.

Pumping is always a problem for high pressure systems. Metering pumps are frequently used in hydrothermal oxidation studies. However, these pumps may suffer issues when handling aqueous dispersions containing larger solid particles which is common in real wastewater and liquid waste feedstocks. Meanwhile, if the effluent also contains particles (because of incomplete reaction or the formation of new carbonaceous solids), the back pressure regulator may suffer from clogging as well.

1.2.6 Hydrothermal oxidation reactor design

To solve problems (including corrosion and salt precipitation) in hydrothermal oxidation, several types of continuous reactor configurations have been developed. Tubular reactors are designed with small diameters, in order to have high linear flow velocities and thus to avoid precipitation of solids. This type of reactor is now frequently used in research and industrial settings (Vadillo et al. 2013). The MODAR reactor was developed to have a container with two zones. In the upper zone at higher temperature, supercritical conditions prevailed and oxidation reactions take place whereas the lower zone is at a lower, subcritical temperature. The latter allows salts to be dissolved in the lower zone and to be removed from the reactor by draining the brine that collects in the lower zone of the reactor, as shown in Figure 1-5 (Huang et al. 1992, Fang 2014).

The cooled-wall reactor has been developed to separate temperature and pressure effects in the setup (Cocero et al. 2004). This reactor has an inner reaction chamber where oxidizer is separately pumped in, as shown in Figure 1-6. The reaction chamber is surrounded by the high pressure feed stream. The feed stream flows into the reaction chamber though a gap. This design allows pressure inside and outside of the reaction chamber to be equal. Because the oxidizer is only fed in the reaction chamber, the outer reactor wall is not in contact with the oxidizer and less corrosion resistant materials may be used, and the inner reactor wall doesn’t need to resist the high pressure.

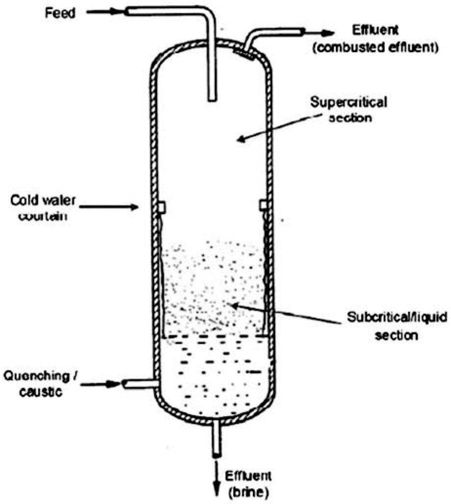


Figure 1-5 The MODAR vessel reactor (Huang et al. 1992)

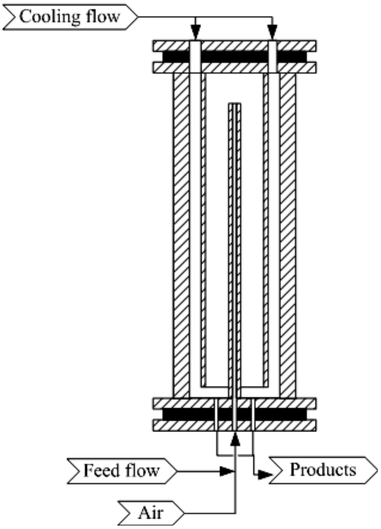


Figure 1-6 Basic structure of the cooled wall reactor (Pérez 2012)

The transpiring-wall reactor is a reactor design having a porous wall which allows subcritical water to permeate in the reactor, as shown in Figure 1-7. This cooler, subcritical water forms a film isolating precipitating salts from the wall and preventing them from attaching to the reactor wall (Mitton et al. 2001, Wellig et al. 2005, Xu et al. 2014).

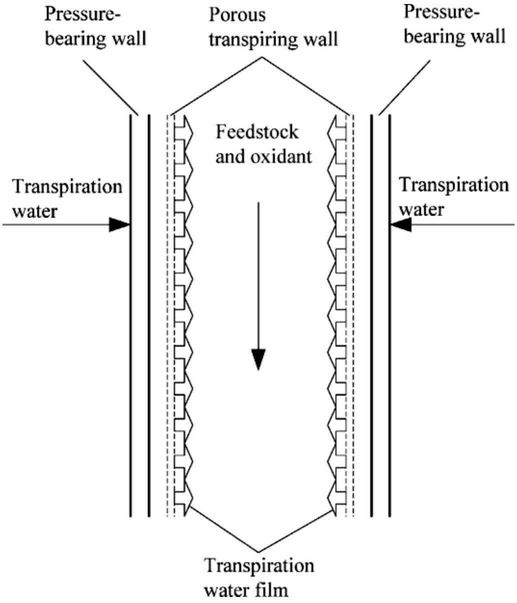


Figure 1-7 Basic structure of the transpiring wall reactor (Xu et al. 2014)

As shown in Figure 1-8, reactors with multi-oxidizer and cooling water injections have also been developed (Vadillo et al. 2013, Fang 2014). Oxidizer is injected into a tubular reactor by several injection ports, placed at varying distances from the point where the feed is injected, in order to distribute the oxidizer more evenly over the tubular reactor. An even distribution of oxidizer as opposed to a single injection into the entrance of the tubular reactor along with the feedstock, also avoids the occurrence of hot spots at the entrance.

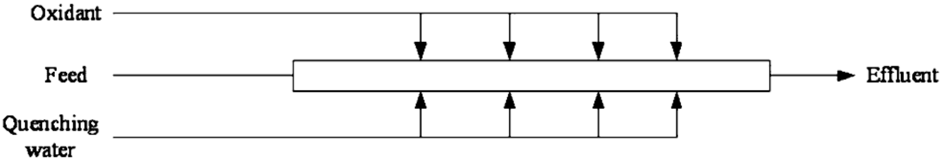


Figure 1-8 Tubular reactor with multiple injections (Vadillo et al. 2013, Fang 2014)

1.3 Conclusion

Hydrothermal oxidation has been demonstrated to be a viable treatment technology for recovery of resources from solid wastes. Compared with many other technologies to treat organic wastes, hydrothermal oxidation has much higher oxidation efficiency (especially for resistant fiber materials) and faster reaction rates which can be a great benefit in the scope of CELSS which needs high material turnover rates. Nevertheless, safety is challenging in CELSS for hydrothermal oxidation running at high temperatures and pressures. Hydrothermal oxidation requires a large volume of oxidizer and releases a large volume of CO_2 in a short time which might harm the atmospheric composition in a CELSS. In summary, the direct application of hydrothermal oxidation to treat solid wastes from CELSS is possible but has some problems and challenges to overcome.

The main work in this dissertation is to combine hydrothermal oxidation and MELiSSA research project to maximize the advantage of the former to solve the requirement from the latter.

Chapter 2 Introduction to the experimental reactors

There were two type of reactors used in this dissertation, namely a batch reactor and continuous reactor. The batch reactor was used to study the oxidation of sludge containing particles (Chapter 4 and 5). The continuous type reactor has two designs, one of which was used to study the oxidation of homogenous feeds (Chapter 3, 6 and 7). The other design was specifically used to evaluate the oxidation performance of sludge which contained particles (Chapter 5). This chapter is to give an introduction of the tested reactors, their structure, basic functioning, maintenance, debugging, and general operational procedures.

2.1 Continuous tubular reactor

As shown in Figure 2-1, the coiled tubular reactor has 2 diaphragm metering pumps. The two-pump configuration allows to separately feed the waste feedstock and the hydrogen peroxide solution. Both pumps are LEWA EK1 with different capacities. Electric heaters are used to preheat both streams prior to entry into the reactor. The two streams are mixed after preheating but before introduction into the tubular reactor. The mixture stream goes through the reactor within a given residence time. A tap water cooled heat exchanger is used to cool down the reactor effluent to room temperature followed by a gravity settler to precipitate particles. The effluent passes through a sintered-metal filter and is depressurized by a pressure regulator (Tescom, 26-1762-26-S). After separating the liquid effluent and the gas effluent, the gas is passed through a gas flow meter (Omega FLR 1004 or 1005, Omega Engineering, Norwalk, US). A picture of the setup can be found in Figure 2-2.

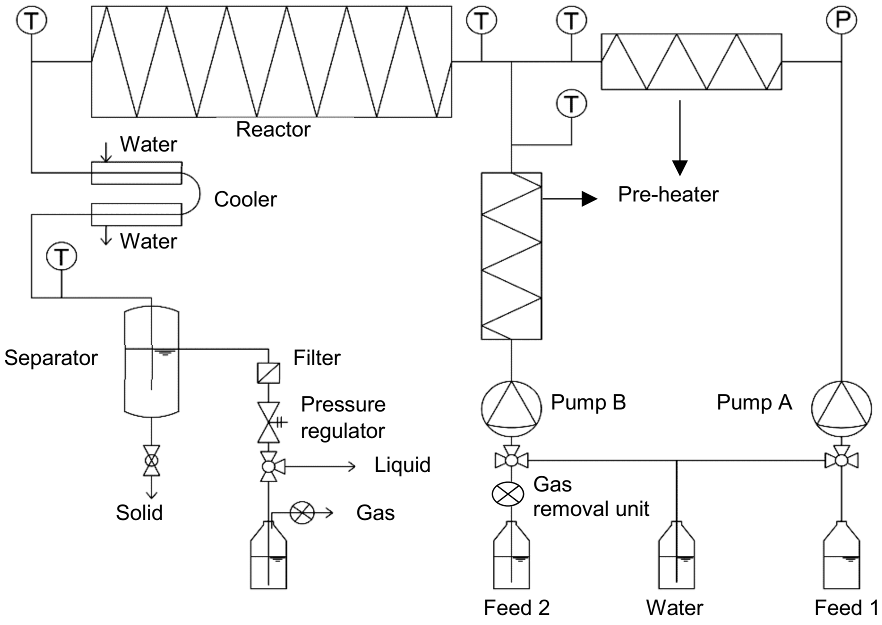


Figure 2-1 Schematic diagram of the experimental apparatus (T: thermocouple; P: pressure transducer).

The general experimental procedure starts by increasing the pressure gradually to the desired value while feeding demineralized water to both pumps, the system is then still at room temperature. The electrical heaters are switched on when the pressure stabilizes. After temperature stabilization at the desired value, the water is switched to waste feed and oxidizer streams for pump A and B respectively. The first liquid effluent sample is taken once 2000 mL of effluent has been collected. In the meantime, the gas flow rate should be stable. The second liquid effluent sample is taken 500 mL after the first sample, the third sample is taken 500 mL after the second one and so on. Finally, the experiment is shut down by switching both pumps to demineralized water again, turning down the electrical heating and lowering the system pressure gradually until ambient pressure.

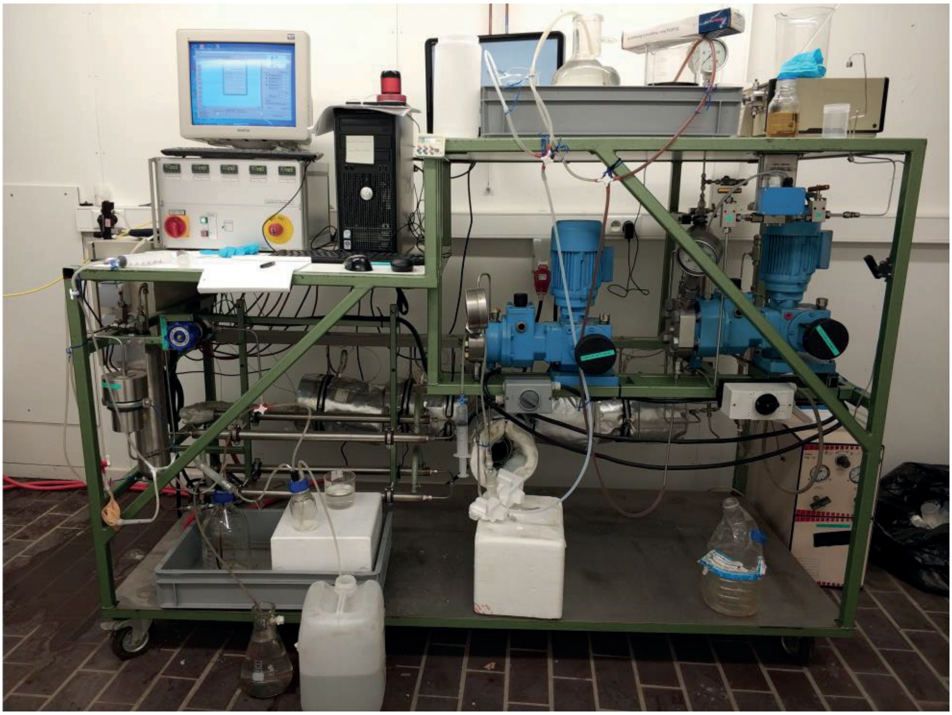


Figure 2-2 Picture of the continuous reactor

2.1.1 Pump and feed flow

Because of the age of the pumps and the fact they already underwent revisioning with membrane and valve replacement, the pump characteristics have to be remeasured. The Pump A was measured to have a maximum pure water flow rate of 1.977 g/s at a pressure of 0.1 MPa and a maximum stroke length of 15 mm. Pump B was measured to have a maximum pure water flow rate of 0.716 g/s at a pressure of 0.1 MPa and a maximum stroke length of 15 mm. The pump flow rate can be changed by adjusting the backpressure and/or the stroke length. By measuring the flow rate at different pressures and stroke lengths, software (*Matlab R2015b*) was used to perform regression analysis on > 100 of data points. Two empirical equations (Equation 2-1 and 2-2) were established to express the relationship between flow rate (Φ, g/s) and the two adjustable pump variables, being pressure (*P,* MPa) and stroke length (*S, mm*). Φ_A and Φ_B are flow rate of pump A and B, respectively. The tested pressure range was 0 - 30 MPa; the tested stroke range was 4 - 15 mm. The empirical equations for the pump characteristics are:

$$\Phi_A = -0.223 - 2.396 \times 10^{-2} \times P + 0.147 * S$$

$$(R^2 = 0.9996)$$

Equation 2-1

$$\Phi_B = -0.653 \times 10^{-1} - 7.472 \times 10^{-3} \times P + 8.904 \times 10^{-2} \times S + 3.181 \times 10^{-4} \times P \times S - 2.463 \times 10^{-3} \times S \times S$$

$$(R^2 = 0.9986)$$

Equation 2-2

Pump A is used to deliver organic feed. Pump B is used to deliver oxidizer (hydrogen peroxide). Hydrogen peroxide was bought from VWR International (Leuven, Belgium) as a 33 *wt.%* solution and diluted to the desired concentration according to the set oxidizer equivalence ratio (OER).

The feed stream for pump A should be free from particles to avoid pump or valve blocking. The oxidizer stream for pump B passes through a gas removal unit prior to the pump to remove any gas bubble resulting from premature decomposition of the hydrogen peroxide.

2.1.2 Reactor and residence time

The volume of the whole setup, shown in Figure 2-1, is around 1300 mL, including preheating and cooling sections. The preheater section consisted of two, serially connected 6 m high pressure coiled pipes (inner diameter: 3.09 mm, outer diameter: 6.35 mm, Alloy 600) for feed stream and one single 6 m high pressure coiled pipe for the oxidizer stream. The preheating section could increase both streams to temperatures around 180 - 200 °C before mixing and entering the oxidation reactor. The time the streams spent in the preheater was 90 ~ 180 s for the feed stream and 90 ~ 120 s for the oxidizer stream depending on stream flow rate. The reactor itself is also a coiled pipe (inner diameter: 3.09 mm, outer diameter: 6.35 mm, Alloy 600) with a reaction volume of 100 mL (Albrecht 2006). Residence time (τ, in s) is calculated by the following equation:

$$\tau = \frac{\rho_{R(P,T)} * V_R}{\Phi_{feed}}$$

Equation 2-3

Where $\rho_{\mathrm{R(P,T)}}$ is the density (in g/cm^3) of the mixture that enters the reactor at set temperature (in °C) and pressure (in MPa) (Harvey 1998), V_R is the reactor volume (in cm^3), and Φ_{feed} is the flow rate of the feedstock mixture (in g/s). The density of the mixture is assumed to be the same as that of pure water given the low concentrations in dispersed/dissolved organics in water.

At high pressure, both pump A and B cannot work with smaller flow rates to maintain system pressures which are needed during the experiments. Thus, the flow rates have to be set sufficiently high to yield stable system pressure, especially at higher pressures. Consequently, the ‘workable’ residence time will be shorter as the set system pressure increased. Meanwhile, the density of the mixture varies with temperature and pressure. Table 2-1 gives an overview of the residence time ranges which could be operated in at given temperature and system pressure.

Table 2-1 Operable residence time ranges in the continuous, tubular reactor

Temperature (°C)	Pressure (MPa)	Residence time (s) Upper limit	 Lower limit
380	25.0	50	25
360	21.0	60	30
340	16.0	70	35
300	10.5	80	38

2.1.3 Heaters

Three electrical heating units are used to heat the reactor. Two preheater units are used to preheat the feed stream and the oxidizer stream. Both streams are preheated to 180 ~ 200 °C prior to mixing. Water is used to flush the system while heating from room temperature to the desired reaction temperature (up to 400 °C for the setup). After the system reached the desired temperature, water is switched to feed stream and oxidizer stream to start the oxidation experiments.

2.1.4 Cooler and separator

There is no heat recovery in the system. Effluent out of the reactor is directly cooled down by a cooler using tap water. Typically, effluent temperature is reduced to 30 °C. The 30 °C effluent goes through a gravity settler and solids accumulated at the bottom of the settler are removed after the experiment. A sintered metal filter is installed between the gravity settler and the back pressure regulator to avoid entrainment of potentially present smaller particles. Unfortunately, the back pressure valve demonstrated to work improperly if the effluent was viscous, which happened when oxidation was incomplete, especially at low OER.

2.1.5 Sample collection

After depressurization, gases and liquids were separated using a separator flask. Gas flow rate was continuously measured by two gas flow meters (Omega FLR 1004 and 1005, Omega Engineering, Norwalk, US) depending on flow ranges. Gas samples were taken with a plastic syringe. Liquid samples were collected in a 100 mL plastic or glass container.

2.1.6 Cleaning procedure

After each experiment, a three-way valve is used to switch feed stream to pure water for cleaning the reactor. At least 1300 mL pure water is required to go through the reactor for cleaning before another run. In some cases, more water is needed because of residuals present from a previous run.

2.1.7 Shut down procedure

After running the reactor with water for the purpose of cleaning, the electrical heaters are turned down. As the temperature gradually decreases, the pressure can be reduced as well by adjusting the back pressure valve. However, pressure always has to be higher than the vapor pressure at the corresponding temperature. When temperature drops to be below 100 °C, pressure can be fully released. Tap water flow to the cooler is shut down when temperature in the reactor drops below 50 °C.

2.1.8 Problems

The continuous reactor has strict requirements for the feed in that no dispersed particles should be present. A magnetic stirrer (IKA) is used to homogenize the feed. On the other hand, the diaphragm metering pump has no tolerance to gas as well. Gas is easily compressed in the pump chamber leading to zero flow rate situations. Hydrogen peroxide slightly decomposes in the feed vessel and feed tubing forming oxygen gas. A gas removal flask is installed before the pump to remove any oxygen gas bubbles. The amount of oxygen gas separated upstream of the pump was measured, as this represented a loss in reactive oxygen going into the system. On average, the loss due to premature hydrogen peroxide decomposition constituted less than 0.22 % of the hydrogen peroxide supplied and can thus be considered negligible. Another problem is that solid products are formed in the reactor effluent in some cases (like at low OER). Despite the integration of a filter and a solids separator, it is not possible to quantify the solid product in each single run as this requires complete depressurization and disassembly of the setup.

2.2 Batch reactor

The batch reactor used for the experiments in this thesis was located in the high pressure lab of Twente University (the Netherlands). The setup (Figure 2-3) is a micro-autoclave with a volume of 45 ml (inner diameter: 22 mm, outer diameter: 30 mm, Incoloy 825). The autoclave is heated by immersion in a hot fluidized sand bed which is preheated with hot air. Three temperatures are measured during the experiments with thermocouples: inner temperature of the reactor (denoted as reactor temperature), temperature of the sand bed and temperature of the heating air. Air temperature is variable and usually 10 °C higher than sand bed temperature, while sand bed temperature is normally 10 °C higher than the reactor temperature. When the autoclave is immersed into the sand bed, it takes a certain time to reach the desired temperature which depended on the process conditions (set-point temperature, reactor loading, etc.). Reactor pressure is measured by an on-line pressure transmitter. The experimental setup picture can be found in Figure 2-4.

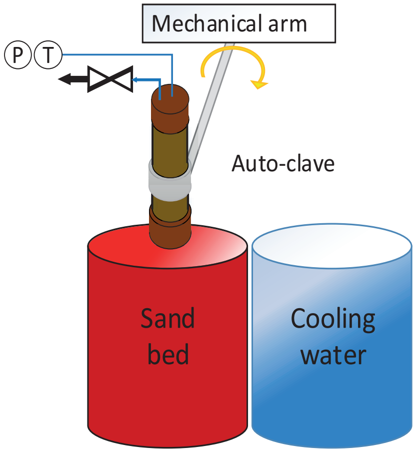


Figure 2-3 Scheme of the batch reactor

Figure 2-4 Picture of the batch reactor

2.2.1 General operational procedure

Before each test, feed and oxidizer were loaded into the autoclave which was then sealed and connected to the pressure transmitter with a metal tube. The end of the metal tube contains a valve that sealed the autoclave and also worked as the outlet for the gas product (after reaction) and the inlet of nitrogen gas (before reaction). After sealing the autoclave, nitrogen gas was introduced to remove inside air as well as to perform a leak test. The latter was performed by increasing the nitrogen pressure to an elevated level and checking whether the pressure was maintained after several minutes. After successful leak testing, the inner reactor pressure was decreased to 0.3 MPa before the autoclave was immersed into the sand bed (the nitrogen gas added is excluded from nitrogen recovery calculations). After the set-point temperature was reached, the autoclave was kept at this temperature for a pre-set residence time interval and then retracted from the sand bed and immersed into cold water for cooling down. Cooling down is very quick from the reaction temperature to around 200 °C (i.e. 30 s for going from 500 to 200 °C). Once the temperature dropped to ambient, gas was released into a collector (eudiometer). A syringe was used to take samples for micro-GC analysis after which the volume of produced gas was measured. Liquid product was transferred from the autoclave to a glass bottle for storage, after which TOC and other measurements were performed.

2.2.2 Experimental parameters

Waste feed

Sludge was taken from the C1 fermenter at CMET running on a simulated space waste under standard MELiSSA conditions (anaerobic, 55 °C, pH 5.3, 10 day hydraulic residence time, 80 - 100 days sludge residence time, 2 g dry matter $L_{reactor}^{-1}$ day^{-1} organic loading rate for the fermenter). The simulated space waste (or called standard MELiSSA waste) was a homogenized mixture with the following composition (in g dry weight per liter): wheat straw (5.4) , red beet (5.4), lettuce (5.4), human feces (3.0) and toilet paper (1.8), diluted in demineralized water (Luther et al. 2018). After production and prior to use, the sludge was kept frozen (- 20 °C). Upon thawing and prior to micro-autoclave testing, the sludge was stirred to form a homogeneous aqueous dispersion with a dry matter content of 4 *wt.%*. The concentration of sludge in the mixture in the reactor was kept constant to only 2 *wt.%* as a result of adding distilled water and hydrogen peroxide solution.

Temperature

The reaction temperature in the batch micro-autoclave experiments was set at 300, 400, 450 and 500 °C. It took several minutes for the reactor to reach set-point temperature. This heating time was considered long (sometimes even more than 400 s, see Figure 2-5) which might have affected the overall SCWO reaction outcome, which will be discussed in the respective chapters 4 and 5.

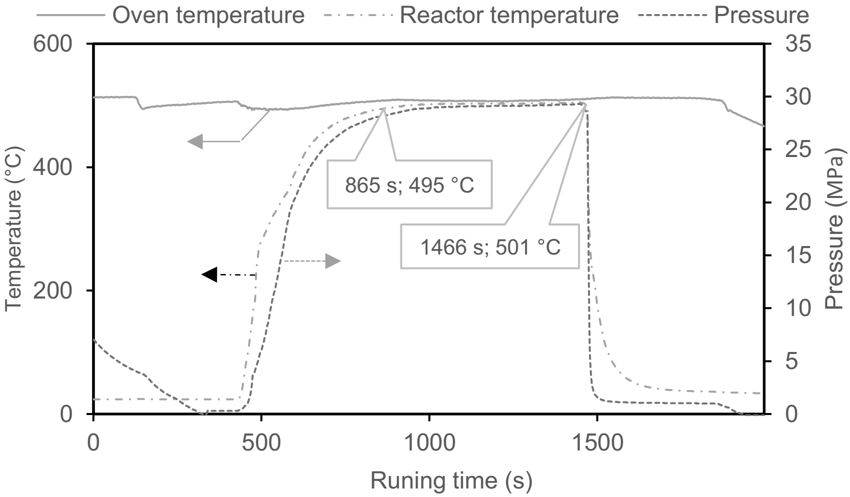


Figure 2-5 Example of pressure and temperature changes in the micro-autoclave in a test with reaction temperature of 500 °C and a residence time of 10 min.

Oxidizer equivalence ration, OER

The OER calculation is the given at continuous reactor experiments (section 3.2.2). Hydrogen peroxide was used as oxidizer. The original concentration of hydrogen peroxide stock solution was 33 *wt.%*. Hydrogen peroxide decomposes easily during the preheating stage. 1 mole of hydrogen peroxide is thought to release 1 mole of reactive O and 1 mole of water.

Pressure

The micro-autoclave was operated at the equilibrium pressure of 11 MPa at 300 °C and 30 MPa for temperatures of 400 °C and above. In a closed high temperature autoclave, the reaction pressure is decided by the amount of water added to the reactor prior to heating. In order to calculate this amount of water, water density data at specific temperatures and pressures were taken from the compressed water and superheated steam tables (Harvey 1998). The water amount (M_{water}, in g) is calculated using the following flowing equation:

$$M_{water} = \rho_{R(P,T)} * V_R$$

Equation 2-4

Where $\rho_{\mathrm{R(P,T)}}$ is the density (in g/cm^3) of the mixture that enters the reactor at set temperature (in °C) and pressure (in MPa) (Harvey 1998), V_R is the reactor volume (in cm^3), The density of the mixture is assumed to be the same as that of pure water given the low concentrations in dispersed/dissolved organics in water

Consequently, at lower temperature, more water was used, the exact amounts are shown in Table 2-2. However, one has to bear in mind that the actual pressure obtained in the autoclave could be slightly higher than the one obtained from its calculation, as the gaseous products being formed in the oxidation reaction contribute to pressure build-up as well, but were not taken into account in the theoretical pressure calculations.

Table 2-2 Weight of water needed for reach set reaction pressure in the micro-autoclave

Pressure (MPa)	Temperature (°C)	Weight of water to be added (g)
11	300	16.1
30	400	16.1
30	450	6.7
30	500	5.2

Residence time

Residence time was tested at 3 levels being 60 s, 300 s and 600 s. Residence time starts recording when the reactor temperature reached set-point (i.e. the time for heating and cooling are not within the residence time). After the set residence time had passed, the autoclave was withdrawn from the heated sand bed and submerged into cold water for cooling.

2.2.3 Problems

Given the overall small amount of reaction product present in the micro-autoclave, any amount of char or tar that could have formed (esp. at low OER) was too small for proper quantification. During the slow heating period before reaching the set point temperature, some reactions could already have taken place which could ultimately affect the outcome of the oxidation process. Besides, precise controlling of residence time remained a challenge. Further discussion on these problems will be given in the respective chapters.

2.3 Continuous plug-flow reactor

The continuous tests of MELiSSA waste was carried out in a coiled plug-flow reactor, as shown in Figure 2-6. The setup was owned and operated by Biomass Technology Group BV (BTG, Enschede, the Netherlands). The coiled reactor was 3.3 m of 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.

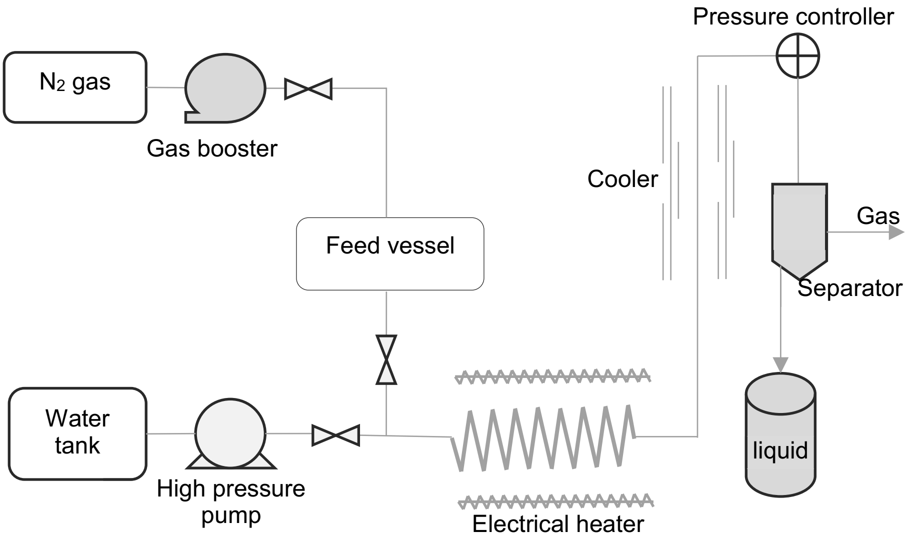


Figure 2-6 Diagram of the continuous SCWO setup

2.3.1 General operational procedure

The feed vessel was filled with feed and oxidizer. 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. It has to be remarked that this method of pumping the mixture and the oxidizer is different than the one used in the continuous setup in Chapters 3, 6 and 7 where two separate pumps were used and the feed and oxidizer were only mixed after pressurization and preheating. In the setup used in this Chapter however, the mixture of feedstock and oxidizer is prepared cold, and then pressurized before heating.

The reactor coil was purged with water during the heating of the setup. 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 water stream was turned off and the valve connecting the feed vessel with the reactor coil was simultaneously opened. The continuous run stopped when the feed vessel was empty.

Chapter 3 Hydrothermal oxidation of five model compounds

Five model compounds were tested to study the feasibility of hydrothermal oxidation in a continuous reactor and to identify the favorable process conditions which could be used in future oxidation studies with real waste feedstocks. Temperature (300, 350 and 380 °C), residence time (28 – 120 s) and OER (0.5, 1.0, 1.5 and 2.0) were studied to understand their influence in the oxidation of different model compounds. The model compounds selected were representative for the plant fibers found in the MELiSSA waste (i.e. cellulose and lignin), as well as for the intermediates formed in the decomposition of said plant fibers (i.e. furfural and phenol) and finally also acetic acid was included as the fifth model compound as this compound is known to be the most difficult to degrade in hydrothermal oxidation. From the results it is demonstrated that reaction temperature is the most influencing process variable, since oxidation experiments carried out at temperatures of 300 and 350 °C showed low oxidation extents with fractions of the raw materials (i.e. cellulose and acetic acid) even present in the final effluent. Tar or char was found in the oxidation of phenol, furfural and lignin. Oxidation at temperature of 380 °C with OER = 2.0 was able to deliver a clear and tar/char-free effluent.

3.1 Introduction

Hydrothermal oxidation of a variety of organic wastes has been studied during the past decades (Schmieder et al. 1999, Jin et al. 2001, Li et al. 2018, Yang et al. 2018). Higher temperature, longer residence time and higher oxidizer injection always have been found to lead to a higher degree of organics decomposition. However, it is also important to investigate the optimized parameters for different individual feeds as well as their corresponding behavior in hydrothermal oxidation. On the other hand, it is necessary to know the reaction phenomena and product distributions in both mild (i.e. subcritical) and harsh (i.e. supercritical) conditions, to operate hydrothermal oxidation in a proper way. Previous hydrothermal oxidation studies focused on reaching higher decomposition by applying harsher conditions. By-products (e.g. char and tar) were seldom produced and discussed. Literatures about oxidation processes under mild conditions are hard to find. In order to better understand hydrothermal oxidation at different reaction conditions, we studied the hydrothermal oxidation at temperatures ranging from 300 to 380 °C.

Among many hydrothermal oxidation studies, oxidation of model compounds have drawn significant attention. Most studied model compounds are small molecules as well as intermediates in hydrothermal oxidation. The study of model compounds could be the key to reveal mechanisms of oxidation in order to achieve full decomposition of organic wastes. Phenol is a model pollutant in industrial processes. Mechanistic and kinetic studies have been conducted by many researchers (Portela Miguélez et al. 1997, Matsumura et al. 2000, Kruse et al. 2003). Additionally, because the aim of the research in this dissertation is to study the degradation of plant fibers, phenol is also considered as an intermediate model compound in the degradation of lignin. Oshmia et al. (Oshima et al. 1998) obtained phenol conversion of 39.2 % at a temperature of 395 °C with an OER > 20 and at a residence time of 7.8 s. But there was no information about experimental phenomenon and residuals. Cellulose and lignin oxidation have gotten few research interest as opposed to phenol as they are not harmful and usually not necessary to be decomposed by hydrothermal oxidation. However, cellulose and lignin are the most abundant organic polymers in nature and the main residuals after fermentation of the MELiSSA waste (which is a simulated MELiSSA waste composed of beet, lettuce, wheat straw, toilet paper, and human feces). Wet air oxidation of lignin was conducted by Hasegawa et al. (Hasegawa et al. 2011) to convert a maximum of 45 % lignin into organic acids at 200 °C. Furfural is a by-product from the decomposition of hemicellulose, the latter being a common cell wall constituent in plants. To fully decompose hemicellulose containing organic wastes for recovery, it is interesting to study the performance of furfural in hydrothermal oxidation. Full oxidation of furfural was achieved in 5 hours at a low temperature of 100 °C (Saleem et al. 2017). Hydrothermal treatment study of furfural at temperatures >300 °C were normally carried out for hydrolysis purpose rather than oxidation (Kruse et al. 2003). Acetic acid is widely accepted as the most refractory intermediate in hydrothermal oxidation. The decomposition of acetic acid is the slowest step in many organic oxidation processes (Lee et al. 1990, Meyer et al. 1995, Gong et al. 2014). Hence, in this chapter the model compounds selected were phenol, acetic acid, furfural, cellulose and lignin.

This chapter aims at studying the oxidation performance of the selected five model compounds using the continuous reactor described in Chapter 2 (Figure 2-1). Effect of temperature (300, 350 and 380 °C) , residence time (28 - 120 s) and OER (0.5, 1.0, 1.5 and 2.0) were investigated to understand the behavior of model compounds under various working conditions. Both subcritical and (mild) supercritical water were studied to carry out the oxidation. In order to understand the behavior of each model compound, we studied their oxidation separately. A mixture of model compounds would require less experiments, but could have a complex behavior in oxidation, i.e. with interactions between model compounds occurring, hence the focus on the study of individual model compounds only.

3.2 method and materials

3.2.1 Materials

Cellulose, lignin, acetic acid, phenol and furfural were all bought from Sigma-Aldrich (Overijse, Belgium), analytical reagent grade. Alkali lignin was brought in the form of a powder (Alkali Lignin, Sigma-Aldrich). Although various forms of lignin exist (depending on the procedure to extract the lignin from a lignocellulosic matrix), only alkali lignin was selected. Comparison of oxidation behavior of different kinds of lignin was outside the scope of this study. The oxidizer was a 33 *wt.%* hydrogen peroxide in water solution, obtained from VWR International (Leuven, Belgium). The concentration of the model compounds in the feed stream was 1.0 *wt.%* for lignin and 2.0 *wt.%* for the other model compounds because the dispersion of lignin had a high viscosity, causing potential blocking of the high pressure pump – hence the need to reduce the lignin concentration.

3.2.2 Apparatus and experimental procedure

The continuous reactor, described in Chapter 2, was used to conduct the experiments. Upon mixing of the feed stream containing the model compound and the oxidizer stream, the actual concentration of the model compound going into the reactor was 1.0 *wt.%* (0.5 *wt.%* for lignin). Temperatures of 300, 350 and 380 °C were studied. Residences times were chosen within the range that was operable by the reactor system. As already laid out in Chapter 2, the maximum operable residence time is also temperature dependent. Specifically, residence times of 28, 35 and 50 s were studied at 380 °C, 35 and 60 s were studied at 350 °C and 60 and 120 s were studied at 300 °C. Oxidizer equivalence ratio for each temperature and residence time had 4 levels, OER = 0.5, 1.0, 1.5 and 2.0, respectively. Lignin has three common monolignols, namely p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. OER of lignin is calculated by assuming that the three monolignols are equal in mole concentration in the lignin. Although the monolignol concentration in lignin is variable (depends on the biomass type from which it is extracted) the latter assumption is reasonable considering the OER for lignin with only one single monolignol constituent was calculated to be in a narrow range of 1.9 - 2.1. Table 3-1 shows the different oxidizer amounts (expressed as a mass ratio) needed for the 5 model compounds. Provided sufficiently long and stable steady-state operation during which effluent samples were collected, each process condition (residence time, temperature, OER) was only performed once experimentally.

Table 3-1 Mass ratio (g/g) of H_2O_2 to model compound at given OER

Model compounds	OER = 0.5	OER = 1.0	OER = 1.5	OER = 2.0
Acetic acid	1.14	2.27	3.41	4.54
Furfural	1.77	3.54	5.31	7.08
Phenol	2.53	5.06	7.60	10.13
Cellulose	1.26	2.50	3.78	5.04
Lignin	2.18	4.35	6.53	8.70

3.2.3 Product analysis

Gas volumetric flow rate was recorded by an in-line gas flow rate meter (Omega FLR 1004 and 1005, Omega Engineering, Norwalk, US). The gaseous effluent was analyzed with a micro GC Varian 4900 (Agilent Technologies, Machelen, Belgium) equipped with two analytical columns: 10 m Molesieve 5 A (with backflush) and 10 m PPQ with TCD detectors, using helium and argon as carrier gases. The following compounds were measured by the micro-GC: H_2, N_2, CH_4, CO, CO_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8 and C_4H_{10}. The TOC (total organic carbon) of the liquid products (after filtering to remove any suspended solids) was measured with a TOC analyzer (TOC-5000 Shimadzu, Kyoto, Japan). After diluting the sample with Milli-Q water to bring its TOC to the range of determination (0 - 100 mg/L), the liquid sample was introduced into the analyzer through a 45 μm filter to remove any solids (if present) and the measurement was repeated at least 3 times.

3.2.4 Data processing and interpretation

OER is defined as the ratio of oxidizer fed to the stoichiometric amount needed for complete oxidation of carbon. When the OER is equal to 1, one mole of carbon requires 2 moles of hydrogen peroxide according to:

$$C+2H_2O_2 \rightarrow CO_2+2H_2O$$

Equation 3-1

A number of performance parameters were defined to evaluate the oxidation process. Carbon recovery (CR, in %) is defined to evaluate the carbon conversion efficiency:

$$CR\ (\%) = \frac{[CO_2 - C]_{gas} \times \Phi_{gas}}{[TOC]_{feed} \times \Phi_{feed}} \times 100$$

Equation 3-2

Where $[CO_2 - C]_{gas}$ represents the concentration of carbon as carbon dioxide in the gaseous effluent (in mg/g), $[TOC]_{feed}$ represents the concentration of total organic carbon in the influent mixture (in mg/g). Φ_{gas} represents the mass flow rate of gas effluent (in g/s), Φ_{feed} represents the mass flow rate of influent mixture (in g/s).

The oxidation process is also evaluated by the *TOC* removal efficiency (*TRE*). The *TRE* quantifies the mass fraction (in %) of the total organic carbon in the feed mixture ($[TOC]_{feed}$ in mg/g) that is removed through oxidation:

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

Equation 3-3

In which Φ_{feed} and Φ_{effl} are the flow of the influent mixture and the liquid effluent, respectively (in g/s). $[TOC]_{effl}$ is the total organic carbon in the liquid effluent (in mg/g). It is important to note that generally, the *TRE* is higher than the *CR* of a given process, as some of the feedstock carbon may end up in other forms than CO_2 (i.e. as CO, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8 or C_4H_{10} in the gas stream or as carbonaceous solids).

As not all of the reactive oxygen supplied by the hydrogen peroxide takes part in the oxidation reaction or some of the reactive oxygen yields oxidation intermediates (e.g. acetic acid), the oxidizer use efficiency (*OUE*) is defined as,

$$OUE\ (\%) = \frac{[O]_{H2O2} - [O]_{gas}}{[O]_{H2O2}} \times 100$$

Equation 3-4

Here $[O]_{H2O2}$ is the total amount of reactive oxygen supplied to the reactor (in mg) while $[O]_{gas}$ being the amount of oxygen in the gaseous effluent (in mg). In this calculation, it was assumed that 1 mole of H_2O_2 supplies 1 mole of reactive O or 0.5 mole of O_2 for the oxidation of organic compounds, according to the reaction $H_2O_2 \rightarrow H_2O + 0.5\ O_2$. However, the aforementioned reaction is the result of a multistep reaction involving the formation of both hydroxyl and hydroperoxyl radicals (Croiset et al. 1997). Because this decomposition occurs during heating of the reaction mixture containing the feedstock, other reactions involving these peroxide-derived radical intermediates and the supplied model compounds may occur.

The *OUE* thus quantifies how efficiently the oxygen was used in the oxidation reaction. A too low *OUE* indicates an inefficient oxidation by H_2O_2 and hence a higher dependence on the externally supplied oxidizer, which is an additional constraint in life support systems for long-term space applications.

Finally, carbon balance closure (CB) is defined as:

$$CB\ (\%) = (W_{TOC} + W_{TIC} + W_{CO_2} + W_{rest-gas-C})\ \times 100$$

Equation 3-5

Where W_i represents the mass fraction of carbon in product i to total carbon from the feed. Specifically for the gas phase, distinction is made between CO_2, CO as well as minor and trace carbon-containing components (CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8 and C_4H_{10}) which are lumped together as $W_{rest-gas-C}$.

One of the problems in the study of hydrothermal oxidation, is that the thermal intensity of the process is determined by both the temperature as well as the residence time. As already highlighted in Chapter 1, lower temperature processes could often reach similar results compared to higher temperature processes provided the residence time is sufficiently long in the former. So, to make comparison simpler it is useful to recombine both process variables into a single new variable which correlates to the overall thermal intensity. One such attempt is the so-called severity factor (Kabel et al. 2007), and is defined below as:

$$\log R_0 = \log(\tau \times \exp(\frac{T - 100}{14.75}))$$

Equation 3-6

Where $\log R_0$ is the severity factor, τ is the residence time (in min, preheating time not included), and T is the reaction temperature (in °C). The value of 14.75 (kJ/mol) is the fitted parameter which is commonly used (Kim et al. 2014).

3.3 Results and discussion

3.3.1 Hydrothermal oxidation at 300 °C

Products in all studied cases at 300 °C contained a large number of unreacted organics (e.g. in cellulose experiments) or dark solids, as shown for example in Figure 3-1. Some of the darker solids could also have been repolymerized intermediates, in the form of tar or char. No further attempt was made to analyze the composition of the tar or char products. It was also not possible for us to identify these solid products and their occurrence did not have any visible regularity. Carbon recovery in these experiments at 300 °C did not exhibit a clear trend, as shown in Appendix-figure 1. Gas flow rate fluctuated strongly during these experiments. Gas composition and liquid analysis results were unstable in most runs. We assumed that oxidation at 300 °C was ineffective, and the product distribution was not stable at the studied residence times (60 and 120 s). It can be concluded that a low working temperature of 300 °C at the tested (short) residence times could not fully decompose any of the 5 tested model compounds.

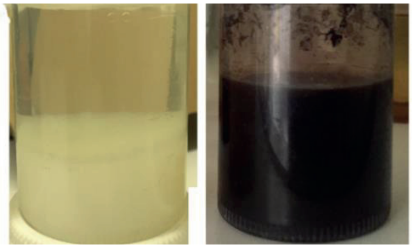


Figure 3-1 Effluent from cellulose (left) and phenol (right) oxidation at 300 °C, 120 s and OER = 2.0.

3.3.2 Effect of operational parameters on carbon recovery at 350 and 380 °C

Organic oxidation carried out at 350 and 380 °C were far more effective and consistent than at 300 °C. The effluent had a more favorable quality (i.e. clear liquid with little or no solid products in some cases), as shown in Figure 3-2. Detailed, tabulated results of the gas composition and the carbon distribution can be seen in Appendix, table 1-5.

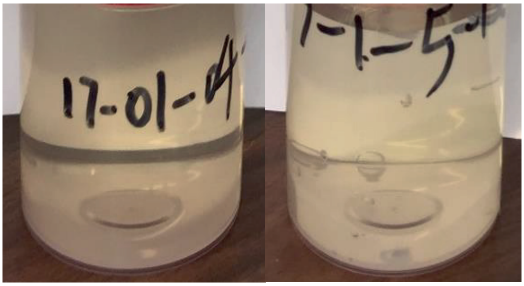
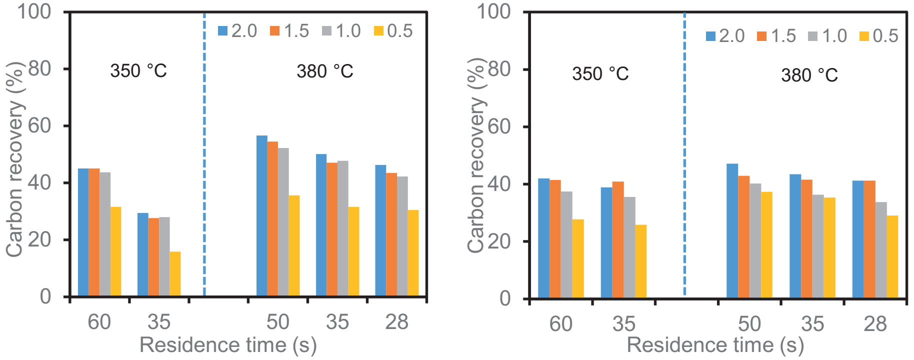


Figure 3-2 Effluent from cellulose (left) and phenol (right) after oxidation at 380 °C, 35 s and OER = 2.0.

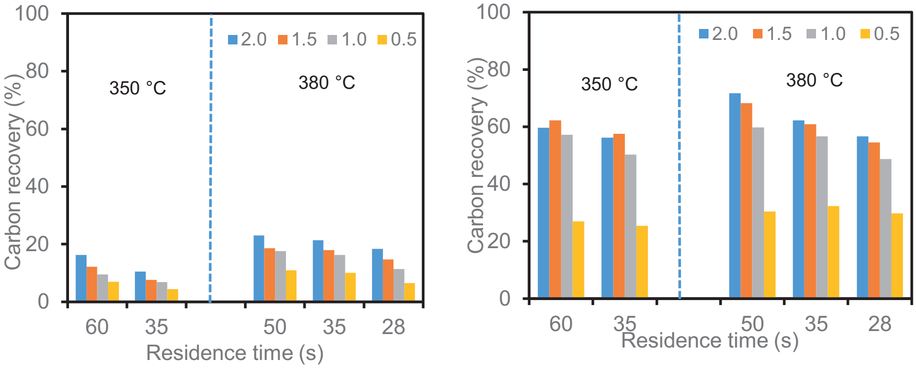
The obtained carbon recovery (CR) of the five model compounds is shown in Figure 3-3. The selected five model feedstocks performed differently due to their different chemical properties. Acetic acid is the most resistant chemical whose maximum CR was only 23.1 % under the tested conditions which is in line with previous studies (Meyer et al. 1995, Suzuki et al. 2006). Acetic acid was a common reported product in many researches (Chen et al. 1995, Aymonier et al. 2001). Its activation energy (> 100 kJ/mol) was reported to be much higher than most organics and consequently this results in the low oxidation efficiencies as observed. Lignin is less resistant than acetic acid and a maximum CR of 43.0 % was obtained. The other 3 model compounds all get their maximum CR higher than 50.0 % under the tested conditions. As shown in Figure 3-3 (b), lignin seems the least affected by the variation in the studied process conditions. It is assumed that lignin probably underwent decomposition (hydrolysis) and subsequent oxidation reactions. Reactions like lignin hydrolysis could be quick. But further degradation to smaller molecules could be slow at the given temperatures or alternatively, intermediates could be prone to repolymerization at low OER. The oxidation of intermediates appears to be slow while the oxidation of smaller molecules is fast, hence imposing more severe reaction conditions at given residence time range did not appear to greatly improve intermediates degradation, resulting in slow increasing overall lignin carbon oxidation. The maximum CR of 5 feedstocks are all achieved at 380 °C at which water is already at supercritical phase. Comparing obtained CR’s at 350 with those obtained at 380 °C, the oxidation in supercritical water had a big lead in efficiency over subcritical water. Supercritical water, as a more active reaction medium and the fact that radical reactions dominate in supercritical water, contribute to the oxidation of the target model compounds. With respect to the influence of residence time, longer residence times had a positive effect on CR and this effect is more obvious when the OER is higher than 1.0. The latter can be explained by the oxygen deficiency (at OER < 1.0) which is the primary limiting factor. As long as the oxygen supply is in excess, more time to complete the reaction will lead to higher oxidation efficiencies.

Considering each feedstock, the combined effect of OER, temperature and residence time is different. For example, lignin oxidation is less sensitive to increases in OER compared to the other model compounds tested as previously discussed. Prolonging the residence time is more effective in increasing acetic acid and furfural oxidation. Consequently, the composition of organics in a given waste feedstock has to be identified before applying optimized process conditions.



(a) Cellulose

(b) Lignin



(c) Acetic acid

(d) Furfural

(e) Phenol

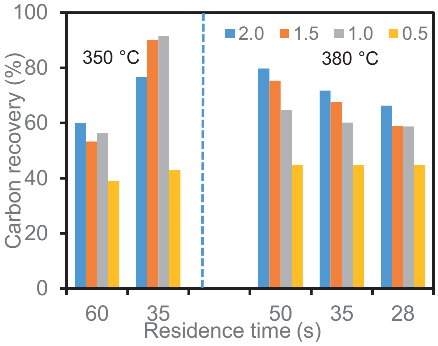


Figure 3-3 Carbon recovery (in %) of (a) cellulose, (b) lignin, (c) acetic acid, (d) furfural and (e) phenol oxidation at OER = 2.0, 1.5, 1.0 and 0.5.

The severity factor, a combination factor of temperature and residence time, is used to understand its effect on the carbon recovery, as shown in Figure 3-4. The carbon recovery followed a mostly continuous trend when plotted against the severity factor, with the exception of phenol and furfural where discontinuities (corresponding to the shift in temperature from 350 to 380 °C) were noticed.

Higher severity factors increase carbon recovery of most model compounds but to a different extent. These results confirm previous studies that higher temperature and longer residence time would enhance carbon recovery. However, the effect of the severity factor was greatly affected by the OER. As shown in Figure 3-5, for the case of acetic acid oxidation, the influence of the severity factor was enhanced by an increasing OER. This enhancement is more obvious when OER > 1.0. The effect of OER is not considered by most researchers when studying the effect of the severity factor.

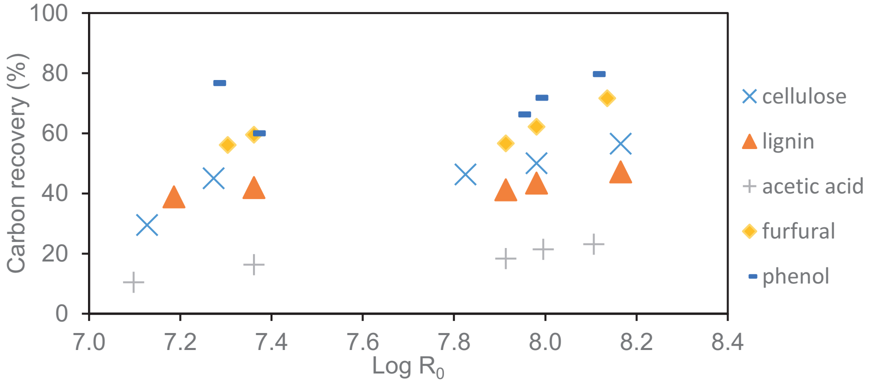


Figure 3-4 The carbon recovery (in %) obtained from hydrothermal oxidation of 5 model compounds at OER = 2.0 as a function of the severity factor, log R_0.

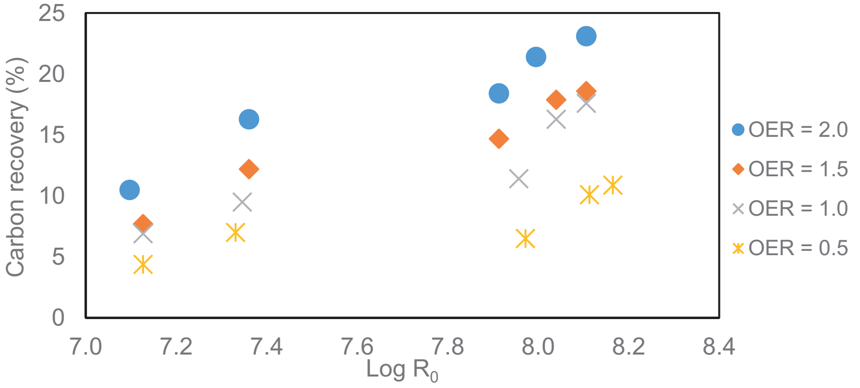


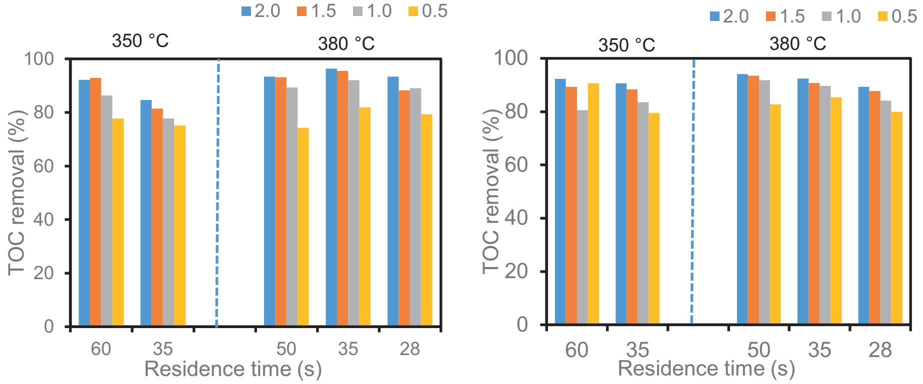
Figure 3-5 The carbon recovery (in %) obtained from the hydrothermal oxidation of acetic acid at OER = 2.0. 1.5, 1.0 and 0.5 as a function of the severity factor, log R_0

3.3.3 Effect of operational parameters on TOC removal and carbon balance at 350 and 380 °C

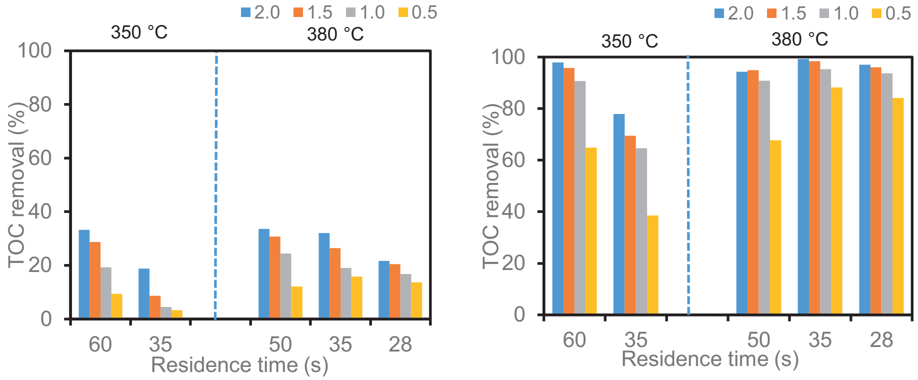
The value of TOC removal efficiency (TRE) should always be greater than or equal to carbon recovery (CR), as the calculation of TRE only considers the fraction of the feedstock carbon that is removed from the liquid phase (and either ends up in the gas phase including any gas other than CO_2 or the solid phase), whereas CR only considers the fraction of feedstock carbon that is fully oxidized to CO_2. From this it is important to bear in mind that carbon ending up in solid products is considered as ‘removed TOC’. Nevertheless, carbon in solid reaction products cannot be really considered the result of a successful decomposition. These carbonaceous solids have to be further decomposed. Hence, TOC removal efficiency in only solid-free studies is considered a good indicator for the decomposition of organics (Al-Duri et al. 2015, Cabeza et al. 2015, Xu et al. 2015). As shown in Figure 3-6, TOC removal efficiencies in all cases except acetic acid are much higher than the carbon recovery. Considering solids found in the effluent, we believe that the carbon in the form of solids ‘contributes’ largely to the TOC removal efficiency. The assumption is confirmed by the TOC removal of acetic acid: Its TOC removal efficiency is only slightly higher than the carbon recovery. The carbon in carbon dioxide can almost completely compensate the loss of carbon in the aqueous effluent, which indicates that the oxidation of acetic acid could only produce negligible quantities of carbonaceous solids, which is confirmed by the clear final liquid effluent. Effect of operational parameters on TOC removal is hard to analyzed as solid products were not quantified. It is however apparent that TOC removal is the lowest when OER is 0.5.

From Appendix-Table 1–5, it is interesting to see the difference (gap) between TOC removal and carbon recovery evolving with reaction conditions. In general, higher temperature, longer residence time and higher OER would decrease the discrepancy between TRE and CR resulting from lower formation of solid products not accounted for in the carbon recovery. However, the discrepancy in cellulose and lignin tests at 380 °C seems unaffected by OER changes. We assume that the decomposition (hydrolysis) of these organic polymers is slow compared to the oxidation of the intermediates to CO_2. The initial decomposition (hydrolysis) appears to be less affected by the oxidizer concentration.

(a) Cellulose (b) Lignin



(c) Acetic acid (d) Furfural



(e) Phenol

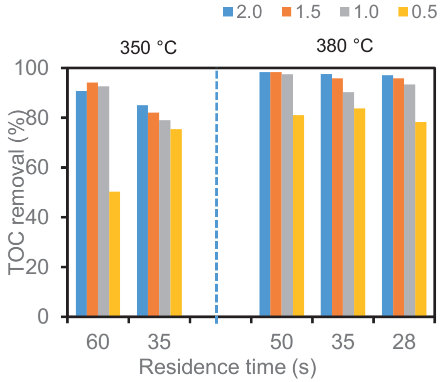


Figure 3-6 TOC removal (in %) of (a) cellulose, (b) lignin, (c) acetic acid, (d) furfural and (e) phenol at OER = 2.0, 1.5, 1.0 and 0.5.

Carbon balance closures of cellulose, lignin, furfural and phenol were less than 100 % (shown in Table 3-2), resulting from the unquantified solid products in the effluent. Carbon balance closures in subcritical cases are lower than in supercritical ones. One reason could be the low reaction rate in the subcritical water. Organics are not fully decomposed and left as soluble residues, which is obvious in the case of cellulose, shown in Figure 3-1. Low reaction rates can also result in high concentrations of intermediates shifting to polymerization where new solids are formed. Acetic acid has a better carbon balance closure compared with the other four feedstocks. Undecomposed acetic acid stays dissolved in the aqueous effluent which is supported by the smell of the effluent. On the other hand, no solid products in the effluent were observed from acetic acid oxidation (Meyer et al. 1995, Suzuki et al. 2006).

Table 3-2 Carbon balance closure in the oxidation of five model compounds.

T (°C)	τ (s)	OER	Carbon balance closure (%)				
			cellulose	lignin	acetic acid	furfural	phenol
380	50	2.0	70.1	53.2	89.5	77.4	81.3
		1.5	65.5	49.5	87.9	73.3	77.0
		1.0	67.3	48.5	93.2	70.8	68.4
		0.5	67.2	55.9	99.6	74.2	66.5
	35	2.0	61.2	51.1	89.3	63.0	74.2
		1.5	59.1	50.9	91.4	62.5	71.8
		1.0	62.4	46.7	97.2	62.7	71.4
		0.5	56.4	51.5	95.3	47.8	65.6
	28	2.0	61.3	52.0	96.7	60.7	69.2
		1.5	63.7	53.5	94.2	60.1	63.1
		1.0	59.9	49.7	95.2	57.2	67.5
		0.5	59.3	50.5	93.8	49.4	70.2
350	60	2.0	59.1	49.7	83.1	61.8	76.7
		1.5	56.2	52.1	83.4	66.4	62.0
		1.0	63.3	57.6	90.2	70.2	66.0
		0.5	59.8	38.5	97.6	65.9	92.6
	35	2.0	51.0	48.3	91.6	78.2	95.1
		1.5	52.8	52.6	99.0	88.0	110.9
		1.0	56.8	53.2	102.4	88.1	116.5
		0.5	46.2	47.9	101.1	89.9	71.4

The oxidizer use efficiency is shown in Appendix-table 6. Oxidizer use efficiency has a negative correlation with carbon recovery. Higher carbon recovery required more oxidizer (i.e. more than proportional) which decreased oxidizer use efficiency. In OER = 0.5, oxidizer use efficiencies were mostly higher than 80% in case of cellulose, lignin, furfural and phenol. Under these oxygen depleted conditions, any of the reactive oxygen supplied is readily consumed for oxidation. In terms of acetic acid, oxidizer use efficiency was always low indicating that the decomposition of acetic acid is suppressed by other factors than excess oxygen. A low temperature is assumed to be one of these factors.

3.3.4 Effluent gas composition

Details of the effluent gas composition can be found in Appendix-table 1-5. As an example, the gas composition in cellulose oxidation is given as Figure 3-7. Carbon dioxide is the main product containing carbon in the gas phase. Small concentrations of carbon monoxide and traces of ethylene also appeared in some cases. The concentration of carbon monoxide decreased with higher OER, which is reasonable as carbon monoxide is further oxidized to carbon dioxide. Hydrogen gas was also frequently obtained in low OER cases. Oxygen balance closure was calculated based on the amount of oxygen before and after reaction. Oxygen balance closure was always found to be higher than 80 % and around 100 % in most low OER cases. This indicates that oxygen from the oxidizer is mostly used by the oxidation process. The flow rate of gas effluent increased with higher OER because of the excess oxygen which was discharged to the gaseous effluent.

Longer residence times in most cases increased the formation of carbon dioxide, and decreased the production of carbon monoxide and hydrogen gas. Carbon monoxide and hydrogen are further oxidized by prolonging residence time. As hydrothermal oxidation is an irreversible process, the direction of organics oxidation towards formation of carbon dioxide is likely to be enhanced by prolonged residence time.

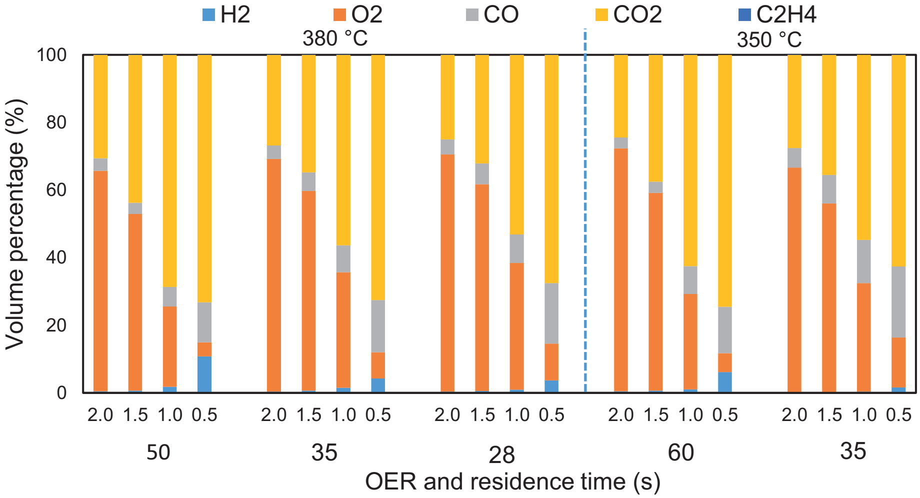


Figure 3-7 Gas composition (in vol.%) in the oxidation of cellulose at different reaction conditions.

Phenol, furfural and cellulose oxidation are likely to generate more carbon monoxide at low temperature and lower OER. The maximum CO/CO_2 ratio of 0.336 : 1 was found in cellulose oxidation at OER = 0.5, temperature = 350 °C and a residence time = 35 s. Carbon monoxide formation in acetic acid and lignin oxidation were only found when OER was low.

3.4 Conclusion

Complete conversion of the five selected model compounds to carbon dioxide was not obtained within the studied operational variables. We investigated the effect of each process variable (temperature, residence time, OER) on hydrothermal oxidation. Although there are differences in the oxidation of each model compound with respect to these aforementioned process variables, the general conclusion is that longer residence time, higher temperature and higher OER enhances the hydrothermal oxidation process. If OER is too low (<1), then decomposition and repolymerization reactions dominate over the competing oxidation reactions, leading to the formation of carbonaceous solids. Longer residence time is required for improved oxidation performance at any given reaction condition. To decrease the formation of solid products, higher OER is necessary. Complex and polymeric organics (e.g. lignin and cellulose) at the given conditions would have an initial decomposition reaction along with oxidation of the intermediates. The decomposition step is less dependent on oxidizer concentration and is assumed to be the slowest. For future oxidation experiments with sludge (containing large proportion of fibers), it is better to increase the residence time for the decomposition of fibers while increasing the OER in order to suppress any repolymerization reaction which would produce solids.

Carbon dioxide was the dominant gas constituent in all cases, while minor quantities of carbon monoxide and hydrogen gas were obtained as well depending on the type of model compound being oxidized. For example, cellulose is more likely to generate carbon monoxide. Also, cellulose and furfural are likely to generate hydrogen gas. Higher OER suppresses the production of carbon monoxide and hydrogen gas.

Chapter 4 Sub- and supercritical water oxidation of anaerobic fermentation sludge for carbon and nitrogen recovery in a regenerative life support system

In Chapter 3, some selected model compounds were subject to hydrothermal oxidation in both subcritical and supercritical water. In this chapter, the focus shifts towards the oxidation of real feedstocks. 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 11 - 30* MPa *and at temperatures of 300 - 500 °C using hydrogen peroxide as oxidizer. Residence times of 1, 5 and 10 min were tested. Carbon recovery increased as temperature increased, with marginal improvements beyond the critical temperature of water. Prolonging the residence time improved only slightly the carbon recovery. 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 liquid effluent. Nitrogen recovery was high at 1 min residence time (> 94.5 %) and decreased for longer residence times (down to 36.4 % at 10 min). Higher temperature and higher OER would be preferred for the nitrogen conversion to ammonium but they also lead to the undesired decomposition of ammonium to gas phase nitrogen products. Higher OER led to the oxidation of ammonium to nitrate which is also preferred in nitrogen recovery. Nitrogen in the liquid effluent was mostly in the form of ammonium in this study.*

This chapter has been redrafted from 'Zhang, D., Clauwaert, P., Luther, A., López Barreiro, D., Prins, W., Brilman, D.W.F., Ronsse, F.: Sub- and supercritical water oxidation of anaerobic fermentation sludge for carbon and nitrogen recovery in a regenerative life support system. Waste Management 77, 268-275 (2018)'.

4.1 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, CO_2, ammonium 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 (Brunner et al. 1994, Bermejo et al. 2006), in the 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 fermentation 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 et al. 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 carbon recovery (Krajnc et al. 1996, Rice et al. 1998). SCWO to process organic waste streams has been studied by several research groups (Helling et al. 1988, Lee et al. 1990, Savage 1999, Schmieder et al. 1999, Portela et al. 2001, Wang et al. 2011, Li et al. 2013, Al-Duri et al. 2015). Chen et al., (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, 24 MPa, an oxidizer equivalence ratio (OER) of 2 and 60 s residence time was 99.7 % and 94.5 %, respectively. Li et al. (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, 30 MPa, an OER of 2 and 10 min residence time. The use of model compounds has also attracted some attention (Schmieder et al. 1999). The results of these model compound studies indicate that temperature, OER and residence time are proportional to the carbon recovery which was also demonstrated in Chapter 3.

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 (Takahashi et al. 1992, Bubenheim et al. 1994, Kudenko et al. 2000, Drysdale et al. 2003). 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 chapter, 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-CO_2 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.

4.2 Materials and methods

4.2.1 Materials

Fermentation sludge was collected from a thermophilic membrane bioreactor fermenting a mixture constituting the MELiSSA model waste, as detailed in section 2.2.2. 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 4-1. 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 (Overijse, Belgium). 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 4.2.2.

Table 4-1 Fermentation sludge (undiluted) properties

	Dry matter *wt.%* wet basis	Carbon *wt.%* dry basis	Nitrogen	Hydrogen	Ash	TOC g/cm³ wet basis
Value	4.0	44.5	2.2	6.2	6.4	17800

4.2.2 Apparatus and experimental procedure

All experiments were performed in the batch autoclave as shown in Figure 2-3. 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 11 MPa (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 30 MPa 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 10 MPa N_2 was performed, which also served to purge any air in the reactor's headspace. Following this, the reactor was pressurized using 0.3 MPa 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. Higher temperature experiments had a lower water load (i.e. less mass to heat up) while lower temperature experiments required a higher water load. As a result, the heating times for all experiments were all around 400 ~ 450 s. 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. Once the temperature dropped to ambient, gas was released into a eudiometer. A syringe was used to take samples for micro-GC analysis after the volume of produced gas was measured. Liquid product was transferred from the autoclave to a glass bottle for storage in a fridge (- 20 °C), after which TOC measurement was performed for at least three times.

To study the influence of temperature, residence time and OER upon oxidation, a 3^3 factorial design was adopted. Based on earlier experimental reports as referenced in the introductory section, the following levels were chosen: temperature (300, 400 and 500 °C), residence time (1, 5 and 10 min.) and OER (0.5, 1.0, 1.5 and 2.0). Every unique combination of process conditions in the micro-autoclave experiments was carried out once, with the exception of experiments at 500 °C, residence times (τ) of 10 min and OER of 0.5, 1.0, 1.5, and 2.0, which were all executed 3 times in order to estimate the experimental error. The maximum experimental error was 4 %. It was further assumed that this experimental error was indicative for the whole range of conditions tested.

4.2.3 Product analysis

The gaseous effluent and TOC results of aqueous effluent were measured with the same methods as in section 3.2.3. Qualitative analysis of the residual organic compounds dissolved in the liquid effluent was performed by GC-MS (Thermo Scientific Trace GC Ultra, Thermo Scientific ISQ Single Quadrupole MS). Dichloromethane (DCM) was used to extract organic components in liquid effluent with a volume ratio of DCM: effluent= 1 : 10. The GC column was a Restek capillary column (Rtx-1707, 60 m × 0.25 mm × 0.25 µm, *L* × *ID* × df). Helium was used as a carrier gas flow of 1 mL/min. 2 µL of sample was introduced for each analysis which was repeated 3 times. The GC oven temperature program started with a 5 min hold at 40 °C followed by heating to 100 °C at 3 °C/min and holding for 4 min and followed by heating to 280 °C at 7 °C/min. The final temperature was held constant for 4 min. Product compounds were identified using a single quadrupole MS. The MS used 70 eV electron ionization and the mass selective detector scanned within an m/z-range of 29–300 amu. Identification methods are reported elsewhere (Yildiz et al. 2016).

Quantitative analysis of the volatile fatty acids (C2-C8 fatty acids (including isoforms C4-C6)) in the liquid (solid-free) effluent were measured in triplicate by gas chromatography (GC-2014, Shimadzu®, The Netherlands). The GC was equipped with a DB-FFAP 123-3232 column (30 m x 0.32 mm x 0.25 µm, *L* × *ID* × *df*; Agilent, Belgium) operated at 140 °C and a flame ionization detector (FID) at 250 °C. The detection limits (lower, upper in mg/L) were as follows: C2 (40, 600), C3/C4 (7,900), C5/C6 (8, 1000). Liquid (reactor effluent) samples were conditioned with sulfuric acid and sodium chloride and 2-methyl hexanoic acid was added as internal standard for quantification. Extraction of the volatile fatty acids was performed with diethyl ether.

The total Kjeldahl nitrogen (organic and ammonium nitrogen) in the sludge was measured by the Kjeldahl method according to Standard Methods for the examination of water and wastewater (Eaton et al. 1995). Nitrate and total nitrogen were determined photometrically using the Nanocolor ® Nitrate 8 kit and total nitrogen TNb 22 kit (Macherey-Nagel, Duran, Germany), respectively. Ammonium concentrations were determined photometrically following the Berthelot reaction (Bucur et al. 2006). Reactions and measurements were performed in 96-well plates and absorbance was measured by a Tecan infinite plate reader. All measurements have been carried out 3 times.

4.2.4 Data processing and evaluation

TOC removal efficiency (*TRE*) within batch experiments is calculated as following, in a slightly different way from Equation 3-3.

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

Equation 4-1

In which M_{feed} and M_{effl} are the weight of the liquid influent and effluent before and after reaction, respectively (in g). $[TOC]_{feed}$ and $[TOC]_{effl}$ are the total concentration of organic carbon in the liquid influent and effluent respectively (in mg/g).

The nitrogen distribution was calculated by means of ammonium nitrogen recovery, nitrate nitrogen recovery and total nitrogen (TN) removal. In the equations below, $[NH_4^+\text{-}N]_{\mathrm{effl}}$, $[NO_3^-{-}N]_{\mathrm{effl}}$ and $[TN]_{\mathrm{effl}}$ represent the concentration of nitrogen in its respective form (nitrate, ammonium and total nitrogen) in the liquid effluent (in mg/g). $[TN]_{\mathrm{feed}}$ represents the concentration of TN (in mg/g) in the respective feed:

$$NH_4^+ - N\ recovery\ (ANR, \%) = \frac{[NH_4^+ - N]\ _{effl}}{[TN]_{feed}} \times 100$$

Equation 4-2

$$NO_3^- - N\ recovery (NNR, \%) = \frac{[NO_3^- - N]\ _{effl}}{[\ TN]_{feed}} \times 100$$

Equation 4-3

$$TN\ removal\ (\%) = \left[1 - \frac{[TN]\ _{effl}}{[\ TN]_{feed}}\right] \times 100$$

Equation 4-4

4.3 Results and discussion

4.3.1 Effect of residence time

The effect of residence time on *TRE* and *CR* of the fermentation sludge oxidation was investigated at an OER of 1.5, and residence times (τ) of 1, 5 and 10 min. Figure 4-1 illustrates the effect of residence time on total organic carbon removal (*TRE*) and carbon recovery (*CR*). The *TRE* was found to be the lowest at τ = 1 min for both 300 and 400 °C. At 300 °C, the *TRE* increased from 77.5 % at τ = 1 min to 80.8 % at τ = 10 min. At 400 °C, the *TRE* increase was higher, from 77.9 % at τ = 1 min to 88.1 % at τ = 10 min. For 450 and 500 °C, around 94 % *TRE* was achieved for both temperatures at τ = 10 min. However, improvement at 500 °C over 450 °C was negligible.

While a minimal positive effect from prolonging the residence time from 1 to 5 min could be observed, the TOC removal efficiency was clearly bigger at τ = 10 min. One possible reason might be the long heating times inherent to this kind of setup (micro-autoclave): over 400 s were needed to reach the desired set-point temperature in the autoclave before recording residence time. This heating stage is considered quite long compared to the typical residence times achieved in continuous reactors under study (see also Chapter 3, 5 and 7). Organic constituents in the sludge could already have undergone reactions like decomposition, polymerization and oxidation during this heating stage resulting in the formation of refractory intermediates. As demonstrated by (Cui et al. 2011), one of those refractory intermediates is acetic acid, which competes with the formation of CO as an intermediate. The oxidation reaction of CO to CO_2 however, is slow. Prolonged residence times are expected to induce additional degradation of those refractory intermediates like acetic acid (Meyer et al. 1995).

The above conclusion is also valid for the carbon recovery rate. As shown in Figure 4-1, longer residence times improve the carbon recovery but only to a small extent (compared to the effect of temperature) while the improvement is more noticeable when going from subcritical to supercritical conditions. Additionally, the difference between *TRE* and *CR*, which is indicative for the fraction of organic carbon that is converted but not to CO_2, is significantly smaller at supercritical conditions than at subcritical conditions. The improved performance of the oxidation of organic constituents in water at supercritical conditions and the role of the residence time therein is consistent with previous literature reports (Thornton et al. 1990, Savage 1999).

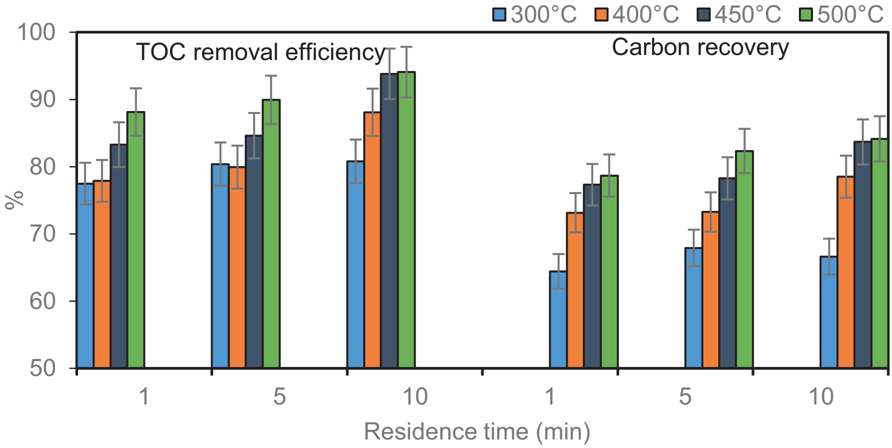


Figure 4-1 Influence of residence time on *TRE* and *CR* in the oxidation of 2 *wt.%* fermentation sludge feedstock (*OER* = 1.5 and *T* = 300, 400, 450 and 500 °C)

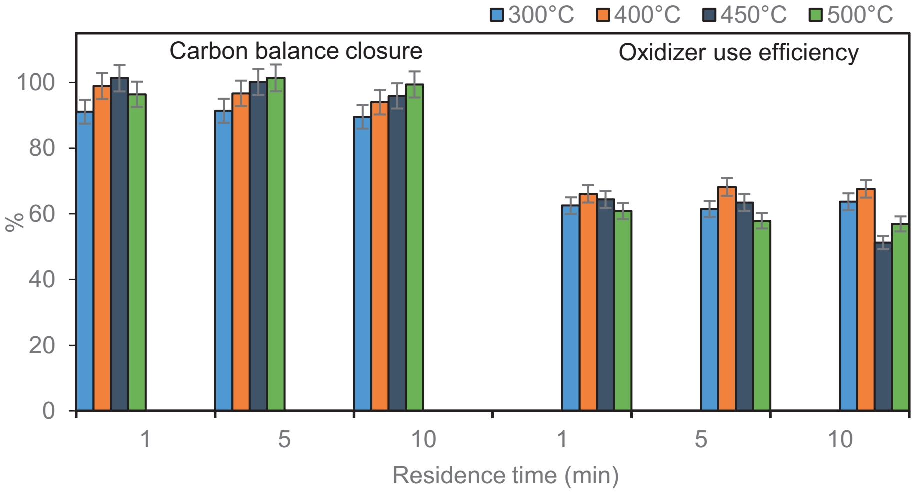


Figure 4-2 Influence of residence time on *CB* and *OUE* in the oxidation of 2 *wt.%* fermentation sludge feedstock (*OER* = 1.5 and *T* = 300, 400, 450 and 500 °C)

Figure 4-2 shows the effect of residence time on *CB* and *OUE*. Around 90 % of the carbon mass balance is closed at 300 °C suffering a near imperceptible decrease from prolonged residence times. Carbon mass balance closure drops from 98.9 % to 94 % at 400 °C and from near 100 % to 96 % at 450 °C with τ = 1 min increasing to τ = 10 min. Incomplete mass balance closure for carbon can be attributed to coke deposits (observed on the inner reactor wall but not quantified) and C-containing gas species that were not analyzed for (i.e. other than CO, CO_2, CH_4, C_2H_6, C_3H_8 and C_4H_{10}). When the temperature was 500 °C, a near 100 % carbon mass balance closure was achieved: oxidation was assumed to be enhanced, with little to no coke deposit formation, at these more intense process conditions (see Figure 4-3).

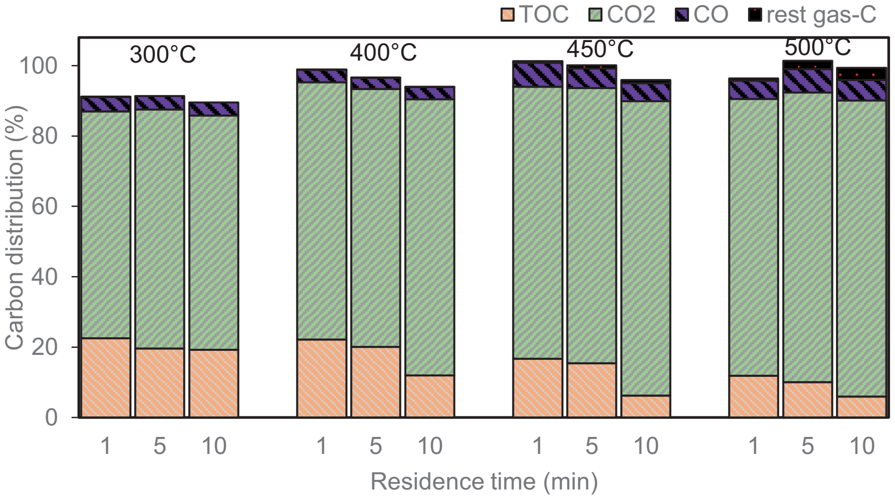


Figure 4-3 Influence of residence time on the carbon distribution in the oxidation of 2 *wt.%* fermentation sludge feedstock (OER = 1.5 and T = 300, 400, 450 and 500 °C)

After calculating the fraction of the supplied reactive oxygen that manages to oxidize feedstock carbon to CO_2, most of the oxygen consumed from the feed was found as carbon dioxide (*OUE* > 60 %), and the residence time was found to have no effect on the O*UE*. Considering the residence time studied in previous SCWO studies (Wang et al. 2011, Dong et al. 2014, Qian et al. 2015) and in our tests, a residence time of 1 min was accepted as being sufficient in all subsequent experiments. Longer residence times, though marginally beneficial, were not deemed useful as they would translate to larger reactor volumes and higher energy consumption in future full-scale continuous reactors (Marrone et al. 2005).

4.3.2 Effect of oxidizer equivalence ratio, OER

The effect of the *OER* on the performance of the oxidation of the fermentation sludge feedstock, as expressed by both the *TRE* and *CR*, was studied. Oxidation experiments were carried out at τ = 1 min, and *OER* of 0.5, 1.0, 1.5 and 2.0. As shown in Figure 4-4, the *TRE* at all temperatures increases significantly with the increasing *OER*. At an *OER* of 0.5, the *TRE* is about 50 %, meaning that half of the organic carbon in the liquid feed is removed by oxidation. The oxidizer use efficiency attains near 100 % values at this low *OER* (also seen in Figure 4-5). With the *OER* increasing from 0.5 to 2.0, the *TRE* increased significantly, especially at supercritical conditions reaching 92.2 % at 500 °C with *OER* = 2.0. The net gain in TOC oxidation improvement reduces as the *OER* is increased, meaning that the more reactive oxygen is provided beyond what is stoichiometrically needed, the less efficiently it is consumed in the oxidation. For instance, at *OER* = 2.0, the oxygen use efficiencies have dropped below 60 %.

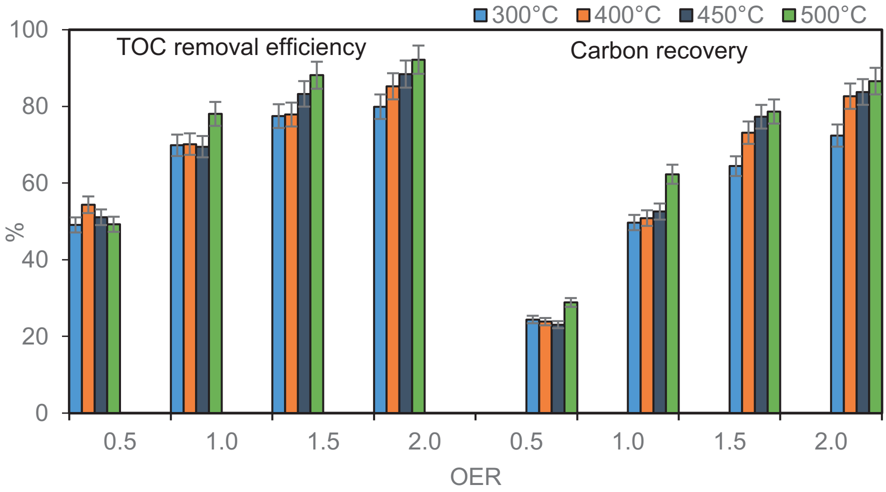


Figure 4-4 Influence of OER on TRE and CR in the oxidation of 2 *wt.%* fermentation sludge feedstock (τ = 1 min and T = 300, 400, 450 and 500 °C)

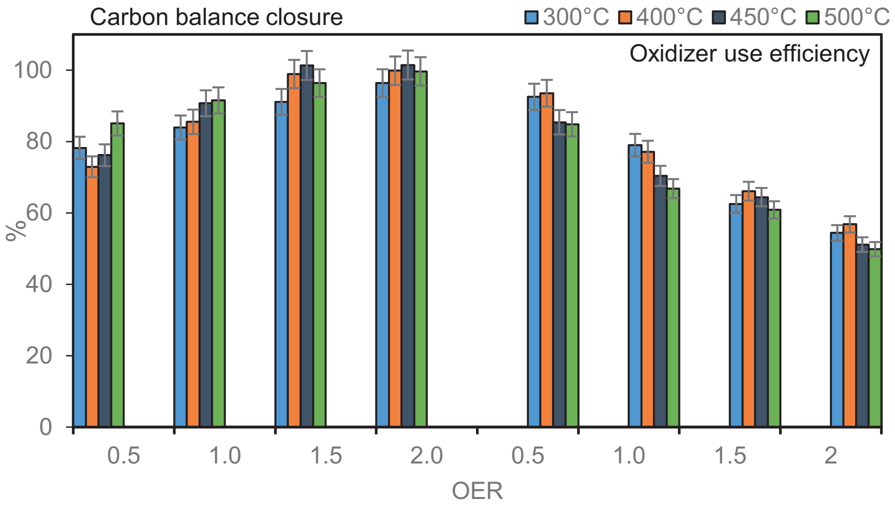


Figure 4-5 Influence of OER on CB and OUE in the oxidation of 2 *wt.%* fermentation sludge feedstock (τ = 1 min and T = 300, 400, 450 and 500 °C)

TRE values up to 92.2 % (and *CR* of 86.6 %) could be reached for the conditions studied and using a residence time of 1 min. Higher temperatures may have to be applied to obtain still higher oxidation efficiencies. This is in agreement with Qian *et al.* (Qian et al. 2015) who stated that moderate temperatures caused difficulties in completely decomposing high organic content feed streams. Depending on the carbon cycling rates in the life support system in which this oxidation process is to be applied, these efficiencies of oxidation, as given by the *TRE* and *CR*, may be considered too low due to the accumulating carbon losses that will occur upon carbon cycling. Longer residence times were also studied with the aim of improving *TRE* and *CR*. Prolonging the residence time to 10 min at an *OER* = 2.0, improved the *TRE* up to 98.6 % and the *CR* up to 97.1 %. Most likely, refractory intermediates were further decomposed at longer residence times in the presence of a high concentration of oxidizer (high *OER*) - see also section 4.3.4.

Due to changes in solubility of oxygen and organics in the supercritical phase, the increasing trend of *CR* versus *OER* diverges at *OER* = 1.0, where oxidation at 500 °C yields a significantly higher efficiency versus 300 °C. As the *OER* increases, the gains in *CR* become progressively smaller. The findings agree well with previous literature reports (Zou et al. 2013, Gong et al. 2014, Wen 2014) in which water at supercritical conditions was found to enhance the effect of higher *OER* (> 1.0) on the carbon recovery rate. On the other hand, the difference (*TRE* – *CR*) becomes smaller when the *OER* is increased, an effect which is enhanced at supercritical conditions. The explanation of the latter is that at low *OER*, there is insufficient reactive oxygen available in the reaction medium to fully oxidize the formed intermediates, the latter ultimately yielding carbon-containing gas species like CH_4 and CO as well as carbonaceous solids (which are not measured in the TOC of the liquid effluent).

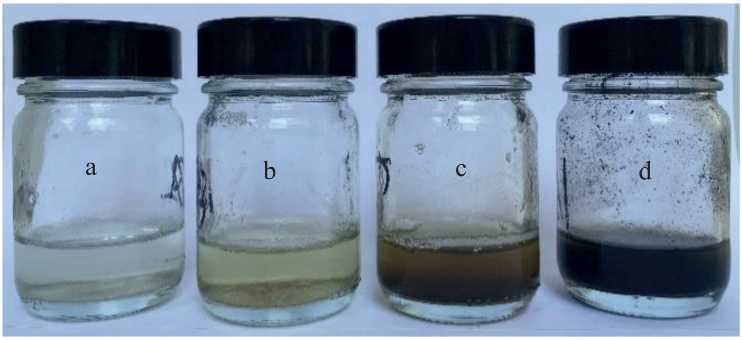


Figure 4-6 Liquid effluents of fermentation sludge oxidation at 400 °C, τ = 1 min, OER being (a) 2.0, (b) 1.5, (c) 1.0 and (d) 0.5

The effect of *OER* on the carbon mass balance closure (*CB*) and *OUE* is displayed in Figure 4-5. Carbon mass balance closure was considered poor at substoichiometric conditions (*OER* = 0.5), being 85 % but increasing to 99.6 % at *OER* = 2.0 in the case of a reactor temperature of 500 °C. The liquid effluent (see Figure 4-6) at *OER* ≤ 1.0 was a black dispersion with pungent and acrid odor, clearly indicating the presence of soluble and volatile intermediates (see analyses in section 4.3.4) and suspended carbonaceous solid particles, the latter which are not quantified and thus result in the large deficiencies in the carbon balance closure. As concluded by Park *et al* (Park et al. 2008), when hydrogen peroxide is present in limiting quantities in the presence of hydrocarbons in water, it may act as a radical initiator in polymerization reactions to form coke-like carbon-containing solids. With *OER* increasing, the aqueous effluent becomes clear and less smelly, indicating that higher *OER* suppresses the presence of soluble and insoluble organic compounds in the liquid effluent.

4.3.3. Effect of temperature

The effect of temperature on *TRE* and *CR* of fermentation sludge oxidation was investigated at a residence time of 1 min, *OER* of 1.5 and 2.0, and temperatures of 300, 400, 450 and 500 °C. Results are shown in Figure 4-4 while the effect on carbon distribution is given in Figure 4-7 and Figure 4-8. There is an obvious higher increase in *TRE* and CR especially when increasing the temperature from the subcritical phase to supercritical phase. Clearly, the capacity of supercritical water to increase the rate of radical reactions, including those with hydroxyl (·OH) and hydroperoxyl(·OOH) radicals formed out of H_2O_2, contributes to the improvement of the oxidation of the feedstock. These observations of carbon recovery versus temperature are consistent with the results reported in (Gong et al. 2014). Having more oxidizer present (*OER* = 2.0) enhances *CR* and *TRE*, with a maximum of *TRE* = 92.2 % and *CR* = 86.6 % at 500 °C. The observation of enhancement of higher *OER* on the carbon recovery agrees well with previous studies (Miller et al. 2015).

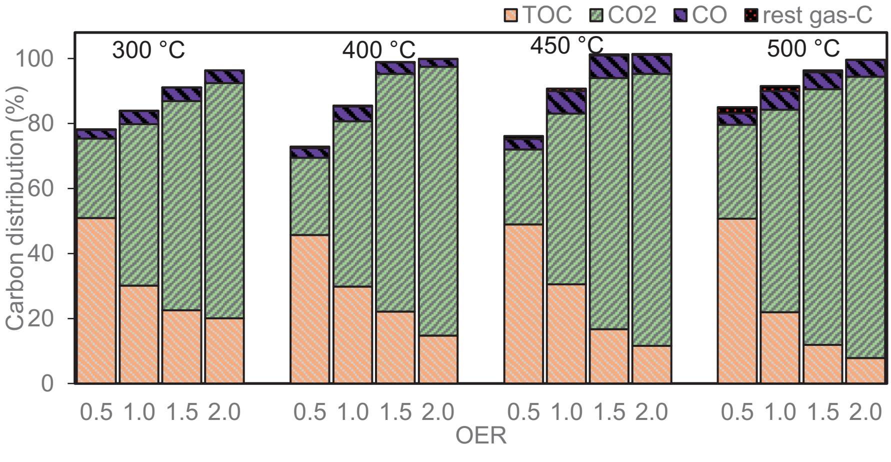


Figure 4-7 Influence of OER on the carbon distribution in the oxidation of 2 *wt.%* fermentation sludge feedstock (τ = 1 min and T = 300, 400, 450 and 500 °C)

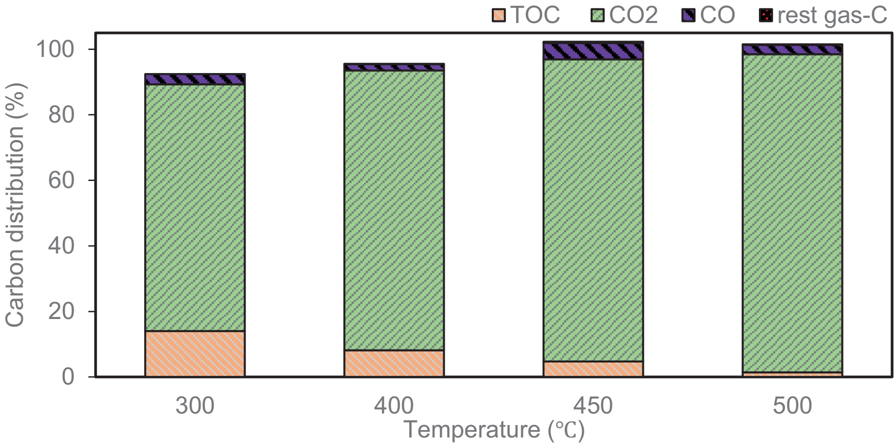


Figure 4-8 Influence of temperature on the carbon distribution in the oxidation of 2 *wt.%* fermentation sludge feedstock (τ = 10 min and OER = 2.0)

As also shown in Figure 4-5, *CB* was always higher than 90%, and was positively correlated with the carbon recovery likely because a proper oxidation yields less carbonaceous solids which have not been quantified and not included in the carbon mass balance.

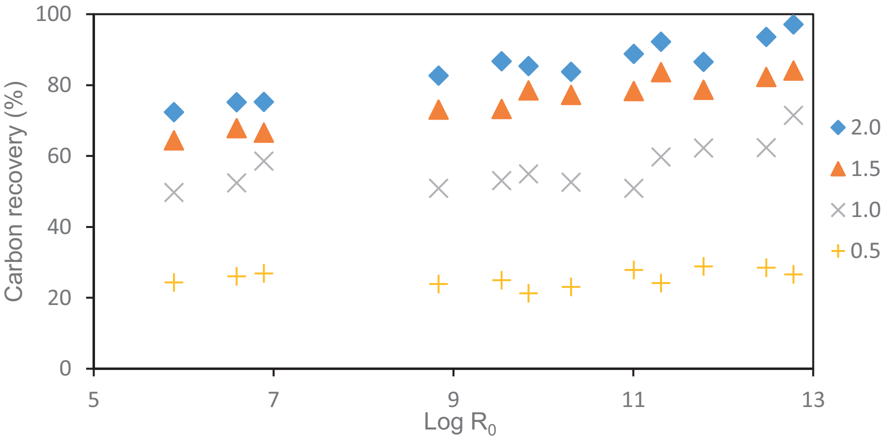


Figure 4-9 The carbon recovery obtained from hydrothermal oxidation of sludge at OER = 2.0. 1.5, 1.0 and 0.5 as a function of the combined severity factor, log R_0.

To further study the combination effects of temperature and residence time on carbon recovery, the severity factor was calculated, as shown in Figure 4-9. Carbon recovery improves slightly with higher severity factor within the range of conditions tested. And the improvement is enhanced by higher OER. The severity factor has a minor effect upon carbon recovery although higher OER leads to higher sensitivity of carbon recovery to the severity factor. As the function of oxidation being the main pathway to generate carbon dioxide, it is reasonable to see the great influence of OER on carbon recovery. It could be possible to achieve a much higher carbon recovery by increasing OER while keeping the severity factor in a milder range where nitrogen recovery is easier to reach as discussed in the following section.

4.3.4 Nitrogen distribution and VFA removal analysis

In the fermentation sludge used in the experiments, the total nitrogen concentration was 897.5 mg N/L and was mostly in the form of organic N compounds next to 101 mg NH_4^+-N/L. No nitrate was present in the feedstock. The oxidation of N compounds in the feedstock leads to different species, distributed over the different product fractions (N-heterocyclic compounds in soluble and insoluble form in the liquid effluent; NO_3^- and NH_4^+ in the liquid effluent; N_2, N_2O, NO_x in the gaseous effluent (Cabeza et al. 2014, Shimoda et al. 2016, Lousteau et al. 2017)). All tested parameters in the oxidation had an effect on the nitrogen distribution. After the oxidation experiments, low concentrations of nitrate were detected, as shown in Table 4-2. Less than 10 % of the feedstock nitrogen was converted into nitrate depending on reaction conditions and even no nitrate was measured in the liquid effluent when the temperature was 450 °C. The ammonium-N retention increased greatly starting at 11.3 % and varied depending on reaction conditions. Under subcritical conditions, ammonium-N retention showed an increasing trend from 79.1 % at τ = 1 min to 87.2 % at τ = 10 min, which is opposite with the trend observed in the supercritical phase where a longer residence time yielded less ammonium in the liquid effluent. Nitrogen compounds from the feedstock decomposed into ammonium in the subcritical phase and peptides/protein decomposition is further enhanced with increasing residence time.

Table 4-2 Ammonium nitrogen recovery (ANR), nitrate nitrogen recovery (NNR) and total nitrogen (TN) removal results in the oxidation of 2 *wt.%* fermentation sludge feedstock (τ = 1 min and OER = 1.5), all values are expressed as weight percentage (%).

	300 °C			400 °C			450 °C		
	ANR	NNR	TN removal	ANR	NNR	TN removal	ANR	NNR	TN removal
1 min	79.1 ± 3.9	10.1 ± 1.1	5.5 ± 0.4	93.6 ± 8.1	6.3 ± 0.7	2.9 ± 0.2	66.4 ± 3.8	n/a*	5.4 ± 0.5
5 min	79.4 ± 7.7	7.5 ± 0.8	6.1 ± 0.1	91.6 ± 1.5	8.2 ± 0.5	9.9 ± 0.2	56.2 ± 6.2	n/a*	22.4 ± 1.8
10 min	87.2 ± 8.8	6.8 ± 0.2	7.3 ± 0.1	74.1 ± 3.7	5.2 ± 0.4	20.7 ± 0.1	35.2 ± 2.4	n/a*	63.6 ± 7.7

* Nitrate was not found.

Table 4-3 Identities and relative amounts of components as analyzed by GC-MS, in the effluent of fermentation sludge oxidation at 450 °C, 30 MPa, OER = 2.0 and 1 min residence time.

No.	Time (min)	Name	Peak area (%)
1	10.5	2-Propanone, 1-hydroxy-	18.52
2	10.61	Heptane, 2,4-dimethyl-	7.45
3	11.91	2,4-Dimethyl-1-heptene	3.51
4	12.43	Octane, 4-methyl-	3.41
5	14.56	1,2-Ethanediol	3.09
6	15.02	1-Hydroxy-2-butanone	1.67
7	15.14	Acetic acid	2.98
8	17.18	Butanedial	3.58
9*	29.06	1,4-Dibromobenzene	5.36
10	43.81	D-Allose	4.43

* 50 mg/L 1,4-Dibromobenzene was used as internal standard.

In contrast under supercritical conditions, organic N compounds decompose quickly and the ammonium itself can further be converted leading to lower ammonium concentrations with longer residence times. The conversion of feedstock N into ammonium or nitrate is favorable for use in a regenerative life support system, as the nitrogen-containing liquid effluent can be used as plant fertilizer. Comparing the tests performed at 300 and 400 °C, both had at least 50 % of the feedstock N converted to ammonium, however at supercritical conditions (400 °C), the conversion was higher, see Table 4-2. Another pathway of N conversion is the production of NO_x. Al-Duri *et al.* (2016) stated that higher oxygen supply favors NO_x production as opposed to N_2 production, this could not be verified in this study as NO_x was not analyzed in the gas product. In order for nitrogen to be oxidized, higher temperatures (650 °C and above) are required (Osibo 2011, Al-Duri et al. 2016). Another gas constituent that is formed out of the feedstock N is N_2. Unfortunately, no accurate measurement of N_2 could be made because nitrogen was already used to flush and pre-pressurize the headspace of the autoclave prior to the experiment. As such, no accurate distinction could be made between N_2 formed in the oxidation and N_2 initially added.

Total nitrogen removal from the effluent, by comparing total nitrogen before and after reaction was always below 25 % at $\tau \leq 5$ min, which means that the majority of the feedstock nitrogen is still in the aqueous phase after reaction, especially in the form of ammonium. Comparing the test performed at 450 versus the one at 400 °C, the ammonium-N recovery dropped and no nitrate was detected while the TN removal increased. As such, we can assume that most feedstock nitrogen was converted into gas product (N_2, N_2O or NO_x) at elevated temperatures, and in combination with longer residence times. Consequently, the conditions which favor carbon oxidation do not favor the retention of feedstock N in the form of ammonium in the effluent.

Fermentation sludge is the product from biological treatment and contains complex components that cannot be readily decomposed by microorganisms. Some of these components are also hard to be removed in the H_2O_2-mediated hydrothermal oxidation process leading to residual TOC in the liquid effluent. Refractory intermediates in the oxidation process contribute to the residual TOC. As shown in the GC/MS analysis results in Table 4-3, few residual constituents can be identified. VFAs are reported to be refractory intermediates during the SCWO process. Lactate, formate, acetate, propionate and butyrate were measured as VFA. As shown in Table 4-4, VFA (expressed in mg C per L of effluent) constitute the main fraction of the residual organic matter. It has to be noticed though that these VFAs could be intermediates formed in sludge oxidation as well as unconverted original constituents of the feedstock as the liquid phase of fermentation sludge contained a large amount of VFAs. At 400 °C and with $\tau = 1$ min, both the concentration of VFA and final TOC decrease with increasing *OER*. On average, the VFA make up 38.4 *wt.%* of all residual TOC, indicating the difficulty in eliminating these VFA in the oxidation process. Comparing the results from experiments held at a residence time of 5 min and 10 min, it is clear that longer residence times improve TOC and VFA removal. The trends in residual VFA concentration correlate well with carbon recovery and consequently, oxidation in subcritical water (300 °C) still yields high concentrations of VFA (> 1000 mg C/L) while in the most efficient of the tested conditions, i.e. 500 °C and *OER* = 2.0, only 282 mg C/L VFA remained.

Table 4-4 The effect of reaction conditions in the oxidation of 2 *wt.%* fermentation sludge on residual VFAs in the liquid effluent.

Temperature (°C)	OER	τ (min)	VFAs (mg C/L)*	Final TOC (mg/L)
300	2.0	1	1121	1950
400	0.5	1	1316	4343
	1.0	1	1273	2820
	1.5	1	812	2103
	2.0	1	710	1445
	2.0	5	550	1031
	2.0	10	143	795
500	2.0	1	282	774

* The concentration of carbon from VFAs.

4.3.5 Reaction mechanism and discussion

It is a widely accepted hypothesis that the free radical reaction mechanism is best suited to describe the oxidation in supercritical water (Shanableh 2005, Xu et al. 2015). This reaction mechanism contains two major steps, namely, thermal decomposition and oxidation. Thermal decomposition is the hydrolytic formation of smaller intermediate molecules, some of which could end up as a final product (like acetic acids and other VFA). Oxidation is the second step in which the smaller intermediates are converted (oxidized) into the end products which are recovered in the effluent. These two processes occur simultaneously with other parallel reactions, including polymerization. According to previous studies (Jin et al. 2001), thermal decomposition is faster than oxidation in subcritical water, but the opposite is true in supercritical water.

In this study, the thermal decomposition dominated during heating time leading to the decomposition of the fermentation sludge and accumulation of soluble organic matter. Meanwhile, polymerization reactions also took place explaining the formation of carbonaceous solids and tar-like, heavier organic compounds. During the subsequent oxidation, these accumulated soluble organic compounds were consumed, although some of these intermediates only tend to be oxidized at a slow rate. The more oxidizer available (*OER*), the better these intermediates were oxidized toward CO_2. However, the rate of oxidation was much slower at 300 °C than in supercritical water, which explained the lower *TRE* and *CR* at 300 °C. Prolonged residence time did not increase *TRE* and *CR* to a great extent probably because of the high reaction activation energy needed for the oxidation of some of the intermediates (Fang 2014). In supercritical tests, thermal decomposition still dominated during heating time. Nevertheless, oxidation, by means of free radical reactions, took the lead in the supercritical phase. At 500 °C, 30 MPa, *OER* = 2.0 and 10 min residence time, the SCWO process can remove 98.6 % of the TOC and it converts 97.1 % organic carbon to carbon dioxide. Nitrogen conversion occurred over the entire temperature range studied. Ammonium was formed as main intermediate. It accumulated during the subcritical phase and decomposed at higher temperatures, as also demonstrated in (Shimoda et al. 2016). Because high temperatures play an important role in decomposing ammonium to N_2, N_2O and ultimately NO_x, and as temperatures used in the tests in this study were not considered high, ammonium accumulated and only minor amounts of nitrate were recovered. With increasing temperature and OER, ammonium and other aqueous nitrogen compounds further decomposed. Higher temperature and OER together with longer residence time could improve the carbon recovery and restrict the ammonium accumulation. Detailed reaction pathways are hard to obtain because of the complicated organic matter composition in the fermentation sludge used.

In our study, the organic waste was not directly introduced into SCWO system which was different from many literature reported studies (Takahashi et al. 1989, Takahashi et al. 1992, Bubenheim et al. 1994, Kudenko et al. 2000, Drysdale et al. 2003, Czupalla et al. 2004). Organic waste was first treated in anaerobic fermentation during which a large fraction of the waste-TOC was converted to CO_2 and soluble organics, and only the remaining residuals were subjected to subsequent hydrothermal oxidation. As such, the processing capacity requirements and oxidizer need in the SCWO (or subcritical oxidation) step have been largely reduced.

4.4 Conclusion

Temperature, *OER* and residence time are all positively correlated with organic carbon removal efficiency and carbon recovery rate. Supercritical water is better suited for waste oxidation than subcritical water. Both *TRE* and *CR* increased significantly with temperature increasing from 300 to 400 °C. At temperatures above 400 °C, the improving tendency was kept but less pronounced (i.e. smaller marginal gains in *TRE* and *CR* with increasing the temperature). With regard to the amount of oxidizer added, as quantified by the *OER*, it strongly correlated with TOC removal, carbon recovery and resulted in more carbon dioxide being produced. Low oxidizer use efficiencies at high *OER* implied that increasing *OER* at levels above stoichiometric could become uneconomical. Residence time had the least effect on TOC removal and conversion to carbon dioxide.

Regarding the nitrogen conversion, prolonged residence times at supercritical conditions yielded a reduction of ammonium in the aqueous effluent. Hence, in applying supercritical water oxidation for recovering both carbon (as CO_2) and nitrogen (as NH_4^+ or NO_3^-) balanced reaction conditions should be considered (i.e. short residence times, temperatures marginally above the critical point and higher OER).

More work on completely converting carbon to carbon dioxide and fully recycling the nitrogen is necessary. For instance, the addition of a catalyst can be considered to improve conversion efficiency. Future work should also focus on recycling the excess (and unreacted) O_2 in the effluent gas as a necessity to lower oxidizer requirements.

Chapter 5 Feasibility of carbon recovery from fermentation sludge via supercritical water oxidation in either batch or continuous reactor

In Chapter 3, some selected model compounds were subjected to hydrothermal oxidation in both subcritical and supercritical water. The results in the previous chapter clearly pointed out the benefit of working at higher temperature, and in supercritical water, with respect to the extent of oxidation of feedstock carbon to CO_2*. Consequently, the work in this Chapter focusses on the supercritical water oxidation (SCWO) only, applied to the anaerobic fermentation sludge for carbon recovery. Continuous and batch reactor systems were studied and compared. The fate of non-carbon/nitrogen compounds were demonstrated. The oxidizer equivalence ratio (OER) has a significant influence on the carbon recovery and products distribution. It is surprising to see the minor influence of temperature on sludge oxidation within the range of conditions tested. Continuous and batch reactors are different in operational procedures, oxidation efficiency and products distribution. Compared against continuous reactors, batch reactors have the ability to handle feeds that contain particulate matter but suffer from low capacity, poor heat integration (hence low energy efficiency) and inter-batch variability. Carbon distribution in the continuous reactor setup was more leaning towards* CO_2 *production. Solid product (i.e. carbonaceous particulates) were found to a lesser extent in the effluent from continuous reactor experiments. Up to 97 % and 93 % of the feed carbon were recovered (as* CO_2*) in continuous and batch reactor setups, respectively. Inorganic compounds from sludge were only recovered to a low extent and most probably precipitated inside the reactor system. The high oxidation efficiency of the sludge and extremely fast reaction make SCWO a promising technology to improve the efficiency of carbon recovery from organic wastes in a regenerative life support system.*

This chapter has been redrafted from 'Zhang, D., Luther, A., Clauwaert, P., Ronsse, F.: The feasibility of carbon recovery from fermentation sludge for a closed system by supercritical water oxidation. Waste and Biomass Valorization (under review)'.

5.1 Introduction

Supercritical water oxidation (SCWO) has been studied for decades as a green technology to process organic waste streams. Water, as an environmentally friendly solvent, becomes a non-polar solvent that enables the dissolution of both organic compounds and oxidizer in the supercritical phase. This homogeneous (i.e. supercritical) phase of water together with feedstock and oxidizer greatly accelerates the oxidation reactions. Meanwhile, the high concentration of active free radicals in supercritical water further enhances organics oxidation. SCWO is capable of fully oxidizing various organic wastes in as little as a few seconds, which is far faster than most conventional waste treatment methods (Fang 2014). Final products are carbon dioxide, dissolved and/or suspended inorganics (i.e. salts) and water – and ideally - without additionally formed pollutants. Nitrogen-containing organics could generate nitrate, nitrite, ammonium, N_2 and NO_x depending on reaction conditions (Segond et al. 2002, Al-Duri et al. 2017). 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).

Resources in regenerative ecological life support systems, like those needed for long-term, crew-operated space missions, are limited. Waste has to be recycled and/or maximally reused. Human waste (i.e., faeces, urine and hygienic products) and non-edible parts of plants are the main constituents of organic waste streams in such systems (Nelson et al. 2010). Most existing regenerative life support systems are not able yet to completely recycle solid waste (Gitelson et al. 1989, Allen et al. 2003, Guo et al. 2014, Fu 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 at a high rate. This high turnover of resources is important for regenerative life support systems since volume is limited, and is important for proper process control. SCWO is capable of oxidizing most organics, but is used here to target compounds which are not or are only slowly decomposed by micro-organisms such as plant fibers, as well as the microbial biomass produced during the anaerobic fermentation step (the so-called compartment I, see Chapter 1). The major end products of SCWO are water and carbon dioxide. Water can be easily recycled and CO_2 is an input for photosynthesis to produce oxygen and edible biomass, typically plant or microbial biomass. As a result, SCWO is considered as a potential technology to recover resources from wastes in the MELiSSA project (ESA 2015 e). Prior studies have demonstrated that organic wastes could be directly oxidized under supercritical water and near 100% organics were removed (Takahashi 1989, Takahashi et al. 1989). In order to minimize the mass of waste to be treated with SCWO (and hence reduce energy consumption, process risks and the use of oxidizer), and maximize resource recovery from the organic wastes, a membrane anaerobic fermentation is applied prior to SCWO to degrade readily biologically available constituents in the waste stream. This step yields CO_2 and small molecules (volatile fatty acids) that can be recycled or processed in downstream processes of the MELiSSA loop, and concentrates the solids in a slurry of accumulated undigested plant fibers and microbial biomass. Only these residues are to be subjected to SCWO to produce benign final products (carbon dioxide and water) and further approach 100 % of resource recovery. 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 mass throughput. A combination of anaerobic fermentation and SCWO, proposed as a possibility for the MELiSSA loop, 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 (Elliott et al. 1994, Vadillo et al. 2012, Chen et al. 2015). 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. These disadvantages are not present in batch reactors: loading feed and oxidizer, 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 oxygen equivalence ratios (OER) compared to continuous reactors (Chen et al. 2017). There are some differences between continuous and batch reactors in operating organic oxidation. Owing to these differences and the fact that the majority of lab research is done in batch reactors, study to compare continuous against batch reactors in SCWO is necessary.

In this study, the aim is to study the feasibility of supercritical water oxidation of MELiSSA sludge. The performance of batch and continuous reactors were compared to reveal the advantages and disadvantages of each reactor system for space use. The sludge was obtained upon anaerobic fermentation of a simulated space organic waste stream. The influence of operating conditions was investigated on carbon recovery (as CO_2) and compared for both reactor systems. Organic and inorganic residuals were analyzed to evaluate the effect of SCWO on sludge treatment.

5.2 Materials and methods

5.2.1 Materials

Fermentation sludge was produced by fermentation in an anaerobic fermenter 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. The standardized MELiSSA waste is to be considered as a simulant for space solid organic waste. The details of the fermentation sludge and how it had been obtained, have been reported in Chapter 4. Hydrogen peroxide (33 *wt.%*, bought from VWR International (Leuven, Belgium)) was used as oxidizer. For batch tests, the sludge concentration in the reactor was set to be 2 *wt.%* (dry matter concentration). For the continuous tests, the sludge concentration in the feed mixture was set at 1 *wt.%* (dry matter concentration). Additionally, 0.25 *wt.%* of hydrolyzed starch was added to stabilize the feed (sludge and oxidizer mixture) and avoid settling in the feed vessel (only in the continuous experiments, details in section 2.2). The organic carbon contribution from the added hydrolyzed starch was accounted for in the OER calculations.

5.2.2 Apparatus and experimental procedures

The continuous tests were carried out in a coiled plug-flow reactor, as shown in Figure 2-6. 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 a desired amount of hydrogen peroxide had been added. The continuous run stopped when the feed vessel was empty which held a volume of mixture to run for approximately 1 hour 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 in the course of a single experiment. 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 procedure can be found in more detail in section 2.2. We studied the effect of temperature, residence time, and OER as shown in Table 5-1. The batch and continuous systems had different operational conditions (such as residence and heating times) because of the inherent working differences of both reactors. Five minutes of residence time was selected in the batch system as to minimize the influence of the relatively long heating and cooling periods in the overall obtained results.

Table 5-1 Studied parameters in batch and continuous experiments

Continuous reactor (5 experimental conditions)	Batch reactor (12 experimental conditions)				
450 °C, OER = 2.0, τ = 1 min;	300 °C,	x	OER = 0.5,	x	τ = 5 min.
500 °C, OER = 1.0, τ = 1 min;	400 °C,		OER = 1.0,		
500 °C, OER = 2.0, τ = 1 min;	450 °C,		OER = 2.0.		
500 °C, OER = 3.0, τ = 1 min;	500 °C.				
550 °C, OER = 2.0, τ = 1 min.					

5.2.3 Product analysis

The gaseous effluent of the continuous tests was analyzed with a GC-2014 Shimadzu gas chromatograph equipped with an FID detector. TOC analysis were the same as in section 3.2.3. The VOC analysis of the liquid effluent from continuous tests were obtained by head-space technique without any pH adjustment. Aliquots of the liquid solution were put in a tight glass containers at 80 °C and flushed with helium. The vapors and gases were transferred into an empty cold trap at -160 °C, and then injected into a Proton Transfer Mass Spectrometry Time of Flight detector (PTR-TOF-MS 8000 model supplied by Ionicon Analytik) for identification and quantification. The analysis of volatile fatty acids in the aqueous effluent from the batch tests were same as in section 4.2.3. The elemental analysis on the aqueous effluent from the continuous tests were performed with Inductively-Coupled Plasma Mass Spectrometry (ICP-MS), as this 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 of which can be directly determined by MS through the measurement of the intensity of m/z ion peaks produced in the spectra. A nebulizer is used to produce a supersonic expansion 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 Ar 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 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 mg/L multi-element standard solution 6 provided by Sigma-Aldrich (Overijse, Belgium). 1-10 mL of each solution were used for sample analysis. To get a quantitative evaluation of P, the ICP-MS system was calibrated by determining the content of P as ortophosphate with a colorimetric method. 10 mL aliquots of the solutions were mixed with proper amounts of ammonium molybdate, to form a complex that by reduction with stanneous chloride produces a blue colored complex, whose content in the solution can be quantified by spectrophotometry as it strongly absorbs 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 contribution of polyphosphates and organic phosphates in the solution to the total phosphorus concentration were negligible with respect to the orthophosphate concentration.

5.3 Results and discussion

5.3.1 Gas products

The conversion (oxidation) of carbon in the fermentation sludge to carbon dioxide is the primary objective of the study. Carbon recovery, as defined in section 3.2.4, quantifies the fraction of feed carbon converted to carbon dioxide indicating the efficiency of SCWO, of which the results are shown in Figure 5-1 and Figure 5-2. Sludge oxidation was tested within both batch and continuous reactors under slightly different operational conditions because of 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 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). From the results, the carbon recovery for 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 temperature in the ranges tested, for both batch and continuous reactors.

The effect of OER is significant in the batch tests, as shown in Figure 5-1. 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 (Savage 1999, Bermejo et al. 2006) in which the OER impacted the carbon oxidation greatly. With more oxidizer present in the reactor, sludge is more likely to be oxidized to generate carbon dioxide. In terms of continuous reactor testing, 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 the tested temperatures, but less effectively, by increasing the OER within continuous reactor systems compared to batch reactor systems.

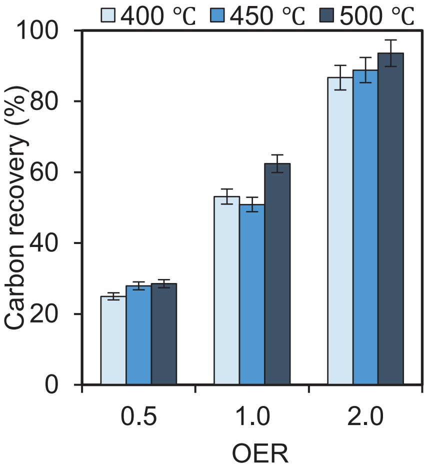


Figure 5-1 Carbon recovery as a function of OER and temperature in batch reactor testing at 5 min residence time.

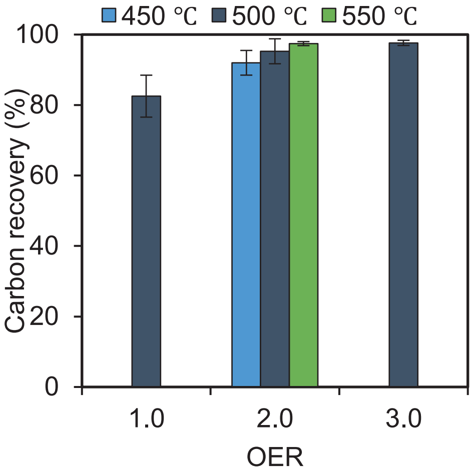


Figure 5-2 Carbon recovery as a function of OER and temperature in continuous reactor testing at 1 min residence time.

When considering the two operational setups 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 mins before reaching 500 °C), during which time sludge components and derived intermediates might undergo significant polymerization reactions along with oxidation and other reactions at relatively 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 oxidizer 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, as is the case in batch reactor systems. Nevertheless, the positive effect of increased OER's only results in a marginally improved CR (of only 2.37 % when increasing OER from 2.0 to 3.0 at 500 °C) at high OER, within the continuous reactor system.

Temperature was reported to affect carbon recovery greatly (Qian et al. 2015, Amrullah et al. 2018, Xu et al. 2018). In our study, carbon recovery is found to be less sensitive to temperature in the studied range. We observed a slight improvement from elevated temperatures. In batch tests at OER = 2.0, carbon recovery at 500 °C is 6.9 % higher than at 400 °C at equal OER. In continuous tests at OER = 2.0, carbon recovery at 550 °C is 5.4 % higher than at 450 °C. The majority of the carbon in the sludge can be oxidized at temperatures around 400 °C with some residuals even resistant to complete oxidation at higher temperatures. Temperatures higher than the tested range might be necessary for complete oxidation and recovery of the carbon from the waste sludge.

Besides CO_2, carbon could also be converted to other gaseous by-products. Carbon dioxide, carbon monoxide and to a lesser extent, methane and ethene are all possible products from SCWO of sludge. Gaseous carbon-containing by-products were more frequently observed in batch tests than in continuous tests. The by-product species and their distribution vary with reaction conditions as is shown in Table 5-2. Carbon monoxide is one of the most common gaseous by-products within the batch tests. The concentration in carbon monoxide had a trend from initial rise to subsequent decline with increasing OER. The maximum CO yield was obtained at OER = 1.0, as shown in Table 5-2. We assume that polymerization reactions play an important role at OER < 1.0 which is confirmed by the low carbon balance closure indicating the formation of solid products (which were not accounted for in the carbon balance). The oxidation reaction is also limited, resulting in low yields in carbon monoxide as well as in carbon dioxide. When the OER is 1.0 or above, presumed polymerization reactions are starting to become suppressed because of the abundance of oxidizer. Oxidation reactions dominate and lead to the formation of carbon dioxide and carbon monoxide (in case of partial oxidation). With excess oxidizer (OER = 2.0), carbon monoxide is likely to be oxidized to carbon dioxide, hence the declining trend in CO-yield with OER increasing from 1.0 to 2.0 – although this decline in CO-yield is less pronounced when process temperatures increased.

Table 5-2 Carbon distribution in batch oxidation tests

Experimental conditions		Carbon distribution (mass fraction in %)				
		Liquid effluent	Gaseous effluent			
T (°C)	OER	TOC	CO_2	CO	Rest gas-C*	CB (%)
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}

5.3.2 Liquid products

Figure 5-3 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 (Nunoura et al. 2003, Svishchev et al. 2006, Ma. 2014). TOC removal indicates the removal of organic carbon from the liquid phase to either solid or gas phases. The aqueous effluent from the continuous tests was clear with little solid products, and carbon dioxide was found to be the only carbonaceous gas. TOC removal values were close to carbon recovery values within the continuous tests, indicating that the majority of removed carbon is completely converted into CO_2. To the contrary, TOC removal efficiency values (Figure 5-3) were much higher than carbon recovery values (Figure 5-1) in the batch tests, especially at low OER (≤ 1). The discrepancy between carbon recovery and TOC removal efficiency results from the formation of uncollectable solid products, dissolved and incompletely oxidized organic compounds (quantified by the effluent TOC) and non-CO_2 gas products as shown in Table 5-2. These non-CO_2 end products are not considered to be desired nor easily recoverable in a life support system and hence need further processing. With elevated OER, the formation of solid particulates, dissolved organics and non-CO_2 gaseous species was observed to a lower extent; carbon recovery improved and got closer to the TOC removal efficiency.

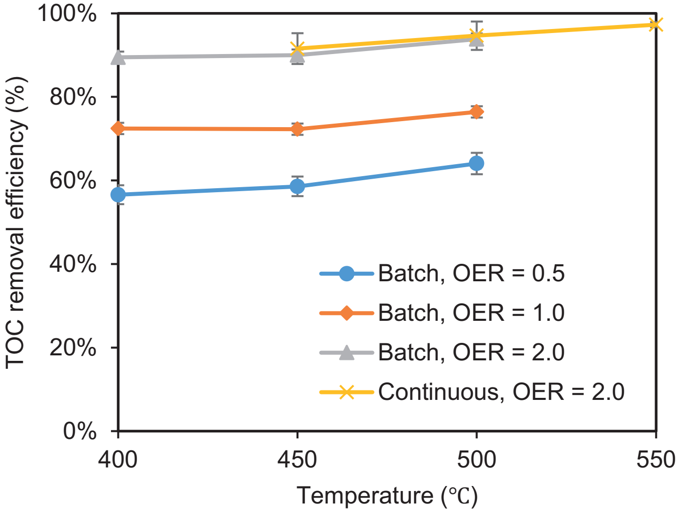


Figure 5-3 The effect of temperature and OER on TOC removal

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 the influent, as these are typical intermediates formed in anaerobic fermentation. After the oxidation process, aldehydes and ketones became the dominant compounds in the VOC fraction of the liquid effluent (Appendix-table 7). 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 (Appendix-figure 2). 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. VFA’s 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 Appendix-table 8). This residual carbon in the aqueous effluent is hard to dispose of and needs further study.

Table 5-3 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

Supercritical water oxidation is conducted under severe process conditions which can result in corrosion and salt precipitation problems. As a results 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. Sludge contains both organic and inorganic compounds. 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 nutrients are required for further compartments of the MELiSSA loop (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 of which the results are shown in Table 5-3. Batch samples were not analyzed as no sufficient effluent quantities were available.

Table 5-3 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, which would lead to resources shortage and system blocking in long term running. The proper recovery of all feedstock elements while simultaneously avoiding leaching of reactor wall materials needs to be further investigated.

5.3.3 Feasibility 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 differently influenced by process conditions in batch compared to continuous reactors. Higher temperature and higher OER both have positive influence 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 economical, 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 and 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 to 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 insider the batch reactor will yield the desired equilibrium pressure at a given temperature, and so (wet) feedstock and oxidizer solution 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). In conclusion, continuous setups have higher processing capacity than batch setups with same reactor volume.

Pressure in the continuous reactor was controlled by a back pressure regulator. The residence time is inversely proportional to the feed rate flow at a fixed temperature and pressure. SCWO processes commonly include pre-heating, reaction and cooling stages. The pre-heating and cooling stages are much longer than the fast SCWO reactions, and this is especially true for batch reactors. During the batch tests at 500 °C, 7 and 2 min were required for heating and cooling stages, respectively, while reaction time was shorter (≤ 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 feed in continuous setups. However, a pressurized 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, sludges, etc.

Table 5-4 Comparison of SCWO capacity between continuous and batch reactor (24 hours (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	2	1	2
Oxidizer	H_2O_2	H_2O_2	H_2O_2	H_2O_2
Residence time	60 s	60 s	60 s	60 s
Heating and cooling time (per run[a], in s)	/	540	/	540
Total heating and cooling time (s)	3600 [b]	540×6×24 [c]	3600 [b]	540×6×24 [c]
CO2 recovery (%)	> 97.6	> 93.8	> 90	> 90
Major end product	CO_2	CO_2	CO_2	CO_2
Throughput (L)	/	/	124.2 [d]	12.96 [e]

a. Batch reactor need heating and cooling for each load.
b. Continuous reactor need only one heating stage at the very start and one cooling at the end.
c. Total heating and cooling time includes 540 s per run, 6 runs per hour and 24 h per day.
d. $(\frac{90\ \mathrm{mL}}{60\ s})$ × (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.

The theoretical scale-up of a 1 L reactor is given in Table 5-4. A 1 L continuous reactor is capable of dealing with 124.2 L influent (1 *wt.%* dry matter content) in a 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 produced 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 et al. 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 (above 1 L), which poses additional safety issues in terms of expansion volume (in case of leak/rupture). Heat transfer and reactor design is not discussed here as they need specific knowledge. We only compared the capacity difference and overall benefits of each reactor.

In comparison with other waste treatment methods (being hydrothermal liquefaction, stand-alone anaerobic fermentation), supercritical water oxidation is superior in its high oxidation efficiency within short residence time while only needing a small setup size. One of the previous studies (combining aerobic fermentation with worm conversion (He et al. 2010)) was operated for 93 days to reach the degradation of cellulose and lignin reached 98.6 % and 93.1 %, respectively, and the carbon recovery of only 65 %. With the combination of anaerobic fermentation and SCWO, the organic load in the waste can be removed up to maximum of 98 %. Nevertheless, the recovery of inorganic compounds is not efficient in SCWO. Inorganic components are mainly deposited inside the setup. The leaching of toxic heavy metals from the reactor alloys are 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.

5.4 Conclusion

Temperature and oxidizer addition (OER) affect sludge oxidation during SCWO. Each parameter variation behaved slightly different in continuous versus batch systems. OER had a greater influence than temperature on oxidation efficiency in batch and continuous tests, with the oxidation in the continuous reactor being less sensitive to OER variation than in a batch reactor. Higher temperatures (outside the tested range in this study) can be recommended to approach complete recovery of carbon. However, undesired phenomena like salt deposition, reactor corrosion and nitrogen oxidation to gas products could be enhanced as well at higher temperatures. Hence, the optimal temperature in SCWO for recovery in a regenerative life support system is likely to be a trade-off.

There are differences between continuous and batch reactors in terms of product distribution and operational procedures. Continuous reactors have the advantage of high processing capacity and tend to be more favorable for scale-up while batch reactors are more suitable to handle particle-containing wastes.

SCWO proves to be suitable for carbon recovery from organic wastes for its high efficiency and capacity. Organic components can be nearly completely oxidized and recycled while inorganic components are only partly recovered. The recovery efficiency of inorganics (including salts, nitrogen and phosphorus) in SCWO clearly needs to improve for application of this technology in life support systems, which should be a focus of follow up studies. The aqueous effluent can be easily recycled to various stages of the regenerative life support system, depending on the required quality of the water to be reused. Carbon dioxide is the main oxidation product which can be reused to grow plants.

Chapter 6 Mild temperature hydrothermal oxidation of anaerobic fermentation filtrate for carbon and nitrogen recovery in a regenerative life support system

Although the principal aim in this dissertation was to investigate the degradation of fibrous materials in the sludge that was formed upon fermentation of the organic waste (Chapters 4 and 5), it was also considered whether the filtrate (which was rich in dissolved organic compounds, mainly volatile fatty acids) could also be subjected to hydrothermal oxidation for recovery of nitrogen and carbon.

In this chapter, hydrothermal oxidation of fermentation filtrate was conducted in a tubular reactor to recover carbon (as CO_2*) and nitrogen (as* NH_4^+ *or* NO_3^-*) at mild temperature in a regenerative life support system. Because simultaneous with the recovery of carbon, also the recovery of nitrogen was targeted, it was opted to work under more mild process conditions. Temperature, residence time (*τ*), and the oxidizer equivalence ratio (OER) were the experimental variables in the oxidation tests. The highest carbon recovery achieved in our tests was 68.2 %, and with 91.8 % of the total nitrogen being in form of* NH_4^+ *or* NO_3^- *at 380 °C,* τ *= 48 s and OER = 4.0. The effect of temperature, residence time and OER on carbon and nitrogen distribution were discussed. Moreover, a first-order reaction rate was applied by means of regression analysis to estimate the carbon conversion rates. Prolonging the residence time at 380 °C with OER = 3.0 is proposed to be a promising modification to increase both carbon and nitrogen recovery from the filtrate.*

This chapter has been redrafted from 'Zhang, D., Luther, A., Clauwaert, P., Ronsse, F.: Mild temperature hydrothermal oxidation of anaerobic fermentation filtrate for carbon and nitrogen recovery in a regenerative life support system. The Journal of Supercritical Fluids 145, 39-47 (2019)'.

6.1 Introduction

Mass recovery is a primary requirement for a regenerative life support system. A long term crewed mission into deep space or an extraterrestrial outpost will require a regenerative life support system, which requires the recycling of carbon, nutrients and water from waste streams generated by the crew and the food production system (Nelson et al. 2010). The European Space Agency's life support system, envisioned by the MELiSSA (Micro-Ecological Life Support System Alternative) project, utilizes anaerobic thermophilic fermentation as the first step to degrade organic MELiSSA waste. To test the concepts within the MELiSSA project, a simulated waste (a mixture of red beet, lettuce, wheat straw, toilet paper, and human feces) mimicking actual human solid waste generated in space, is being used. However, the waste fermentation process can greatly decompose organics but far from fully degradation, which results in a large number of recalcitrant and unconverted plant fibers in the fermentation sludge and volatile fatty acids (VFAs) dissolved in the filtrate (also termed 'permeate') (Lissens et al. 2004). It is important to further degrade the partially or non-decomposed organic waste constituents. The fiber rich sludge are frequently drained from the anaerobic fermenter for further processing and VFA rich filtrate is the continuous effluent of this bioreactor. Though with higher costs and risks, hydrothermal oxidation is capable of effectively decomposing the organic compounds survived from fermentation process in both the sludge and the VFAs in the filtrate (Nelson et al. 2010, Miller et al. 2015). Nitrogen is simultaneously oxidized during this process, albeit partially or completely depending on the process conditions (Yang et al. 2017). The filtrate obtained from the anaerobic fermenter contains water soluble organics, while most unconverted carbon is in the form of plant fibers and other insoluble organics in the fermentation sludge. Processing the sludge and the filtrate by means of hydrothermal oxidation are assumed to differ in oxidizer needs, as well as in their optimized reaction conditions. Sludge hydrothermal oxidation has been previously studied in chapter 4 and 5. The filtrate, with a lower total organic carbon (TOC) content and having as major constituents VFAs, organic nitrogen and NH_4^+, is subjected in this study to oxidation in a continuous tubular reactor with excess oxygen addition (in the form of H_2O_2) at around critical temperature to maximize carbon and nitrogen recovery.

Nitrogen in the MELiSSA waste is mainly in the form of organic nitrogen and is partly degraded to ammonium in the filtrate after the anaerobic thermophilic fermentation. However, ~ 40 % of the nitrogen in the filtrate is in the form of organic nitrogen. The MELiSSA project aims to recover all organic nitrogen as either NH_4^+ or NO_3^- rather than gas-phase NO_x or N_2 that are respectively toxic or hard to be recycled (Luther et al. 2018). NH_4^+ and NO_3^- can be directly reused by plants or microorganisms as nitrogen source (Lissens et al. 2004). Hydrothermal oxidation for the degradation of residual organic nitrogen aims both at the conversion towards NH_4^+ and/or NO_3^-, and at the same time, avoiding the formation of N_2 and NO_x.

As studied by (Rice et al. 1998, Goto et al. 1999, Jin et al. 2001), supercritical water oxidation is an ideal process to transfer carbon from dissolved organics to carbon dioxide while potentially retaining the nutrients dissolved in an organic-free liquid effluent. Both batch and continuous processes have been studied to successfully oxidize different feedstocks (Chen et al. 2017, Lin et al. 2017, Stavbar et al. 2017, Zhang et al. 2017). Continuous reactors have the advantage of continuous feeding and require little to no buffer vessels as the waste is typically continuously being generated in a life support system. Without sequential heating, reaction and cooling stages, which are specific to batch processes, continuous reactors in which heat exchangers are used to recover effluent heat to the influent, work in a thermally efficient way. However, batch reactors have the advantage of offering more flexibility in terms of feedstock types that can be processed. Homogeneous reactions and heterogeneous reactions could both happen during hydrothermal oxidation. Fibers are known to be recalcitrant in supercritical water oxidation and more likely to undergo heterogeneous reactions which are rate-limited by mass transfer (Ma et al. 2015, Chen et al. 2017) whereas soluble organics undergo homogeneous reactions which are governed by free radical mechanisms (Li et al. 1991, Brunner 2009, Brunner 2009). Researchers have studied oxidation of many hazardous and recalcitrant materials to convert them into harmless products (Chen et al. 2017, Lin et al. 2017, Stavbar et al. 2017). However, the hydrothermal oxidation of volatile fatty acids hasn't been widely investigated (Lee et al. 1990, Azadi et al. 2013).

To summarize, in most organic oxidation studies, feedstock carbon was converted into carbon dioxide. High organic decomposition could be achieved but under varying optimized conditions depending on the type of organic waste being processed (Lee et al. 2002, Tan et al. 2014). Nitrogen is converted into diverse products depending on reaction conditions and its oxidation is highly affected by temperature (Chen et al. 2016, Chen et al. 2016). Temperatures higher than 450 °C start to generate NO_x and N_2 (Gong et al. 2016). Ammonium, nitrite and nitrate are the main components in the effluent when temperature is around the critical point with higher oxygen equivalence ratios (being the ratio at which excess oxygen for complete oxidation has been added, OER for short) shifting the nitrogen distribution to nitrate (Yang et al. 2018). Higher OER would favor nitrate production, which is in a lot of cases the preferred nitrogen source for crop production. Studies with the purpose of simultaneously recovering carbon and nitrogen are rare. Most hydrothermal oxidation studies aimed to decompose organics while in this study, we focus on the recovery of both carbon and nitrogen from waste.

In this chapter, we studied the hydrothermal oxidation of filtrate in a continuous reactor at temperatures around the critical point of water. We studied the conversion of carbon to carbon dioxide as well as the degradation of organic nitrogen resulting in dissolved nitrogen species (org-N, NH_4^+ or NO_3^-) in the liquid effluent or N-species in the gas phase (i.e. NH_3). The effect of operational parameters on carbon and nitrogen recovery was studied. A reaction kinetic of TOC (total organic carbon in the liquid phase) removal was also derived.

6.2 Materials and methods

6.2.1 Materials

Filtrate was obtained from an anaerobic fermenter from CMET (Ghent University) as in section 4.2.1. A mixture of wheat straw, red beet, lettuce, faeces, and toilet paper (MELiSSA waste) was thermophilically fermented at 55 °C and a pH of 5.3. Filtrate was collected through a 45 µm membrane from the anaerobic fermenter. Table 6-1 illustrates the properties of the filtrate. Hydrogen peroxide (H_2O_2, 33 *wt.%*, VWR International (Leuven, Belgium)) was obtained as oxidizer and diluted with distilled water to desired concentration.

Table 6-1 Chemical characteristics of undiluted filtrate (wet mass)

Parameters	Value
Dry matter (*wt.%*)	0.77
Total organic carbon (TOC) (mg/L)	3300
Total inorganic carbon (TIC) (mg/L)	25
Total nitrogen (TN) (mg/L)	246.46
Total nitrate (mg/L)	0.45
Total organic nitrogen (mg/L)	101.17
pH	5.3
Color	Black brown

6.2.2 Apparatus and experimental procedure

All experiments were performed in a coiled tubular reactor system, as shown in Figure 2-1. An electromagnetic stirrer was used to homogenize the contents of the vessel holding the filtrate to be fed to the system. An assembly unit was applied to get rid of the gas from the H_2O_2 stream before accessing the pump.

Pure water was pumped through both pumps at set flow (determined by the desired residence time) to start. The back pressure valve was adjusted to control system pressure to 2 MPa higher than the equilibrium vapor pressure at corresponding set temperature. The accuracy of pressure setting was ± 0.3 MPa. Heaters were then turned on to heat the system (feed and oxidizer preheaters as well as reactor heater) to set temperature. The accuracy of reaction temperature control was ± 0.1 °C. After temperature and pressure were stable, water streams were switched to feed stream and oxidizer stream for pump A and B respectively. The first liquid (effluent) sample was collected after 1.5 times mixture (compared to the system volume, ~ 2000 mL) had passed through the system, meanwhile gas flow and composition were stable. Later, the second and third sample were taken after every 500 mL of mixture passed through the system. Set point temperatures ranged from 300 to 380 °C. Filtrate concentration in the mixture was 0.44 *wt.%* for all experiments after mixing filtrate with oxidizer. Hydrogen peroxide concentration in the oxidizer stream was decided by the desired oxidizer equivalence ratio.

6.2.3 Product analysis

The gaseous effluent and TOC results of aqueous effluent were measured with the same methods as in section 3.2.3. Total nitrogen (TN) was measured by elemental analyzer (Thermo Scientific Flash 2000). Total Kjeldahl nitrogen (TkN) and ammonium ($NH4^{+)}$ was measured by steam distillation on a Vapodest 30 steam distillation unit as described in (Eaton et al. 1992). Nitrite and nitrate was measured directly using a NANOCOLOR® nitrite and nitrate kits (Machery-Naegel GmbH & Co., Düren, Germany). Organic nitrogen in liquid samples was determined by subtracting ammonium, nitrate and nitrite from the total nitrogen. For convenience of calculation, the missing N in the mass balance of N was assumed to be NH_3 as no other gas products of nitrogen were found. Quantitative analysis of the volatile fatty acids (C2-C8 fatty acids (including isoforms C4-C6)) in the liquid effluent were measured the same methods as in section 4.2.3.

6.2.4 Data processing and interpretation

Hydrogen yield (Y_{H_2}, mg/g) is defined as :

$$\mathrm{Y}_{H_2}\,(\mathrm{mg/g}) = \frac{[H_2 - H]_{gas} \times \Phi_{gas}}{[Filtrate]_{feed} \times \Phi_{feed}}$$

Equation 6-1

Where Y_{H_2} is the yield of H_2. $[H_2 - H]_{gas}$ represents the hydrogen gas yield in gas effluent (in mg/s). $[Filtrate]_{feed}$ represents the dry matter concentration of filtrate in feed (in *wt.%*). Φ_{gas} represents the flow of gas effluent (in g/s), Φ_{feed} represents the flow of influent mixture (in g/s).

Organic nitrogen decomposition (OND) is defined as:

$$OND\ (\%) = (1 - \frac{[ON]_{effl} \times \Phi_{effl}}{[ON]_{feed} \times \Phi_{feed}}) \times 100$$

Equation 6-2

Where $[ON]_{effl}$ represents the concentration of organic nitrogen in the liquid effluent (in mg/g). $[ON]_{feed}$ represents the concentration of organic nitrogen in the influent mixture (in mg/g). Φ_{effl} represents the flow of liquid effluent (in g/s).

Nitrogen recovery (NR) is defined as:

$$NR\ (\%) = \frac{([NH_4^+ - \mathrm{N}]_{effl} + [NO_3^- - \mathrm{N}]_{effl} + [NO_2^- - \mathrm{N}]_{effl}) \times \Phi_{effl}}{[TN]_{feed} \times \Phi_{feed}} \times 100$$

Equation 6-3

Where $[NH_4^+ - \mathrm{N}]_{effl}$, $[NO_3^- - \mathrm{N}]_{effl}$ and $[NO_2^- - \mathrm{N}]_{effl}$ represent the concentration of nitrogen in ammonium, nitrate and nitrite (considered to be the useful recovered N-species in the effluent) in the liquid effluent (in mg/g). $[TN]_{feed}$ represents the concentration of total nitrogen in the influent mixture (in mg/g).

6.3 Results and discussion

6.3.1 Effect of operation parameters on carbon recovery

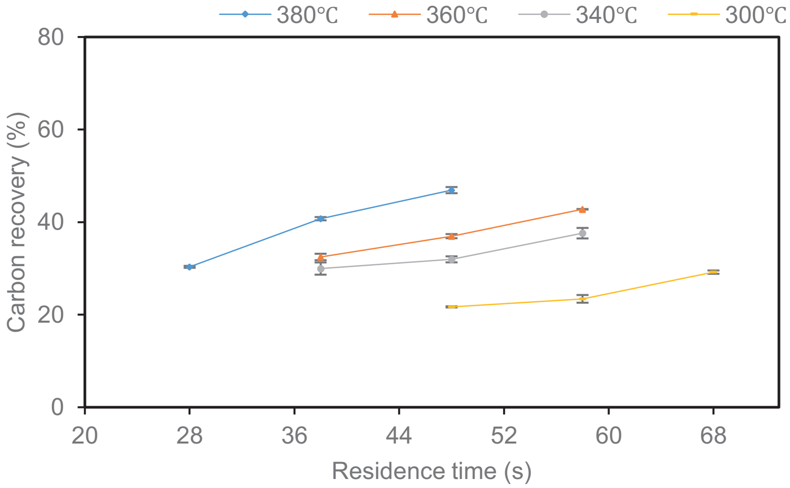


Figure 6-1 Effect of residence time on CR under 300, 340, 360 and 380 °C and at OER = 2.0.

The effect of residence time on hydrothermal oxidation of filtrate is illustrated in Figure 6-1. Experiments under different temperatures were conducted (300 to 380 °C) at diverse residence times (28 to 68 s) which were within the limits of the setup. Filtrate consists of volatile fatty acids including acetic acid which is hard to decompose in SCWO. Filtrate is not fully oxidized as shown in Figure 6-1. Only up to 46.9 % of carbon from the filtrate can be converted into carbon dioxide at the given reaction conditions. However, carbon recovery is enhanced by prolonging residence time at all temperatures tested. The effect of residence time under high temperature (380 °C, the only temperature tested above critical point) is more obvious than at low temperature (300 °C) which can be explained by the free radical reaction mechanism which dominates in supercritical water (Gong et al. 2014). Owing to increasing tendency of carbon recovery from prolonged residence time, we assume that more carbon could be recovered from the filtrate if longer residence times were applied.

Figure 6-2 shows the effect of OER on carbon recovery at τ = 48 s under various temperatures. It can be observed from Figure 6-2 that OER has significant impact on carbon recovery. There is a positive correlation between OER and carbon recovery, a result which is in line with previous reports (Qian et al. 2015, Qian et al. 2016, Lin et al. 2017, Stavbar et al. 2017). The influence of OER can be enhanced by applying higher temperatures. As a result, CR benefits more from increasing OER at 380 °C than at 300 °C. Up to 68.2 % carbon recovery is achieved at OER = 4.0, τ = 48 s and temperature = 380℃. High temperature and OER are expected to generate more free radicals that enhance the oxidation of VFAs. However, the given temperature cannot be completely take the advantage of given high OER. The improvement from increasing OER diminishes when OER is high. CR gains 8.2 % as OER increased from 3.0 to 4.0 while this improvement was still 13 % when OER increased from 2.0 to 3.0. Meanwhile, oxygen is largely released in the gas product as O_2 and wasted (i.e. do not take part in the oxidation reactions) at high OER. Either OER = 3.0 or 4.0 is enough for filtrate carbon oxidation. For better recovery of carbon from filtrate, temperatures higher than 380 °C are considered to be necessary.

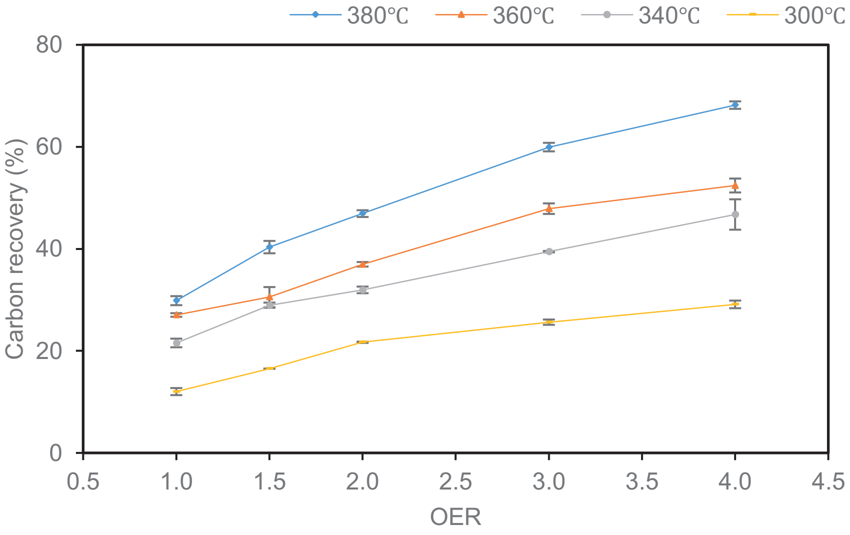


Figure 6-2 Effect of OER on CR under 300, 340, 360 and 380 °C at τ = 48 s.

Experiments at 360 and 380 °C were conducted under various residence times and OER to observe the sub- and supercritical water oxidation of filtrate for better analysis of carbon recovery, as shown in Figure 6-3. Trials at 360 and 380 °C were performed with different residence times owing to reactor limitations. Supercritical water oxidation with τ = 48 s and OER = 4.0 achieved 68.2 % carbon recovery, surpasses the 52.4 % of carbon recovery at same residence time and OER under subcritical water phase, and also be higher than the 60.4 % of carbon recovery at same OER with longer residence time (58 s) under subcritical water phase. Compared to subcritical water oxidation at OER = 4.0, supercritical water oxidation at OER = 4.0 increases more significantly from prolonging the residence time. Hydrogen peroxide in supercritical water produces reactive hydroxyl radicals OH• (Savage et al. 1998), which could react with the filtrate organic constituents effectively. The accumulation of OH• radicals from prolonging residence time leads to significant improvement in carbon recovery at longer residence times. By contrast, thermal degradation dominates in subcritical water. Unfortunately, the major components of filtrate, being VFAs, are difficult to decompose at subcritical temperature. Prolonging residence time only slightly boosts carbon recovery. The positive effect from higher OER is less significant.

Carbon from filtrate distributes into insoluble organic carbon that is discharged from the separator, soluble organic carbon remaining in the liquid effluent and carbon in the gas effluent. Carbon recovery aims to convert as much carbon into gas phase as possible. As studied by Lee (Lee et al. 1990) and Meyer (Meyer et al. 1995), CO, CO_2 CH_4 and H_2 were the major gas products from acid oxidation. Our gas analysis is consistent with their studies but without CO formation. CH_4 concentrations in studied cases were lower than 0.1 Vol.%. Carbon in gas products of filtrate oxidation is mainly in the form of carbon dioxide, which is favorable for carbon recovery. The result has no difference between subcritical water oxidation and SCWO. Hydrogen gas is a by-product from filtrate oxidation and only appeared at 360 and 380 °C. H_2 formation is probably restrained at low temperature. Water-gas shift reaction was stated as the mechanism of H_2 formation (Muangrat et al. 2010). SCWO tended to produce more H_2 than subcritical water oxidation under same OER and residence time, as shown in

Table 6-2. It can be explained that more OH• and higher temperature in supercritical phase might shift the water-gas shift reaction to H_2 formation (Ratnasamy et al. 2009). However, H_2 yield decreased with OER increasing. It is reasonable considering the strong oxidizing property of •OH. H_2 yield is found to be enhanced by prolonging residence time, which is more obvious at lower OER, probably resulting from the assumption that the oxidation of H_2 is less effective than the formation of H_2. A maximum of non-negligible 62.9 mg/g H_2 yield was reached at 380 °C, OER = 1.0 and $\tau = 48$ s. H_2 is considered a by-product from filtrate oxidation that has to be further removed or recovered.

Table 6-2 also illustrates the TOC removal efficiency and carbon balance. Carbon balance closure in most cases was nearly 100 %, especially at higher OER. Near 100 % carbon balance indicates that carbon from filtrate is almost completely found in gas and liquid effluents, which is confirmed by the absence of solid particles in the liquid effluent. TOC removal efficiency was always marginally higher than carbon recovery, proving that the majority of the removed organic carbon from the filtrate is converted into carbon dioxide as expected while a small minority remains as unconverted or partially converted compounds in the reaction effluent.

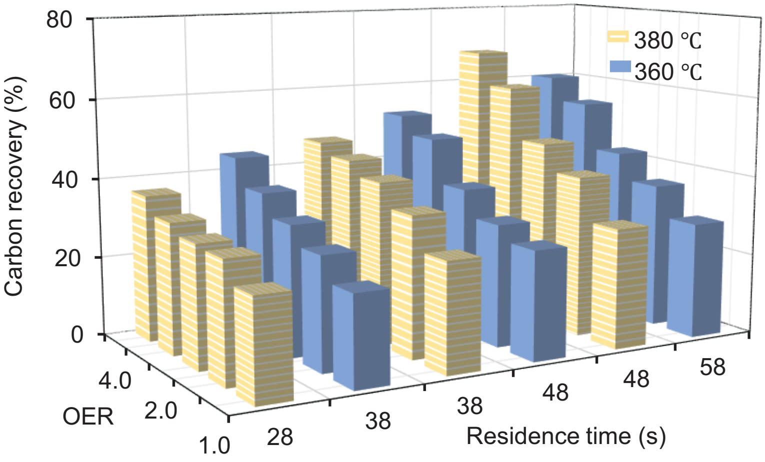


Figure 6-3 Effect of OER, residence time on carbon recovery of filtrate at 360 and 380 °C.

The oxidation of volatile fatty acids was studied in more detail and the results are shown in Table 6-3. Volatiles acids compose the majority of all total organic carbon in the filtrate. Acetic acid and butyric acid are two major compounds of VFAs. After hydrothermal oxidation at given conditions, butyric acid and most listed acids are largely removed. Acetic acid, however, is resistant and remains as the major organic constituent in the effluent. As stated in previous reports (Meyer et al. 1995, Suzuki et al. 2006), acetic acid is a refractory intermediate in hydrothermal oxidation.

Table 6-2 Effect of operation parameters on TOC removal efficiency, carbon balance, H_2 yield.

Temperature (°C)	τ (s)	OER	TRE (%)	CB (%)	H_2 yield (mg/g)
380	28	4.0	37.8	99.0	17.6
		3.0	34.5	98.2	18.5
		2.0	32.0	98.3	21.8
		1.5	31.1	98.7	34.7
		1.0	25.7	98.9	39.8
	38	4.0	49.5	97.3	25.3
		3.0	46.5	97.6	27.7
		2.0	41.6	99.1	35.8
		1.5	36.5	98.7	48.5
		1.0	27.9	99.2	60.9
	48	4.0	69.7	98.5	22.2
		3.0	60.2	99.7	23.8
		2.0	47.3	99.6	38.7
		1.5	42.7	97.6	53.6
		1.0	32.7	97.1	62.9
360	38	4.0	44.6	99.9	0.0
		3.0	40.6	97.2	0.0
		2.0	34.3	98.2	5.7
		1.5	29.6	98.4	23.9
		1.0	25.2	97.1	25.9
	48	4.0	52.9	99.5	2.6
		3.0	48.0	99.9	8.2
		2.0	37.0	99.9	16.4
		1.5	32.6	98.0	38.1
		1.0	27.4	99.6	33.4
	58	4.0	60.5	99.9	0.0
		3.0	54.8	99.6	3.5
		2.0	44.0	98.8	15.9
		1.5	40.0	96.3	42.3
		1.0	33.4	95.3	37.5

Table 6-3 Concentration of volatile fatty acids before and after hydrothermal oxidation at T = 380 °C, τ = 48 s and OER = 4.0

Acids	Concentration of volatile fatty acids (mg C/L)		
	Original filtrate	Influent mixture*	Effluent product
Acetic acid	689	395	272
Propionic acid	72	42	16
Isobutyric acid	69	40	0
Butyric acid	967	555	33
Isovaleric acid	42	24	0
Valeric acid	22	13	0
Caproic acid	161	93	13
Isocaproic acid	0	0	0
Heptanoic acid	0	0	0
Octanoic acid	0	0	0
Sum	2023	1161	334

*The concentration obtained after mixing with peroxide solution and is ultimately the concentration in the reactor

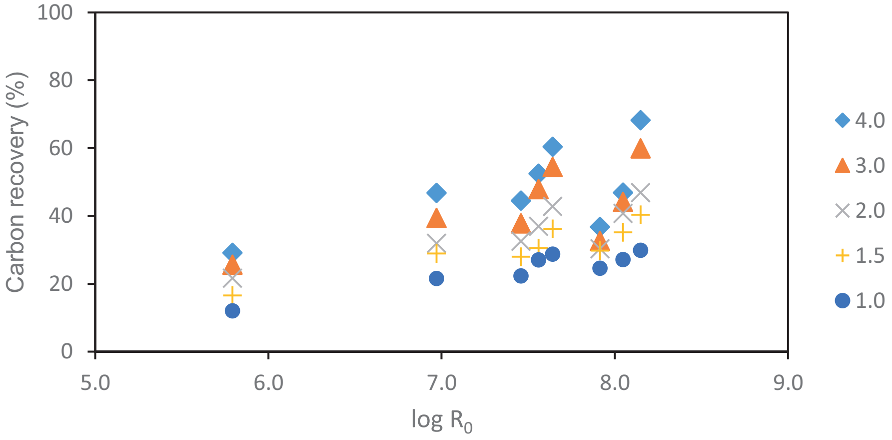


Figure 6-4 The carbon recovery obtained from hydrothermal oxidation of sludge at OER = 4.0, 3.0, 2.0, 1.5 and 1.0 as a function of the combined severity index, log R_0

It is a general tendency that higher carbon recovery is obtained by increasing the severity factor. The correlations between carbon recovery and severity index were met with several discontinuities. Nevertheless, a larger effect of the oxidizer is observed, especially when compared to the severity index in its lower tested tange. The improvement of carbon recovery at OER = 1.0 is 17.8 % by increasing the severity factor from 5.8 to 8.1, while the improvement is 39.1 % at OER = 4.0. To improve carbon recovery, the joint effects from OER and severity factor both need to be considered.

6.3.2 Effect of operation parameters on nitrogen recovery

The organic nitrogen in the MELiSSA waste was partly converted into ammonium after anaerobic fermentation (~ 40 %). The filtrate contained 145 mg NH_4^+-N per liter and 101 mg organic nitrogen per liter. The objective in this work was to decompose this remaining 41% organic nitrogen by means of hydrothermal oxidation. Nitrogen recovery efficiency of hydrothermal oxidation is evaluated by means of organic nitrogen decomposition towards either NH_4^+, NO_2^- or NO_3^-. Under the studied process conditions in hydrothermal oxidation, a maximum of 80.1 % of the organic nitrogen can be decomposed, resulting in a total of 91.8 % recovery of the nitrogen if the combined processes of fermentation and hydrothermal oxidation are considered. Final nitrogen products are nitrate, ammonium, few nitrogen in organics in the liquid effluent and some ammonium in the gas effluent.

Figure 6-5.a demonstrates the results of organic nitrogen decomposition at OER = 2.0 under different temperatures. Organic nitrogen compounds in the filtrate are mainly amino acid and peptide. The big lead of organic nitrogen decomposition in supercritical water over subcritical water indicates the positive effect of temperature on nitrogen decomposition. What’s more, the single-phase reaction under supercritical phase could further boost the effect of temperature. Decomposition of organic nitrogen increases as the residence time is prolonged. It is promising to obtain higher organic nitrogen decomposition with longer residence time (Phuong Thu et al. 2016). However, the effect of longer residence time is not as significant as stated by previous studies (Yang et al. 2017, Yang et al. 2018), probably resulting from the low working temperatures used in this study. The effect of longer residence time can be enhanced in higher temperature as shown from tests at 380 °C in Figure 6-5.a.

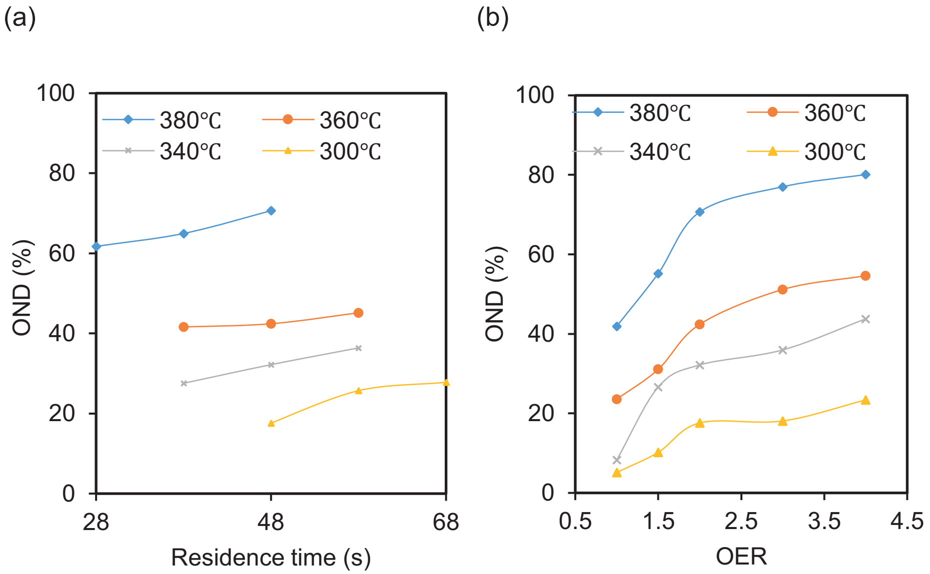


Figure 6-5 Effect of (a) residence time at OER = 2.0 and (b) OER at τ = 48 s on organic nitrogen decomposition.

The effect of OER on organic nitrogen decomposition is shown in Figure 6-5.b. Organic nitrogen decomposition increase significantly when increasing OER from 1.0 to 2.0. In this study, the OER is calculated solely based on the TOC concentration of the filtrate, the latter which is around 10 times higher than organic nitrogen concentration. The ratio between reactive oxygen added to nitrogen present in the filtrate is greatly increased when increasing OER from 1.0 to 2.0. As shown in Figure 6-5.b, further increasing the OER slightly increased organic nitrogen decomposition at OER > 2.0, resulting from much higher excess ratio between oxygen to nitrogen. Due to low concentration of organic nitrogen in the feedstock, OER = 2.0 is sufficient for organic nitrogen decomposition and recovery.

Nitrogen oxidation occurred simultaneously with nitrogen decomposition. Ammonium is oxidized to nitrate as shown in Figure 6-6. Ammonium could originate from the filtrate before hydrothermal treatment or as a decomposition product of organic nitrogen formed during the hydrothermal process. N_2 and NO_x were not detected in the gas product probably due to the relatively low working temperatures as studied (Osibo 2011, Xu et al. 2015, Shimoda et al. 2016), this observation is favorable for proper recovery of nitrogen in a life support system. Nitrite concentration in the liquid effluent was insignificant under the studied process conditions, probably because of the high oxygen concentration. Nitrate can be directly used by plants and is considered to be more favorable than harmful ammonium for a regenerative life support system (Clauwaert et al. 2017). The conversion from ammonium to nitrate is low (< 20 %) and is greatly affected by temperature and OER. The conversion to nitrate at 380 °C is obviously higher than in subcritical water. These observations are consistent with previous reports in which conversion from ammonium to nitrate in subcritical water is restrained but enhanced in supercritical water (Xu et al. 2015, Yang et al. 2017). Figure 6-6 also indicates a positive correlation between residence time as well as OER and nitrate recovery. Maximum conversion to nitrate obtained was 16.7 % at 380 °C with τ = 48 s and OER = 4.0.

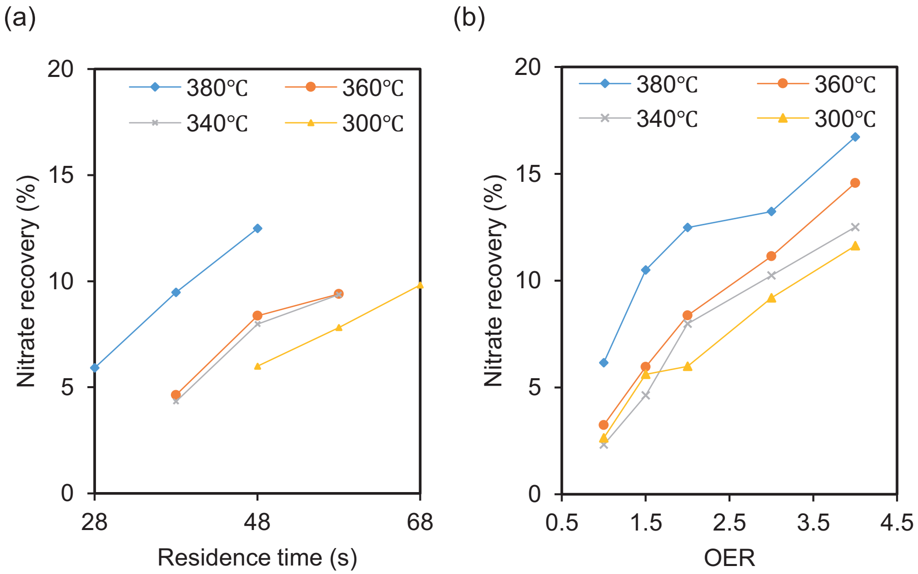


Figure 6-6 Effect of (a) residence time at OER = 2.0 and (b) OER at τ = 48 s on nitrate recovery.

Carbon recovery from the filtrate can be well conducted under OER = 3.0, the high OER is needed given the recalcitrance of one of the main constituents in the filtrate, being acetic acid. Higher OER will increase carbon recovery but less effectively. In terms of nitrate formation, higher OER is thought to be better but also less economical (i.e. higher reliance on hydrogen peroxide). Longer residence times are positive, albeit limited, for both nitrogen and carbon recovery at given reaction conditions. Supercritical water is preferred over subcritical water for filtrate oxidation. However, temperatures higher than 380 °C might potentially lead to the undesired formation of N_2 and NO_x in the effluent gas (Gong et al. 2016).

6.3.3 Global kinetics for TOC removal

By comparing TOC removal with carbon recovery, we stated that most carbon removed from the effluent is in the form of carbon dioxide under the conditions tested.

The global reaction rate for the removal of TOC by hydrothermal oxidation can be described as follows:

$$r = -\frac{d[TOC]}{d\tau} = \kappa\ [TOC]^a\ [O_2]^b\ [\mathrm{H}_2O]^c$$

Equation 6-4

Here, r is the global reaction reaction rate. [*TOC*] is the TOC concentration (mol/L). [O_2] is the oxygen concentration (mol/L). In here and for the sake of simplicity, the assumption is made that hydrogen peroxide is fully decomposed into water and oxygen during preheating. κ represents the reaction rate constant ($(\mathrm{mol/L})^{1-a-b}$/s). τ is the reaction time (s). a, b and c are reaction orders of TOC, O_2 and H_2O respectively. Assuming an Arrhenius temperature dependence, reaction rate constant can be expressed as

$$\kappa = A\ exp\left(-\frac{E_a}{RT}\right)$$

Equation 6-5

and

$$\ln k = -\frac{E_a}{RT} + \ln A$$

Equation 6-6

Here, E_a represents the activation energy (J/mol). A represents the Arrhenius pre-exponential constant specific for the reaction ((mol/L)$^{1-a-b}$/s). R is the universal gas constant (8.314 J/(mol K)). T is the reaction temperature (K).

The reaction order of water is considered to be zero since water consisted of more than 99% in reaction medium (Sanchez-Oneto et al. 2008). As published by many researchers (Portela et al. 2001, Erkonak et al. 2008, Al-Duri et al. 2015, Chen et al. 2015), hydrothermal oxidation of organic compounds can be assumed with a reaction order of unity. The pseudo-first order approximation was used to evaluate the reaction's activation energy and Arrhenius pre-exponential constant. The oxidizer concentration was assumed to change insignificantly in the experiments carried out with OER > 3, making b = 0. Global rate was modified to following equation to evaluate κ.

$$r = -\frac{d[TOC]}{d\tau} = \kappa'[TOC]_0$$

Equation 6-7

The initial TOC is expressed as $[TOC]_0$. κ' is the reaction rate at given temperature (s^{-1}). Calculated κ' at different temperatures is shown in Table 6-4.

Table 6-4 TOC removal reaction rate constant κ' at different temperature

T (K)	635	613	577
$\kappa' = ([\mathrm{TOC}]/[\mathrm{TOC}]_0 \text{ vs } \tau)$	0.01565	0.01219	0.00711

As expressed in the Arrhenius equation of Equation 6-6, E_a is evaluated from the slope of ln κ' versus 1/T and the corresponding pre-exponential factor A is calculated from intercept, shown in Figure 6-7. Consequently, E_a is calculated to be 95.7 kJ/mol and A is 42.0 s^{-1}.

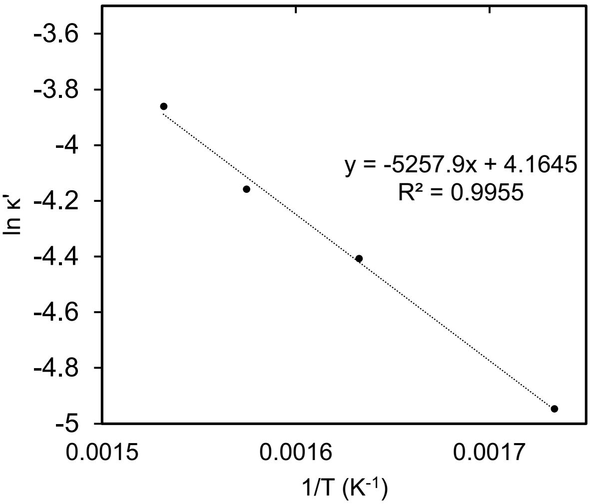


Figure 6-7 Arrhenius plot for TOC removal (Pseudo-first-order model to evaluate E_a and A).

By assuming TOC removal being a first order reaction, by integrating the Equation 6-4.

$$X = 1 - exp\left(-A\ exp\left(\frac{E_a}{RT}\right)\tau[O_2]_0^b\right) \text{ (a = 1 and c = 0)}$$

Equation 6-8

Where *X* is the TOC removal (equal to *TRE*), the subscript 0 of oxygen represents values at the reactor entrance. *E*a and A values were obtained above.

A genetic algorithm method was used to minimize the sum of squared differences of the experimental and predicted removal (Portela et al. 2001, Söğüt et al. 2009). By inputting all the 44 data points into software, the reaction order of oxygen was calculated, being b = 0.41. Thus, the kinetic equation for TOC removal was expressed as follows:

$$r = -\frac{d[TOC]}{d\tau} = 42\, exp\left(-\frac{95699}{RT}\right)\, [TOC]\, [O_2]^{0.41}$$

Equation 6-9

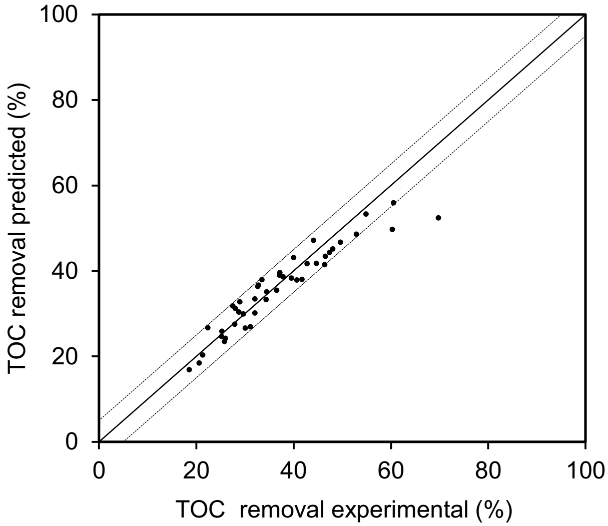


Figure 6-8 Parity plot between experimental TOC conversion (in %) and those predicted (in %) by the kinetic model.

Figure 6-8 shows the parity plot between calculated TOC removal and experimental results. The dashed lines indicate a deviation of ± 5 % conversion on the 45° line. Most predicted data are in good agreement with the experimental data. The only exception are 2 plot points, specifically those corresponding at the conditions in supercritical water, that had higher TOC removal than the kinetic model based prediction. This indicates that the increased temperature, as well as the change in the water proprieties at supercritical phase both have positive influence on TOC removal. The reaction's activation energy is rather high compared with most studied organics (Sanchez-Oneto et al. 2008, Abelleira et al. 2013). For example, it was 70 kJ/mol for semisynthetic cutting fluid (Sánchez-Oneto et al. 2008), 27.8 kJ/mol for textile wastewater (Söğüt et al. 2007) and 45.5 kJ/mol for organic and heavy metallic pollutants (Chen et al. 2016). But this high value of *E*a may be reasonable considering that the tested filtrate contained relative high quantities in recalcitrant VFAs like acetic acid.

6.4 Conclusion

Full recovery of filtrate has not been achieved at given conditions. Carbon recovery and nitrogen recovery appear to have different optimal reaction conditions in terms of temperature, OER and residence time. Carbon dioxide is almost the only gas product from hydrothermal oxidation of the filtrate along with small H_2 yield. A maximum of 68.2 % of carbon recovery was obtained under the studied process conditions. Higher temperature and OER most likely will increase the carbon conversion to carbon dioxide. Up to 80.1 % organic nitrogen was decomposed in hydrothermal oxidation resulting in 91.8 % of total nitrogen recovery if hydrothermal oxidation is combined with a preceding fermentation process. Nitrogen is slightly converted into nitrate with most remaining as ammonium. Both higher temperature and higher OER have positive influence on nitrogen recovery and formation of nitrate. However, temperatures higher than 380 ℃ may be difficult to recommend considering potential (irrespective of the N_2 and NO_x formation) nitrogen recovery but at higher costs. Residence times longer than 48 s with OER = 3.0 ~ 4.0 at around 380 °C are suggested to improve both carbon recovery and nitrogen recovery.

A global rate expression was proposed based on the experimental data for the TOC removal, which was supposed to be similar to carbon recovery as carbon was mostly converted into carbon dioxide. The TOC oxidation was predicted to be first order reaction for TOC. The activation energy for filtrate removal was calculated to be 95.7 kJ/mol. Reaction order of oxidizer was calculated to be 0.41 s^{-1}.

Chapter 7 Effluent recirculation during mild supercritical water oxidation dramatically improves oxidation efficiencies techno-economic viability

From Chapters 4-6, it is clear that increasing the severity of the process (i.e. temperature, residence time and oxidizer addition) is beneficial for carbon oxidation, but at the same time it reduces the capability to recover nitrogen. Additionally, more severe conditions pose additional safety constraints and may considered not to be economical. As such, a new supercritical water oxidation (SCWO) methodology is reported, which should be able to dramatically improve oxidation efficiencies at milder temperatures compared to present methods by recirculating the effluent to the system. Combining recirculation and mild conditions during SCWO thus unlocks a versatile oxidation platform, while safeguarding environmental and technical risks.

This chapter has been redrafted from 'Zhang, D., Ghysels, S., Ronsse, F.: Effluent recirculation during mild supercritical water oxidation dramatically improves oxidation efficiencies techno-economic viability. (In preparation)'.

7.1 Introduction

Supercritical water oxidation benefits from the unique solvent properties of supercritical water (critical point being 374 °C and 22.1 MPa) to establish the oxidation of organic compounds. Within a supercritical environment, reactants (being both the waste as well as the oxidizer) appear as a homogeneous single phase. SCWO fits within a waste management strategy to decompose harmful and high-risk substances (e.g. medical wastes) or high-moisture waste streams (Marrone 2013, Brunner 2014). In such cases, SCWO avoids the emission of toxic and noxious intermediates, e.g. dioxins, which would occur in case of incineration. It also overcomes the energy requirements to dry the feedstock prior to its processing. Additional generic advantages of SCWO comprise the high organic removal efficiency (Savage 1999, Vadillo et al. 2013, Al-Duri et al. 2015, Zhang et al. 2017) and clean final products. Nevertheless, SCWO has to meet several criteria with respect to process conditions in order to satisfy oxidation of different organics effectively, which is one of the main research topics in SCWO. On the other hand, corrosion is a significant problem in SCWO because of harsh working conditions. The corrosion is greatly affected by the presence of oxidizer in supercritical water.

Oxidation of organics under *mild* supercritical conditions, i.e. just above the critical point, generally is ineffective (TOC removal being only 30 - 70 %) (Bermejo et al. 2006). To achieve complete oxidation, SCWO typically operates at temperatures far exceeding the critical point (> 600 °C) (Fang 2014, Tan et al. 2014). Higher oxidizer addition is also found to be positive to improve oxidation efficiency. Such harsh conditions are required for successive oxidation of recalcitrant/refractory intermediates (e.g. acetic acid) formed during SCWO (Meyer et al. 1995, Jin et al. 2001, Portela et al. 2001). Nevertheless, other undesirable side effects that arise from such harsh conditions are: 1) the nitrogen distribution towards NOx at higher temperature and oxidizer load and 2) obviously the corrosive nature of high-supercritical water and oxidizer mixture, which compromises long-term reactor operation (Matsumura et al. 2000). It might be possible to compensate the harsh conditions (higher oxidizer usage and temperature) with longer residence times at milder temperatures as prolonged residence time could benefit oxidation efficiencies (Guo et al. 2010, Fang 2014), but goes in tandem with additional technical requirements, such as an increased reactor size and number of oxidizer injection points. These are considered as disadvantages, while larger reactors require extra investment costs and multiple oxidizer injection points would make the setup more complex and more vulnerable. As most organics subjected to supercritical water oxidation formed a solid-free liquid effluent at a sufficient oxidative environment (i.e. OER higher than 1.5 times the stoichiometrically amount required) (Gong et al. 2016, Phuong Thu et al. 2016, Chen et al. 2017, Gong et al. 2017), we hypothesize the possibility to extend the residence time by recirculating the liquid effluent (the latter containing incomplete oxidation products) while carrying out the oxidation at milder conditions (i.e. just above the critical point of water with oxidizer dosing around 2). Residence time is prolonged by several multiple times depending on the number of recirculations. The recirculated effluent (containing incomplete oxidation products) is taken as reaction medium for fresh waste feedstock. Fresh waste feedstock is continuously fed and oxidized simultaneously with the incomplete oxidation products in the recirculated effluent the same way as in a conventional continuous setup.

While facing lower oxidation efficiencies, mild SCWO offers the advantage of reducing corrosion (especially if the longer residence times provided by the recirculation allow to lower the OER to just above 1.0) and additionally avoiding the evolution of NO_x from N-species in the organic phase (Kritzer et al. 2001, Marrone et al. 2009). Gas products from SCWO are generally composed of carbon dioxide and to a lesser extent, carbon monoxide and methane. The minor gas species (e.g. CH_4 and CO) could be easily converted to carbon dioxide which is a greenhouse gas but can be used in downstream applications (e.g. in plant growth in greenhouses or as chemical feedstock in synthesis), and is safer to dispose of than potentially toxic and oxidation-resistant organics that are present in the waste to be processed.

This chapter presents an original and novel strategy for SCWO, which potentially decreases two problems of SCWO (i.e. corrosion and low feedstock flexibility) and keeps reactor dimensions and associated safety risks considerably low. A continuous setup, fit for operation slightly above the critical point, was investigated for its feasibility to serve operating at constant reaction conditions, and enable to decompose a plethora of organic wastes regardless of the optimal oxidation conditions of individual specific compounds. The proposed process is capable of developing a mobile and compact setup with smaller reactor dimensions and being more versatile to treat different organic wastes, especially toxic ones. To achieve so, recirculation of the effluent was investigated for three pure model compounds: two distinct types of solid organics, being acetic acid which is known as soluble recalcitrant intermediate, and being cellulose and lignin which are the most abundant organics in nature and are resistant in most biodegradation technologies.

7.2 Methods and materials

7.2.1 Theoretical calculation of recirculation process

In chapter 3, the oxidation efficiency of cellulose, lignin and acetic acid at temperature of 380 °C, pressure of 25 MPa, OER of 2.0 and residence time of 28 seconds, were obtained as being 46.4 %, 41.3 % and 18.4 %, respectively. By assuming that the residual organics would have same the oxidation efficiency if recycled back to the reactor at the same conditions (and without addition of fresh oxidizer), the remaining amount of organics after each recirculation can be calculated as shown in Figure 7-1. An oxidation efficiency > 99 % could be reached after 8, 9 and 23 times for the recirculation of cellulose, lignin and acetic acid, respectively. Theoretically, it is possible to achieve near fully oxidation of organics given sufficient number of recirculations.

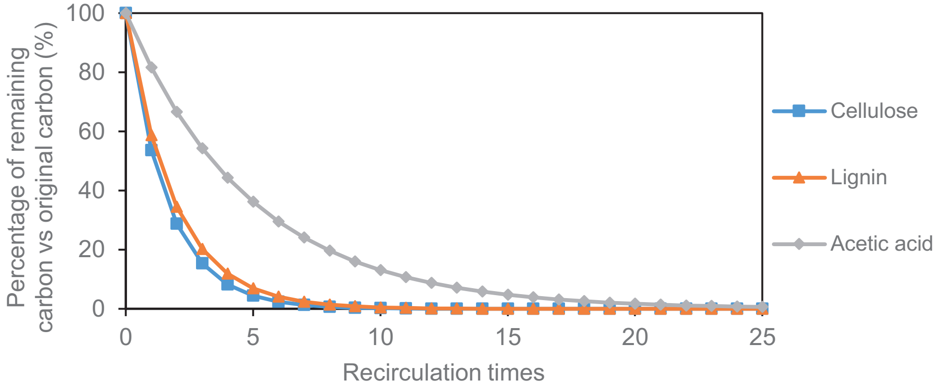


Figure 7-1 Calculated percentage of remaining carbon in the effluent *vs* original carbon in the feedstock as a function of the number of recirculations (380 °C, OER = 2.0 and τ = 28 s) – data based on the oxidation efficiencies obtained for single-pass experiments in Chapter 3.

7.2.2 Product specifications

Cellulose, lignin and acetic acid were analytical reagent grade (Sigma–Aldrich, Overijse, Belgium). All became homogeneous dispersions or solutions after mixing with water. A 33 *wt.%* hydrogen peroxide was bought from VWR International (Leuven, Belgium) and was diluted with distilled water to desired concentration before experiments.

7.2.3 Setup and process

The continuous reactor is used, as shown in Figure 2-1. At start, pure water was pumped through pumps A and B. A back pressure valve was used to control the system pressure at 25 MPa, with an accuracy of ± 0.2 MPa. The system was later preheated to 380 °C by electrical heaters, with an accuracy of ± 0.1 °C. After temperature and pressure were stable, pump A and B were switched to feed stream (feed 1) and oxidizer stream (feed 2) respectively. The former was prepared by mixing either cellulose, lignin or acetic acid with water, so that the fresh organics would reach a 0.78 *wt.%* concentration in the feed stream (Table 7-1). The oxidizer was dosed in such way that it could oxidize twice the amount of organic-C from fresh organics, i.e. the OER = 2.0 (Table 7-1). A magnetic stirrer was used to keep the feed in the supply vessel homogeneous. The liquid effluent was collected after 2000 mL of the organics/water/H_2O_2 mixture had passed through the system. Gas and liquid samples were taken during that time. The collected aqueous effluent was used as reaction medium for the fresh feed in a next run. The residence time was determined using Equation 2-3.

Table 7-1 Operational conditions for a single pass run.

Feed types	Feed flow (g/s)	H_2O_2 flow (g/s)	Feed concentration (*wt.%*)	H_2O_2 concentration (*wt.%*)	Residence time (s)
Cellulose	1.11	0.62	0.78	7.22	26
Lignin	1.11	0.62	0.78	12.12	26
Acetic acid	1.11	0.62	0.78	6.32	26

Figure 7-1. b depicts the experimental workflow. Fresh water and dry feedstock were mixed as feed stream and fed to the setup. Hydrogen peroxide (H_2O_2) as the oxidizer, was separately pumped into the system and the dosing of peroxide corresponded to an OER = 2.0. The ratio of mass of flow rates of feed to H_2O_2 solution was 1.11 : 0.62 in all tests. The continuous setup consisted of a coiled tubular reactor, set to 380 °C and 25 MPa and was operated at a residence time of 26 seconds. Solid product was not found in the liquid effluent. Gas effluent was collected and analyzed after reaction. Aqueous effluent was collected and mixed with fresh feed to serve as input material for the next run. The concentration of fresh feed in water/H_2O_2/organics mixture (i.e. the concentration in the mixture that enters the reactor coil) was always controlled to be 0.5 *wt.%*. Fresh feed and recycled effluent (containing undecomposed residuals from previous run) were oxidized simultaneously.

Within our experimental procedure (Figure 7-2. b), additional water was introduced into the system which stemmed from: (i) the H_2O_2 solution itself, (ii) the water within the waste feedstock (iii) the generation of chemical water from hydrogen present in the organic feedstock. The introduced water increased the absolute quantity of the mixture as well as the subsequent effluent volume as effluent recirculation goes on. Wet wastes containing large amounts of water, as well as the use of diluted oxidizer solutions will need an extra procedure to remove the extra water in the system as to keep the volume of recirculated effluent constant throughout time. Later in this chapter (section 7.3.2), we propose a theoretical extension of the setup to solve the problem of this cumulative effluent.

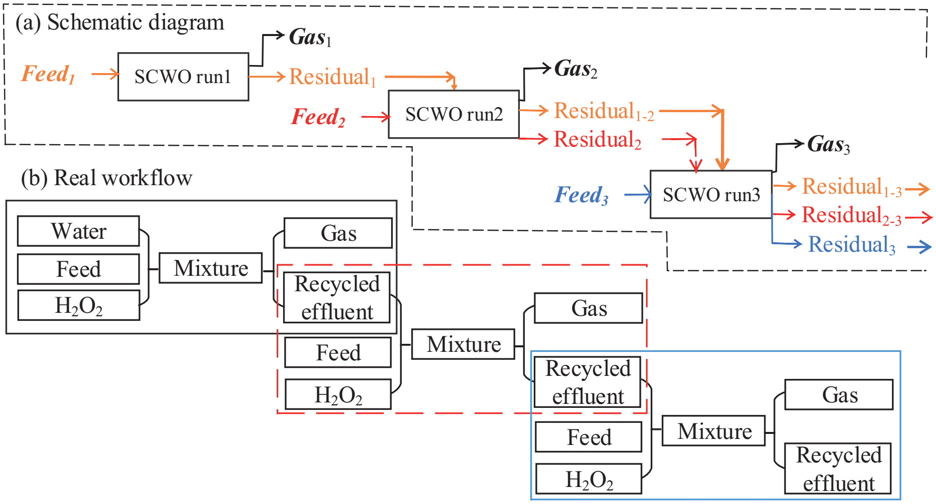


Figure 7-2 Schematic diagram (a) and real workflow (b) of experiments. Residue$_x$ denotes the residual carbon in the liquid effluent stemming from freshly injected feed in the x^{th} SCWO run. Residue$_{x\text{-}y}$ ($x<y$) denotes the residual carbon of the liquid effluent from run y which stemmed from the feedstock injected in the x^{th} run.

7.2.4 Behaviors in organic decomposition during each recirculation

After the first run in the process scheme (Figure 7-2. a), some residual/refractory organics remained in the liquid effluent, as was expected. Indeed, mild conditions with a limited residence time cannot achieve full oxidation. The effluent solution was subsequently re-used as reaction medium in a second run, i.e. mixed with fresh organics and oxidizer in the same concentration as the initial run. While refractory compounds from the initial run were allowed to consecutively degrade, new refractory intermediates from the fresh feed were formed in the second run. Extrapolated, the following hypothesis was put forth: *100 % removal of the initially fed organics is achieved after a finite number of n runs (i.e. after 1 initial run without recycling combined with n-1 runs with recycling).* If this hypothesis holds, 100 % removal of organics introduced is achieved after run *n*. Identifying this *n* is crucial and would preferably be a reasonable low number.

The residual amount of carbon in the effluent of a particular run, stemming from the initially fed waste-C at run one, was obtained from carbon balance closures over the feed, gas and effluent. It was assumed that fresh feed and dissolved residuals in the effluent from previous runs decompose independently without interaction. As a consequence, the carbon in the liquid effluent from run i ($0 < i < n$) was distributed over i pools, stemming from carbon fed in run 1 to i (Figure 7-2. a).

The i pools of dissolved intermediates in the liquid effluent present after run i were assigned a carbon-content based on carbon balance closure. The entire procedure to calculate the cumulative oxidation efficiency of initially fed organic carbon through multiple recycling runs, using the latter assumptions, is exemplified for cellulose, lignin and acetic acid in the Appendix Figures 3 - 5, respectively.

7.2.5 Analysis methods

The gas composition and effluent TOC were analyzed by same methods as described in section 3.2.3. The feedstock soluble residuals in the effluent of cellulose, lignin and acetic acid were analyzed by GC-MS as described in section 4.2.3. Cellulose molecule was assumed to degrade into smaller molecules to some extents. As a result, the TOC value was selected to represent the oxidation degree of organics.

7.2.6 Data processing and interpretation

Oxidation efficiency (OE) is defined as:

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

Equation 7-1

Where $[TOC]_{effl}$ represents the residual TOC concentration in the liquid effluent (in mg/g). $[TOC]_{feed}$ represents the TOC concentration in the influent mixture (in mg/g).

7.3 Results and discussion

7.3.1 Carbon distribution during recirculation

Results of cellulose SCWO in Table 7-2 shows that carbon in the gas phase initially increases successively from run one to run three; thereafter a quasi-steady situation prevails. The same trend was observed for carbon in the effluent, yet, the quasi-steady situation was achieved one run earlier. The earlier transition from build-up to a quasi-steady concentration of carbon in the effluent, compared to carbon in the gas phase, falls within expectations: effluent from run two was recycled to run three, degraded almost entirely into gases and led to negligible carbon build-up in the effluent, while building up carbon in the gas phase.

Figure 7-3 explains why a build-up of carbon in the effluent was apparently reaching a steady state, and how this actually indicates full oxidation of the initially added feedstock's carbon. The horizontal axis displays the number of SCWO runs, while the vertical axis represents the cumulative oxidation efficiency of added cellulose in run *i*. Every line represents the individual oxidation efficiencies of cellulose-carbon that was added prior to the start of run *i*.

Table 7-2 Cellulose-C oxidation in a mild supercritical water oxidation setup with effluent recycling. Carbon concentration is expressed in terms of mg carbon per cubic decimeter of added influent mixture (mg C/L).

Run	Carbon in influent (fresh + residuals)	Carbon in Gas	Carbon in Liquid effluent	Carbonl Balance closure (%)	Cumulative oxidation efficiency of carbon from the initial feed (%)
1	2242	1432 ± 35	798 ± 11	99.5	64
2	2242 + 527	1699 ± 38	1050 ± 9	99.3	82
3	2242 + 696	1862 ± 20	1035 ± 4	98.6	99
4	2242 + 700	1907 ± 20	1025 ± 16	99.7	100
5	2242 + 674	1910 ± 16	1056 ± 5	101.7	100

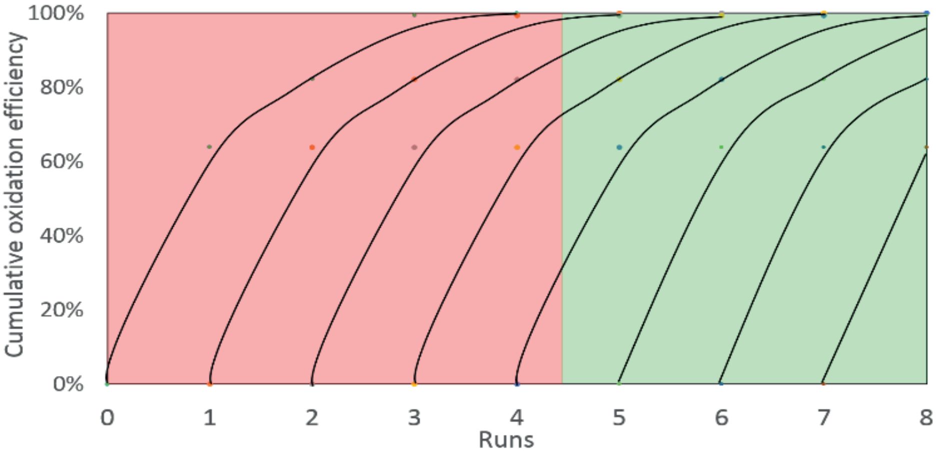


Figure 7-3 Cumulative oxidation efficiency of cellulose-carbon during each run. The red window covers the runs at which initial carbon still is present in the effluent (the green window covers the runs at all carbon from the initial feed was degraded).

After one SCWO run, 64 % of initial cellulose had been oxidized, according to Table 7-2. Upon run 2, a second batch of cellulose-carbon is to be added. After run two, the cumulative oxidation efficiency of the cellulose-carbon that was fed at the start of run 1 was calculated to be 82 %, while the cellulose-carbon added in run 2 oxidized with an efficiency of 64 %. After run three, the cumulative oxidation efficiency of the cellulose-carbon that was fed at the start of run 1 was calculated to be 99 %, while the cumulative oxidation efficiency of the cellulose-carbon added in run 2 was 82 %, and the cellulose-carbon added in run 3 oxidized with an efficiency of 64 %. Because of the incomplete cumulative oxidation efficiencies through runs 1-3, carbon in the liquid effluent built up (Figure 7-3, red-left window). After the fourth run, the liquid effluent was calculated free of cellulose-carbon that was initially injected (i.e. in run 1). From that point forward, every run, *n*, following the fourth run degraded the feed that was added before run *n*-4 completely (Figure 7-3, green window). The steady concentration of carbon in the effluent is also apparent from Table 7-2. Altogether, it is safe to say that recirculation of effluent was definitely able to fully decompose cellulose under mild conditions.

Table 7-3 Lignin-C oxidation in a mild supercritical water oxidation setup with effluent recycling. Carbon concentration is expressed in terms of mg carbon per cubic decimeter of added influent mixture (mg C/L).

Run	Carbon in influent (fresh + residuals)	Carbon in Gas	Carbon in Liquid Effluent	Carbon Balance closure (%)	Cumulative oxidation efficiency of carbon from the initial feed (%)
1	3486	1579 ± 29	1902 ± 16	100.1	45
2	3486 + 1241	2236 ± 6	2480 ± 23	100.2	74
3	3486 + 1621	2377 ± 36	2703 ± 38	100.5	84
4	3486 + 1776	2495 ± 50	2799 ± 26	99.4	96
5	3486 + 1801	2452 ± 57	2856 ± 57	99.6	89

Table 7-3 summarizes results of recycled SCWO experiments with lignin. Similarly as for cellulose, carbon in the gas and effluent rapidly builds up, followed by a quasi-steady situation. The carbon built-up in the effluent transitions to a steady concentration situation from run three to run four; delayed by one run compared to cellulose. This observation indicates an increased recalcitrance of lignin compared to cellulose, which is consistent with other findings in literature(Balakrishnan et al. 2011). The fact that a quasi-steady situation had been reached, indicates an increased conversion (from 45 % without recycling, to 96 % with effluent recycling of minimum 5 times).

From the fourth to the fifth run, the cumulative oxidation efficiency dropped counter intuitively from 96 % to 89 %. This anomaly arose because the carbon-content in the liquid effluent from run 5 was calculated larger than that of run 4. The carbon contents in the effluent streams, assigned to stem from the initial lignin feed, increased from run four to run five. The exact reason for the further increase in carbon content is not exactly clear (could be experimental error), as the currently used carbon measurement method doesn’t allow to determine in what run that carbon (in lignin) was fed. To further elucidate fate of the feedstock-C that is fed in subsequent runs, it could be recommended to use direct measurements of the organic-C in the effluent that was fed at the start by using ^{13}C-labeled feedstock in the initial run. However, we plead that the herein applied calculations overall was valid for lignin as well and uncovered an improved oxidation through circulative mild SCWO.

Table 7-4 Acetic acid-C oxidation in a mild supercritical water oxidation setup with effluent recycling. Carbon concentration is expressed in terms of mg carbon per cubic decimeter of added influent mixture (mg C/L).

Run	Carbon in influent (fresh+ residuals)	Carbon in Gas	Carbon in Liquid Effluent	Carbon Balance closure (%)	Cumulative oxidation efficiency of carbon from the initial feed (%)
1	2030 + 0	575 ± 18	1424 ± 7	101.6	29
2	2030 + 947	748 ± 13	2102 ± 15	104.5	40
3	2030 + 1450	912 ± 13	2612 ± 29	98.8	61
4	2030 + 1671	1121 ± 16	2613 ± 33	99.1	97
5	2030 + 1679	1125 ± 24	2589 ± 46	99.9	99

Even for acetic acid, the most refractory among the tested organics, an increasing cumulative oxidation of initial feed was observed (Table 7-4). Like cellulose and lignin, carbon in the effluent initially increased dramatically, after which carbon in the effluent increased/decreased modestly. From run three to four, carbon in the effluent transitions from a build-up to a steady concentration situation. This transition from build-up to steady situation lags one run (i.e. from run four to five) due to identical reasons as stated before for cellulose. The transition point from build-up to steady state occurs later for acetic acid if compared to cellulose. Acetic acid is harder to decompose through successive recirculation; it achieved the lowest oxidation efficiency after one run. Yet, it cumulatively oxidizes almost completely within a reasonable number of runs. We conclude that recirculation thus enabled a near-complete oxidation of acetic acid as well.

Compared with the results from figure 7-1 (calculated number of recirculations needed based on single-pass experiments), less recirculation times are required to reach near-complete oxidation in the recirculation experiments. It is suspected that the residual organics ending up in the effluent might have higher oxidation efficiency as they are intermediates from previous stages and as such, their oxidation behavior is different than the parent feedstock (or the intermediate from the previous cycle) they derive from. Consequently, simply extrapolating single-pass oxidation efficiencies to the point where all organic compounds in the effluent have been oxidized, is not bound to have a large error.

7.3.2 Advantages and challenges

Though benefits from the greatly enhanced oxidation of organics, the recirculation process suffers from the increased effluent volume (especially when using wet feedstock). The cumulative effluent would require ever increasing operation times as the recirculation continues in time. Thus, it is recommended to provide a means to concentrate the effluent prior to recirculation and mixing with fresh feed.

Reverse osmosis (RO) is considered to be a suitable technology to separate water and dissolved compounds. An RO membrane is able to concentrate dissolved compounds while remove pure water out of the system. One of the major costs of applying RO is the requirement to pressurize the liquid influent. SCWO is an inherent high pressure system and as such, the existing outlet pressure (with a partial reduction thereof) can be used to drive the reversed osmosis, which can further reduce the cost of RO implementation. After RO treatment, the concentrated dissolved compounds (being incomplete oxidation products in our case) will be recirculated to the SCWO reactor and oxidized simultaneously with fresh feed. By discharging extra water using RO, the recirculated effluent volume can be kept constant. The improved conceptual process is shown in Figure 7-4.

Working with RO will likely pose additional challenges. With regards to wastes containing significant quantities of dissolved salts (e.g. Cl, P and S based ones), these salts will also be retained by the RO membrane and as such, the salt concentration in the recirculated effluent will continue to increase – potentially leading to salt plugging problems. Consequently, the removal of these salts from the recirculating system should also be considered. A solution could be to periodically completely discard all effluent recirculating in the system after the salt concentration is higher than a certain threshold value and to refill the reactor and recirculation system with fresh water. The latter solution will require to stop feeding incoming feed *n* cycles before discarding all reactor contents, as to ensure that only salts are discarded and not any partially degraded organics. The discarded effluent with high salt concentration will require further disposal.

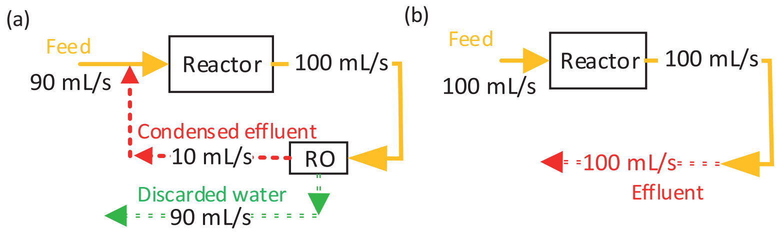


Figure 7-4 Diagram of the aqueous flow in the (a) recirculation system with RO and (b) single-pass conventional system, numerical values are given as illustrative example are not actual experimental results.

Compared to a conventional setup (Figure 7-4), the additional costs will be the RO system and recirculation facilities. Luckily, the major cost of RO, being the pressure boost system, is bypassed. In the example given, where a mass flow ratio of retentate to influent of 1 : 10 is considered, the feed flow rate will be 10 % less compared to a single-pass conventional system. The energy input for heating the feed will be only ~ 10 % more at the same feed load. However, the oxidation efficiency of the recirculation system could reach near 100 % in one setup regardless of the organic waste type. To reach the same level of oxidation efficiency, a conventional setup would need a much longer reactor (larger setup dimension), higher temperature, or more oxidizer. What's worse, a conventional setup will likely require re-optimizing the process parameters when switching to other types of waste feed. Corrosion caused by higher oxidizer usage or higher temperature is inevitable but in a likelihood, less prevalent in the recirculation setup.

7.4 Conclusion and perspectives

In conclusion, all tested model compounds indicated that oxidation efficiencies considerably accumulated: from 64 % to 100 % for cellulose, from 45 % to at least 96 % for lignin and from 29 % to 99 % for acetic acid. Importantly, all these improvements were achieved in a concise set-up, operated at constant mild super critical conditions. The data allowed to pinpoint *n* (i.e. the minimum number of recycling runs for complete oxidation) for cellulose, being four. For lignin and acetic acid, a near-complete oxidation was achieved after five runs.

Through bypassing techno-economical hurdles associated with conventional SCWO, while keeping its advantages, an appealing oxidation platform is offered: (i) lower temperature is required for improved oxidation, (ii) recirculation keeps reactor dimensions and associated safety risks considerably low, (iii) chemical corrosion caused from high oxidizer usage is less an issue and (iv) the applied strategy is versatile, i.e. oxidation conditions are not compound-specific. Future research might also consider higher organic loadings and more types of organic compounds. Overall, this work provides solid indications that the outlined SCWO concept constitute a most interesting route for future research.

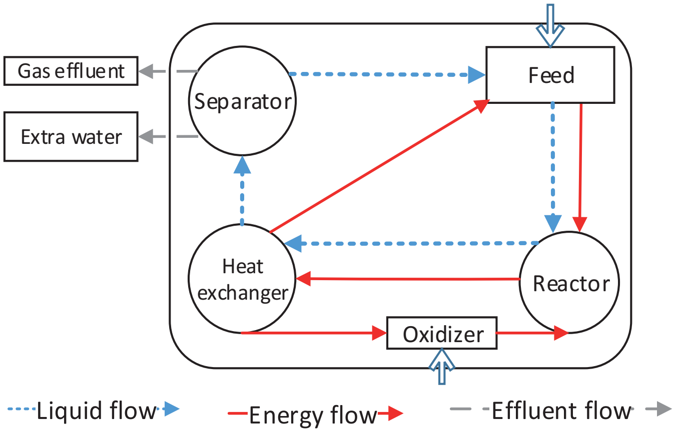


Figure 7-5 Ideal SCWO recycling system diagram.

Finally, we present a SCWO setup in Figure 7-5, based on our results. The system operates at mild conditions, recirculates the residual organics completely, and applies air/oxygen gas as oxidizer. The setup is capable of dealing with different organic compounds. The recirculation method has potential to improve the application of SCWO technology. The circulation method allows: (1) the SCWO reactor being more compact, with a much smaller reactor volume, (2) the residence time is not fixed and is basically infinite which allows complete break-down of refractory compounds. Reactors without circulation (i.e. present CSTR's or tubular reactors) have a residence time determined by design, hence they are custom designed to handle a particular waste stream in mind, a single SCWO setup/strategy with circulation is versatile to deal with different organics compounds, (3) a reactor design with circulation has the potential to operate at less harsh process conditions (in terms of temperature and pressure) and thus putting less stringent requirements on reactor material selection.

7.5 Transformation to CELSS

The recirculation process is capable of working with a compact reactor at relatively low temperature suffering from less rigorous risks associated to high-temperature, high-OER running SCWO technology. The setup would also be able to handle various types of organic wastes which is a requirement in CELSS (i.e. various wastes like plant waste, fecal matter, urine, are all generated). A safer, more compacted and versatile system brings improved maintainability and operability. Besides, the low working temperature should maximize the recovery of nitrogen compounds to useable products.

However, there are some issues that need to be conquered before using SCWO to recover MELiSSA waste. One issue being that minerals are hard to recover in the SCWO process. Corrosion should be limited given the milder process conditions but is likely to remain a major inherent problem of the SCWO technology, even when recirculation is applied.

Chapter 8 Summary and perspective

8.1 Summary

8.1.1 Oxidation of five model compounds

The tests of the five model components confirmed that organics can be degraded by hydrothermal oxidation process. However, the degradation efficiency of different compounds at same process conditions were significantly different. Only low degradation efficiencies were found at the tested reaction conditions. Higher temperature, longer residence time and higher OER were demonstrated to increase the organic degradation by means of oxidation. The effect of temperature was observed to be the most important. Oxidation temperature above the critical point was greatly superior to 300 and 360 °C. Acetic acid was found to be refractory even at 380 °C.

8.1.2 Oxidation of fermentation sludge

Hydrothermal oxidation of fermentation sludge reached efficiencies up to 98.6 % in terms of TOC removal. The oxidation of sludge was found to be improved by higher temperature, longer residence time and higher OER. The effect of each individual process parameter was different with respect to oxidation efficiency and TOC removal. Sludge was more likely to be converted into carbon dioxide at higher OER while higher temperature was the most effective parameter to improve sludge decomposition. The positive effective from longer residence time at given conditions was considered not significant. Nitrogen conversion to soluble nitrogen compounds was greatly affected by the process parameters. Temperature had the greatest influence on nitrogen distribution: higher temperature favors the decomposition of organic compounds to ammonium and also the oxidation of ammonium. However, the formation of NO_x was most likely to be enhanced when temperature was higher than 400 °C which should be avoided. Longer residence times benefited the formation of ammonium from organic compounds which was also the case for the oxidation of ammonium.

The primary objective of the work was achieved: hydrothermal oxidation has the potential to degrade the fermentation sludge in the MELiSSA concept and the maximum carbon recovery (as CO_2) reaches 97.1 %. The harsher the reaction conditions, the better the carbon recovery will be. However, the effect on nitrogen recovery is totally different and extreme SCWO conditions are not favored to maximize nitrogen recovery.

8.1.3 Oxidation feasibility study

Both bath and continuous reactors were applied to decompose sludge obtained from an anaerobic fermenter running on a simulated MELiSSA waste. Oxidation of sludge with efficiencies higher than 90 % were carried out successfully in both reactors. However, their performance was found to be different. Organic oxidation happened in the continuous reactor was less sensitive to OER improvement. Batch reactor need heating and cooling stages for each run, resulting in lower efficiency than continuous reactor in a long-term operation. Yet, it remained a problem to carry feed with particles in a continuous reactor.

Compared to other technology, hydrothermal oxidation was superior in high efficiency and extremely fast reaction. Nevertheless, inorganics recovery was a challenge in hydrothermal oxidation of MELiSSA wastes as major inorganics participated inside the oxidation system. The leaching of heavy metals from the system material would also slightly contaminate the liquid effluent.

8.1.4 Oxidation of filtrate

The major compounds in the filtrate were volatile fatty acids which were resistant to hydrothermal oxidation. Filtrate oxidation under the tested reaction conditions were far below complete decomposition. The maximum carbon (as CO_2) and nitrogen (as either NO_3^- or NH_4^+) recovery was only up to 68.2 % and 80.1 %, respectively. These relatively low values stem from the tested maximum temperatures of 380 °C and short residence times of 48 s which are considered to be mild. Our oxidation experiments were conducted at these mild conditions because of the continuous setup limitations. For the purpose of maximizing filtrate oxidation, a setup with higher working temperature may be recommended. As the filtrate contains no visible particles, a continuous reactor is recommended to carry out the filtrate oxidation.

8.1.5 Effluent recirculation

The effluent recirculation methodology enables an enhanced organic oxidation at a constant temperature, OER and setup scale. Three model compounds were studied to verify the method and a greatly improved organic decomposition was found. The methodology increases the residence time for oxidation by recycling the effluent. The prolonged residence time compensates the requirements of higher temperature and OER. Meanwhile, the recirculation method avoids the use of a larger reactor volume to establish longer residence times.

8.2 Perspective of hydrothermal oxidation in closed life support systems

Figure 8-1 shows the best obtained carbon recovery and nitrogen recovery results in the tested reaction conditions in this dissertation. The highest carbon recovery for both sludge and filtrate were achieved at the harshest tested reaction conditions. The corresponding carbon balance closures were near 100 %. High OER was needed to improve carbon recovery resulting in low oxidizer use efficiency. Highest nitrogen recovery from filtrate was obtained at the highest reaction temperature. Highest nitrogen recovery from sludge was obtained at 400 °C with shortest tested residence time and highest OER.

It was concluded that harsher reaction conditions were better for carbon recovery. Temperatures of 400 °C, along with higher OER (unfortunately resulting in low OUE), would favor the decomposition of organic nitrogen compounds while limit the decomposition of ammonium. Residence time should be carefully controlled to be around 1 min for maximum ammonium retention. The optimized operational conditions (Table 8-2) are suggested to maximize the simultaneous carbon and nitrogen recovery. Meanwhile, a system to recover excess oxygen from gas effluent is required.

Table 8-1 Obtained carbon recovery results.

	Feedstock types	Best obtained results (%)	Corresponding results (%)	Reaction conditions
Carbon recovery	Sludge	97.1	*TRE* = 98.6 *CB* = 101.5 *NR* = /* *OUE* = 51.7	*T* = 500 °C τ = 600 s *OER* = 2.0
	Filtrate	68.2	*TRE* = 69.7 *CB* = 98.5 *NR* = 91.8 *OUE* = 4.1	*T* = 380 °C τ = 48 s *OER* = 4.0
Nitrogen recovery	Sludge	93.8	*TRE* = 85.2 *CB* = 99.8 *CR* = 82.7 *OUE* = 56.8	*T* = 400 τ = 60 s *OER* = 2.0
	Filtrate	91.8	*TRE* = 69.7 *CB* = 98.5 *CR* = 68.2 *OUE* = 4.1	*T* = 380 °C τ = 48 s *OER* = 4.0

* Sample too little for nitrogen analysis.
TRE: total organic removal efficiency; CR: carbon recovery; CB:carbon balance; NR: nitrogen recovery; OUE: oxidizer use efficiency.

Table 8-2 Optimal operation conditions suggested for resource recovery from MELiSSA waste.

Temperature (°C)	Residence time (s)	OER	Reactor	Dry matter concentration (wt.%)
400 - 450	~ 60	2.0 - 4.0	Continuous	> 4

Table 8-3 gives a recommendation of what a 1 L continuous reactor could process. Every crew member would produce around 6.3 L of organic waste (1 *wt.%*, wet basis), which means 28 g carbon per person per day having to be processed. If a 1 L continuous reactor would perform all day running at a concentration of 4 *wt.%* (wet basis) for energy self-sustenance, it could handle organic waste produced from up to 79 crew members. The system could recover up to 2210 g carbon from wastes per day. The oxidizer usage (OER = 2.0) would be 11790 g oxygen (75.9 kg hydrogen peroxide in form of 33 *wt.%* solution, or 8.24 m^3 oxygen gas under STP conditions)

Table 8-3 The calculated processing of a 1 L continuous reactor running on a 4 *wt.%* (wet basis) feed and at OER = 2.0.

Reactor size (L)	Capacity (crews/day)	Carbon recovery (g C/day)	Nitrogen recovery (g N/day)	Oxygen load (g/day)	Oxygen in gas effluent (g/day)
1	79	2210	109	11790	5895

We have to consider the actual situation where the technology would be used. A closed system needs a safe and low resource (i.e. oxidizer input) consuming technology to process the waste. As a result, higher OER's are better to be avoided. Nevertheless, the OER should be carefully controlled as to avoid the formation of solid products. Longer residence times and higher temperatures can be used to compensate when operating at lower OER. In terms of nitrogen recovery, temperature control is of utmost importance. Temperature and residence time greatly affect the nitrogen distribution. Temperatures higher than 450 °C might shift the nitrogen conversion to the undesirable NO_x. Ammonium is the most abundant degradation product. Downstream processes to convert and use ammonium (i.e. in plant growth) are necessary.

It is important to know that hydrothermal oxidation is an exothermic reaction though it needs high temperature to initiate. As the effluent is of high temperature and needs a cooling stage before being discarded, the heat from cooling has to be recovered. In the case of continuous reactors (with or without effluent recirculation), the heat released during cooling can be used to preheat the influent. With a proper concentration of the feedstock, the heat generated from the exothermic oxidation reaction should be sufficient to maintain autothermal operation of the reactor.

Filtrate oxidation did not appear to be a good solution because of the low oxidation efficiency. Filtrate needs higher working temperatures for oxidation which will bring more risks and more corrosion to the oxidation reactor. Otherwise, much longer residence time haves to be used to compensate the benefit of working at higher temperature. Also in here, the recirculation method may prove to be useful. Meanwhile, the low concentration of organics in the filtrate will be incapable of generating enough heat to sustain the reactor temperature. A method to pre-concentrate the filtrate should be developed to render its hydrothermal oxidation energy self-sufficient.

Our work explores to the possibility of hydrothermal oxidation to recover carbon and nitrogen from MELiSSA wastes. A large number of auxiliaries along with hydrothermal oxidation have to be considered. A heat recovery system in hydrothermal oxidation hasn’t been thoroughly studied. The feed system as well as phase separation will also be a challenge in zero-gravity. What’s more, a high-pressure pump that can handle feeds with large particles may prove to be challenging. As fermentation sludge contains large particles, the continuous feeding of sludge will be a problem. Batch reactors could solve the feeding problems but suffer from the low operational efficiency, low energy efficiency and safety risks.

Nutrient recovery is another challenge in the hydrothermal oxidation process. P, N, K and many other inorganic components may deposit inside the reactor during supercritical oxidation. For a long-term running closed life support system, the recovery of these inorganics is also essential. A solution to recover inorganics during hydrothermal oxidation needs further investigation.

8.3 Perspectives of hydrothermal oxidation

Hydrothermal oxidation can degrade organic wastes with a high efficiency with the production of clean end products. However, the working conditions are extremely severe. High temperatures and pressures, and the prospect of corrosion in hot compressed water render the reactor materials less suited for long-term operation. High pressures posit a high requirement to the feeding system. With the methodology of effluent recirculation, hydrothermal oxidation can be operated at a lower temperature with less corrosion problem – though the technique needs further proof of concept on actual waste feeds.

Being high risk and high cost, but also a green and an effective waste treatment technology, hydrothermal oxidation is suitable to treat wastes that are inefficient or incomplete to handle by other waste treatment methods – especially on a small to medium scale. The dichotomy of hydrothermal oxidation being promising for life support systems in space while for waste treatment on earth, more conventional, more cost-effective and yet fairly effective technologies exist, renders the current technological and scientific progress in hydrothermal oxidation technology limited.

Appendix

Appendix-table 1 Cellulose oxidation results

OER	τ (s)	T (°C)	Gas volume percentage					CO_2 (mg/s)	C in CO_2 (mg/s)	C in gas (mg/s)	oxygen out(mg/s)	oxygen in (mg/s)	C in effluent mg/s	C in feed (mg/s)	TOC removal %	CO_2 conversion %
			H_2 (%)	O_2 (%)	CO (%)	CO_2 (%)	C_2H_4 (%)									
2.0	50	380	0.44	65.28	3.71	30.55	0.01	9.35	2.55	2.86	14.5	24.19	0.30	4.51	93.4	56.6
1.5		380	0.66	52.27	3.30	43.75	0.02	8.74	2.38	2.57	7.6	17.97	0.30	4.37	93.1	54.5
1.0		380	1.78	23.74	5.77	68.69	0.01	8.16	2.23	2.41	2.1	11.99	0.45	4.26	89.3	52.3
0.5		380	10.81	4.13	11.86	73.15	0.01	5.92	1.61	1.88	0.2	5.86	1.16	4.52	74.3	35.7
2.0	35	379	0.33	68.86	4.01	26.80	0.01	12.03	3.28	3.77	22.5	37.52	0.24	6.55	96.4	50.1
1.5		378.5	0.62	59.16	5.43	34.77	0.02	11.42	3.11	3.61	14.1	27.69	0.30	6.61	95.5	47.1
1.0		380	1.46	34.26	7.89	56.38	0.02	11.44	3.12	3.56	5.1	18.23	0.52	6.53	92.1	47.8
0.5		380	4.27	7.75	15.44	72.52	0.00	7.57	2.07	2.51	0.6	9.02	1.18	6.54	81.9	31.6
2.0	28	377	0.36	70.20	4.44	25.00	0.01	13.70	3.74	4.40	28.0	47.31	0.54	8.06	93.3	46.4
1.5		379	0.55	61.18	6.13	32.12	0.02	12.73	3.47	4.14	17.6	34.82	0.94	7.97	88.3	43.6
1.0		380	0.92	37.55	8.39	53.11	0.03	12.31	3.36	3.89	6.3	22.79	0.87	7.94	89.1	42.3
0.5		381	3.69	10.92	17.89	67.46	0.04	8.84	2.41	3.05	1.0	11.28	1.64	7.91	79.3	30.5
2.0	60	347	0.49	71.85	3.23	24.38	0.03	6.79	1.85	2.10	14.5	23.24	0.32	4.10	92.1	45.1
1.5		347	0.64	58.57	3.23	37.53	0.03	6.75	1.84	2.00	7.7	18.38	0.29	4.08	92.9	45.1
1.0		347	1.03	28.24	8.21	62.46	0.05	7.33	2.00	2.27	2.4	12.41	0.63	4.57	86.3	43.8
0.5		347	6.19	5.51	13.72	74.54	0.00	5.24	1.43	1.70	0.3	6.06	1.01	4.53	77.7	31.6
2.0	35	355.1	0.15	66.48	5.82	27.54	0.01	13.80	3.76	4.56	24.2	41.96	1.95	12.77	84.7	29.5
1.5		355	0.15	55.85	8.49	35.50	0.02	13.09	3.57	4.43	15.0	31.10	2.40	12.93	81.5	27.6
1.0		355.6	0.37	32.08	12.77	54.78	0.00	13.25	3.61	4.46	5.6	20.75	2.87	12.90	77.8	28.0
0.5		353.1	1.56	14.81	21.04	62.56	0.04	7.49	2.04	2.73	1.3	10.29	3.21	12.86	75.1	15.9

Appendix-table 2 Lignin oxidation results

OER	τ (s)	T (°C)	Gas volume percentage					CO_2 (mg/s)	C in CO_2 (mg/s)	C in gas (mg/s)	oxygen out(mg/s)	oxygen in (mg/s)	C in effluent mg/s	C in feed (mg/s)	TOC removal %	CO_2 conversion %
			H_2 (%)	O_2 (%)	CO (%)	CO_2 (%)	C_2H_4 (%)									
2.0	50	380	0.00	82.50	0.00	17.49	0.01	11.09	3.03	3.03	38.0	43.70	0.38	6.41	94.1	47.2
1.5	50	380	0.02	77.99	0.00	21.98	0.00	9.87	2.69	2.69	25.5	31.53	0.41	6.26	93.5	43.0
1.0	50	380	0.16	59.50	0.00	40.34	0.00	9.03	2.46	2.46	9.7	20.57	0.50	6.11	91.8	40.3
0.5	50	380	1.50	24.62	2.45	71.43	0.00	8.29	2.26	2.34	2.1	10.12	1.05	6.06	82.7	37.3
2.0	35	379	0.00	85.61	0.00	14.38	0.01	10.97	2.99	3.00	47.5	64.70	0.52	6.89	92.4	43.5
1.5	35	379	0.00	82.07	0.00	17.93	0.00	10.27	2.80	2.80	34.2	47.60	0.62	6.73	90.7	41.6
1.0	35	380	0.00	75.75	0.00	24.25	0.00	8.78	2.39	2.39	19.9	31.78	0.68	6.59	89.6	36.3
0.5	35	384	0.28	47.64	2.10	49.98	0.00	8.19	2.23	2.33	5.7	15.59	0.93	6.33	85.3	35.3
2.0	28	380	0.00	85.43	0.00	14.57	0.00	13.35	3.64	3.64	56.9	81.88	0.95	8.82	89.2	41.3
1.5	28	380	0.00	81.53	0.00	18.47	0.00	12.97	3.54	3.54	41.6	60.37	1.05	8.58	87.7	41.2
1.0	28	380	0.00	77.09	0.00	22.91	0.00	10.49	2.86	2.86	25.7	39.77	1.35	8.48	84.1	33.8
0.5	28	383	0.12	56.76	1.79	41.33	0.00	8.47	2.31	2.41	8.5	18.97	1.59	7.93	79.9	29.1
2.0	60	350	0.07	77.71	0.00	22.22	0.00	5.38	1.47	1.47	13.7	21.71	0.27	3.49	92.3	42.0
1.5	60	350	0.10	69.70	0.00	30.20	0.00	5.15	1.40	1.40	8.6	15.86	0.36	3.39	89.3	41.4
1.0	60	350	0.38	56.06	0.72	42.84	0.00	4.62	1.26	1.28	4.4	10.43	0.66	3.37	80.5	37.5
0.5	60	350	1.47	38.37	2.76	57.40	0.00	3.47	0.95	0.99	1.7	5.21	0.32	3.41	90.6	27.8
2.0	35	352	0.00	74.02	0.00	25.98	0.00	18.48	5.04	5.04	38.3	73.38	1.21	12.95	90.7	38.9
1.5	35	353	0.00	64.95	0.00	35.05	0.00	19.47	5.31	5.31	26.2	54.63	1.52	12.99	88.3	40.9
1.0	35	355	0.12	48.66	1.79	49.42	0.00	16.83	4.59	4.76	12.0	35.38	2.12	12.92	83.6	35.5
0.5	35	353	0.65	17.88	4.39	77.09	0.00	12.50	3.41	3.60	2.1	17.76	2.71	13.19	79.4	25.8

Appendix-table 3 Acetic oxidation acid results

OER	τ (s)	T (°C)	Gas volume percentage					CO_2 (mg/s)	C in CO_2 (mg/s)	C in gas (mg/s)	oxygen out(mg/s)	oxygen in (mg/s)	C in effluent mg/s	C in feed (mg/s)	TOC removal %	CO_2 conversion %
			H_2 (%)	O_2 (%)	CO (%)	CO_2 (%)	C_2H_4 (%)									
2.0	50	378	0.57	87.92	0.00	11.51	0.00	3.09	0.84	0.84	17.2	22.12	1.62	3.65	55.8	23.1
1.5	50	378	0.64	87.00	0.00	12.36	0.00	2.44	0.67	0.67	12.5	16.27	1.49	3.58	58.4	18.6
1.0	50	378	1.13	81.16	0.00	17.71	0.00	2.30	0.63	0.63	7.7	10.74	1.82	3.55	48.9	17.6
0.5	50	380	1.96	73.40	1.65	22.99	0.00	1.05	0.29	0.31	2.4	6.96	1.85	2.63	29.7	10.9
2.0	35	379.5	0.15	91.40	0.00	8.45	0.00	3.15	0.86	0.86	24.8	33.61	2.04	4.01	49.1	21.4
1.5	35	381	0.10	90.78	0.00	9.12	0.00	2.59	0.71	0.71	18.7	24.87	2.26	3.94	42.7	17.9
1.0	35	381	0.18	88.22	0.00	11.59	0.00	2.30	0.63	0.63	12.8	16.41	2.49	3.86	35.5	16.3
0.5	35	383.5	0.47	83.81	1.46	14.25	0.00	1.39	0.38	0.42	6.0	8.10	3.82	3.78	-1.0	10.1
2.0	28	380	0.58	92.09	0.00	7.34	0.00	3.76	1.03	1.03	34.3	42.04	2.62	5.58	53.0	18.4
1.5	28	380	0.43	91.27	0.00	8.30	0.00	2.99	0.82	0.82	23.9	31.06	4.40	5.54	20.5	14.7
1.0	28	381.5	0.34	90.14	0.50	9.02	0.00	2.26	0.62	0.65	16.4	20.62	4.10	5.41	24.3	11.4
0.5	28	382	0.64	87.06	1.55	10.76	0.00	1.31	0.36	0.41	7.7	10.22	5.22	5.48	4.8	6.5
2.0	60	350	0.06	91.07	0.00	8.86	0.01	2.46	0.67	0.67	18.4	22.87	1.38	4.13	66.6	16.3
1.5	60	350	0.06	91.04	0.00	8.90	0.00	1.82	0.50	0.50	13.6	16.88	1.16	4.07	71.5	12.2
1.0	60	349.5	0.14	89.35	0.00	10.51	0.00	1.41	0.39	0.39	8.7	11.12	1.63	4.04	59.7	9.5
0.5	60	349	0.41	83.41	0.00	16.18	0.00	1.07	0.29	0.29	4.0	5.52	2.13	4.19	49.3	7.0
2.0	35	349	0.10	89.09	0.00	10.81	0.00	5.05	1.38	1.38	30.3	38.52	10.65	13.12	18.9	10.5
1.5	35	350	0.12	88.43	0.00	11.46	0.00	3.78	1.03	1.03	21.2	27.24	12.26	13.43	8.7	7.7
1.0	35	350	0.26	85.24	0.00	14.51	0.00	3.29	0.90	0.90	14.1	18.80	12.42	13.01	4.5	6.9
0.5	35	350	0.55	80.63	0.00	18.82	0.00	2.10	0.57	0.57	6.6	9.30	12.62	13.05	3.3	4.4

Appendix-table 4 Furfural oxidation results

OER	τ (s)	T (°C)	Gas volume percentage					CO_2 (mg/s)	C in CO_2 (mg/s)	C in gas (mg/s)	oxygen out(mg/s)	oxygen in (mg/s)	C in effluent mg/s	C in feed (mg/s)	TOC removal %	CO_2 conversion %
			H_2 (%)	O_2 (%)	CO (%)	CO_2 (%)	C_2H_4 (%)									
2.0	50	379	0.22	67.20	0.00	32.58	0.00	15.40	4.20	4.20	23.1	35.30	0.33	5.85	94.3	71.7
1.5	50	380	0.73	49.87	0.00	49.40	0.00	14.81	4.04	4.04	10.9	25.67	0.30	5.92	94.9	68.3
1.0	50	380	1.89	25.89	2.10	70.13	0.00	12.24	3.34	3.44	3.3	16.71	0.51	5.58	90.8	59.8
0.5	50	380	15.53	13.89	19.36	51.21	0.00	6.18	1.69	2.32	1.2	8.29	1.79	5.55	67.7	30.4
2.0	35	379	0.00	73.80	0.00	26.20	0.00	16.53	4.51	4.51	33.9	53.97	0.06	7.24	99.2	62.2
1.5	35	380	0.25	58.21	0.00	41.54	0.00	17.62	4.81	4.81	18.0	39.64	0.13	7.90	98.3	60.9
1.0	35	381	1.09	32.09	1.64	65.18	0.00	16.06	4.38	4.49	5.8	25.92	0.36	7.74	95.3	56.6
0.5	35	382	12.12	9.14	8.12	70.62	0.00	8.95	2.44	2.72	0.8	12.73	0.89	7.55	88.2	32.3
2.0	28	380	0.00	74.03	0.46	25.51	0.00	19.66	5.36	5.46	41.5	68.07	0.29	9.46	97.0	56.7
1.5	28	380	0.19	53.07	1.44	45.30	0.00	18.25	4.98	5.14	15.6	49.15	0.36	9.14	96.1	54.5
1.0	28	380	1.81	35.64	2.67	59.88	0.00	16.47	4.49	4.69	7.1	32.48	0.59	9.23	93.7	48.7
0.5	28	380	13.06	9.87	8.42	68.66	0.00	10.08	2.75	3.08	1.1	16.06	1.47	9.22	84.1	29.8
2.0	60	350	0.24	66.04	0.00	33.72	0.00	12.09	3.30	3.30	17.2	35.79	0.12	5.53	97.9	59.6
1.5	60	350	0.81	46.81	0.00	52.37	0.00	12.55	3.42	3.42	8.2	29.24	0.23	5.50	95.7	62.2
1.0	60	350	4.41	19.63	4.54	71.43	0.00	13.06	3.56	3.79	2.6	17.30	0.58	6.22	90.7	57.2
0.5	60	350	9.14	12.38	9.66	68.82	0.00	5.62	1.53	1.75	0.7	8.58	2.00	5.69	64.8	26.9
2.0	35	356	0.00	62.46	0.00	37.54	0.00	23.39	6.38	6.38	28.3	58.51	2.50	11.35	78.0	56.2
1.5	35	356	0.00	46.06	0.00	53.94	0.00	24.79	6.76	6.76	15.4	45.06	3.59	11.76	69.5	57.5
1.0	35	356	1.26	16.86	3.81	78.07	0.00	22.11	6.03	6.32	3.5	28.95	4.24	11.99	64.6	50.3
0.5	35	356	6.57	9.46	8.97	75.00	0.00	10.32	2.81	3.15	0.9	14.26	6.82	11.09	38.5	25.4

Appendix-table 5 Phenol oxidation results

OER	τ (s)	T (°C)	Gas volume percentage					CO_2 (mg/s)	C in CO_2 (mg/s)	C in gas (mg/s)	oxygen out(mg/s)	oxygen in (mg/s)	C in effluent mg/s	C in feed (mg/s)	TOC removal %	CO_2 conversion %
			H_2 (%)	O_2 (%)	CO (%)	CO_2 (%)	C_2H_4 (%)									
2.0	50	378	0.00	69.55	0.00	30.45	0.00	20.69	5.64	5.64	34.4	52.59	0.11	7.08	98.4	79.7
1.5	50	378	0.02	54.29	0.00	45.69	0.00	19.35	5.28	5.28	16.7	38.61	0.11	7.00	98.4	75.4
1.0	50	380	0.46	30.74	1.23	67.57	0.00	16.31	4.45	4.53	5.4	24.68	0.17	6.88	97.5	64.7
0.5	50	380	2.67	18.06	4.37	74.91	0.00	11.57	3.16	3.34	2.0	12.01	1.34	7.04	81.0	44.9
2.0	35	379	0.00	73.41	0.00	26.59	0.00	25.20	6.87	6.87	50.6	79.47	0.23	9.57	97.6	71.8
1.5	35	379	0.00	63.03	0.00	36.97	0.00	23.90	6.52	6.52	29.6	57.87	0.41	9.65	95.8	67.6
1.0	35	379	0.27	35.78	1.56	62.39	0.00	21.28	5.80	5.95	8.9	37.42	0.94	9.65	90.3	60.2
0.5	35	382	5.50	9.85	7.91	76.74	0.00	15.72	4.29	4.73	1.5	18.24	1.56	9.58	83.8	44.8
2.0	28	381	0.00	77.79	0.00	22.21	0.00	26.97	7.36	7.36	68.7	101.39	0.32	11.09	97.2	66.3
1.5	28	381	0.00	68.60	0.00	31.40	0.00	23.86	6.51	6.51	37.9	73.15	0.46	11.04	95.9	58.9
1.0	28	381	0.23	43.94	2.01	53.82	0.00	23.85	6.50	6.75	14.2	47.44	0.73	11.08	93.4	58.7
0.5	28	382	5.99	8.75	6.56	78.70	0.00	17.93	4.89	5.30	1.4	23.00	2.36	10.92	78.4	44.8
2.0	60	350	0.01	68.91	3.44	27.64	0.00	18.46	5.04	5.66	33.5	56.01	0.77	8.40	90.8	60.0
1.5	60	350	0.16	53.27	2.37	44.20	0.00	16.17	4.41	4.65	14.2	37.36	0.49	8.28	94.1	53.3
1.0	60	350	0.74	20.61	2.89	75.76	0.00	16.34	4.46	4.63	3.2	27.10	0.58	7.90	92.6	56.4
0.5	60	350	4.43	9.50	7.70	78.37	0.00	11.25	3.07	3.37	1.0	12.49	3.91	7.86	50.3	39.0
2.0	35	355	0.00	58.86	1.75	39.39	0.00	35.55	9.70	10.13	38.6	87.16	1.89	12.64	85.1	76.7
1.5	35	355	0.00	40.22	1.78	58.01	0.00	40.84	11.14	11.48	20.6	61.43	2.21	12.35	82.1	90.2
1.0	35	355	1.16	4.24	3.94	90.67	0.00	43.51	11.87	12.38	1.5	42.53	2.72	12.97	79.0	91.5
0.5	35	355	1.78	3.14	7.72	87.35	0.00	20.11	5.48	5.97	0.5	20.30	3.13	12.74	75.4	43.0

Appendix-table 6 Oxidizer use efficiency

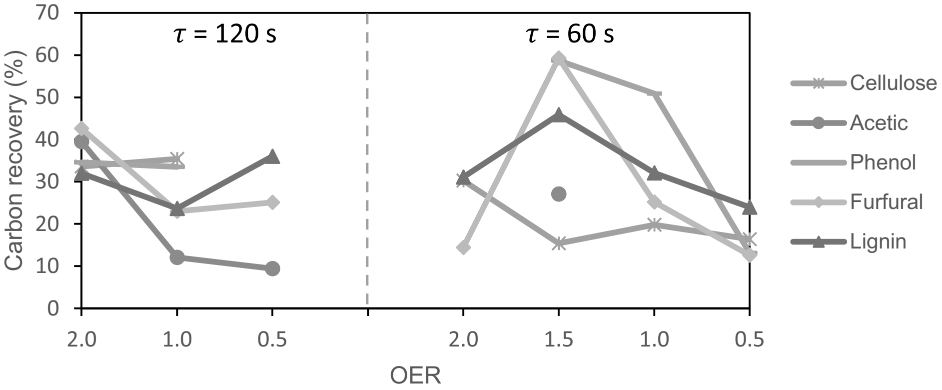
T (°C)	τ (s)	OER	oxidizer use efficiency (%)				
			cellulose	lignin	acetic acid	furfural	phenol
380	50	2.0	39.9	12.9	22.4	34.6	34.6
		1.5	57.7	19.3	23.3	57.6	56.7
		1.0	82.9	52.9	28.8	80.3	78.1
		0.5	95.9	79.5	64.9	85.3	83.1
	35	2.0	40.1	26.5	26.3	37.3	36.3
		1.5	48.9	28.2	24.7	54.7	48.8
		1.0	72.3	37.3	22.3	77.8	76.3
		0.5	93.5	63.6	26.4	93.4	92.0
	28	2.0	40.8	30.5	18.4	39.1	32.2
		1.5	49.4	31.0	23.1	68.4	48.2
		1.0	72.2	35.4	20.4	78.0	70.1
		0.5	90.8	55.4	24.3	93.4	93.7
350	60	2.0	37.4	37.0	19.5	51.9	40.2
		1.5	58.3	45.5	19.6	72.1	62.1
		1.0	80.6	57.8	21.4	84.9	88.1
		0.5	95.4	67.6	27.0	91.4	92.1
	35	2.0	42.3	47.8	21.4	51.6	55.7
		1.5	51.8	52.0	22.0	65.8	66.5
		1.0	72.8	65.9	25.1	88.0	96.5
		0.5	87.5	88.1	29.5	93.4	97.4

Appendix-table 7 VOC (μg/mL) determined by head-space analysis of the aqueous effluent from continuous tests. T = 500 °C and residence time = 1 min

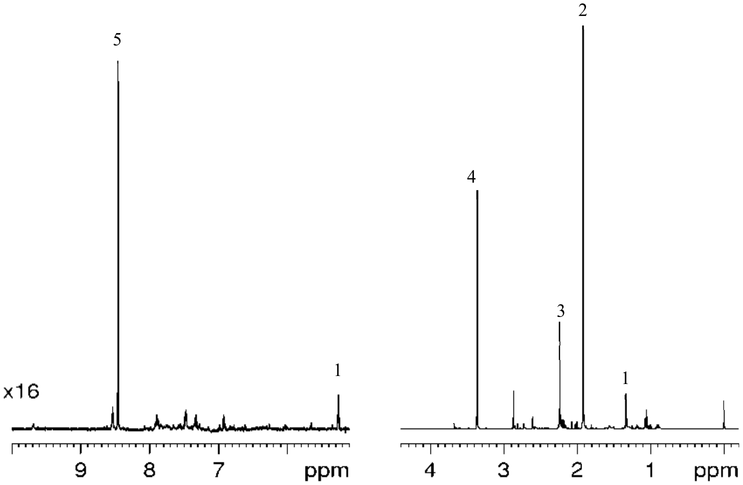
VOC types	Concentration (μg/mL)	
	OER = 1.0	OER = 2.0
Acetaldehyde	6.82	0.11
Glycolaldeyde	5.34	0.36
Propanal	3.59	0.01
2-Propanone	16.21	1.51
Propanal, 2-methyl-	0.11	0
Butanal	0.27	0
2-Butanone	5.63	1.84
Butyrolactone	0	0.53
2-Butanone 3-methyl	0.6	0
3-Buten-2-one,3 methyl	0.51	0
2-Pentanone	0.16	0
3-Pentanone	0.55	0
Unknown ketone	2.89	5.75
Cyclopentanone	0.12	0
3-methyl pentenone	0.1	0
Cyclopentanone, 2-methyl	0.09	0
benzaldehyde	0.24	0.55

Appendix-table 8 Composition of VFAs in the aqueous effluent after (batch) oxidation at 500 °C, OER = 2.0 and Residence time = 5 min.

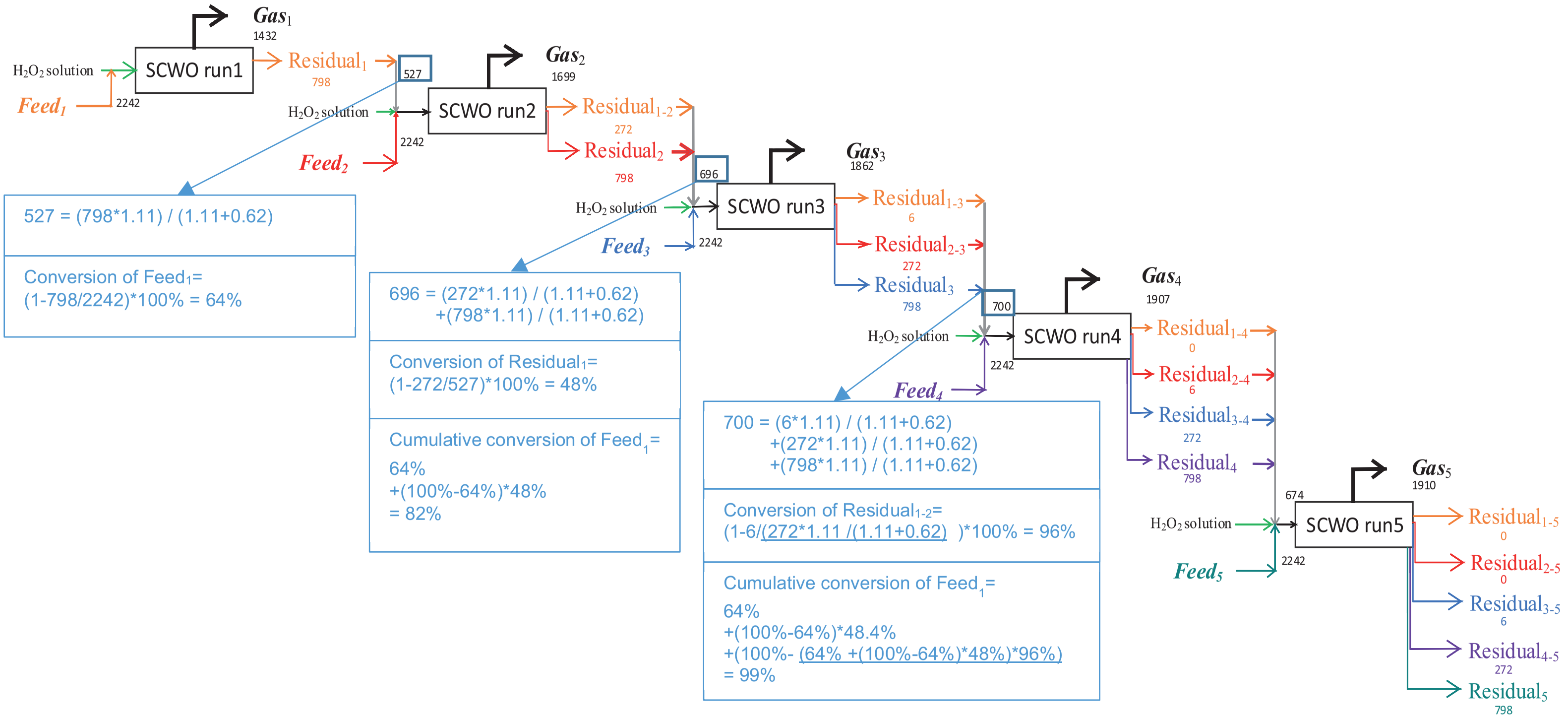
	Lactate	Formate	Acetate	Propionate	Butyrate
Concentration (mg C/L)	4.22	9.97	159.25	3.31	2.49



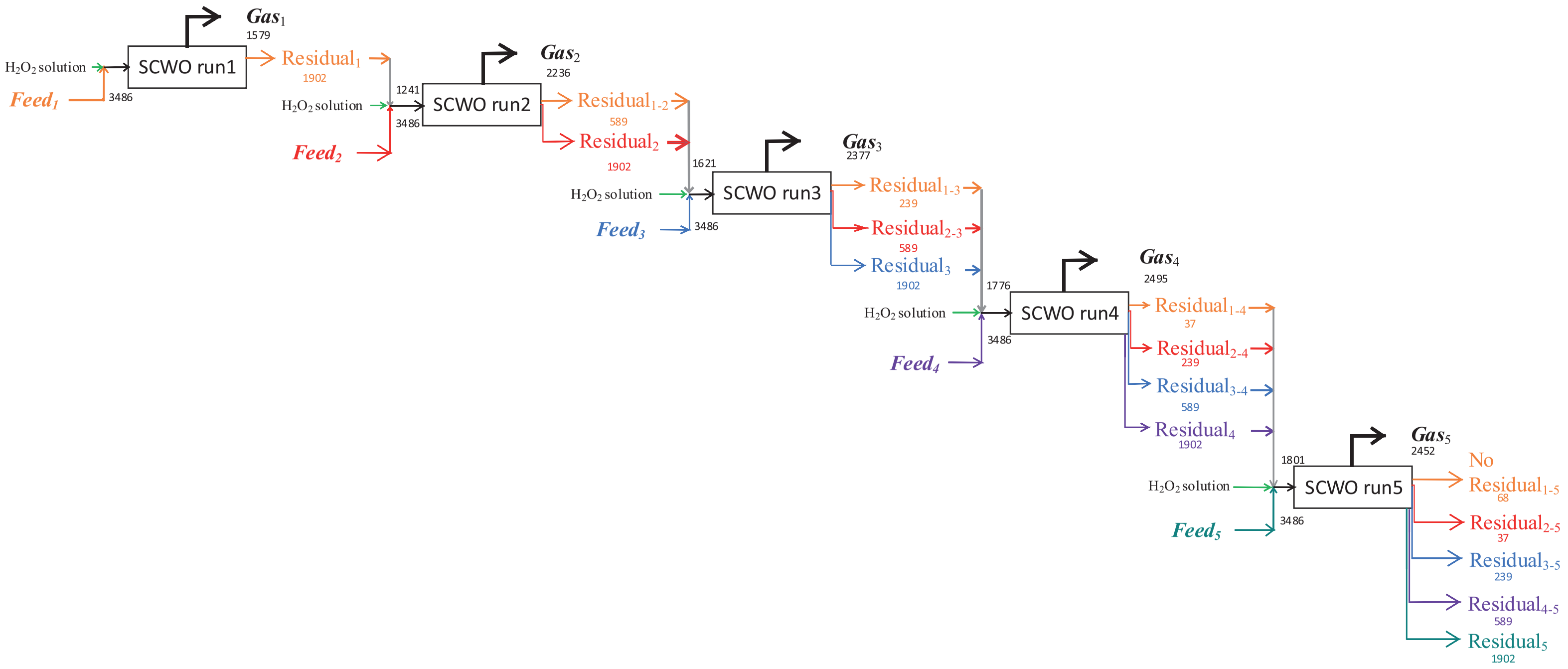
Appendix-figure 1 Carbon recovery in oxidation experiments at 300 °C.



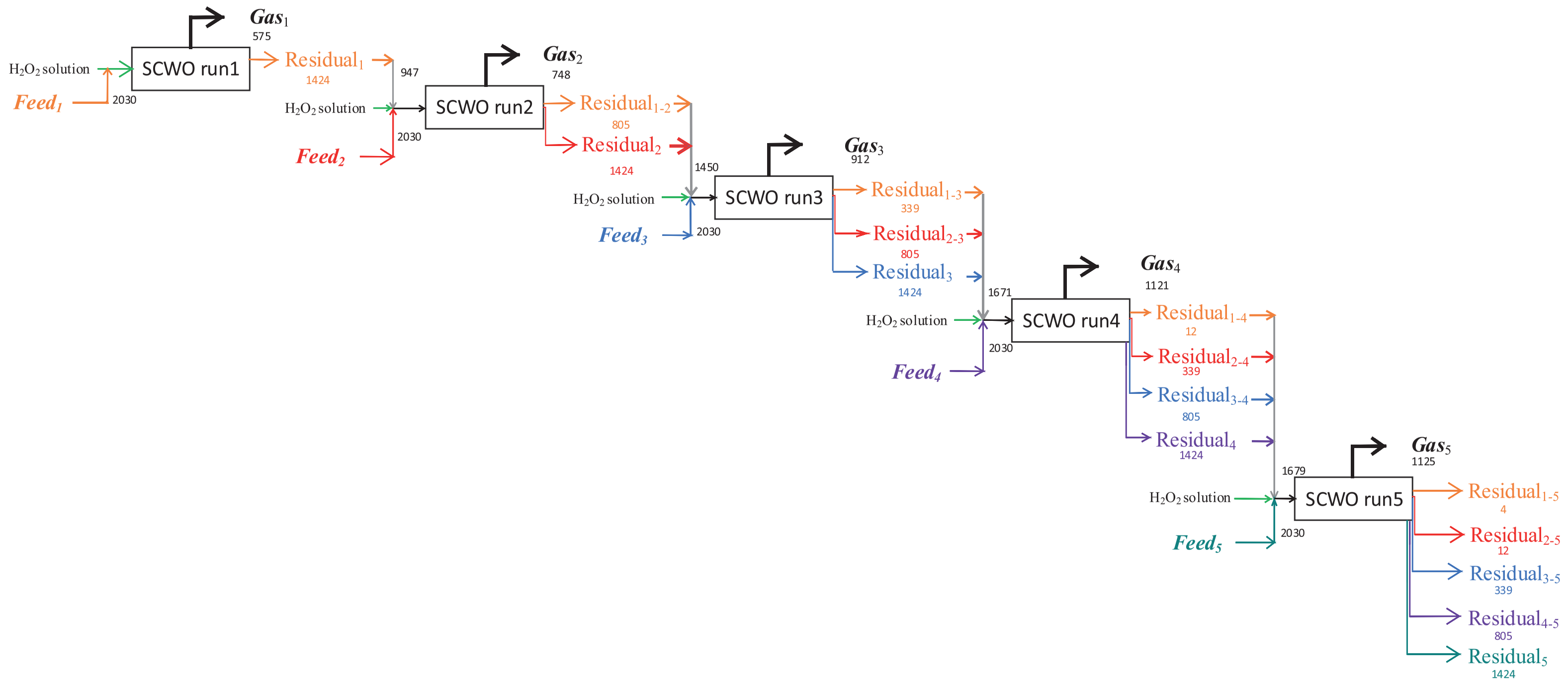
Appendix-figure 2 Organics analyzed by CP/MAS 1H-NMR in the aqueous effluent from continuous tests. T = 500 °C, Residence time = 1 min and OER = 1.0. (1, Acetaldehyde hemiacetal; 2, acetic acid / acetate anion; 3, Acetone; 4, Methanol; 5, Formic acid.)



Appendix-figure 3 Cellulose SCWO with recirculation. Carbon-contents of different residues present in the liquid effluent. The total carbon-content of any effluent was partitioned into multiple residues and assigned a carbon-content based on carbon-balance closure, under the assumption that organics degrade independently.



Appendix-figure 4 Lignin SCWO with recirculation. Carbon-contents of different residues present in the liquid effluent. The total carbon-content of any effluent was partitioned into multiple residues and assigned a carbon-content based on carbon-balance closure, under the assumption that organics degrade independently.



Appendix-figure 5 Acetic acid SCWO with recirculation. Carbon-contents of different residues present in the liquid effluent. The total carbon-content of any effluent was partitioned into multiple residues and assigned a carbon-content based on carbon-balance closure, under the assumption that organics degrade independently.

Reference

Abelleira, J., Sanchez-Onet, J., Portela, J. R., & Martínez de la Ossa, E. J. (2013). "Kinetics of supercritical water oxidation of isopropanol as an auxiliary fuel and co-fuel." Fuel **111**(0): 574-583.

Al-Duri, B., & Alsoqyani, F. (2017). "Supercritical Water Oxidation (SCWO) for the Removal of N— Containing Heterocyclic Hydrocarbon Wastes; Part II: System Kinetics." The Journal of Supercritical Fluids.

Al-Duri, B., Alsoqyani, F., & Kings, I. (2015). "Supercritical water oxidation for the destruction of hazardous waste: better than incineration." Philos Trans A Math Phys Eng Sci **373**(2057): 9.

Al-Duri, B., Alsoqyiani, F., & Kings, I. (2016). "Supercritical water oxidation (SCWO) for the Removal of N− Containing Heterocyclic Hydrocarbon Wastes. Part I: Process Enhancement by Addition of Isopropyl Alcohol." The Journal of Supercritical Fluids **116**: 155-163.

Al-Duri, B., Pinto, L., Ashraf-Ball, N., & Santos, R. (2008). "Thermal abatement of nitrogen-containing hydrocarbons by non-catalytic supercritical water oxidation (SCWO)." Journal of Materials Science **43**(4): 1421-1428.

Albrecht, T. (2006). Conversion of Lignocellulosic Materials and Model Compounds in Sub- and Supercritical Water.

Allen, J. (2002). "People challenges in biospheric systems for long-term habitation in remote areas, space stations, Moon, and Mars expeditions." Life Support & Biosphere Science **8**(2): 67-70.

Allen, J., & Nelson, M. (1987). "Space biospheres." Malabar, FL, Orbit Book Co., Inc., 1987, 94 p.

Allen, J. P., Nelson, M., & Alling, A. (2003). "The legacy of biosphere 2 for the study of biospherics and closed ecological systems." Advances in Space Research **31**(7): 1629-1639.

Amrullah, A., & Matsumura, u. (2018). "Supercritical water gasification of sewage sludge in continuous reactor." Bioresource Technology **249**: 276-283.

Aymonier, C., Gratias, A., Mercadier, J., & Cansell, F. (2001). "Global reaction heat of acetic acid oxidation in supercritical water." The Journal of Supercritical Fluids **21**(3): 219-226.

Azadi, P., Afif, E., Foroughi, H., Dai, T. S., Azadi, F., & Farnood, R. (2013). "Catalytic reforming of activated sludge model compounds in supercritical water using nickel and ruthenium catalysts." Applied Catalysis B-Environmental **134**: 265-273.

Balakrishnan, M., Batra, V. S., Hargreaves, J. S. J., & Pulford, I. D. (2011). "Waste materials – catalytic opportunities: an overview of the application of large scale waste materials as resources for catalytic applications." Green Chem. **13**(1): 16-24.

Barner, H. E., Huang, C. Y., Johnson, T., Jacobs, G., Martch, M. A., & Killilea, W. R. (1992). "SUPERCRITICAL WATER OXIDATION - AN EMERGING TECHNOLOGY." Journal of Hazardous Materials **31**(1): 1-17.

Benjamin, K. M., & Savage, P. E. (2005). "Supercritical water oxidation of methylamine." Industrial & engineering chemistry research **44**(14): 5318-5324.

Bermejo, M. D., & Cocero, M. J. (2006). "Supercritical water oxidation: A technical review." Aiche Journal **52**(11): 3933-3951.

Blüm, V. (2003). "Aquatic modules for bioregenerative life support systems: Developmental aspects based on the space flight results of the C.E.B.A.S. mini-module." Advances in Space Research **31**(7): 1683-1691.

Bo, D., Zhang, F.-S., & Zhao, L. (2009). "Influence of supercritical water treatment on heavy metals in medical waste incinerator fly ash." Journal of hazardous materials **170**(1): 66-71.

Brennecke, J. F., & Chateauneuf, J. E. (1999). "Homogeneous Organic Reactions as Mechanistic Probes in Supercritical Fluids." Chemical Reviews **99**(2): 433-452.

Brunner, G. (2009). "Near and supercritical water. Part II: Oxidative processes." The Journal of Supercritical Fluids **47**(3): 382-390.

Brunner, G. (2009). "Near critical and supercritical water. Part I. Hydrolytic and hydrothermal processes." The Journal of Supercritical Fluids **47**(3): 373-381.

Brunner, G. (2014). Chapter 10 - Oxidation in High-Temperature and Supercritical Water. Supercritical Fluid Science and Technology. G. Brunner, Elsevier. **5:** 525-568.

Brunner, G. (2014). Oxidation in High-Temperature and Supercritical Water. Supercritical Fluid Science and Technology. **5:** 525-568.

Brunner, G., Teich, J., & Dohrn, R. (1994). "Phase equilibria in systems containing hydrogen, carbon dioxide, water and hydrocarbons." Fluid Phase Equilibria **100**: 253-268.

Bubenheim, D. L., & Wydeven, T. (1994). "Approaches to resource recovery in controlled ecological life support systems." Advances in Space Research **14**(11): 113-123.

Bucur, B., Catala Icardo, M., & Martinez Calatayud, J. (2006). "Spectrophotometric determination of ammonium by an rFIA assembly." Revue roumaine de chimie **51**(2): 101-108.

Cabeza, P., Al-Duri, B., Bermejo, M. D., & Cocero, M. J. (2014). "Co-oxidation of ammonia and isopropanol in supercritical water in a tubular reactor." Chemical Engineering Research & Design **92**(11): 2568-2574.

Cabeza, P., Silva Queiroz, J. P., Criado, M., Jiménez, C., Bermejo, M. D., Mato, F., & Cocero, M. J. (2015). "Supercritical water oxidation for energy production by hydrothermal flame as internal heat source. Experimental results and energetic study." Energy **90, Part 2**: 1584-1594.

Cantero, D. A., Tapia, A. S., Bermejo, M. D., & Cocero, M. J. (2015). "Pressure and temperature effect on cellulose hydrolysis in pressurized water." Chemical Engineering Journal **276**: 145-154.

Capanema, E. A., Balakshin, M. Y., Fitzgibbon, P. D., Matyas, K., Mclarty, T. M., & Sanderson, C. S. (2017). Cellulose-containing compositions and methods of making same, Google Patents.

Chang, S.-j., & Liu, Y.-c. (2007). "Degradation mechanism of 2,4,6-trinitrotoluene in supercritical water oxidation." Journal of Environmental Sciences **19**(12): 1430-1435.

Chen, H. Z., Wang, G. W., Xu, Y. J., Chen, Z., & Yin, F. J. (2016). "Green process for supercritical water oxidation of sewage sludge with red mud as CO2 absorbent." Journal of Environmental Chemical Engineering **4**(3): 3065-3074.

Chen, J. Y., Wang, Y. D., Ding, S. Y., Ding, J. Y., Li, M. L., Zhang, C., & Zou, M. H. (2016). "Sub- and super-critical water oxidation of wastewater containing organic and heavy metallic pollutants and recovery of superfine metallic particles." Journal of Environmental Chemical Engineering **4**(3): 2698-2705.

Chen, P., Li, L., & Gloyna, E. F. (1995). Simulation of a Concentric-Tube Reactor for Supercritical Water Oxidation. Innovations in Supercritical Fluids, American Chemical Society. **608:** 348-363.

Chen, S., Qu, X., Zhang, R., & Bi, J. (2015). "Destruction of representative submarine food waste using supercritical water oxidation." Environ Sci Pollut Res Int **22**(6): 4527-4533.

Chen, Z., Chen, Z., Yin, F., Wang, G., Chen, H., He, C., & Xu, Y. (2017). "Supercritical water oxidation of oil-based drill cuttings." J Hazard Mater **332**: 205-213.

Chen, Z., Wang, G. W., Yin, F. J., Chen, H. Z., & Xu, Y. J. (2015). "A new system design for supercritical water oxidation." Chemical Engineering Journal **269**: 343-351.

Clauwaert, P., Muys, M., Alloul, A., De Paepe, J., Luther, A., Sun, X., Ilgrande, C., Christiaens, M. E. R., Hu, X., Zhang, D., Lindeboom, R. E. F., Sas, B., Rabaey, K., Boon, N., Ronsse, F., Geelen, D., & Vlaeminck, S. E. (2017). "Nitrogen cycling in Bioregenerative Life Support Systems: Challenges for waste refinery and food production processes." Progress in Aerospace Sciences **91**: 87-98.

CNSA. (2018). "Lunar Palace I information " Retrieved 1 August, 2018, from http://www.lss-lab.bme.buaa.edu.cn/ygyh/bzsy.htm.

Cocero, M., Vallelado, D., Torio, R., Alonso, E., & Fdez-Polanco, F. (2000). "Optimisation of the operation variables of a supercritical water oxidation process." Water science and technology **42**(5-6): 107-113.

Cocero, M. J., Alonso, E., Sanz, M. T., & Fdz-Polanco, F. (2002). "Supercritical water oxidation process under energetically self-sufficient operation." The Journal of Supercritical Fluids **24**(1): 37-46.

Cocero, M. J., Cabeza, Á., Abad, N., Adamovic, T., Vaquerizo, L., Martínez, C. M., & Pazo-Cepeda, M. V. (2018). "Understanding biomass fractionation in subcritical & supercritical water." The Journal of Supercritical Fluids **133**: 550-565.

Cocero, M. J., & Martínez, J. L. (2004). "Cool wall reactor for supercritical water oxidation: Modelling and operation results." The Journal of Supercritical Fluids **31**(1): 41-55.

Council, N. R. (2001). Evaluation of alternative technologies for disposal of liquid wastes from the explosive destruction system. Washington, D.C., National Academy Press.

Crawford, I. A. (2015). "Lunar resources: A review." Progress in Physical Geography **39**(2): 137-167.

Croiset, E., Rice, S. F., & Hanush, R. G. (1997). "Hydrogen-Peroxide Decomposition in Supercritical Water." AIChE Journal **43**(9): 2343-2352.

Cui, B.-c., Liu, S.-z., Cui, F.-y., Jing, G.-l., & Liu, X.-j. (2011). "Lumped kinetics for supercritical water oxidation of oily sludge." Process Safety and Environmental Protection **89**(3): 198-203.

Curtin, T., O’ Regan, F., Deconinck, C., Knüttle, N., & Hodnett, B. K. (2000). "The catalytic oxidation of ammonia: influence of water and sulfur on selectivity to nitrogen over promoted copper oxide/alumina catalysts." Catalysis Today **55**(1–2): 189-195.

Czupalla, M., Aponte, V., Chappell, S., & Klaus, D. (2004). "Analysis of a spacecraft life support system for a Mars mission." Acta Astronautica **55**(3): 537-547.

Dietrich, M., Randall, T., & Canney, P. (1985). "Wet air oxidation of hazardous organics in wastewater." Environmental Progress **4**(3): 171-177.

Ding, Z. Y., Frisch, M. A., Li, L. X., & Gloyna, E. F. (1996). "Catalytic oxidation in supercritical water." Industrial & Engineering Chemistry Research **35**(10): 3257-3279.

Dong, X., Wang, Y., Li, X., Yu, Y., & Zhang, M. (2014). "Process Simulation of Laboratory Wastewater Treatment via Supercritical Water Oxidation." Industrial & Engineering Chemistry Research **53**(18): 7723-7729.

Dong, Z., Chen, W., Zheng, W., & Guzonas, D. (2012). "Corrosion behavior of chromium oxide based ceramics in supercritical water (SCW) environments." Corrosion Science **65**: 461-471.

Drysdale, A. E., Ewert, M. K., & Hanford, A. J. (2003). "Life support approaches for Mars missions." Advances in Space Research **31**(1): 51-61.

Du, X., Zhang, R., Gan, Z., & Bi, J. (2013). "Treatment of high strength coking wastewater by supercritical water oxidation." Fuel **104**: 77-82.

Eaton, A. D., Clesceri, L. S., & Greenberg, A. E. (1992). Standard methods for the examination of water and waste water, 18th Edition.

Eaton, A. D., Clesceri, L. S., Greenberg, A. E., & Franson, M. A. H. (1995). Standard Methods for the Examination of Water and Wastewater, American Public Health Association.

Elliott, D. C., Sealock, L. J., & Baker, E. G. (1994). "CHEMICAL-PROCESSING IN HIGH-PRESSURE AQUEOUS ENVIRONMENTS .3. BATCH REACTOR PROCESS-DEVELOPMENT EXPERIMENTS FOR ORGANICS DESTRUCTION." Industrial & Engineering Chemistry Research **33**(3): 558-565.

Erkonak, H., Sogut, O. O., & Akgun, M. (2008). "Treatment of olive mill wastewater by supercritical water oxidation." Journal of Supercritical Fluids **46**(2): 142-148.

ESA. (2015 a, 18 August 2015). "Compartment I: The liquefying compartment." Retrieved 18 August 2015, from http://www.esa.int/Our_Activities/Space_Engineering_Technology/Melissa/Compartment_I_The_liquefying_compartment.

ESA. (2015 b). "Compartment II: The photoheterotrophic compartment." Retrieved 18 August 2015, from http://www.esa.int/Our_Activities/Space_Engineering_Technology/Melissa/Compartment_II_The_photoheterotrophic_compartment.

ESA. (2015 c). "Compartment III: The nitrifying compartment." Retrieved 18 August, 2015, from http://www.esa.int/Our_Activities/Space_Engineering_Technology/Melissa/Compartment_III_The_nitrifying_compartment.

ESA. (2015 d). "Compartment IV : The photoautotophic compartment." Retrieved 18 August 2015, from http://www.esa.int/Our_Activities/Space_Engineering_Technology/Melissa/Compartment_IV_The_photoautotophic_compartment.

ESA. (2015 e). "MELiSSA loop." Retrieved 18 August, 2015.

ESA. (2018). "European Space Agency." Retrieved 20/11, 2018, from http://www.esa.int/Our_Activities/Space_Engineering_Technology/Melissa.

Fang, Z. (2014). Near-critical and supercritical water and their applications for biorefineries, Springer.

Fang, Z., Xu, S.-k., & Kozinski, J. A. (2000). "Behavior of Metals during Combustion of Industrial Organic Wastes in Supercritical Water." Ind. Eng. Chem. Res **39**: 4536-4542.

Fauvel, E., Joussot-Dubien, C., Tanneur, V., Moussière, S., Guichardon, P., Charbit, G., & Charbit, F. (2005). "A porous reactor for supercritical water oxidation: experimental results on salty compounds and corrosive solvents oxidation." Industrial & engineering chemistry research **44**(24): 8968-8971.

Fedyaeva, O. N., & Vostrikov, A. A. (2012). "Disposal of hazardous organic substances in supercritical water." Russian Journal of Physical Chemistry B **6**(7): 844-860.

Fu, Y., Li, L., Xie, B., Dong, C., Wang, M., Jia, B., Shao, L., Dong, Y., Deng, S., Liu, H., Liu, G., Liu, B., Hu, D., & Liu, H. (2016). "How to Establish a Bioregenerative Life Support System for Long-Term Crewed Missions to the Moon or Mars." Astrobiology **16**(12): 925-936.

Garcia-Jarana, M. B., Kings, I., Sanchez-Oneto, J., Portela, J. R., & Al-Duri, B. (2013). "Supercritical water oxidation of nitrogen compounds with multi-injection of oxygen." Journal of Supercritical Fluids **80**: 23-29.

Gitelson, I., Terskov, I., Kovrov, B., Lisovskii, G., Okladnikov, Y. N., Sid'Ko, F. Y., Trubachev, I., Shilenko, M., Alekseev, S., & Pan'kova, I. (1989). "Long-term experiments on man's stay in biological life-support system." Advances in Space Research **9**(8): 65-71.

Gitelson, J., & Lisovsky, G. (2003). Man-Made Closed Ecological Systems. London, CRC Press.

Gloyna, E. F., & Li, L. (1993). "Supercritical water oxidation: an engineering update." Waste Management **13**(5): 379-394.

Gloyna, E. F., & Li, L. (1995). "Supercritical water oxidation research and development update." Environmental Progress & Sustainable Energy **14**(3): 182-192.

Gong, Y., Guo, Y., Wang, S., & Song, W. (2016). "Supercritical water oxidation of Quinazoline: Effects of conversion parameters and reaction mechanism." Water Research **100**: 116-125.

Gong, Y., Guo, Y., Wang, S., Song, W., & Xu, D. (2017). "Supercritical water oxidation of quinazoline: Reaction kinetics and modeling." Water Research **110**: 56-65.

Gong, Y. M., Wang, S. Z., Tang, X. Y., Xu, D. H., & Ma, H. H. (2014). "Supercritical water oxidation of acrylic acid production wastewater." Environ Technol **35**(5-8): 907-916.

Goto, M., Nada, T., Ogata, A., Kodama, A., & Hirose, T. (1998). "Supercritical water oxidation for the destruction of municipal excess sludge and alcohol distillery wastewater of molasses." The Journal of Supercritical Fluids **13**(1–3): 277-282.

Goto, R., Shiramizu, D., Kodama, A., & Hirose, T. (1999). "Kinetic analysis for ammonia decomposition in supercritical water oxidation of sewage sludge." Industrial & Engineering Chemistry Research **38**(11): 4500-4503.

Güngören , T. M., Sağlam, M., Yüksel, M., & Ballice, L. (2013). "Simultaneous effect of temperature and pressure on catalytic hydrothermal gasification of glucose." The Journal of Supercritical Fluids **73**(0): 151-160.

Guo, S., Dong, W., Ai, W., Feng, H., Tang, Y., Huang, Z., Shen, Y., Ren, J., Qin, L., Zeng, G., Zhang, L., Zhu, J., Fei, J., & Xu, G. (2014). "Research on regulating technique of material flow for 2-person and 30-day integrated CELSS test." Acta Astronautica **100**: 140-146.

Guo, S. S., Mao, R. X., Zhang, L. L., Tang, Y. K., & Li, Y. H. (2017). "Progress and prospect of research on controlled ecological life support technique." REACH - Reviews in Human Space Exploration **6**: 1-10.

Guo, Y., Wang, S., Gong, Y., Xu, D., Tang, X., & Ma, H. (2010). "Partial oxidation of municipal sludge with activited carbon catalyst in supercritical water." Journal of Hazardous Materials **180**(1–3): 137-144.

Gustan, E., & Vinopal, T. (1982). "Controlled ecological life support system: transportation analysis."

Hao, X. H., Guo, L. J., Mao, X., Zhang, X. M., & Chen, X. J. (2003). "Hydrogen production from glucose used as a model compound of biomass gasified in supercritical water." International Journal of Hydrogen Energy **28**(1): 55-64.

Harvey, A. H. (1998). Thermodynamic properties of water: Tabulation from the IAPWS Formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use, US Department of Commerce, Technology Administration, National Institute of Standards and Technology Boulder, CO.

Hasegawa, I., Inoue, Y., Muranaka, Y., Yasukawa, T., & Mae, K. (2011). "Selective Production of Organic Acids and Depolymerization of Lignin by Hydrothermal Oxidation with Diluted Hydrogen Peroxide." Energy & Fuels **25**(2): 791-796.

He, W., Liu, H., Xing, Y., & Jones, S. B. (2010). "Comparison of three soil-like substrate production techniques for a bioregenerative life support system." Advances in Space Research **46**(9): 1156-1161.

Helling, R. K., & Tester, J. W. (1988). "Oxidation of simple compounds and mixtures in supercritical water: carbon monoxide, ammonia and ethanol." Environmental science & technology **22**(11): 1319-1324.

Hill, W. A., Loretan, P. A., Bonsi, C. K., Morris, C. E., Lu, J. Y., & Ogbuehi, C. (1989). "Utilization of sweet potatoes in controlled ecological life support systems (CELSS)." Advances in Space Research **9**(8): 29-41.

Holtzapple, M. T., & Little, F. E. (1989). Comparison of Waste Combustion and Waste Electrolysis: A Systems Analysis, SAE Technical Paper.

Hong, G. T., Fowler, P. K., Killilea, W. R., & Swallow, K. C. (1987). Supercritical water oxidation: treatment of human waste and system configuration tradeoff study, SAE Technical Paper.

Huang, C., Barner, H., Albano, J., Killilea, W., & Hong, G. (1992). Method for supercritical water oxidation.

Hübner, T., Roth, M., & Vogel, F. (2016). "Hydrothermal Oxidation of Fecal Sludge: Experimental Investigations and Kinetic Modeling." Industrial & Engineering Chemistry Research **55**(46): 11910-11922.

Jin, F.-M., Kishita, A., Moriya, T., & Enomoto, H. (2001). "Kinetics of oxidation of food wastes with H2O2 in supercritical water." The Journal of Supercritical Fluids **19**(3): 251-262.

Jin, F. M., & Enomoto, H. (2011). "Rapid and highly selective conversion of biomass into value-added products in hydrothermal conditions: chemistry of acid/base-catalysed and oxidation reactions." Energy & Environmental Science **4**(2): 382-397.

Kabel, M. A., Bos, G., Zeevalking, J., Voragen, A. G. J., & Schols, H. A. (2007). "Effect of pretreatment severity on xylan solubility and enzymatic breakdown of the remaining cellulose from wheat straw." Bioresource Technology **98**(10): 2034-2042.

Killilea, W. R., Swallow, K. C., & Hong, G. T. (1992). "The fate of nitrogen in supercritical-water oxidation." The Journal of Supercritical Fluids **5**(1): 72-78.

Kim, Y., Kreke, T., Mosier, N. S., & Ladisch, M. R. (2014). "Severity factor coefficients for subcritical liquid hot water pretreatment of hardwood chips." Biotechnology and bioengineering **111**(2): 254-263.

Krajnc, M., & Levec, J. (1996). "On the kinetics of phenol oxidation in supercritical water." AIChE journal **42**(7): 1977-1984.

Kritzer, P., & Dinjus, E. (2001). "An assessment of supercritical water oxidation (SCWO): Existing problems, possible solutions and new reactor concepts." Chemical Engineering Journal **83**(3): 207-214.

Kruse, A., & Dahmen, N. (2015). "Water – A magic solvent for biomass conversion." The Journal of Supercritical Fluids **96**: 36-45.

Kruse, A., & Gawlik, A. (2003). "Biomass conversion in water at 330-410 degrees C and 30-50 MPa. Identification of key compounds for indicating different chemical reaction pathways." Industrial & Engineering Chemistry Research **42**(2): 267-279.

Kruse, A., Henningsen, T., Sinag, A., & Pfeiffer, J. (2003). "Biomass gasification in supercritical water: influence of the dry matter content and the formation of phenols." Industrial & engineering chemistry research **42**(16): 3711-3717.

Kudenko, Y. A., Gribovskaya, I. V., & Zolotukhin, I. G. (2000). "Physical–chemical treatment of wastes: a way to close turnover of elements in LSS." Acta Astronautica **46**(9): 585-589.

Lee, D.-S., Gloyna, E. F., & Li, L. (1990). "Efficiency of H2O2 and O2 in supercritical water oxidation of 2,4-dichlorophenol and acetic acid." The Journal of Supercritical Fluids **3**(4): 249-255.

Lee, G., Nunoura, T., Matsumura, Y., & Yamamoto, K. (2002). "Comparison of the effects of the addition of NaOH on the decomposition of 2-chlorophenol and phenol in supercritical water and under supercritical water oxidation conditions." Journal of Supercritical Fluids **24**(3): 239-250.

Li, D., Sun, C. J., & Ye, J. F. (2013). Removal efficiency of organic substance in municipal sludge by supercritical water oxidation. Advanced Materials Research, Trans Tech Publ.

Li, L., Chen, P., & Gloyna, E. F. (1991). "Generalized kinetic model for wet oxidation of organic compounds." AIChE Journal **37**(11): 1687-1697.

Li, Q., Li, F., Meng, A., Tan, Z., & Zhang, Y. (2018). "Thermolysis of scrap tire and rubber in sub/super-critical water." Waste Management **71**: 311-319.

Lin, G. K., Xu, D. H., Ma, Z. J., Wang, S. Z., & Guo, Y. (2017). "Effect of Oxidation Coefficient on Products of Sewage Sludge Treatment in Supercritical Water." 3rd International Conference on Energy and Environment Research, Iceer 2016 **107**: 357-362.

Lissens, G., Verstraete, W., Albrecht, T., Brunner, G., Creuly, C., Seon, J., Dussap, G., & Lasseur, C. (2004). "Advanced anaerobic bioconversion of lignocellulosic waste for bioregenerative life support following thermal water treatment and biodegradation by Fibrobacter succinogenes." Biodegradation **15**(3): 173-183.

Lousteau, C., Ayadi, H., & Descorme, C. (2017). "Aqueous phase (catalytic) wet air oxidation of ammonia: Thermodynamic considerations." Applied Catalysis B: Environmental **202**: 12-20.

Luck, F. (1999). "Wet air oxidation: past, present and future." Catalysis today **53**(1): 81-91.

Luther, A., eyaert, A. B., Brutsaert, M., Zhang, D., Rebeyre, P., Lasseur, C., Ronsse, F., Rabaey, K., & Clauwaert, P. (2018). Coupling bioelectrochemical oxidation to C1 of the MELiSSA loop. Joint Agrospace-MELiSSA workshop, Roma.

Ma, H. H., Wang, S. Z., Zhou, L., Ma, S. X., Fan, J., & Xu, D. H. (2015). "Kinetics Analysis of Heterogeneous Oxidation of Coal Particles in Supercritical Water." Chemical Engineering & Technology **38**(1): 91-100.

Ma., C. (2014). "Supercritical Water Oxidation of Wastewater-based Drilling Fluid with Glycol Addition." Journal of Advanced Oxidation Technologies **17**(2): 385-388.

Marcus, Y. (2012). Supercritical Water: A Green Solvent: Properties and Uses, Wiley.

Marino, B. D. V., & Odum, H. T. (1999). Biosphere 2: Research Past and Present, Elsevier Science.

Marrone, P. A. (2013). "Supercritical water oxidation—Current status of full-scale commercial activity for waste destruction." The Journal of Supercritical Fluids **79**(0): 283-288.

Marrone, P. A., Cantwell, S. D., & Dalton, D. W. (2005). "SCWO system designs for waste treatment: Application to chemical weapons destruction." Industrial & Engineering Chemistry Research **44**(24): 9030-9039.

Marrone, P. A., & Hong, G. T. (2009). "Corrosion control methods in supercritical water oxidation and gasification processes." The Journal of Supercritical Fluids **51**(2): 83-103.

Matsumura, Y., Nunoura, T., Urase, T., & Yamamoto, K. (2000). "Supercritical water oxidation of high concentrations of phenol." Journal of Hazardous Materials **73**(3): 245-254.

Meyer, J. C., Marrone, P. A., & Tester, J. W. (1995). "Acetic acid oxidation and hydrolysis in supercritical water." AIChE Journal **41**(9): 2108-2121.

Miller, A., Espanani, R., Junker, A., Hendry, D., Wilkinson, N., Bollinger, D., Abelleira-Pereira, J. M., Deshusses, M. A., Inniss, E., & Jacoby, W. (2015). "Supercritical water oxidation of a model fecal sludge without the use of a co-fuel." Chemosphere **141**: 189-196.

Mishra, V. S., Mahajani, V. V., & Joshi, J. B. (1995). "Wet Air Oxidation." Industrial & Engineering Chemistry Research **34**(1): 2-48.

Mitton, D., Eliaz, N., Cline, J., & Latanision, R. (2001). "An overview of the current understanding of corrosion in SCWO systems for the destruction of hazardous waste products." Materials Technology **16**(1): 44-53.

Muangrat, R., Onwudili, J. A., & Williams, P. T. (2010). "Influence of alkali catalysts on the production of hydrogen-rich gas from the hydrothermal gasification of food processing waste." Applied Catalysis B-Environmental **100**(3-4): 440-449.

Muthukumaran, P., & Gupta, R. B. (2000). "Sodium-carbonate-assisted supercritical water oxidation of chlorinated waste." Industrial & engineering chemistry research **39**(12): 4555-4563.

Naoko, A., & Phillip, E. S. (2002). "Roles of water for chemical reactions in high-temperature water." chemical Reviews **102**: 2725-2750.

Nelson, M., Allen, J., Ailing, A., Dempster, W. F., & Silverstone, S. (2003). "Earth applications of closed ecological systems: Relevance to the development of sustainability in our global biosphere." Advances in Space Research **31**(7): 1649-1655.

Nelson, M., Burgess, T. L., Alling, A., Alvarez-Romo, N., Dempster, W. F., Walford, R. L., & Allen, J. P. (1993). "Using a Closed Ecological System to Study Earth's BiosphereInitial results from Biosphere 2." BioScience **43**(4): 225-236.

Nelson, M., Dempster, W., Alvarez-Romo, N., & MacCallum, T. (1994). "Atmospheric dynamics and bioregenerative technologies in a soil-based ecological life support system: initial results from Biosphere 2." Advances in Space Research **14**(11): 417-426.

Nelson, M., Leigh, L., Alling, A., MacCallum, T., Allen, J., & Alvarez-Romo, N. (1992). "Biosphere 2 test module: A ground-based sunlight-driven prototype of a closed ecological life support system." Advances in Space Research **12**(5): 151-156.

Nelson, M., Pechurkin, N. S., Allen, J. P., Somova, L. A., & Gitelson, J. I. (2010). Closed Ecological Systems, Space Life Support and Biospherics. Environmental Biotechnology. L. K. Wang, V. Ivanov, & J.-H. Tay. Totowa, NJ, Humana Press**:** 517-565.

Nitta, K. (1987). "An overview of Japanese CELSS research activities." Advances in space research **7**(4): 95-103.

Nunoura, T., Lee, G., Matsumura, Y., & Yamamoto, K. (2003). "Reaction engineering model for supercritical water oxidation of phenol catalyzed by activated carbon." Industrial & engineering chemistry research **42**(15): 3522-3531.

Oleson, M., Slavin, T., Liening, F., & Olson, R. (1986). "Controlled ecological life support systems (CELSS) physiochemical waste management systems evaluation."

Onwudili, J. A., & Williams, P. T. (2007). "Reaction mechanisms for the hydrothermal oxidation of petroleum derived aromatic and aliphatic hydrocarbons." The Journal of Supercritical Fluids **43**(1): 81-90.

Onwudili, J. A., & Williams, P. T. (2009). "Degradation of brominated flame-retarded plastics (Br-ABS and Br-HIPS) in supercritical water." The Journal of Supercritical Fluids **49**(3): 356-368.

Oshima, Y., Hori, K., Toda, M., Chommanad, T., & Koda, S. (1998). "Phenol oxidation kinetics in supercritical water." The Journal of supercritical fluids **13**(1): 241-246.

Osibo, O. O. (2011). Removal of nitrogen containing hydrocarbons from wastewater by catalytic and non-catalytic hydrothermal oxidation, in sub-and supercritical conditions, University of Birmingham.

Oswald, W. J., Golueke, C. G., & Horning, D. O. (1965). "Closed ecological systems." Journal of the Sanitary Engineering Division **91**(4): 23-48.

Park, K. C., Tomiyasu, H., Morimoto, S., Takeuchi, K., Kim, Y. J., & Endo, M. (2008). "Carbon formation promoted by hydrogen peroxide in supercritical water." Carbon **46**(13): 1804-1808.

Park, Y., Hool, J. N., Curtis, C. W., & Roberts, C. B. (2001). "Depolymerization of Styrene− Butadiene Copolymer in Near-Critical and Supercritical Water." Industrial & engineering chemistry research **40**(3): 756-767.

Pérez, P. C. (2012). Studies in the development of SCWO vessel reactors with hydrothermal flame

as an internal heat source. phd, UNIVERSIDAD DE VALLADOLID.

Pérez, V. I., Rogak, S., & Branion, R. (2004). "Supercritical water oxidation of phenol and 2,4-dinitrophenol." The Journal of Supercritical Fluids **30**(1): 71-87.

Peterson, A. A., Vogel, F., Lachance, R. P., Froling, M., Antal, M. J., & Tester, J. W. (2008). "Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies." Energy & Environmental Science **1**(1): 32-65.

Phuong Thu, L., & Michele, B. (2016). "Carbon and nitrogen removal from glucose-glycine melanoidins solution as a model of distillery wastewater by catalytic wet air oxidation." J Hazard Mater **310**: 108-116.

Pickering, K. D., & Edeen, M. A. (1998). Lunar-Mars life support test project phase III water recovery system operation and results, SAE Technical Paper.

Portela, J. R., Nebot, E., & de la Ossa, E. M. (2001). "Generalized kinetic models for supercritical water oxidation of cutting oil wastes." The Journal of Supercritical Fluids **21**(2): 135-145.

Portela, J. R., Nebot, E., & de la Ossa, E. M. (2001). "Kinetic comparison between subcritical and supercritical water oxidation of phenol." Chemical Engineering Journal **81**(1-3): 287-299.

Portela Miguélez, J. R., López Bemal, J., Nebot Sanz, E., & Martínez de la Ossa, E. (1997). "Kinetics of wet air oxidation of phenol." Chemical Engineering Journal **67**(2): 115-121.

Price, C. M. (1982). Wet oxidation of human waste, Massachusetts Institute of Technology.

Qian, L., Wang, S., Xu, D., Guo, Y., Tang, X., & Wang, L. (2015). "Treatment of sewage sludge in supercritical water and evaluation of the combined process of supercritical water gasification and oxidation." Bioresource Technology **176**: 218-224.

Qian, L., Wang, S., Xu, D., Guo, Y., Tang, X., & Wang, L. (2016). "Treatment of municipal sewage sludge in supercritical water: A review." Water Research **89**: 118-131.

R. L, S. J., Fang, Z., Inomata, H., & Arai, H. (2000). "Phase behavior and reaction of nylon 6/6 in water at high temperatures and pressures." Journal of Applied Polymer Science **76**(7): 1062-1073.

Ratnasamy, C., & Wagner, J. P. (2009). "Water Gas Shift Catalysis." Catalysis Reviews **51**(3): 325-440.

Rice, S. F., & Steeper, R. R. (1998). "Oxidation rates of common organic compounds in supercritical water." Journal of Hazardous Materials **59**(2-3): 261-278.

Sahena, F., Zaidul, I. S. M., Jinap, S., Karim, A. A., Abbas, K. A., Norulaini, N. A. N., & Omar, A. K. M. (2009). "Application of supercritical CO2 in lipid extraction – A review." Journal of Food Engineering **95**(2): 240-253.

Saleem, F., Müller, P., Eränen, K., Warnå, J., Yu Murzin, D., & Salmi, T. (2017). "Kinetics and modelling of furfural oxidation with hydrogen peroxide over a fibrous heterogeneous catalyst: effect of reaction parameters on yields of succinic acid." Journal of Chemical Technology & Biotechnology **92**(9): 2206-2220.

Sanchez-Oneto, J., Mancini, F., Portela, J. R., Nebot, E., Cansell, F., & de la Ossa, E. J. M. (2008). "Kinetic model for oxygen concentration dependence in the supercritical water oxidation of an industrial wastewater." Chemical Engineering Journal **144**(3): 361-367.

Sánchez-Oneto, J., Mancini, F., Portela, J. R., Nebot, E., Cansell, F., & Martínez de la Ossa, E. J. (2008). "Kinetic model for oxygen concentration dependence in the supercritical water oxidation of an industrial wastewater." Chemical Engineering Journal **144**(3): 361-367.

Sato, T., Watanabe, M., Smith Jr, R. L., Adschiri, T., & Arai, K. (2004). "Analysis of the density effect on partial oxidation of methane in supercritical water." The Journal of Supercritical Fluids **28**(1): 69-77.

Savage, P. E. (1999). "Organic Chemical Reactions in Supercritical Water." Chemical Reviews **99**(2): 603-622.

Savage, P. E., Yu, J. L., Stylski, N., & Brock, E. E. (1998). "Kinetics and mechanism of methane oxidation in supercritical water." Journal of Supercritical Fluids **12**(2): 141-153.

Schmieder, H., & Abeln, J. (1999). "Supercritical water oxidation: State of the art." Chemical Engineering & Technology **22**(11): 903-908.

Segond, N., Matsumura, Y., & Yamamoto, K. (2002). "Determination of ammonia oxidation rate in sub-and supercritical water." Industrial & engineering chemistry research **41**(24): 6020-6027.

Shanableh, A. (2005). "Generalized first-order kinetic model for biosolids decomposition and oxidation during hydrothermal treatment." Environmental science & technology **39**(1): 355-362.

Shi, W., Li, S., Jia, J., & Zhao, Y. (2013). "Highly efficient conversion of cellulose to bio-oil in hot-compressed water with ultrasonic pretreatment." Industrial & Engineering Chemistry Research **52**(2): 586-593.

Shimoda, E., Fujii, T., Hayashi, R., & Oshima, Y. (2016). "Kinetic analysis of the mixture effect in supercritical water oxidation of ammonia/methanol." Journal of Supercritical Fluids **116**: 232-238.

Shin, Y. H., Lee, H. S., Veriansyah, B., Kim, J., Kim, D. S., Lee, H. W., Youn, Y. S., & Lee, Y. W. (2012). "Simultaneous carbon capture and nitrogen removal during supercritical water oxidation." Journal of Supercritical Fluids **72**: 120-124.

Silverstone, S., Nelson, M., Alling, A., & Allen, J. (2003). "Development and research program for a soil-based bioregenerative agriculture system to feed a four person crew at a Mars base." Adv Space Res **31**(1): 69-75.

Smith, D., Garland, J., & Rector, T. (2006). A Novel Membrane Bioreactor for Spacecraft Water Recycling. Earth & Space 2006: Engineering, Construction, and Operations in Challenging Environment**:** 1-6.

Söğüt, O. Ö., & Akgün, M. (2007). "Treatment of textile wastewater by SCWO in a tube reactor." The Journal of Supercritical Fluids **43**(1): 106-111.

Söğüt, O. Ö., & Akgün, M. (2009). "Removal of C.I. Basic Blue 41 from aqueous solution by supercritical water oxidation in continuous-flow reactor." Journal of Industrial and Engineering Chemistry **15**(6): 803-808.

Stavbar, S., Hrncic, M. K., Premzl, K., Kolar, M., & Turk, S. S. (2017). "Sub- and super-critical water oxidation of wastewater containing amoxicillin and ciprofloxacin." Journal of Supercritical Fluids **128**: 73-78.

Suzuki, H., Cao, J., Jin, F., Kishita, A., Enomoto, H., & Moriya, T. (2006). "Wet oxidation of lignin model compounds and acetic acid production." Journal of Materials Science **41**(5): 1591-1597.

Svishchev, I. M., & Plugatyr, A. (2006). "Supercritical water oxidation of o-dichlorobenzene: degradation studies and simulation insights." The Journal of Supercritical Fluids **37**(1): 94-101.

Takahashi, Y. (1989). "Water Oxidation Waste Management System for a CELSS-The State of the Art." Biological Sciences in Space **3**(1): 45-54.

Takahashi, Y., Nitta, K., Ohya, H., & Oguchi, M. (1987). "The applicability of catalytic wet-oxidation to CELSS." Advances in Space Research **7**(4): 81-84.

Takahashi, Y., & Tanaka, K. (1992). "Material recycling in a regenerative life support system for space use: Its issues and waste processing." Advances in Space Research **12**(5): 65-73.

Takahashi, Y., Wydeven, T., & Koo, C. (1989). "Subcritical and supercritical water oxidation of CELSS model wastes." Advances in Space Research **9**(8): 99-110.

Tan, Y., Shen, Z., Guo, W., Ouyang, C., Jia, J., Jiang, W., & Zhou, H. (2014). "Temperature sensitivity of organic compound destruction in SCWO process." J Environ Sci (China) **26**(3): 512-518.

Tester, J. W., Holgate, H. R., Armellini, F. J., Webley, P. A., Killilea, W. R., Hong, G. T., & Barner, H. E. (1993). "SUPERCRITICAL WATER OXIDATION TECHNOLOGY - PROCESS-DEVELOPMENT AND FUNDAMENTAL RESEARCH." Acs Symposium Series **518**: 35-76.

Thornton, T. D., & Savage, P. E. (1990). "Phenol oxidation in supercritical water." The Journal of Supercritical Fluids **3**(4): 240-248.

Tibbits, T., & Alford, D. K. (1982). "Controlled ecological life support system: Use of higher plants."

Timberlake, S. H., Hong, G. T., Simson, M., & Modell, M. (1982). Supercritical water oxidation for wastewater treatment: preliminary study of urea destruction, SAE Technical Paper.

Turc, H., Pintena, J., Bagarri, P., Gibiat, F., & Fabreguettes, V. (1999). "A combined modeling and experimental approach for achieving a simplified closed ecosystem." Advances in Space Research **24**(3): 351-360.

Vadillo, V., Garcia-Jarana, M. B., Sánchez-Oneto, J., Portela, J. R., & Martínez de la Ossa, E. J. (2012). "New feed system for water-insoluble organic and/or highly concentrated wastewaters in the supercritical water oxidation process." The Journal of Supercritical Fluids **72**(0): 263-269.

Vadillo, V., Garcia ‐ Jarana, M. B., Sάnchez ‐ Oneto, J., Portela, J. R., & de la Ossa, E. J. M. (2011). "Supercritical water oxidation of flammable industrial wastewaters: economic perspectives of an industrial plant." Journal of Chemical Technology and Biotechnology **86**(8): 1049-1057.

Vadillo, V., Sánchez-Oneto, J., Portela, J. R., & Martínez de la Ossa, E. J. (2014). Chapter 9 - Supercritical Water Oxidation for Wastewater Destruction with Energy Recovery A2 - Anikeev, Vladimir. Supercritical Fluid Technology for Energy and Environmental Applications. M. Fan. Boston, Elsevier: 181-190.

Vadillo, V., Sánchez-Oneto, J., Portela, J. R. n., & Martínez de la Ossa, E. J. (2013). "Problems in supercritical water oxidation process and proposed solutions." Industrial & Engineering Chemistry Research **52**(23): 7617-7629.

Veriansyah, B., & Kim, J. D. (2007). "Supercritical water oxidation for the destruction of toxic organic wastewaters: A review." Journal of Environmental Sciences-China **19**(5): 513-522.

Villegas, L. G. C., Mashhadi, N., Chen, M., Mukherjee, D., Taylor, K. E., & Biswas, N. (2016). "A Short Review of Techniques for Phenol Removal from Wastewater." Current Pollution Reports **2**(3): 157-167.

Wahyudiono., Kanetake, T., Sasaki, M., & Goto, M. (2007). "Decomposition of a Lignin Model Compound under Hydrothermal Conditions." Chemical Engineering & Technology **30**(8): 1113-1122.

Wang, Q., Lv, Y. K., Zhang, R., & Bi, J. C. (2013). "Treatment of cotton printing and dyeing wastewater by supercritical water oxidation." Desalination and Water Treatment **51**(37-39): 7025-7035.

Wang, S., Guo, Y., Chen, C., Zhang, J., Gong, Y., & Wang, Y. (2011). "Supercritical water oxidation of landfill leachate." Waste Management **31**(9–10): 2027-2035.

Wang, T., & Zhu, X. F. (2003). "Sulfur transformations during supercritical water oxidation of a Chinese coal." Fuel **82**(18): 2267-2272.

Wellig, B., Lieball, K., & Rudolf von Rohr, P. (2005). "Operating characteristics of a transpiring-wall SCWO reactor with a hydrothermal flame as internal heat source." The Journal of Supercritical Fluids **34**(1): 35-50.

Wen, S. (2014). "Supercritical Water Oxidation of Oily Wastewater." Journal of Advanced Oxidation Technologies **17**(2): 339-342.

Wheeler, R. M. (2003). "Carbon balance in bioregenerative life support systems: Some effects of system closure, waste management, and crop harvest index." Advances in Space Research **31**(1): 169-175.

Williams, P. T., & Onwudili, J. (2005). "Composition of products from the supercritical water gasification of glucose: A model biomass compound." Industrial & Engineering Chemistry Research **44**(23): 8739-8749.

Xu, D., & Savage, P. E. (2018). "Supercritical water upgrading of water-insoluble and water-soluble biocrudes from hydrothermal liquefaction of Nannochloropsis microalgae." The Journal of Supercritical Fluids **133**: 683-689.

Xu, D., Wang, S., Huang, C., Tang, X., & Guo, Y. (2014). "Transpiring wall reactor in supercritical water oxidation." Chemical Engineering Research and Design **92**(11): 2626-2639.

Xu, D., Wang, S., Tang, X., Gong, Y., Guo, Y., Wang, Y., & Zhang, J. (2012). "Design of the first pilot scale plant of China for supercritical water oxidation of sewage sludge." Chemical Engineering Research and Design **90**(2): 288-297.

Xu, D. H., Wang, S. Z., Gong, Y. M., Guo, Y., Tang, X. Y., & Ma, H. H. (2010). "A novel concept reactor design for preventing salt deposition in supercritical water." Chemical Engineering Research and Design **88**(11): 1515-1522.

Xu, D. H., Wang, S. Z., Zhang, J., Tang, X. Y., Guo, Y., & Huang, C. B. (2015). "Supercritical water oxidation of a pesticide wastewater." Chemical Engineering Research & Design **94**: 396-406.

Yang, B., Cheng, Z., Tang, Q., & Shen, Z. (2018). "Nitrogen transformation of 41 organic compounds during SCWO: A study on TN degradation rate, N-containing species distribution and molecular characteristics." Water Research **140**: 167-180.

Yang, B., Shen, Z., Cheng, Z., & Ji, W. (2017). "Total nitrogen removal, products and molecular characteristics of 14 N-containing compounds in supercritical water oxidation." Chemosphere **188**(Supplement C): 642-649.

Yao, G., Chen, Z., Chen, Q., Li, D., Xie, Z., Zhou, Y., Xiong, X., & Xu, Y. (2018). "Behaviors of Organic and Heavy Metallic Pollutants during Supercritical Water Oxidation of Oil-Based Drill Cuttings." Water, Air, & Soil Pollution **229**(3): 102.

Yesodharan, S. (2002). "Supercritical water oxidation: an environmentally safe method for the disposal of organic wastes." CURRENT SCIENCE-BANGALORE- **82**(9): 1112-1122.

Yildiz, G., Ronsse, F., Vercruysse, J., Daels, J., Toraman, H. E., van Geem, K. M., Marin, G. B., van Duren, R., & Prins, W. (2016). "In situ performance of various metal doped catalysts in micro-pyrolysis and continuous fast pyrolysis." Fuel Processing Technology **144**: 312-322.

Zhang, F., Shen, B., Su, C., Xu, C., Ma, J., Xiong, Y., & Ma, C. (2017). "Energy consumption and exergy analyses of a supercritical water oxidation system with a transpiring wall reactor." Energy Conversion and Management **145**: 82-92.

Zhang, H.-f., Su, X.-l., Sun, D.-k., Zhang, R., & Bi, J.-c. (2007). "Investigation on degradation of polyethylene to oil in a continuous supercritical water reactor." Journal of Fuel chemistry and Technology **35**(4): 487-491.

Zhang, J., Wang, S., Li, Y., Lu, J., Chen, S., & Luo, X. (2017). "Supercritical water oxidation treatment of textile sludge." Environ Technol **38**(15): 1949-1960.

Zhao, h. (2007). "Man on moon possible within 15 years." Retrieved 20/11, 2018, from http://www.chinadaily.com.cn/china/2007-03/07/content_821256.htm.

Zhao, Q., Dong, X., Zhou, M., & Jingchang, W. (2014). Dioxin destruction by supercritical water oxidation. Environmental Engineering, Pts 1-4. H. Li, Q. Xu, & H. Ge. **864-867:** 1709-1712.

Zou, D., Chi, Y., Dong, J., Fu, C., Wang, F., & Ni, M. (2013). "Supercritical water oxidation of tannery sludge: Stabilization of chromium and destruction of organics." Chemosphere **93**(7): 1413-1418.

Curriculum Vitae

Name: Dongdong ZHANG

Date of birth: 5th December 1989,

Citizenship: People's Republic of China

Email: dongdongzhang.ac@gmail.com

Education

PhD candidate

2014-2018, Ghent University, Belgium

Master of Engineering

2012-2014, China Agricultural University, China

Bachelor of Engineering

Bachelor of Arts

2008-2012, China Agricultural University, China

Publications and patents

Peer-reviewed journal papers

1. **Zhang. D.**, Clauwaert. P., Luther, A., Barreiro. D.L., Prins. W., Brilman. W., Ronsse. F., Sub- and supercritical water oxidation of anaerobic fermentation sludge for carbon and nitrogen recovery in a regenerative life support system, Waste management, 77 (2018) pp. 268-275.

2. **Zhang. D.**, Luther. A., Clauwaert. P., Ronsse. F., Hydrothermal oxidation of anaerobic fermentation filtrate for carbon and nitrogen recovery in a regenerative life support system, The Journal of supercritical fluids,145 (2019) pp. 39-47.

3. Clauwaert, P., Muys, M., Alloul, A., De Paepe, J., Luther, A., Sun, X., Ilgrande, C., Christiaens, M., Hu, X., **Zhang, D.**, Lindeboom, R., Sas, B., Rabaey, K., Boon, N., Ronsse, F., Geelen, D., Vlaeminck, S., Nitrogen cycling in Bioregenerative Life Support Systems: Challenges for waste refinery and food production processes, Progress in Aerospace Sciences 91 (2017), 87-98.

4. Dong. H., **Zhang. D.**, Liu. Q., etc. Effect of Different Concentrations and Durations of NaCl and KCl Treatment on Yield and Quality of Cherry Tomato Fruit [J]. Modern Agricultural Science and Technology, 23 (2011), 156-160.

Articles intended for publication

1. **Zhang. D.**, Luther. A., Clauwaert. P., Ronsse. F., Feasibility of carbon recovery from fermentation sludge for a closed life support system by supercritical water oxidation, Waste and Biomass Valorization (under review).

2. **Zhang. D.**, Ghysels. S., Ronsse. F., Approach fully decomposition of organics under mild supercritical water oxidation by circulation (in preparation).

Patents

1. Song. W., **Zhang. D.**, LI. B., A Method to Produce Qinya in Greenhouse in North China, authorized data 20110803 [P] CN102138414A.

Conference presentations

1. **Zhang. D.**, Ronsse. F., Luther, A., Clauwaert. P., Hydrothermal oxidation of anaerobic fermentation filtrate for use in a regenerative life support system, 12th International Symposium on Supercritical Fluids. 22th-25th April 2018, ANTIBES, France. (Oral presentation)

2. **Zhang. D.**, Ronsse. F., Luther. A., Clauwaert. P., Carbon and nitrogen recovery by hydrothermal oxidation. Joint AgroSpace-MELiSSA Workshop. 16th-18th May 2018, Roma, Italy. (Oral and poster presentation)

3. **Zhang. D.**, Ronsse. F., Luther. A., Clauwaert. P., Barreiro, D.L., Prins, W., Brilman, W., Hydrothermal oxidation of fermentation sludge for use in a regenerative life support system. 7th international conference on engineering for waste and biomass valorization.2th - 5th July 2018, Prague, Czech Republic. (Oral presentation)

4. Luther A, Beyaert A, Brutsaert M, **Zhang D**, Rebeyre P, Lasseur C, et al. Coupling bioelectrochemical oxidation to C1 of the MELiSSA loop. Joint AgroSpace-MELiSSA Workshop. 16th-18th May 2018, Roma, Italy.

Invited reviewer in international scientific journals

Waste and Biomass Valorization, Journal of the Taiwan Institute of Chemical Engineers.