Valorization of waste fractions through HydroThermal Liquefaction. Conversion of plastics, lignocellulosic materials, and organic residues into biocrude and recovery of valuable products

Conti, Federica

Publication date:
2020

Document Version
Publisher's PDF, also known as Version of record

Citation for published version (APA):
Conti, F. (2020). *Valorization of waste fractions through HydroThermal Liquefaction. Conversion of plastics, lignocellulosic materials, and organic residues into biocrude and recovery of valuable products*. Aalborg Universitetsforlag.

VALORIZATION OF WASTE FRACTIONS THROUGH HYDROTHERMAL LIQUEFACTION. CONVERSION OF PLASTICS, LIGNOCELLULOSIC MATERIALS, AND ORGANIC RESIDUES INTO BIOCRUDE AND RECOVERY OF VALUABLE PRODUCTS

BY
FEDERICA CONTI

DISSERTATION SUBMITTED 2020

AALBORG UNIVERSITY
DENMARK

Valorization of waste fractions through HydroThermal Liquefaction. Conversion of plastics, lignocellulosic materials, and organic residues into biocrude and recovery of valuable products

Ph.D. Dissertation

Federica Conti

Aalborg University

Department of Energy Technology

Dissertation submitted: May 2020

PhD supervisor: Professor Lasse Aistrup Rosendahl,
Aalborg University, Aalborg, Denma

Assistant PhD supervisor: Associate Professor Thomas Helmer Pedersen,
Aalborg University, Aalborg, Denmark

PhD committee: Associate Professor Jens Bo Holm Nielsen (chair)
Aalborg University

Professor, PhD David Chiaramonti
RE-Cord/University of Florence

Senior Scientist, PhD, Brajendra Kumar Sharma
University of Illinois Urbana-Champaign

PhD Series: Faculty of Engineering and Science, Aalborg University

Department: Department of Energy Technology

ISSN (online): 2446-1636
ISBN (online): 978-87-7210-646-5

Published by:
Aalborg University Press
Langagervej 2
DK – 9220 Aalborg Ø
Phone: +45 99407140
aauf@forlag.aau.dk
forlag.aau.dk

Printed in Denmark by Rosendahls, 2020

Preface

This PhD thesis was made as a completion of the PhD project that I have conducted within the Advanced Biofuels research group at the Faculty of Engineering and Science, Aalborg University, Denmark.

When I first came to Denmark, I soon realized how flat the country was… However, I cannot say the same on this PhD journey, which has been full of ups and downs! This said, I wish to express my sincere gratitude to my supervisor, Prof. Lasse A. Rosendahl, for having given me the chance to work in this field, for his guidance and motivation throughout the PhD, for showing understanding, and for having a friendly attitude. I have really enjoyed doing research within your group.

Moreover, I would like to address a special thanks to my co-supervisor, Associate Prof. Thomas H. Pedersen, and to Associate Prof. Saqib S. Toor for their guidance and support, for their contribution to this project, and for sharing their expertise during laboratory activities.

Furthermore, I would like to thank Associate Prof. Asbjørn H. Nielsen for the fruitful collaboration. An additional thank goes to the past and present colleagues of the Advanced Biofuel research group, to the technicians from the workshop, and to the employees of Steeper Energy ApS for sharing their knowledge on the CBS1 plant. I would like to thank the PhD committee as well, for the time they allocated for the revision of this work.

Finally, a special thanks goes to my parents and to my boyfriend, who encouraged me and were supportive throughout the project period.

Contents

Nomenclature

Abbreviations, acronyms, and units:

Al	aluminum
BACs	bioactive chemicals
BPA	Bisphenol A
BTX	benzene, toluene, xylene
Ca	calcium
Cd	cadmium
CF	crude fats
CH_4	methane
CM	cow manure
CO	carbon monoxide
CO_2	carbon dioxide
CP	crude proteins
Cr	chromium
C_{rec}	carbon recovery
Cu	copper
d.a.f.	dry ash free
d.b.	dry basis
DEE	diethyl ether
E_{rec}	energy recovery
EU	European Union
FC	fixed carbon
Fe	iron

FS	fish sludge
FT-IR	Fourier transform infrared spectroscopy
GC	gas chromatograph
GC-MS	gas chromatography- mass spectrometry
GHG	greenhouse gas
HEFA	hydroprocessed esters and fatty acids
HHV	higher heating value
HTL	hydrothermal liquefaction
HVOs	hydrotreated vegetable oils
H_2	hydrogen
H_2O	water
ICP-AES	inductively coupled plasma- atomic emission spectroscopy
ILUC	indirect land use change
Mg	magnesium
Mn	manganite
MSW	municipal solid wastes
Mtoe	million tonnes of oil equivalent
Ni	nickel
N_2	nitrogen
P	phosphorus
Pb	lead
PBT	Polybutylene terephthalate
PC	Polycarbonate
p_c	critical pressure
PET	Poly(ethylene terephthalate)
PLA	Poly(lactic acid)
PMMA	Poly(methyl methacrylate)
POM	Poly(oxymethylene)
ppm	parts per million (by volume)
PPO	Poly(p-phenylene oxide)
PVA	Poly(vinyl alcohol)

REDII	revised directive on renewable energy
SB	Styrene-butadiene
SDS	sustainable development scenario
SM	swine manure
SS	sewage sludge
T_c	critical temperature
TGA	thermogravimetrical analysis
TN	total nitrogen
TOC	total organic carbon
TPA	Terephtalic acid
VM	volatile matter
vol.%	volume fraction
wt.%	mass fraction
WW	wastewater
Zn	zinc
2DS	2 °C scenario

Thesis details

Thesis Title: Valorization of waste fractions through HydroThermal Liquefaction. Conversion of plastics, lignocellulosic materials, and organic residues into biocrude and recovery of valuable products.

Ph.D. Student: Federica Conti

Supervisors: Prof. Lasse Aistrup Rosendahl, Aalborg University
Associate Prof. Thomas Helmer Pedersen, Aalborg University

The main body of this thesis is based on the following papers:

[A] T. H. Pedersen, F. Conti, "Improving the circular economy via hydrothermal processing of high density waste plastics", *Waste Management* 68 (2017) 24–31

[B] F. Conti, S. S. Toor, T. H. Pedersen, A. H. Nielsen, L. A. Rosendahl, "Biocrude production and nutrients recovery through hydrothermal liquefaction of wastewater irrigated willow", *Biomass and Bioenergy* 118 (2018) 24–31

[C] F. Conti, S. S. Toor, T. H. Pedersen, T. H. Seehar, A. H. Nielsen, L. A. Rosendahl, "Valorization of animal and human wastes through hydrothermal liquefaction for biocrude production and simultaneous recovery of nutrients", Energy Conversion and Management 216 (2020) 112925

In addition to the main papers, the following publications and contributions have also been made:

Publications

[D] S. S. Toor, F. Conti, A. A. Shah, T. H. Seehar, L. A. Rosendahl, "Hydrothermal Liquefaction-A Sustainable Solution to the Sewage Sludge Disposal Problem", *Advances in Waste-to-Energy Technologies* (2019), Chapter 9, 143-163 ISBN 978-1-138-39042-3

[E] A. A. Shah, S. S. Toor, F. Conti, A. H. Nielsen, Lasse A. Rosendahl, "Hydrothermal liquefaction of high ash containing sewage sludge at sub and supercritical conditions", *Biomass & Bioenergy* 135 (2020) 105504

Conference contributions

- F. Conti, T. H. Pedersen, "Improving the circular economy via hydrothermal processing of high-density waste plastics", Oral presentation at 6th International Symposium on Energy from Biomass and Waste, Venice (Italy), 14th-17th November 2016

- F. Conti, S. S. Toor, T. H. Pedersen, A. H. Nielsen, L. A. Rosendahl, "Hydrothermal processing of wastewater willow with integrated nutrients recovery", Oral presentation at EUBCE 2017, Stockholm (Sweden), 12th-15th June 2017

- F. Conti, S. S. Toor, L. A. Rosendahl, "Distribution of inorganic elements among products from HTL of manure", Poster presentation at tcbiomass 2017, Chicago (USA), 19th-21st September 2017

- F. Conti, S. S. Toor, D. Castello, T. H. Pedersen, L. A. Rosendahl, "Conversion of Swine Manure into High Quality Biocrude through Hydrothermal Liquefaction", Poster presentation at EUBCE 2018, Copenhagen (Denmark), 14th-17th May 2018

- F. Conti, T. H. Pedersen, D. Castello, S. S. Toor, L. A. Rosendahl, "Simultaneous Production of Biocrude Oil and Recovery of Nutrients through Hydrothermal Liquefaction of Organic Wastes", Poster presentation at EUBCE 2018, Copenhagen (Denmark), 14th-17th May 2018

- F. Conti, T. H. Pedersen, S. S. Toor, L. A. Rosendahl "Effect of sub and super critical water conditions on the conversion of organic wastes into biocrude through hydrothermal liquefaction", Poster presentation at EUBCE 2019, Lisboa (Portugal), 27th-30th May 2019

This thesis has been submitted for assessment in partial fulfillment of the PhD degree. The thesis is based on the submitted or published scientific papers which are listed above. Parts of the papers are used directly or indirectly in the extended summary of the thesis. As part of the assessment, co-author statements have been made available to the assessment committee and are also available at the Faculty.

Abstract

The increasingly visible effects of climate change demand for a larger use of renewable fuels, especially in the transportation sector, in order to reduce GHG emissions and to move forward against fossil fuels dependence. Hydrothermal liquefaction (HTL) is a prospective technology, capable of producing renewable advanced biofuels via thermochemical conversion of the feedstock into biocrude and its consequent upgrading. The peculiarity of HTL is to be able to process a large variety of feedstock regardless from their chemical composition, including wet biomasses, and therefore allowing even the treatment of inhomogeneous wastes. The present work investigated the HTL of three highly diverse waste fractions with the common aim of valorizing the organic fraction by producing biocrude and, at the same time, investigating the potential recovery of valuable by-products for an improved circular economy.

In the first study, HTL was proposed to process unrecyclable mixed fractions of plastics: to investigate its potentials, nine high-density polymers were individually processed under supercritical water conditions. In most cases, the liquefaction of the plastics resulted in high yields of synthetic crude oils; in particular, PC almost fully converted into biocrude (99.8%), and very high biocrude yields (ca. 80%) were obtained from SB and PPO conversion. From the qualitative characterization, the biocrudes result suitable for fuels and chemicals applications. Furthermore, biocrudes derived from polymers with an aromatic structure may also be used for BTX production, as they contain aromatic compounds. Moreover, monomers were identified in the products after liquefaction of PC, SB, PLA, PBT, and PET; as a result, monomeric compounds may be reclaimed for the production of new plastics. For example, although PET and PBT liquefaction did not produce any biocrude, their conversion resulted in the precipitation of the monomeric compound TPA. From the results of this work, HTL is found being highly prospective for chemical recycling of high-density polymers.

In the second study, HTL was proposed to convert willow used for a particular application: the lignocellulosic biomass was grown on fields irrigated with wastewater

for absorbance of nutrients and metals from the waste stream. The supercritical liquefaction of the willow produced high yields (40%) of biocrude oil, a mixture of ketones and phenols, that could be upgraded for the production of fuels. Around 60% of the biocrude was in fact found being made of compounds whose boiling point is in the same range as gasoline, jet fuel, and diesel. The quality of the biocrude was not affected by the presence of the inorganics in the biomass, as most of the investigated inorganics (e.g. Ca, P, Mg, Fe) were primarily recovered in the solids after HTL processing. Potassium and sodium showed a different behavior being, instead, primarily dissolved in the aqueous phase. The concentration of the inorganics in the solids result favorable to both separate undesired heavy metals and recover nutrients for reutilization as fertilizers.

In the third study, HTL was proposed as treatment for the disposal and simultaneous valorization of animal and human organic residues. Swine manure, cow manure, fish sludge, and sewage sludge were thus processed at both sub- and supercritical conditions, in presence and in absence of K_2CO_3 catalyst. The organic fraction of these wastes was substantially valorized through HTL: up to two thirds of the feedstock introduced in the reactor was converted into biocrude (59% for fish sludge, 46% for sewage sludge, and 41% for the manures at the most favorable process conditions). Though higher yields were obtained when operating at lower temperature (350 °C), the quality of the biocrude was enhanced by the use of supercritical conditions (400 °C), especially for the manure-derived biocrudes, for which more severe conditions resulted in a higher deoxygenation extent. Likewise, the addition of K_2CO_3 catalyst allowed reducing the final oxygen content in the biocrudes, with a stronger effect on the biocrudes derived from the manures. Similarly as for the processing of woody biomass, most of the inorganics (Al, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Zn) were primarily recovered (>70%) in the HTL solids after hydrothermal processing. Since these waste fractions have high inorganic content (around 10% in the manures and >20% in the sludges) and are a particularly abundant source of phosphorus, HTL holds great potential for the recovery of a large volume of phosphorus.

The outcomes of the present PhD work confirm the high flexibility of the HTL process towards the processing of highly inhomogeneous and diverse waste streams. The results of the experimental activities conducted within this work are also intended for utilization in support of the development and upscaling of the HTL technology.

Resumé

De stigende negative effekter af klimaforandringerne øger efterspørgslen af vedvarende brændstoffer, i særdeleshed inden for transportsektoren, til at reducere drivhusgasudledningerne og mindske afhængigheden af fossile brændstoffer. Hydrothermal liquefaction (HTL) er en potentiel teknologi, der er i stand til at producere vedvarende, avancerede biobrændstoffer via våd termokemisk omdannelse af organisk materiale til bio-olie, efterfulgt af opgradering af bio-olien til færdige brændstoffer. HTL er i stand til at konvertere en lang række bio-materialer uanset deres kemiske sammensætning, herunder våd biomasse, hvilket endda muliggør omsætning af inhomogent affald til brændstoffer.
I denne afhandling er omdannelsen af tre meget forskellige affaldsfraktioner via HTL undersøgt med det fælles formål at øge værdien af den organiske fraktion ved at producere bio-olie og samtidig undersøge en potentiel nyttiggørelse af værdifulde biprodukter til en forbedret cirkulær økonomi.

I det første studie testes hypotesen, at HTL kan anvendes til at forædle ikke-genanvendelige plastfraktioner. Til understøttelse af hypotesen testes potentialet af ni højdensitets-polymerer, alle behandlet individuelt under superkritisk HTL. I de fleste tilfælde resulterede plastmaterialet i høje udbytter af syntetisk olie; især blev polykarbonat (PC) næsten fuldstændigt omdannet til syntetisk olie (99,8 %), og meget høje olie-udbytter (ca. 80 %) blev opnået ved konvertering af styren-butadien (SB) og polyphenylenoxid (PPO). Udfra en kvalitativ karakterisering konkluderes det, at de syntetiske olie fra plasten er velegnet til produktion af brændstoffer og andre kemikalier. Endvidere kan polymerer af en aromatisk struktur nedbrydes til aromatiske stoffer, som kan anvendes til BTX-produktion. Derudover blev der identificeret monomerer i produkterne fra PC, SB, polylaktisk syre (PLA), polybutylen terephthalat (PBT) og polyethylen terephthalat (PET); som et resultat heraf kan monomererne indvindes til fremstilling af ny plast. F.eks. resulterede konverteringen af PET og PBT ikke i nogen produktion af olie men derimod i faststof-monomeren terephthalat syre (TPA). Fra resultaterne af dette studie konkluderes det, at HTL er en yderst potentiel teknologi til kemisk genanvendelse af polymerer med høj densitet.

I det andet studie blev HTL undersøgt til konvertering af fytoremedierende pil; det vil sige, pil dyrket på marker, der er overrislet med spildevand til absorption af næringsstoffer og tungmetaller. Superkritisk HTL bevirkede, at pilen producerede høje udbytter (39,7 %) af bio-olie, primært bestående af en blanding af ketoner og fenoler, der kunne opgraderes til produktion af biobrændstoffer. Det blev identificeret af cirka 60 % af bio-olien falder inden for kogepunkter i samme område som konventionel benzin, jetbrændstof og diesel. Kvaliteten af bio-olien blev ikke påvirket af tilstedeværelsen af uorganiske stoffer i biomassen, da de fleste af de undersøgte uorganiske stoffer (f.eks. Ca, P, Mg, Fe) primært blev udvundet i den faste fraktion efter HTL-behandling. Kalium og natrium var primært opløst i den vandige fase. Koncentrationen af de uorganiske stoffer i den faste fraktion resulterede i en gunstigt separation af både uønskede tungmetaller og genindvinding af næringsstoffer til genanvendelse som gødning.

I det tredje studie blev HTL undersøgt som behandlingsmetode til bortskaffelse og samtidig valorisering af organiske restfraktioner fra dyr og mennesker. Svinegylle, kvæggylle, fiskeslam og spildevandsslam blev således behandlet under både sub- og superkritiske forhold, både med og uden tilsætning af K_2CO_3. Den organiske fraktion af dette affald blev i væsentlig grad valoriseret gennem HTL: op til to tredjedele af det råmateriale, der blev introduceret i reaktoren, blev omdannet til bio-olie (59 % for fiskeslam, 46 % for spildevandsslam og 41 % for gyllen under de mest gunstige procesbetingelser). Hvor der blev opnået de højeste udbytter ved konvertering ved lavere temperatur (350 °C), blev kvaliteten af bio-olie forbedret ved anvendelse af superkritiske betingelser (400 °C), især for gylleafledte bio-olier, for hvilke mere barske betingelser resulterede i en højere grad af iltfjernelse. På samme måde bidrog tilsætning af K2CO3 generelt til reduktion af det endelige iltindhold i bio-olierne, med den stærkeste effekt på bio-olierne fra gylle. Tilsvarende behandlingen af pil blev de fleste uorganiske stoffer (Al, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Zn) primært udvundet (> 70 %) i en fast fraktion efter HTL. Da disse affaldsfraktioner har et højt uorganisk indhold (ca. 10 % i gyllen og >20 % i slammene) og samtidig er en væsentlig kilde til fosfor, besidder HTL et stort potentiale til genindvinding af store mængder fosfor.

Resultaterne af dette Ph.d.-projekt bekræfter HTL-processens høje fleksibilitet og evne til at behandle særdeles inhomogene og forskellige affaldsstrømme.
Resultaterne af det eksperimentelle arbejde anses som understøttende til den videre udvikling og opskalering af HTL-teknologien.

Part I: Extended summary

Chapter 1

Introduction

1.1 Climate change and CO_2 emissions

The average surface temperature of the Earth has increased by 0.8 °C since 1880 and two-thirds of this temperature rise has taken place since 1975 [1]. The effects of the climate change are already visible and are projected to become more pronounced: warming and acidification of the oceans, rising of sea levels, melting of polar ice, glacial retreat, and increasingly intense and frequent extreme events, such as hurricanes, heavy rains, or heat waves [2]. The recent increase in anthropogenic greenhouse gas (GHG) emissions, which produce a heat-trapping effect, is recognized to be the dominant reason for global warming. The present atmospheric concentrations of carbon dioxide, methane, and nitrous oxide have reached unprecedented levels in the last 800,000 years. Moreover, in the last 150 years, atmospheric CO_2 level has rapidly increased from 280 ppm to 400 ppm. In particular, CO_2 emissions, produced from fossil fuel combustion and industrial processes, are the main contributors (accounting for 78%) to the sharp GHG increase measured from 1970 to 2010 [3]. Without any mitigation, in 2100 the global average surface temperature is predicted to rise by 3.7-4.8 °C compared with pre-industrial levels [3]. Such increase in the global temperature would have irreversible effects, and compromise water availability and food security for future generations.

To fight climate change, 195 countries have signed the Paris Agreement in 2015. This includes a limitation to the increase of the global average temperature to well below 2 °C compared with pre-industrial levels, and to pursue concrete efforts to limit this increase eventually to 1.5 °C [4]. In response to the Paris Agreement, the International Energy Agency has outlined the “2 °C scenario” (2DS). It proposes a reduction of CO_2 emissions by 70% respect to the present level by 2060 in order to have at least a 50% chance of limiting the average global temperature increase to 2 °C by 2100 [5].

The key factor behind present and future CO_2 emissions is the increase in energy demand driven by the continuous growth in population and the economic development. Electricity, heat generation, and transport are the main contributors to CO_2 emissions, producing more than two thirds on the total CO_2 emissions (see Figure 1). The transport sector by itself produced 27% of total EU-28 GHG emissions in 2016, with GHG emissions from international aviation, for example, increased by 114% respect to 1990 [8]. The transportation sector is still highly dependent on petrol consumption, with the road transport sector sharing the highest percentages of CO_2 emissions (74%), followed by the aviation and maritime sectors (see Figure 1).

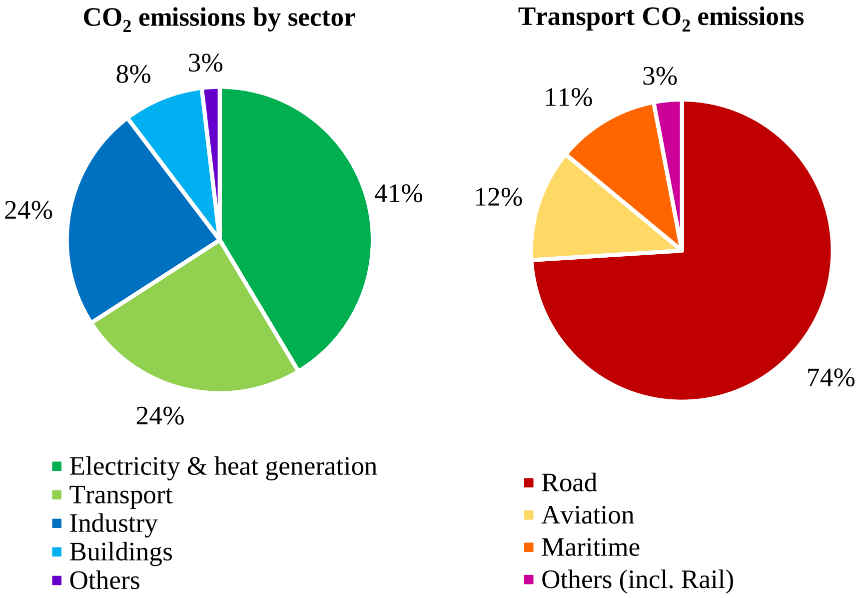


Figure 1: On the left side, Global CO_2 emissions by sector in 2017 (based on data from [6]). On the right side, Global transport CO_2 emissions by sub-sector in 2016 (based on data from [7]).

1.2 Renewables in the transport sector

The transport sector is still heavily relying on fossil fuels respect to the electricity and heat generation sectors. On a global scale, the share of renewable energies in the transport sector only accounted for 3.4% in 2017, respect to 23.9% of the electricity and 10.3% of the heat generation [9]. In EU, a higher share of renewables in the transport sector (7.6%) was reported for the same year, although more efforts are still required to achieve the 10% target set for 2020 and on a longer scale [10].

By 2050, the passenger vehicle stock is expected to more than double, and the aviation and shipping sectors are expected to more than triple [11]. It is therefore straightforward to understand that to ensure future energy demands and, at the same time, respect the limits defined in the Paris Agreement, more sustainable alternatives require to be implemented. Both biofuels and electric mobility will play a key role towards the decarbonization of the transport sector. To date, the use of renewable electricity in transport is primarily associated to the rail system. Electrification already represents an alternative for light vehicles, and, though it is currently limited, it is estimated to grow. Electrification will likely be unfeasible for the aviation, marine, and long-haul road freight sectors, which are expected instead to largely rely on biofuels.

Biofuels are currently the main alternative to petroleum fuels as they can be blended and directly used in existing combustion engines. However, their production only accounts for about 3% of the total fuel demand (88.01 Mtoe in 2018); it requires to triple, in order to reach the 10% goal (252 Mtoe in 2030) established in the sustainable development strategy (SDS). The use of biofuels is, at present, almost exclusively associated to light passenger vehicle and road freight, while it is minimal in the aviation and marine sectors: for example, the aviation biofuel production accounted for less than 0.01% of the aviation fuel demand in 2018 [12].

To ensure a reduction in GHG emissions and sustain the large growth in fuel demand, an increasing use of drop-in fuels will be required. This will particularly apply for the aviation sector, whose requirements towards fuels characteristics are very restrictive. Drop-in biofuels are in fact defined as *"liquid bio-hydrocarbons that are functionally equivalent to petroleum fuels and are fully compatible with existing petroleum infrastructure"* [13]. From a chemical point of view, they are liquid hydrocarbons with low oxygen content, low water solubility, and high degree of carbon bond saturation. One of the main advantages of drop-in fuels is that they allow to overcome blending wall issues, typical of conventional biofuels (bioethanol and biodiesel). The physicochemical properties of drop-in fuels (e.g. boiling point range, carbon number, viscosity, freezing point, flash point, aromatic content) must resemble those of petroleum fuels to be mixed with them. The main processing routes to produce drop-in biofuels are:

- oleochemical: from the hydroprocessing of lipid feedstock (e.g. oil crops, algae, or waste cooking oils) resulting in HVOs (hydrotreated vegetable oils) and HEFA (hydroprocessed esters and fatty acids);
- biochemical: from the biological conversion of sugars or cellulosic materials to single product hydrocarbons, alcohols (e.g. isobutanol to jet and ethanol to jet) or fatty acids that can be further upgraded to drop-in biofuels;
- thermochemical: from thermal conversion of biomass (pyrolysis, hydrothermal liquefaction, or gasification) producing intermediates, which are then upgraded to hydrocarbon fuels.

1.3 Advanced biofuels

Biofuels are renewable fuels produced from biomass, which is any organic matter derived from plants, algae, animals, or wastes (e.g. wood, agricultural crops, energy crops, forestry residues, animal manure, municipal organic wastes, or sewage sludge). Conventional biofuels, also called “1st generation biofuels”, are produced from agricultural crops, and, for this reason, they have been in the center of the “food vs fuel” debate. Advanced biofuels, or “2nd generation” biofuels, are, instead, produced from non-edible biomass or wastes, hence they mitigate land-use change concerns and their life-cycle results in lower GHG emissions respect to conventional biofuels.

Advanced biofuels have lately received increasing attention after EU revised directive on renewable energy (REDII) has entered into force in December 2018. It encompasses a specific target for renewables in the transportation sector: a minimum of 14% of the energy consumed in road and rail transport must come from renewable energy by 2030. Aviation and maritime sectors are not subjected to any obligation; however, they can contribute to the overall target. Crop-based biofuels are capped at a maximum level of 7%, and high indirect land use change (ILUC)-risk biofuels will gradually phase out. ILUC biofuels are produced from feedstock requiring a significant expansion on high carbon stock land (i.e. forests, wetlands, peatlands), and therefore result in high release of CO_2 stored in trees and soil. Lastly, REDII sets a dedicated target for advanced biofuels: (at least) 0.2 % in 2022, 1 % in 2025, and 3.5 % in 2030. Additionally, a detailed and restrictive list of which biomasses and wastes can be used for the production of advanced biofuels is also included in the directive [14].

Among the technologies used to produce advanced biofuels, Hydrothermal Liquefaction has a unique feature: it is highly feedstock-flexible, therefore both dry or wet biomasses and wastes can be processed, and regardless of their chemical composition.

1.4 Hydrothermal Liquefaction

Hydrothermal liquefaction (HTL) is a thermochemical process which converts biomass under hot compressed water, at relatively high temperatures (300-450 °C) and high pressures (15-35 MPa) into biocrude, a high energy-density renewable crude oil. HTL reproduces in few minutes (ca. 30 min), what Nature has done to produce fossil fuels in millions of years.

HTL exploits the changes in water properties near and above its critical point (T_c = 374 °C and p_c = 22 MPa). Rising the temperature from 300 °C to 450 °C at pressure above p_c, the density of water decreases from liquid-like values (~800 kg m^{-3}) to gas-like values (~150 kg m^{-3}), without a phase change. At the same time, the dielectric constant drops down (from ~ 80 at 25 °C to ~ 2 at 450 °C) making water behaving like a non-polar solvent. The ionic product ($K_w = [H_3O^+]\,[OH^-]$), which indicates whether ionic or radical reactions would prevail, first increases and then quickly drops down around the critical point [15]. This would result in an increased production of char and gases at supercritical conditions. However, when operating at high pressures (i.e. 350 bar), this drop is smoothed, and ionic reactions still prevail over radical reactions. This makes it feasible to perform HTL at supercritical conditions, where increased reaction rates often result in higher deoxygenation extents [16].

Since water is the reaction medium and the reactant of the process, wet feedstocks (70-85 wt% of H_2O) are particularly suitable as raw materials in HTL. This particular feature of hydrothermal processing alleviates the overall process economy as the energy intensive drying step can be avoided. Moreover, a large variety of feedstock can be processed through HTL, regardless from their chemical structure (carbohydrates, lignin, protein, and lipids) [15, 17]. Co-liquefaction of different feedstock is also an option in the HTL process; this has been, and still is, widely investigated to exploit potential synergetic effects towards biocrude production and quality [18, 19]. As a result, the high flexibility towards different feedstock is one of the most important advantages of HTL.

When biomass/water slurries are heated under pressure, the organic fraction starts depolymerizing and decomposing through a number of reactions including hydrolysis, dehydration, decarboxylation, forming water-soluble intermediates. These re-polymerize through various condensation reactions producing biocrudes and hydrochars. An aqueous phase, containing water-soluble organics, and a gas phase, primarily constituted by CO_2 and minor amounts of H_2, CH_4 and CO, are formed as well (see Figure 2).

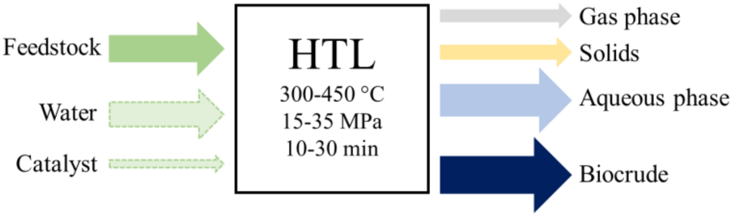


Figure 2: Scheme of the input and output streams in the HTL process.

When biomass is liquefied into biocrude, the overall chemical goal is to reduce the oxygen content. Biomasses, in fact, contain large amount of oxygen (30-50 wt.%, see Table 1), while conventional petroleum only have trace amounts (<1 wt.%). Under HTL processing, oxygen heteroatoms are mainly removed by dehydration and decarboxylation in the form of water and carbon dioxide, respectively. As H_2O and CO_2 have no heating value (HHV), the result is a densification of the energy in the biocrude: from 15-20 MJ kg^{-1} of biomasses to 30-38 MJ kg^{-1} of HTL biocrudes. About 60-70 % of the carbon in the biomass is usually transferred to the biocrude. Biocrude yields, as well as its quality, are highly variable and depend upon various factors, above all on the biomass used as feedstock, but also on process parameters, such as temperature, pressure, residence time, addition of catalyst/pH modifier in the feed slurry. By selecting the right parameters, high biocrude yields and energy recoveries (> 80%) can be achieved through HTL.

A great deoxygenation extent is already achieved through HTL processing (O_2 in the biocrude is about 10-20 wt.%, see Table 1); however a further deoxygenation is required to transform the biocrude into “fuel-like” products. The upgrading of the biocrude is also aimed to remove nitrogen and sulfur heteroatoms, whose concentrations in the biocrude are highly dependent on the type of biomass used as raw material. Depending on its quality and its level of blending with standard petroleum, the biocrude can be directly upgraded in standard refinery units, or alternatively, it can be partially or fully upgraded and fractionated in stand-alone units to drop-in fuels. To ease the upgrading step, which still relies on catalysts specifically developed for crude oil, and at the same time to reduce capital costs associated to the upgrading, it is fundamental to deliver best-quality HTL biocrudes. These two processes, HTL and biocrude upgrading, should therefore be considered as a whole process in prospective of delivering drop-in fuels of high quality.

Table 1: Elemental compositions and heating values of different biomass feedstocks, biocrudes, upgraded biocrudes, and petroleum for comparison.

	C (%)	H (%)	O (%)	N (%)	S (%)	HHV (MJ kg^{-1})	Reference
Feedstock:							
woody biomass	44-53	5.5-6.5	38-49	0-2	0.05-0.1	15-19	[20]
manure	49-59	4.9-7.7	31-42	1.1-4.3	0.3-1.1	20-23	[21]
sewage sludge	43-51	5.9-8.0	37-47	2.3-6.1	1.0	15-20	[D]
Biocrude:							
woody biomass	80.6	9.1	10.1	0.15	0.03	37.2	[22]
manure	71.2	9.5	15.6	3.7	0.12	34.7	[23]
sewage sludge	73-79	8.7-10.1	6.2-8.1	4.3-5.1	0.6-1.2	35-38	[24]
Upgraded biocrude:							
woody biomass	88.4	11.6	0.0	0.99	0.02	42.1	[22]
sewage sludge	83-85	12-14	0.0-1.2	0.03-3.6	0.002	43-46	[24] [25]
Petroleum	83-87	10-14	0.05-1.5	0.1-2	0.05-6	44.4	[26] [27]

1.5 Waste fractions in HTL

One of the factors that has most impact on biofuel production costs is the price of the feedstock [28]. The price of the raw material can in fact account for about a third on the fuel final price [29]. Hence, a way to be competitive with traditional fossil fuels is to use waste fractions as feedstock. Applying the principles of the circular economy: rather than disposable and useless, wastes become resources exploited for the production of new valuable products, which are reintroduced on the market. The result is that both the environment and biofuel production technologies will benefit.

However, the handling and processing of waste fractions can be highly challenging due to a series of reasons. Organic wastes (e.g. animal manure, sewage sludge, municipal solid wastes, industrial food waste) are often highly inhomogeneous and wet. Despite being composed of organic matter, they contain large quantities of inorganics as well. These inorganic elements may precipitate and accumulate resulting in blockages of the reactor or the set-up in continuous units. They may also interfere with the catalyst resulting in its deactivation. A further issue with organic wastes of animal or human origin is the presence of pathogens. This imposes the necessity of a safe handling to prevent contamination towards the personnel working in direct contact, as well as, restrictions on wastes and products disposal to prevent contaminations of the environment.

These issues are overcome due to the high flexibility of the HTL towards various and wet feedstock, making feasible even the use of waste fractions as raw materials. As a result, using HTL, both the organic and the inorganic fractions are valorized; the former is converted into a mixture of renewable hydrocarbons, the biocrude; the latter is a source of valuable elements, among which nitrogen, phosphorus and potassium are fundamental nutrients for agriculture (the so-called N-P-K fertilizers). Phosphorus is, at present, primarily extracted from phosphate rocks, which are a finite, non-renewable resource. Nitrogen fertilizers are produced from nitrogen in the air, but the overall production process consumes large quantities of natural gas. Therefore, HTL ensures an essential circular approach, as the inorganics are recovered in the products (see Figure 3). A further advantage of processing organic wastes through HTL is the elevated temperature of the process that destroys all the biologically active organisms and thus results in products which are free from pathogens, and therefore safe for its handlers.

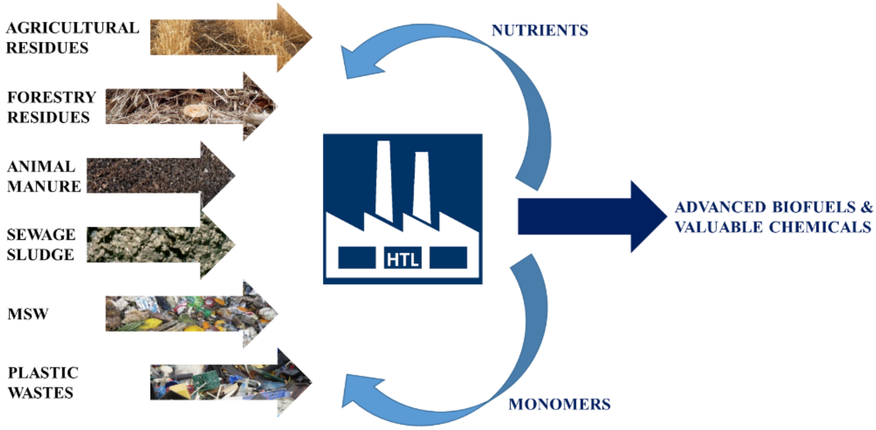


Figure 3: Waste fractions used as feedstock in the HTL process for the production of renewable advanced biofuels or for the extraction of valuable chemicals and the simultaneous recycling of nutrients and monomeric compounds.

1.6 Overview of the PhD project and thesis outline

Given the background just described, the PhD project aims to investigate the conversion of different waste fractions in the HTL process, to assess the production of biocrude oil, and to explore the recovery of valuable by-products. HTL is a highly prospective technology, able to produce sustainable advanced biofuels; however, it is not yet proven beyond pilot scale (TRL 5-6). Therefore, investigating the use of new sources as feedstock is fundamental to contribute to its development and upscaling. Demonstrating the capacity of HTL to handle and process various waste fractions is a double achievement: it enhances the HTL flexibility and environmental concerns are addressed (i.e. the re-use and valorization of waste fractions, the recycle of nutrients, pathogens are destroyed due to the elevated temperatures, microplastics can be processed along with the organic wastes).

The PhD project is structured into three sub-projects: each of them with focus on different types of wastes, which were all converted through HTL under similar processing conditions. An outline of the PhD project is delineated in Figure 4.

The first study explores the decomposition of nine different plastic polymers under hot compressed water, with focus on the potential recovery of the monomers in the HTL products. The choice of using those specific polymers was based on the outcome of an investigation, pointing the complexity of recycling high-density waste plastics when they are mixed.

The second study investigates the HTL of a particular type of lignocellulosic biomass: willow wood cultivated using household wastewater for irrigation. Fast-growing willows are used as vegetation filters: their natural tendency to absorb nutrients and metals from the soil is exploited to absorb the inorganics released when irrigating the plants with household wastewater. The added value, in this case, is associated to the recovery of nutrients from the HTL products.

The third project focuses on the use of organic wet wastes from animal and human origin in the HTL process. More specifically, cow manure, swine manure, fish sludge, and sewage sludge are used to produce biocrude under sub- and supercritical HTL conditions. Simultaneously, the recovery of the inorganics (e.g. N, P, K) in the HTL product phases are assessed.

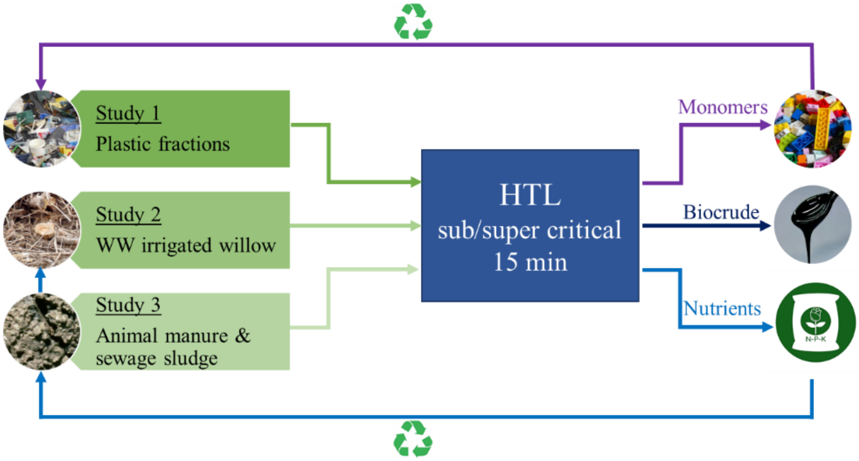


Figure 4: Outline of the PhD project.

The thesis is structured into two parts: Part I and Part II.

Part I, the extended summary, provides a background to the research field, and it reports the methodology and the main outcomes obtained from the PhD project with reference to the main publications (paper A, paper B, and paper C). The extended summary is structured into Chapters:

- Chapter 1 provides an introduction to the research field;
- Chapter 2 discusses the methodology used for the experimental activities and the challenges that were faced;
- Chapter 3 reports the results from study 1 on plastics;
- Chapter 4 reports the results from study 2 on wastewater irrigated willow;
- Chapter 5 reports the results from study 3 on animal and human organic wastes;
- Chapter 6 summaries the main outcomes and conclusions of the PhD project;
- Chapter 7 provides recommendations for future studies.

Part II of the thesis contains all the publications, of which the first three articles are based on the outcomes of PhD project: paper A refers to study 1, paper B to study 2, and paper C to study 3. The other two publications (paper D and paper E) are additional works in which I was directly involved. “Paper D” is a book chapter where the HTL technology is proposed as alternative processing route for sewage sludge, while “Paper E” is an article based on a study conducted on sewage sludge with high-ash content.

Chapter 2

Methodology

This chapter provides details on the methodologies used within this PhD project. These information are of relevance for a broader understanding of the results, as these strictly depend upon the choice made for the processing of the feedstocks and the recovery of the products (e.g. experimental set-up used, process conditions adopted, choice of solvents in the recovery of the products). Additionally, this chapter presents and discusses the major challenges encountered, so that they may be avoided in future investigations.

2.1 Feedstock characterization

The plastic polymers were bought from various petrochemical producers and they were used "as received" in the HTL experiments, without undergoing any pretreatment or characterization. The willow wood was provided by a local producer; and similarly, the animal manures and the sewage sludge were collected from Danish farms and a wastewater treatment plant, respectively, near Aalborg (Denmark). The fish sludge was obtained from a fish farming industry in Norway. It was highly relevant to know the collection point of the biomasses respect to their processing line (i.e. sewage sludge was collected after secondary treatment) and if any treatment was performed before they were supplied to us (e.g. the manures were mechanically dewatered while polymer flocculants were added to the fish sludge and the sewage sludge to facilitate the dewatering). Once received, the willow stems with bark were chopped and ground to fine sawdust (particle size below 0.5 mm) using a cyclone mill (Foss, Cyclotec 1093). The organic wastes were stored in a refrigerator before being analyzed and used in the HTL experiments. Safety precautions were strictly followed in order to avoid contamination: samples were handled in dedicated areas for biohazards and personnel was vaccinated against hepatitis A, Polio, and Tetanus. On the other hand, the same precautions were not necessary when handling HTL products as the high temperature of the process destroys all the pathogens, as already described.

Before investigating the conversion of the feedstocks through HTL, the raw materials were characterized to establish their moisture content, inorganic content, and elemental composition. The moisture content was measured with a moisture analyzer (Kern, MLS) by heating the samples from room temperature to 120 °C. The moisture mass fraction, expressed in weight percent (wt%), was reported by the instrument after weight stabilization. These results were successively used to calculate the amount of water necessary to be added to the biomass to produce a slurry with the desired dry matter (20%) for the HTL experiments.

The inorganic content, or ash content, was determined with an electric muffle furnace (Protherm Furnaces), in which the pre-dried samples were heated in air up to 775 °C, hold isothermally for 3 h, and then cooled down to room temperature. The remaining fraction of the samples was weighted and defined as the ash mass fraction. The reason for drying the samples before measuring the ash content was of minimizing errors due to the presence of large amounts of water respect to the inorganic content. For example, from the results reported in Table 1 of Paper [C], the swine manure was found to contain 75.5 wt% moisture and 11.4 wt% ash on dry basis (d.b.). The inorganic content of the feedstocks was measured also by thermogravimetric analysis (TGA). However, as only a small amount of sample (5-10 mg) could be loaded in the pan for analysis, an increased uncertainty of the results was observed respect to the measurements obtained from the furnace, in which a higher amount of sample (ca. 2 g) could be loaded in the crucible.

The elemental composition of the pre-dried feedstocks was determined with an elemental analyzer (Perkin Elmer, 2400 Series II CHNS/O), which directly measured C, H, and N mass fractions, while the O mass fraction was calculated by difference. Though the instrument is developed to be operated also in CHNS mode, it was previously observed that accurate results are obtained when it is operated in CHN mode. Therefore the S mass fraction was determined, together with the other inorganics, with ICP analysis. Before analyzing the samples, the elemental analyzer was calibrated using Acetanilide (C: 71.09 %, H: 6.71 %, and N: 10.36 %). By using the elemental composition of the feedstocks, hydrogen to carbon and oxygen to carbon atomic ratios were calculated as follow:

$$\frac{H}{C} = \frac{\frac{weight\ percent\ Hydrogen}{atomic\ weight\ Hydrogen}}{\frac{weight\ percent\ Carbon}{atomic\ weight\ Carbon}}$$

$$\frac{O}{C} = \frac{\frac{weight\ percent\ Oxygen}{atomic\ weight\ Oxygen}}{\frac{weight\ percent\ Carbon}{atomic\ weight\ Carbon}}$$

The H/C and O/C atomic ratios of the feedstocks were then reported in the Van Krevelen diagram, together with the atomic ratios relative to the biocrudes in order to visualize the decarboxylation and dehydration extent achieved with the HTL conversion.

The feedstocks used in the third study (animal manures and sewage sludge) were additionally characterized in terms of higher heating value (HHV), volatile matter (VM), fixed carbon (FC), lignocellulosics, crude proteins (CP), and crude fats (CF) content. The HHV were measured with a bomb calorimeter (IKA, C2000). The VM was measured with a DSC/TGA system (TA Instrument, Discovery SDT 650), in which the samples were heated up to 775 °C under inert N_2 atmosphere. The VM was then calculated as the loss in weight when raising the temperature from 105 °C to 775 °C. The FC, on dry basis, was calculated as indicated in the formula below:

$$FC\ (\%) = 100\ (\%) - ash\ (\%) - VM\ (\%)$$

Lignocellulosics and crude proteins were calculated using the following formula adapted from the literature:

$$lignocellulosics\ \ (\%) = (VM + FC)\ (\%) - (CF + CP)(\%) \qquad [30]$$

$$CP\ (\%) = N\ (\%) * 6.25 \qquad [31]$$

Crude fats, or lipids, were instead measured after Soxhlet extraction with petroleum ether for 24 h.

2.2 Experimental set-up for HTL experiments

The HTL experiments were performed using stainless steel (grade 316) micro-batch reactors (see Figure 5), with 10-12 cm^3 volume, which were built in the department workshop (Aalborg University, Aalborg, Denmark) using tubes and fittings by Swagelok. Biomass/water slurries were loaded into the reactors by means of a spatula or a syringe without needle. The reactors were closed, sealed using high temperature grease, and then purged to remove air with inert N_2 gas through a valve placed on top of the reactor unit. Pressure transducers and thermocouples were connected to the reactors to monitor the pressure and the temperature during the HTL conversion. The heat to reach the reaction temperature (350 °C or 400 °C) was provided by a fluidized sandbath (Techne SBL-2D, see Figure 5) in which up to two reactors could be submerged simultaneously, once the temperature was stable. The mixing inside the reactors was instead provided by a mechanical agitator, mounted above the sandbath. The cooling of the reactors was done by quenching in a water bucket.

Figure 5: On the left: an example of micro-batch reactor, used for the HTL experiments. On the right: the fluidized sandbath to provide the heat for the reaction.

The reason for having chosen to process the feedstock in batch reactors is that batch operations allow a practical screening, especially when processing new raw materials or when different process conditions have to be tested. At the same time, the feed slurries can be loaded into the reactors without encountering the challenges due to the pumping of high dry matter streams, which would likely have been the case with organic wastes containing inorganics and plastic materials. Among batch reactors, microbatch reactors reproduce in a better way the continuous HTL processing of the biomass due to their small scale [32]. The use of an autoclave reactor would have instead implied a long time to heat up the reactor to the process conditions; moreover, it would not have been able to grant a rapid cooling and, therefore, increasing the chance for re-polymerization and char formation. When microbatch reactors are submerged into the pre-heated sandbath, the reaction temperature is rapidly reached, as high heating rate are granted (250-450 K min^{-1} [33]). Low heating rates should in fact be avoided as they result in char formation due to re-polymerization of the intermediates [34]. At the same time, high cooling rates (1000 K min^{-1} [33]) were ensured with the quenching of the reactors in a water bucket. However, microbatch reactors present also downsides: the small size results in the production of small amounts of products, which in turn increases the chance of products losses and errors in the consistency of the results, and it may prevent from carrying out some analysis. Their high surface-to-volume ratio may produce catalytic wall effects. For example, new stainless steel reactors were reported promoting the dehydration of cyclohexanol in water at 380 °C respect to when seasoned stainless steel reactor were used [35]. Likewise, the surface of stainless steel 316 reactors was found acting as a heterogeneous catalyst for the hydrolysis of benzamide [36].

In order to overcome some of the above-mentioned issues, future studies could implement the use of batch reactors with a larger volume (e.g. 40-50 cm^3). Nevertheless, microbatch reactors offer a practical solution for screening investigations of new feedstock and/or process conditions and they are believed to lead to reliable results.

2.3 HTL process conditions

2.3.1 Reaction temperature

Though most of the publications on HTL available in literature are conducted at subcritical conditions (usually below 350 °C) there are multiple reasons for performing HTL at supercritical conditions instead (above 375 °C). When feedstocks are processed at higher temperatures, a higher degree of depolymerization can be achieved due to the increased reaction rates. Consequently, biocrudes with an improved quality (i.e. decreased oxygen content, increased HHV, and lower viscosity) can be obtained [37, 38]. At the same time, as recently highlighted in a review on continuous HTL processing, it is not too energy intensive and costly to reach and maintain a system under supercritical conditions, due to the low compressibility of liquids and to fluctuations in specific heat capacity [16].

The HTL experiments conducted within this PhD project were performed at sub- and/or supercritical process conditions depending on the feedstock used and on the rationale of the experiment. The experiments within the first and second study, on plastic polymers and on willow irrigated with wastewater, were performed at supercritical conditions (at 400 °C). Previous investigations on lignocellulosic biomass, both at batch scale and in the continuous "CBS1" unit at Aalborg University (Aalborg, Denmark), have reported an improved biocrude quality when operating at this temperature [39-41]. For what concern plastics, from the decomposition curves of the polymers reported in literature, it appeared necessary to operate at higher temperatures to achieve a sufficient depolymerization extent. Furthermore, the choice of working at supercritical conditions was driven by a broader aim: to prove that the plastic polymers could be processed at the optimal conditions already in use for lignocellulosic biomass, so that to ensure the co-processing of the two fractions. The study on organic wastes included experiments both at sub- and supercritical conditions; here the main goal was to investigate the effect of the two regimes on the biocrude yield and quality and in relation to the biomass constituents (carbohydrates, crude proteins, and crude fats).

2.3.2 Catalyst

HTL conversion is often performed in the presence of a homogeneous or heterogeneous catalyst. Among the various roles, catalysts are used to enhance the initial degradation rate of the biomass and suppress char formation. Both acidic and basic conditions are known to favor hydrolysis reactions [42]. Under acidic conditions higher hydrolysis rates can be reached as respect to basic conditions but, on the other hand, acidic environments promote charring reactions. Hence, acidic conditions are preferred in hydrothermal carbonization, where the goal is to produce a solid fuel in the form of char, rather than in HTL, where the aim is to produce a liquid fuel, the biocrude oil. In HTL, basic conditions are often achieved by adding a homogeneous catalysts (i.e. water-soluble basic compounds) to the feed slurry. Carbonates, bicarbonates, and hydroxides of an alkali or alkaline earth metal are all proven effective catalyst. These homogeneous catalysts cannot be recovered in the HTL products in the same form, as they will react with other compounds. Therefore, even though they are commonly referred to as catalyst, it would be more appropriate to refer to them as additives or pH modifiers [32].

Regarding the experimental activities conducted within the present PhD project, potassium carbonate (K_2CO_3) was used in the HTL of willow biomass. This catalyst had in fact previously resulted to be particularly effective in promoting biocrude production from lignocellulosic material, achieving higher de-oxygenation extents and, at the same time, suppressing coke formation [43]. The catalyst (2.5 wt% of the total reactor loading) was therefore added to the wood/water feed before introducing the slurry into the reactors. The experimental activities on animal manures and sewage sludge, conducted within the third study, were performed both with and without the addition of K_2CO_3 in order to explore whether the catalyst had any beneficial effect on biocrude yield and its quality. The experiments on plastics were conducted instead without any catalyst, as we wanted to investigate the behavior of the individual polymers under the supercritical hydrothermal environment.

2.3.3 Feedstock loading

Another parameter affecting HTL conversion is the loading of solid material in the feed. On one hand, solids loading above 15-20 wt% are recommended to make continuous HTL conversion economically viable: lower concentrations would not sustain the capital costs associate to heat exchangers, heat losses and the expenses related to the pumping of larger quantities of water [15]. On the other hand, pumping feeds with high loading is highly challenging on larger continuous scale. This has been the focus of a previous research, where different methods have been applied to increase the dry matter of lignocellulosic feed slurry. The recirculation of the produced biocrude in the fresh wood/water slurry, a hydrothermal alkaline pretreatment, and the co-processing of wood with algae or other biomasses with water holding capacity and thickening properties were proposed and successfully tested [44]. The first and second treatment were also successfully demonstrated at continuous scale in the CBS1 plant at Aalborg University (Aalborg, Denmark) reaching 20 wt.% and 25 wt.% wood loading, respectively.

The experiments conducted in the second study (on willow) and in the third study (on animal manures, fish sludge, and sewage sludge) were all performed at 20 wt.% dry matter loading to simulate the conditions which could be used at larger continuous scale. To achieve such loadings, demineralized water was added to the biomasses, taking into account the level of moisture already contained in the feedstocks (see Table 2).

Table 2: Moisture mass fractions in the feedstocks, measured by moisture analyzer at 120 °C, and corresponding dry matter contents.

Feedstock	Moisture (wt.%)	Dry matter (wt.%)	Reference
Willow	5.5	94.5	[B]
Swine manure	75.5	24.5	[C]
Cow manure	63.0	37.0	
Fish sludge	5.6	94.4	
Sewage sludge	78.7	21.3	

Swine manure and cow manure were mechanically dewatered, before being delivered to our laboratories in Aalborg University (Aalborg, Denmark), by means of a screw press, which allows reaching up to ~ 35 wt.% of dry matter. Therefore, potentially we could have received the feedstock with the dry matter content already in line for direct feeding into the HTL.

Sewage sludge was processed as received, without the addition of water, being its dry matter content already close to 20 wt.% (21.3 wt.%, as reported in Table 2). Moreover, its paste-like consistency allowed a smooth feeding into the reactors, by means of a needleless syringe. The same feeding procedure could not be applied when using manures, as the water would separate out from the dry fraction when pressing the syringe plunger.

Fish sludge was delivered in the form of powder with low moisture content (5.6 wt.%) achieved after a mechanical treatment and the addition of a polymer flocculants. When fish sludge was collected from fish ponds it had instead low dry matter content (about 5 wt.%). The fish sludge could potentially be delivered with a higher moisture content for direct feeding into the HTL. To compare the outcomes of the conversions, the experiments on fish sludge, conducted within the third study on organic wastes, were performed with 20 wt.% dry matter. However, fish sludge particles did not show enough interaction with water at 20 wt.% dry matter, and the fish/water mixture could not be pumped by a syringe. Additional pumping tests using a syringe were performed at increasing dry matter loading (see Figure 6), and a smooth pumpability was observed at 40 wt.% dry matter content. Therefore, supplementary experiments on fish sludge were conducted with 40 wt.% loading.

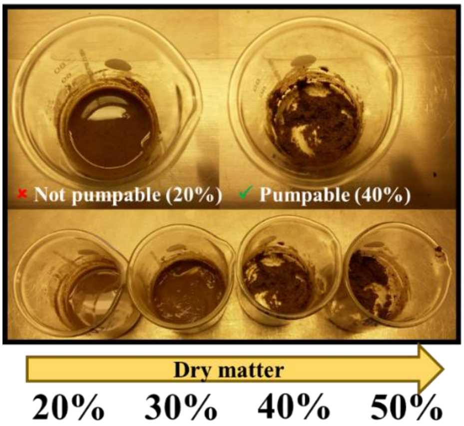


Figure 6: Fish sludge and water mixtures at increasing dry matter content: from left, 20 wt.%, 30 wt.%, 40 wt.%, and 50 wt.

The feedstock loading in the experiments conducted on plastic fractions was set to 10 wt.%, as in a future prospective of co-processing plastic with biomass, the plastic loading would not exceed the 50% of the total dry matter loading (20 wt.%).

2.3.4 Reaction time

The reaction time is a fundamental parameter in HTL processing: overly short reaction times can result in low biocrude productions, while overly long reaction times could cause a repolymerization of the products, with consequent production of char. In the current PhD study, all the experiments were performed with a reaction time of 15 min, including the heating time, as reactors reached the reaction temperature in a very short time (below 1 min) thanks to the high heating rate granted by the experimental set-up in use. The choice of this specific time was based on a previous successful investigation on lignocellulosic model systems [33].

2.3.5 Reaction environment

Once sealed, reactors were checked for leaking using N_2 gas up to ~8 MPa. Reactors were then purged three times with N_2 to remove residual air. When using organic wastes and willow as feedstock, reactors were slightly pressurized (1.5-2.0 MPa) to avoid the presence of biomass in the upper capillary section of the reactor unit, as this occurred in unconverted material and/or blockages.

2.4 Recovery of HTL products

As previously introduced, when biomass is hydrothermally processed through HTL, a multiphase product is obtained, and, consequently, the different phases need to be separated. The recovery procedure can affect the products final yield and quality. For example, the solvents used to recover the biocrude can influence the amount of product collected and its chemical composition. Therefore, when comparing the outcomes of two studies performed on the same biomass material, it is necessary not only to look at the reactor set-up and at the process conditions, but also at the recovery procedure.

In the current PhD project, all the studies applied the same procedure for recovering HTL products. A schematic overview on the main steps involved in the procedure is presented in Figure 7 and additional details can be found in the publications [A, B, C]. The procedure was adapted from a method previously developed for the recovery of HTL products, produced from lignocellulosic model compounds [33].

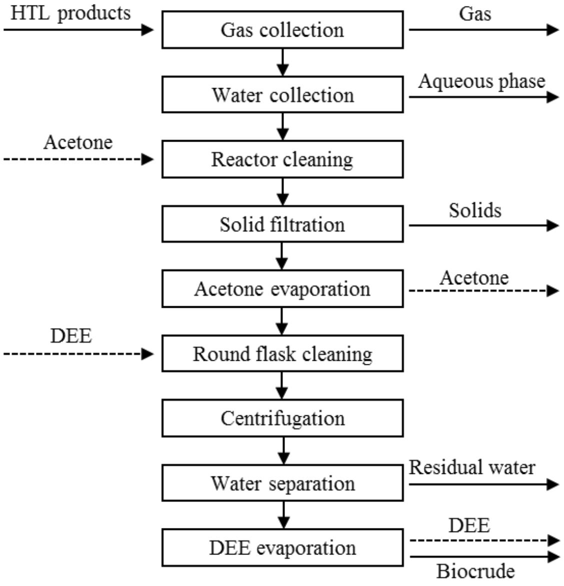


Figure 7: Recovery procedure for the collection of Hydrothermal Liquefaction products (gas, aqueous phase, solids, residual water, and biocrude). Solvents: Acetone and Diethyl Ether (DEE).

The first step of the recovery procedure was to collect the gas by opening a valve placed on the top of the reactors. The gas was either vented out or recovered in a gas collector device for further qualitative characterization. The second product to be collected was the aqueous phase by turning the reactors upside down without the addition of any solvent, to preserve the chemical composition for analysis. The remaining mixture of products (solids, biocrude, and residual water) was collected by rinsing the reactors with acetone. The solids were then separated by filtration: solids were defined as the dried fraction (overnight at 105 °C), insoluble in acetone, collected on a filter paper (particle retention: 5–13 μm). The acetone was successively removed by evaporation using a rotary evaporator, while the remaining fraction (biocrude with some residual water) was collected from the rotavap round flask using Diethyl ether (DEE). The mixture, consisting of biocrude, residual water, and DEE solvent, was centrifuged to enhance the separation of the residual aqueous phase, which was separated out as bottom layer, while the biocrude dissolved in the DEE constituted the top phase. After the removal of the aqueous phase by means of a syringe, the DEE was evaporated using a centrifuge evaporator, and the residual fraction was defined as the biocrude.

The procedure successfully recovered HTL products; nevertheless, some steps resulted more challenging: for example, the recovery of the biocrude from the rotavap round flask and the removal of the residual water. The difficulties encountered in recovering the biocrude were probably associated to the dissolution extent of the biocrude in the DEE. On the other hand, the solvent was chosen due to its high immiscibility with water and its low boiling point. The high immiscibility was exploited to enhance water/biocrude separation, while, thanks to its low boiling point, the solvent could be easily evaporated limiting the loss of biocrude light fractions. Regardless from the recovery procedures adopted, the number of steps involved, and the choice of the solvents, working at small scale with a reduced amount of products would anyway increase the chance of encountering losses of products. However, as previously described, the use of micro-batch reactors allowed for a practical screening of different feedstock under different process conditions.

2.5 Characterization of HTL products

Once recovered, HTL product phases were characterized using various analytical techniques. The composition of the gas phases was determined using a Gas Chromatograph (GC), which was calibrated for the detection of H_2, CH_4, CO, and CO_2. The aqueous phases were characterized in terms of pH, total organic carbon (TOC), and total nitrogen (TN). In the study conducted on willow biomass, the concentrations of chloride, phosphate, and sulphate in the aqueous phases were additionally measured. The CHN elemental compositions of the solids and of the biocrudes were determined with an elemental analyzer. The functional groups in the biocrudes obtained from plastics were investigated by Fourier Transform Infrared Spectroscopy (FT-IR). Biocrudes were qualitatively characterized by Gas Chromatography Mass Spectrometry (GC-MS). However, GC-MS provided information only on the volatile fraction, which for biocrudes may sometimes account only for half of the total mass. The volatility of the biocrudes was investigated by Thermogravimetrical Analysis (TGA). The outcomes of the TGA measurements were also used to assess the ash content of the biocrudes and solids obtained from HTL of organic wastes. More detailed information on the equipment used for the analysis and on the methodology are reported in the publications [A, B, C].

Some analysis could not be performed, due to the reduced amount of products, as a result from working at small scale. For example, the HHV of the biocrudes could not be measured with the bomb calorimeter, as it was done for the feedstocks. HHV were therefore calculated using the correlation developed by Channiwala and Parikh [45], as reported below:

$$HHV = 0.3491\,C + 1.1783\,H + 0.1005\,S - 0.1034\,O - 0.0151\,N - 0.0211\,A$$

where C, H, S, O, and N are the mass fractions of the elements, and A refers to the ash mass fraction. For the same reason, the ash mass fractions of the solids and of the biocrudes were determined by TGA, instead of using the furnace, as for biomass materials.

2.6 Methodology for measuring inorganic elements

In the studies conducted on willow and on organic wastes, the focus was set both in the production of biocrude and in the recovery of the inorganic elements in the HTL products. For this reason, the composition of the inorganic fraction of both feedstocks and HTL products (i.e. solids, aqueous phases, and biocrudes) was investigated using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The samples were acid digested in a microwave to extract the elements, and successively analyzed through ICP, which provided information on the concentration of the elements. The investigated elements were: aluminum (Al), calcium (Ca), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganite (Mn), sodium (Na), nickel (Ni), phosphorus (P), lead (Pb), sulfur (S), zinc (Zn). The concentrations of these elements were then combined with the results on the yields of the product phases, to estimate where the single elements tended to be recovered (i.e. in the solids or in the aqueous phase or in the biocrude) after the hydrothermal processing. Therefore, the results on the inorganics are presented in the publications and in the thesis as distributions of the different elements in the HTL products, rather than as mass balances. The reason for this choice is that for some elements mass balances cannot be closed properly: in fact, for some elements, recoveries above 100% are obtained primarily in the HTL solids. In particular, recoveries of nickel (Ni) and chromium (Cr), well above 100%, were obtained in the HTL solids for all the organic wastes regardless of the process conditions. Since the reactors used were made of stainless steel 316, which contains 10-14% Ni and 16-18% Cr [46], the high recoveries in these elements may be explained with a partial loss from the inside walls of the reactors during biomass processing. This aspect requires further investigations for being able to establish whether reactors should have limitations on the number of times they can be used to prevent the release of walls material.

Chapter 3

HTL of plastic fractions

3.1 Waste plastic fractions

The widespread use of plastic materials has produced a rapid growth in plastic production, which has increased by twenty times in the last half century, and it is projected to double over the next 20 years and almost quadruple by 2050 [47]. In 2018, the global annual plastic production has almost reached 360 million tons, of which 61.8 million tons produced in EU [48]. The direct consequence of this massive production of plastic materials, which are often meant for single-use applications, is the generation of large amounts of wastes, whose recycling is still limited, primarily due to the inhomogeneity of the waste streams [49]. Moreover, it is estimated that, every year, over 8 million tons of waste plastics end up in the ocean [47], representing an environmental concern as well as being harmful to wildlife. Furthermore, the release of microplastics to both marine and terrestrial environments is a global problem, as it is dangerous also for humans if they enter the food chain.

In many EU-countries, landfilling of waste plastics is still practiced : on average, about one third of the waste plastics are landfilled; this corresponds to about 8 million tons of landfilled plastics per year [50]. In countries where restrictions on landfilling were introduced, the recycling rate has increased – however only to a moderate extent – as incineration is still the primary alternative for the disposal of waste plastics. In Denmark, for example, it is estimated that 64% of waste plastics are incinerated, while only 34% are recycled [51, 52]. An outline on how waste plastics are currently handled in Europe (on average) and in Denmark is presented in Figure 8. Incineration offers a sustainable alternative to landfilling, resulting in both waste reduction and energy recovery by heat and/or power generation. However, recycling should always be the first approach for the handling of wastes, particularly for waste plastics. Plastic materials are in fact almost exclusively produced from fossil feedstock; therefore, their mechanical or chemical recycling can significantly affect the consumption of virgin feedstock. Recycling of plastics is straightforward for separated fractions of pure polymers (e.g. when separated collection systems are in place for PET bottles). On the other hand, the main challenges for plastic recycling enterprises are fractions of mixed plastics (e.g. from household collection) and plastics mixed with organic waste (e.g. packaged food). In fact, these waste streams cannot always be sorted into fractions of a sufficient level of purity for being recycled, either due to technological barriers or to economic unfeasibility. As a consequence, large amount of waste plastics are still incinerated or landfilled, cutting off the recycling loop of plastic materials.

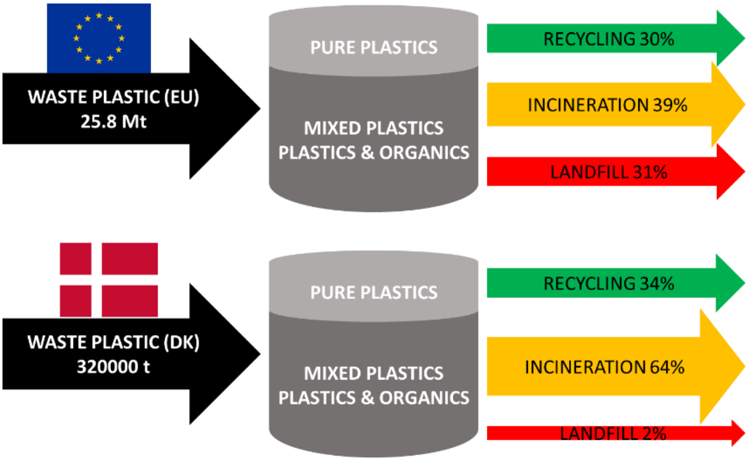


Figure 8: Overview on the current handling of waste plastics in Europe (above) and in Denmark (below) [50, 52].

Mixed plastics can be separated up to some extent by gravitational density in wet separators controlling the density of the wet medium [49]. With this technique, plastics with lower densities are collected from the surface of the wet medium, while those with higher densities are recovered from the bottom of the tank. The float, the fraction recovered from the top, and the sunk, the fraction recovered from the bottom, can be further separated in successive tanks. However, in order to achieve the levels of purity required for the recycling, many steps are necessary, resulting in extensive and expensive processes. In particular, this applies for mixed fractions of high-density waste plastics, which are ultimately sent to incineration, as reported after our consult with the largest plastic recycling enterprise in Denmark.

Here, an alternative solution is proposed to improve the circular economy of waste plastics: the lighter fractions will be treated for primary recycling, while the unrecyclable high-density plastics will be hydrothermally processed. As a result, through HTL the plastic polymers would decompose into valuable chemicals and into their monomeric constituents, which will be used for the production of new polymers. An overview of the proposed process configuration is outlined in Figure 9. The scope of Study 1 in the present PhD project was to investigate the decomposition of high-density plastics in presence of supercritical water and to assess the potential recovery of monomeric compounds in the HTL products.

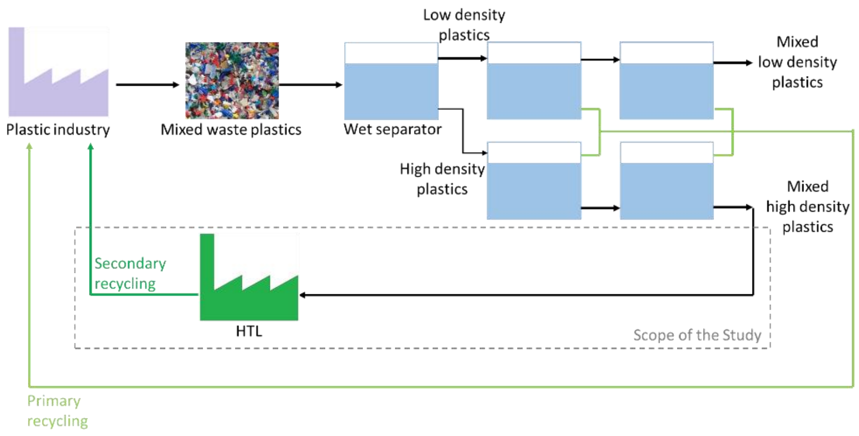


Figure 9: Conceptual scheme highlighting the scope of Study 1: improving plastic circular economy via HTL of unrecyclable high-density polymers.

HTL potentially offers a sustainable answer to the management of waste plastics, resulting in a prospective solution for the treatment of a broader range of waste streams: in particular, organic waste streams contaminated with plastics (e.g. food waste with packaging material or sewage sludge containing microplastics).

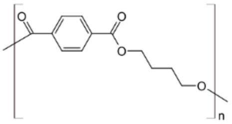
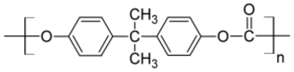
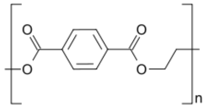
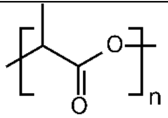
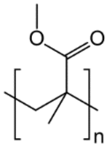
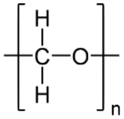
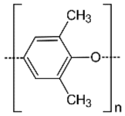
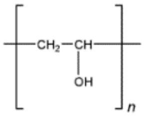
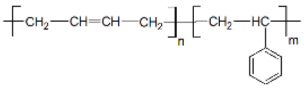
At the time Study 1 was initiated (January 2016), studies on thermochemical conversion of plastics focused primarily on pyrolysis, while a limited amount of literature was available on HTL of plastic materials. However, in the last couple of years, HTL has undergone to a rapid development towards its commercialization, and an Australian company, Licella^{TM}, leader in the commercialization of the HTL technology has publicly announced the construction of a new plant, designed for the handling of unrecyclable waste plastics. Licella^{TM}, in joint venture with Armstrong

Chemicals, will build a commercial scale hydrothermal upgrading plant to convert end-of-life plastic into chemicals using their Cat-HTR^{TM} platform [53]. The plant by ReNew ELP, whose construction is expected to start in 2020, will have an initial capacity of 20,000 tons of waste plastic per year, expandable up to 80,000 tons, and will be located in Wilton (UK) [54, 55]. Another example of chemical recycling of waste plastics comes from BASF project ChemCycling. In joint venture with Quantafuel, expert in pyrolysis of plastics, BASF will construct a plant in Skive (Denmark) for converting thermochemically unrecyclable waste plastics into feedstock and monomers to be used for the production of new plastics. The construction is planned to start in in the fourth quarter of 2019 and it will have a capacity 16,000 tons per year [56, 57].

3.2 High-density polymers

The high-density polymers selected for investigation in Study 1 are reported in Table 3, where short and full names are provided together with the chemical structure of the repeating units and their main applications. The plastics were individually processed under supercritical water conditions (400 °C) to assess the decomposition extent of the pure polymers and the distribution of the products among the different HTL phases (gas, aqueous phase, biocrude, and solids). In addition, preliminary investigations using mixtures of the selected polymers were performed and the results are reported in Paragraph 3.4. Observing the chemical structure of the repeating units presented in Table 3, it appears that most of the investigated plastics have aromatic structure (e.g. PC, PPO, SB); therefore, in these cases, biocrudes will likely show aromatic structure. Similarly to the monomers, which can be recycled for the production of new plastic materials, the aromatics complexes can be reintroduced into the petrochemical industry for the production of Benzene, Toluene, Xylene (BTX compounds).

Table 3: List of the high-density polymers investigated in Study 1.

	Plastic	**Repeating unit**	**Applications**
PBT	Polybutylene terephthalate		electrical (plug connectors), electronic (keyboards), automotive
PC	Polycarbonate		electronic (CD/DVD, phones), automotive, medical, safety helmets, construction (greenhouse)
PET	Poly(ethylene terephthalate)		food packaging (bottles, microwave trays), synthetic clothes
PLA	Poly(lactic acid)		food packaging, medical & healthcare, 3D printing, diapers
PMMA	Poly(methyl methacrylate)		transparent glass substitute (aquarium glasses, aircraft windows), medical, acrylic paint
POM	Poly(oxymethylene)		mechanical gears, automotive, electrical
PPO	Poly(p-phenylene oxide)		electronic, electrical automotive
PVA	Poly(vinyl alcohol)		rubber reinforcement (in tires), nets, sewing thread
SB	Styrene-butadiene		automotive (tires), mats, shoes soles, chewing gum, conveyor belts

3.3 Conversion of high-density plastics through HTL

3.3.1 Biocrude production and product distribution

When hydrothermally processed under supercritical conditions, most of the investigated high-density polymers converted into biocrude oil, also named ‘synthetic crude’. The yields in biocrude obtained from plastics conversion are reported in Figure 10, where the polymers are presented by decreasing values of biocrude yield. PC, SB, and PPO almost exclusively converted into biocrude with yields of 99.8%, 80.7%, and 78.9%, respectively [A]. These values of biocrude yields are particularly high when compared to the yields in biocrude generally obtained from the conversion of biomasses as wood, algae or manure (25-45%) [20]. Biocrude was also the main product recovered from PMMA and PVA conversions, despite lower yields were registered (48.0% and 35.3%, respectively) [A]. For these two polymers, the remaining fraction of carbon was transferred to the aqueous phase, as higher TOC values were measured (23.4 g L^{-1} and 12.2 g L^{-1}, respectively) as compared to the aqueous phases collected from the other polymers (see Table 1 in Paper [A] for more details). After POM conversion, carbon was more equally distributed among the HTL phases, leading to a lower biocrude yield (13%).

A different behavior was observed for PET, PBT, and PLA plastics, whose conversion did not result in the production of any biocrude. PET and PBT primarily converted into solid products with yields of 68.5% and 50.8%, respectively (see Figure 10). No solvents were required for the collection of the products after PBT and PET conversion. Neither biocrude nor solids were detected when converting PLA. On the other hand, a high TOC value of the water phase (19.1 g L^{-1}) [A] suggested a significant presence of organics in the aqueous phase and, at the same time, a significant production of gas was registered (approximately 20 bar). The elemental compositions of the biocrudes and the solids are reported in Table 4; the carbon mass balance can be found in Paper [A].

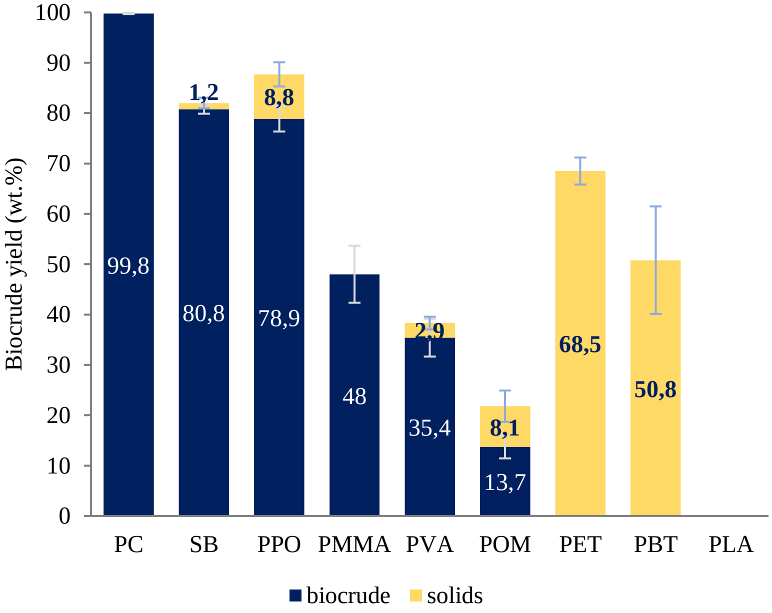


Figure 10: Yields in biocrude and solids obtained from the conversion of high-density plastics. Neither biocrude nor solids were recovered from PLA conversion.

Table 4: Elemental compositions (wt.%), H/C, and O/C ratios of the biocrudes and solids obtained from HTL of the high-density plastics (elaborated from Table 1 in Paper [A]).

	Biocrudes					Solids				
	C	H	O	H/C	O/C	C	H	O	H/C	O/C
PBT	-[a]	-[a]	-[a]			57.6	3.4	39.0	0.70	0.51
PC	75.0	8.0	17.0	1.27	0.17	-[a]	-[a]	-[a]		
PET	-[a]	-[a]	-[a]			34.9	1.4	63.7	0.48	1.37
PMMA	63.6	9.0	27.4	1.69	0.32	-[a]	-[a]	-[a]		
POM	78.7	7.7	13.6	1.17	0.13	64.3	4.3	31.3	0.80	0.37
PPO	85.7	8.2	6.1	1.14	0.05	83.8	7.1	9.1	1.01	0.08
PVA	81.5	9.0	9.5	1.32	0.09	29.3	3.5	67.3	1.42	1.72
SB	90.5	8.6	0.9	1.13	0.01	-[a]	-[a]	-[a]		

-[a] The product was not detected or not enough for the measurements

The main product of interest from biomass liquefaction is generally the biocrude, either whether the final purpose is the production of liquid fuels or the extraction of valuable chemicals. Instead, the production of solids is usually undesired, as they consist in char due to repolymerization of the products. Therefore, at a first glance, it could appear that PET, PBT, and PLA polymers are not suitable for being processed in HTL, since biocrude was not detected after their conversion. However, after a deeper investigation including a qualitative characterization of the solids obtained from PET and PBT, it was concluded that for plastic materials the production of solids is as relevant as the biocrude. In fact, the monomeric constituents of the plastics were detected in the HTL solids after liquefaction of PET and PBT. The presence of monomers in the HTL products is discussed in the next paragraph.

3.3.2 Plastic circular economy

As previously introduced, the interest behind processing waste plastics in HTL is to provide a sustainable alternative for their management with secondary recycling of the monomers for the production of new polymers and tertiary recycling of valuable chemicals. The quality of the biocrudes, solids, and aqueous phases obtained from the conversion of the polymers was therefore investigated in this prospective. The qualitative characterization of the biocrudes by GC-MS highlighted that synthetic crudes obtained from the conversion of plastics have a simple product slate, or, in other words, they are constituted of a very limited amount of compounds. In comparison, biomass-derived biocrudes are usually a mixture of a large amount of chemical compounds [15, 58]. The simplicity in the composition of the plastic-derived biocrudes will be advantageous for the separation and recovery of the monomers and/or chemicals.

The biocrude obtained from HTL of PC consisted of only four compounds: phenol, isopropylphenol, isopropenylphenol, and Bisphenol A (BPA) (see the chromatogram in Figure 11). Under hot compressed water, the ether bonds within carbonates (in PC) underwent to hydrolysis, producing BPA, whose partial cracking formed the other three phenolics. Phenolic compounds are valuable commodity chemicals [59], commonly used in household products or as intermediates for industrial synthesis. BPA is instead the monomer used in PC production, as highlighted in the reaction reported in Figure 11. In order to increase the recovery in BPA, its cleavage into smaller compounds should be prevented, for example applying more moderate process conditions (i.e. reduced temperature and/or shorter residence time) [60]. The process conditions used in this work were in fact optimized for biomass conversion and used for plastics in prospective of biomass/plastic co-liquefaction. However, reducing the severity of the process conditions could result in PC depolymerization to BPA, without further degradation. Hence, with high recovery in biocrude (99.8%) containing PC monomer and valuable chemicals, HTL offers a highly promising solution for an improved circular economy of PC plastics.

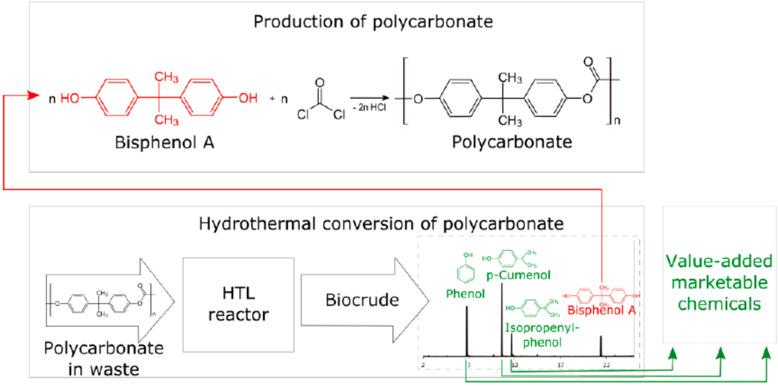


Figure 11: Schematic overview on how PolyCarbonate (PC) circular economy could be improved through HTL with targeted recovery of its monomeric constituent (Bisphenol A) and valuable chemicals.

Similarly as for PC, the biocrude obtained from the hydrothermal conversion of SB showed a simple product slate: it was constituted of a limited number of compounds of aromatic structure in the C_8-C_{16} range (see the GC-MS chromatogram reported in Figure 12). These chemicals, monoaromatics and biphenyls, may be handled by standard refineries as a BTX pool or as a pool of gasoline compounds. Moreover, among the aromatic compounds, the monomeric Styrene was identified (compound n.3 in Figure 12); this may be used for the production of new SB plastic. The other monomer, butadiene, was not detected instead. Due to its high volatility (it is a gas at standard conditions), it is likely that butadiene was transferred to the gas phase; future investigations should confirm this. Furthermore, to uncover the full potential of chemical recycling through HTL, the heavy fraction of the SB biocrude, accounting for 60% in weight (see the TGA curve in Figure 4 of Paper [A]), should be qualitatively investigated. In contrast, the biocrude obtained from PC conversion was almost fully characterized by GC-MS, as the volatile fraction represented the 80% of the biocrude. From the elemental composition (Table 4) and the GC-MS qualitative characterization, it appears that SB primarily converted into hydrocarbons; this eased the recovery of the biocrude, which spontaneously separated from the aqueous phase without recurring to any solvent. All in all, SB resulted highly susceptible to hydrothermal processing, with a consistent production of biocrude (80.8%), which may be used both for the production of new polymers and for the recovery of value-added chemicals.

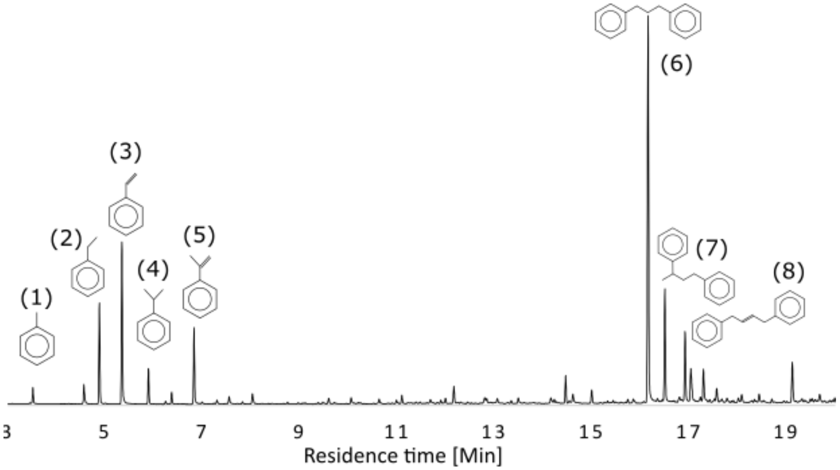


Figure 12: Chromatogram of the volatile fraction of the biocrude obtained from hydrothermal processing of Styrene-butadiene (SB). From the left to the right, at increasing residence time, the following compounds were identified: (1) toluene; (2) ethylbenzene; (3) styrene; (4) benzene, (1-methylethyl)-; (5) amethylstyrene; (6) benzene, 1,10-(1,3-propanediyl)bis-; (7) benzene, 1,10-(1-methyl-1,3-propanediyl)bis-; (8) benzene, 1,10-(2-butene-1,4-diyl)bis- [A].

Another example of how HTL processing can improve plastic circular economy is represented by PLA conversion. In this case, the focus of the investigation was on the aqueous phase, since neither biocrude nor solids were produced while from the carbon balance a great extent of the carbon was recovered in that phase. The organic compounds were extracted following the procedure described in [61], and successively analyzed by GC-MS, which detected the presence of various compounds: primarily carboxylic acids (e.g. acetic acid, propanoic acid, butyric acid, lactic acid, valeric acid, 2-methyl butyric acid), alcohols, and ketones in the C_5-C_6 range [A]. Lactic acid, the monomer from which PLA is produced, may therefore be extracted for the production of new plastic, while the other compounds hold potentials as marketable chemicals. Additionally, the fact that compounds are recovered in the aqueous phase may be advantageous when co-processing PLA with other plastics, which convert into biocrude, as the recovery would be eased by the fact that the products distributes in different phases.

A fourth example of an improved circular economy of the plastics through HTL is represented by PBT and PET conversion. In line with a previous study showing that these two polymers are intolerant to hot water [62], the present work observed that PBT and PET were subjected to hydrolysis and that full degradation was achieved within short residence times. In fact, high yields of solid products were obtained after HTL of PBT (50.8%) and PET (68.5%). The solids were qualitatively characterized and it was successively found that they consisted of an individual compound: terephtalic acid (TPA), one of the two monomers from which both PBT and PET are produced (see the chromatogram in Figure 13). The other monomers (butanediol for PBT and ethylene glycol for PET) were not detected; however, they may be dissolved in the aqueous phase, as previously observed in [62]. Moreover, the authors observed a decrease in ethylene glycol yields at increasing temperature; this was linked to the presence of acetaldehyde and diethylene glycol, formed by dehydroxylation and dimerization of ethylene glycol. The precipitation of the monomeric constituent TPA facilitated its chemical recovery through HTL, resulting highly prospective for the co-processing of PBT/PET with polymers converting into biocrude, as, also in this case, the recovery of the products is expected to be simplified by the spontaneous distribution among different phases.

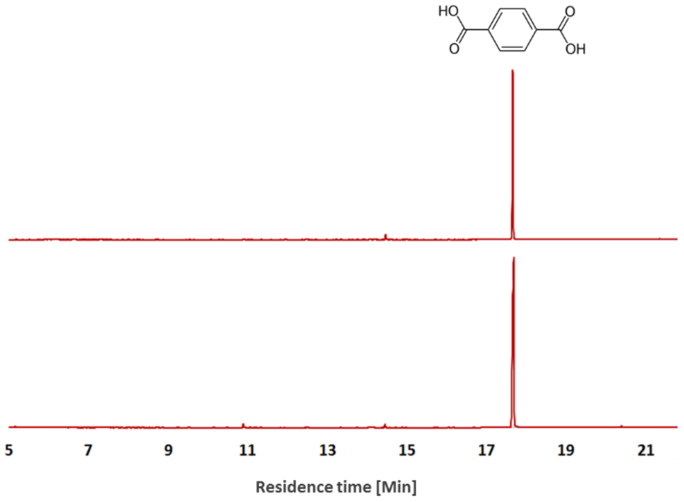


Figure 13: Chromatograph of the solids obtained from hydrothermal processing of PBT (top) and PET (bottom) showing the presence of a single compound: the monomeric Terephthalic acid.

The characterization of the biocrudes derived from PPO, PMMA, PVA, and POM conversion was not as straightforward as for the other investigated polymers, either because of the reduced volatility of the biocrudes or as the monomeric compounds could not be identified. The main outcomes from the conversion of these polymers in HTL from Paper [A] are reported below:

PPO conversion produced high yields of biocrude (78.9%), which resulted the least volatile of the investigated polymers with the residual non-volatile fraction accounting for 70% of the total weight (see TGA curves, Figure 4 of Paper [A]). The volatile fraction (30 wt.%), analyzed by GC-MS, was found being constituted of various methyl-, ethyl-, and propyl- substituted benzenes in line with the H/C ratio of 1.15 (see Table 4), which suggested the biocrude would have aromatic structure. The elemental analysis detected the presence of oxygen (6%); however, as no oxygenated compounds were identified from the GC-MS, these are assumed to be in the heavy fraction of the biocrude.

PMMA conversion produced a biocrude (48.0%) almost fully characterized by GC-MS, as it is constituted of low boiling point compounds (at 300 °C more than 80% was volatilized from TGA curves in Figure 4 of Paper [A]) . The biocrude was a mixture of esters and carboxylic acids in the C_6-C_9 range. Esters were formed from PMMA cracking and cyclization, while carboxylic acids were the result of esters hydrolysis. The main identified compounds were: cyclohexane carboxylic acid, methyl ester, pentanoic acid, 4-methyl, methyl ester; pentanedioic acid, 2,4-dimethyl-, dimethyl ester and 4,4-dimethyl mono-methylglutarate, methyl ester. The monomer MMA was not detected; however, the high TOC of the aqueous phase together with its marked acidity (pH 2.8) suggests that MMA may be dissolved in the aqueous phase.

PVA conversion led to a substantial production of biocrude (35.4%), of which the majority was volatile (60%). The GC-MS showed that the volatile fraction of the biocrude has aromatic structure (e.g. phenol, benzyl alcohol, benzoic acid, cumenol), in line with the elemental analysis, which suggested the presence of aromatic oxygenated, showing a H/C of 1.32 and an oxygen content of 9%. Having the biocrude an aromatic structure, PVA conversion through HTL results prospective for co-processing with PC, SB, and PPO, whose conversion similarly led to biocrudes with aromatic structure.

Respect to the other polymers converting into biocrude (i.e. PC, SB, PPO, PMMA, and PVA), POM liquefaction led only to a smaller production of biocrude (13.7%), and some solids (8.0%), while most of the carbon was recovered in the aqueous phase (with highest TOC of 25.0 g L^{-1}). This high carbon content may be explained by the presence of formaldehyde and methanediol, as the thermal decomposition of POM produces formaldehyde by end-chain initiation followed by depolymerization [63], and formaldehyde is highly soluble in water and, reacting, produces methanediol by hydration [64]. The biocrude was found to be a mixture of high (40%) and low (60%) boiling point compounds, with the latter being made of phenols (e.g. dimethyl, trimethyl, and tetramethyl phenols) and ketons (e.g. 2-pentanone (4-hydroxy-4methyl) and 2-cyclopenten-1-one (2,3,4-trimethyl-)).

Although at this stage the monomeric constituents were not detected in case of PPO, PMMA, PVA, and POM, the conversion of these polymers through HTL still remains a prospective solution for their valorization via chemical recycling.

3.4 Co-processing of plastics

Based on the outcomes of the study conducted on single polymers, preliminary investigations on mixed fractions of plastics explored possible synergetic effects. The following four plastic mixtures were therefore examined: PC/PMMA, PC/SB/PPO, PC/PBT, and SB/PBT. The PC/PMMA mixture (50:50) was chosen as both polymers, when hydrothermally processed individually, converted into biocrudes primarily constituted of volatile compounds (approx. 80% volatilized at 300 °C, see Figure 4 in Paper [A]). The PC/SB/PPO mixture (33:33:33) was chosen as all polymers converted into biocrudes with an aromatic structure, though PC-derived biocrude was primarily constituted of light compounds, while the biocrudes obtained from SB and PPO were found to be the least volatile. Finally, PC/PBT and SB/PBT mixtures (both 50:50) were selected since one of the polymer (PC or SB) primarily converted into biocrude, while the other one (PBT) into solids. The main reason for the latter investigation was to assess whether Terephtalic acid could still be precipitated out as a solid, while simultaneously obtaining a high yield of biocrude.

The yields in biocrude and solids obtained from the hydrothermal processing (400 °C, 15 min, no catalyst) of the above mentioned plastic mixtures are reported in Figure 14 and Figure 15, respectively. The calculated yields are presented next to those obtained from the experiments, based on the values obtained from the conversion of the single polymers and the ratios used in the mixtures.

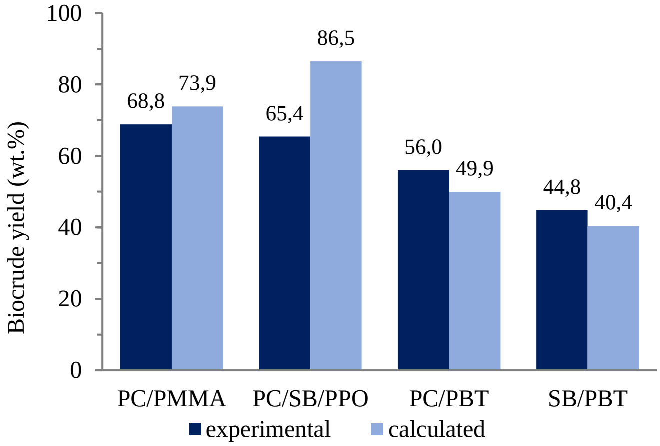


Figure 14: Biocrude yields obtained from HTL conversion of plastic mixtures.

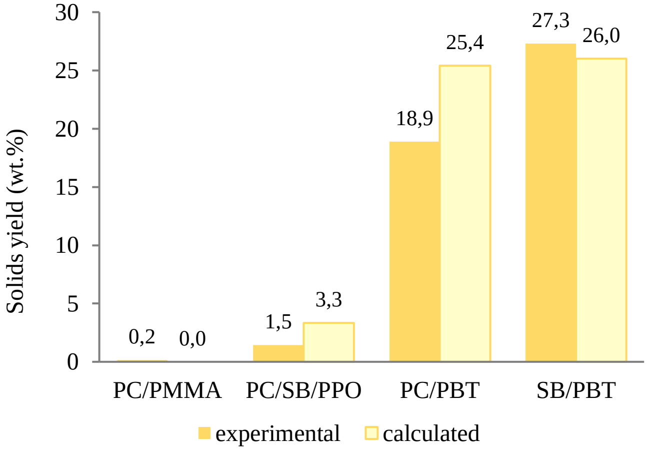


Figure 15: Solids yields obtained from HTL conversion of plastic mixtures.

PC/PMMA conversion resulted in a high yield of biocrude (68.8%), only slightly lower than the expected calculated value (73.9%), while no solids were produced as similarly observed when the two polymers were individually processed. Further investigations will be required to assess the quality of PC/PMMA derived biocrude, which is expected to be a combination of both aromatic and non-aromatic compounds. Likewise, PC/SB/PPO conversion primarily resulted in the production of biocrude

(65.4%). Though biocrude production was elevated, it was significantly inhibited since a higher value was expected from the calculated yield (86.5%). The solids yield (1.5%) in Figure 15 refers to the fraction of solids, which could be effectively collected; however, PC/SB/PPO conversion produced more solids and unconverted material, which explains the reduction in biocrude yield. Finally, the HTL conversion of PC/PBT and SB/PBT mixtures simultaneously produced high yields of biocrude oil (56.0% and 44.8%, respectively), which are higher when compared to the calculated ones (49.9% and 40.4%, respectively). Moreover, high recoveries of solids were obtained; that could be linked to the precipitation of Terephtalic acid. A partial dissolution of the TPA in the biocrude may explain the higher recoveries in the biocrude and lower recoveries in solids obtained from the PC/PBT mixture. The outcomes of this preliminary investigation on mixture of polymers appear prospective and, once again, indicate that HTL is able to offer a sustainable alternative for the handling of waste plastic encompassing their chemical recycling.

3.5 Challenging plastic polymers

The behavior of high-density plastics when hydrothermally processed was the main focus of Study 1 in this PhD project, since the recycling of these polymers represents a great challenge for plastic recycling industries. However, with exception of PET, these high-density plastics are not the most used. In fact, half of the plastic demand is associated to Polypropylene (PP), low-density Polyethylene (LD-PE), and high-density polyethylene (HD-PE), as shown in Figure 16.

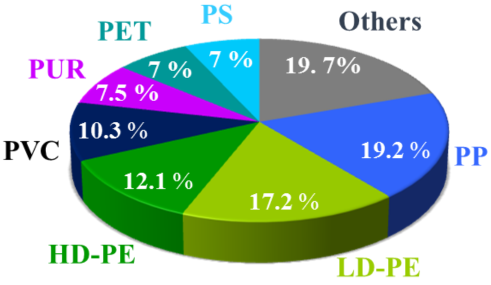


Figure 16: European plastic demand by polymer type [65].

As a direct consequence, large amounts of plastic wastes are produced from the use of these polymers. If properly sorted, their recycling appears straightforward; however, if mixed with other plastics or especially with organic material, their recycling may be compromised. There is to date an increased interest in assessing how these polymers behave when hydrothermally processed and therefore, a preliminary investigation was also conducted on two largely consumed plastics. PP and LD-PE were individually processed at 400 °C for 15 min. However, only unconverted plastic material was detected inside the reactors, as shown in Figure 17.

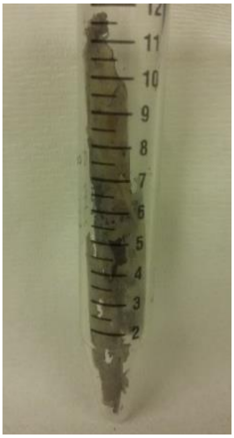


Figure 17: Unconverted plastic material collected after hydrothermal processing of LD-PE using the following conditions: 400 °C, 15min, without catalyst.

The incomplete degradation of these plastic polymers, under the same process conditions adopted for high-density plastics, suggested the need for applying more severe process conditions for PP or LD-PE conversion: higher reaction temperatures or longer residence times. The isothermal decomposition of LD-PE was investigated through TGA in N_2 atmosphere at 400 °C, 425 °C, and 450 °C. This investigation showed that applying higher temperatures (in particular when comparing 400 °C to 450 °C) the polymer is decomposed in a short time (see TGA curves in Figure 18).

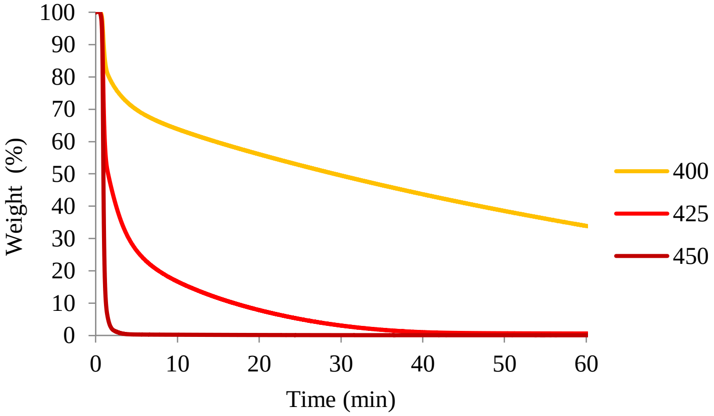
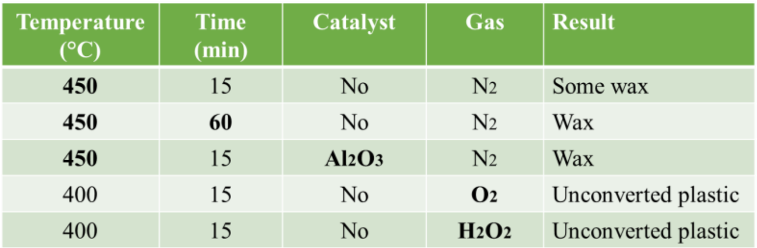


Figure 18: Isothermal decomposition curves of LD-PE in N_2 atmosphere.

Therefore, the first attempt for successfully converting LP-PE was to increase the reaction temperature to 450 °C; however, this still resulted in the recovery of waxy compounds. A second attempt was consequently done using the same higher temperature in addition to a longer residence time of 60 min. More wax was recovered, though the conversion remained very limited. In order to maintain a shorter residence time (15 min), the addition of Al_2O_3 catalyst was also investigated; still leading to a limited amount of waxy product. Therefore, although LD-PE showed to be prone to thermal degradation in N_2 (without water as medium), when hydrothermally processed it showed to be recalcitrant to degradation, even when more severe processing conditions (i.e. 450 °C and 60 min) were applied. Slower degradation of PE in supercritical water respect to thermal cracking was previously observed by [66], who additionally reported that water molecules also intervene and inhibit the further decomposition or recombination of the degradation products. Thermal cracking is the preferred depolymerization mechanism as no heteroatoms or reactive sites are found in PE plastics [67].

As oxidation of LD-PE is known to effectively degrade the polymer [68], the use of oxidizing agents (i.e. O_2 and H_2O_2) was additionally investigated. Despite the successful result reported in literature using O_2 as oxidizing agent, only unconverted material was collected in the present study both when using O_2 and H_2O_2. All the conditions additionally explored for LD-PE decomposition under hot compressed water are summarized in Table 5. Regardless of various attempts, the degradation LD-PE through HTL still remains to be further investigated: using higher temperatures (above 450 °C), using a lower plastic loading, and in co-processing with biomass.

Table 5: Conditions used to investigate the hydrothermal processing of LD-PE. The changes in the process conditions respect to the initial conditions (400 °C, 15 min, no catalyst, in N_2) are highlighted in bold.



Temperature (°C)	Time (min)	Catalyst	Gas	Result
450	15	No	N_2	Some wax
450	**60**	No	N_2	Wax
450	15	**Al_2O_3**	N_2	Wax
400	15	No	**O_2**	Unconverted plastic
400	15	No	**H_2O_2**	Unconverted plastic

Chapter 4

HTL of willow irrigated with wastewater

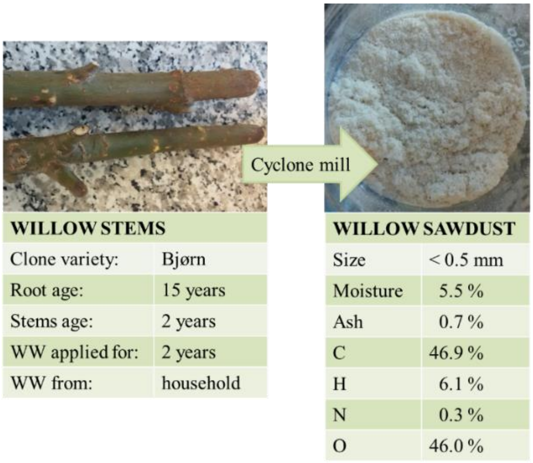
4.1 Willow vegetation filters

Willows are increasingly cultivated in short rotation coppice (SRC), where their fast-growing characteristic is exploited for producing large amounts of biomass, primarily used as renewable carbon source for heat and power generation [69]. Willows find further application in the phytoremediation of contaminated soils. In this case, their optimal capacity to absorb elements from the soil through their roots is exploited for purification of soils from the presence of heavy metals [70-72]. Similarly, willow are increasingly used as vegetation filters for the purification of wastewater. The wastewater effluent is used for irrigation of willow plants, which are planted in confined areas; in this way, nutrients and metals contained in the wastewater are absorbed through the roots and transferred to the plants avoiding or limiting the need for external input of fertilizers. The use of willows as vegetation filters is of particular interest, as they offer a solution to the management of wastewater streams, while, at the same time, crops yields are increased [73, 74]. When willows are combusted for heat and power generation, the heavy metals contained in the biomass are recovered in the ashes [75]. Various technologies are available and still under investigation for the recovery of heavy metals and nutrients, as phosphorus, from combustion ashes [76, 77]; however some elements, as sulfur and nitrogen, are irreversibly lost when biomass is combusted [78, 79].

In Study 2 of the present PhD project we propose to alternatively process wastewater irrigated willow through HTL: the willow biomass is converted to biocrude oil, while the inorganics are transferred to the HTL products. According to this new process configuration, the produced biocrude may be upgraded for fuel production; the nutrients, in particular the fundamental macronutrients (e.g. N, P, K), may be circulated back to the land as fertilizers, if properly recovered. Therefore, the aims of Study 2 were to investigate the supercritical hydrothermal processing of wastewater irrigated willow, to assess biocrude yield and its quality, and to explore in which phases the inorganics tended to be recovered after HTL.

4.2 Characterization of the willow

The wastewater irrigated willow was a clone variety (Bjørn), specifically developed to achieve high biomass yield and, at the same time, high absorption of the nutrients. The willow plants were irrigated with untreated household wastewater (WW) and sludge for two years before stems were cut and provided to us (see Figure 19, left side). Since the biomass was delivered in the form of stems, it was necessary to cut it into smaller pieces and to successively mill it, in order to obtain a fine sawdust (see Figure 19, right side). The milling procedure, that in our case resulted necessary to ease the loading into the micro-batch reactors, would have been done also at larger continuous scale to allow the pumping of the feed-slurry. For example, in the continuous unit CBS1 at Aalborg University the particle size of woody biomass is reduced using a hammer mill [43].



WILLOW STEMS	
Clone variety:	Bjørn
Root age:	15 years
Stems age:	2 years
WW applied for:	2 years
WW from:	household

WILLOW SAWDUST	
Size	< 0.5 mm
Moisture	5.5 %
Ash	0.7 %
C	46.9 %
H	6.1 %
N	0.3 %
O	46.0 %

Figure 19: On the left, willow stems as received with details relative to the plant and the irrigation regime. On the right, the willow sawdust obtained after milling the stems, with results from moisture analysis, ash content, and CHN elemental composition (details from [B]).

The moisture content measured after the milling was 5.5 wt.% [B]; therefore, demineralized water was added to produce a 20 wt.% dry matter slurry. The ash content, after 3 h at 775 °C, resulted being 0.7 wt.%. Comparing the ash content of the willow used in the present study with the ash content of various willows not irrigated with wastewater from the Phyllis 2 database [80], the latter result having a higher ash content (1.06-2.50 wt.% on d.b.). As we could not directly compare the ash content of the investigated willow biomass with the values of other wastewater irrigated willows, it remains unclear whether we should have expected higher levels of ash or the ash content was representative for willows irrigated with wastewater. The HHV of the willow biomass, calculated with the formula described in [45], resulted being 18.8 MJ kg^{-1}.

The composition of the inorganic fraction was examined by ICP and the results on the concentrations of the investigated elements are reported in Figure 20. It appears that calcium and potassium have significantly higher concentrations (4-7 times higher) as respect to the other explored inorganics. The concentration of phosphorus, iron, magnesium, and sulfur resulted in range of 200-300 ppm, while a minor amount or traces of copper, manganese, sodium, and zinc were detected. It was further observed that the mass fraction of the elements investigated through ICP does not sum up to the detected level of ash; therefore, the remaining part could be associated to the presence of other elements, such as aluminum, lead, or nickel, which were not investigated through ICP [B].

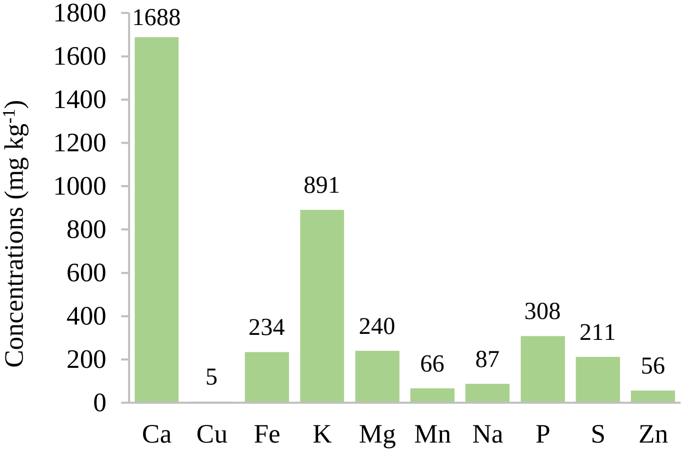


Figure 20: Concentrations of inorganic elements in the dried willow sawdust detected through ICP (data from [B]).

4.3 Biocrude production

The supercritical HTL conversion of wastewater irrigated willow produced high yields of energy-dense biocrude (39.7%) and minor quantities of solids (10.8%) (see Figure 21). The remaining fraction was recovered as organics dissolved in the aqueous phase (TOC of the aqueous phase: 25.1 g L^{-1}) and in the gas phase (75.2 vol.% of CO_2, 19.0 vol.% of H_2 and minor fractions of CH_4 and CO) [B]. The liquefaction of the willow biomass led to a concentration of the carbon in the biocrude: the carbon mass fraction increased from 46.9% in the willow to 78.2% in the biocrude, with a corresponding carbon recovery of 66.1% [B]. The use of supercritical conditions resulted in a significant reduction of the oxygen mass fraction from 46.0% in the biomass to 12.4% in the biocrude. As a consequence, the HHV doubles from 18.8 MJ kg^{-1} in the willow biomass to 36.0 MJ kg^{-1} in the biocrude, with a corresponding energy recovery of 76.1%.

The effects of hydrothermal processing on the elemental composition of the willow biomass are highlighted in the Van Krevelen diagram (see Figure 21), which shows that decarboxylation reactions prevailed on dehydration reactions in the production of biocrude.

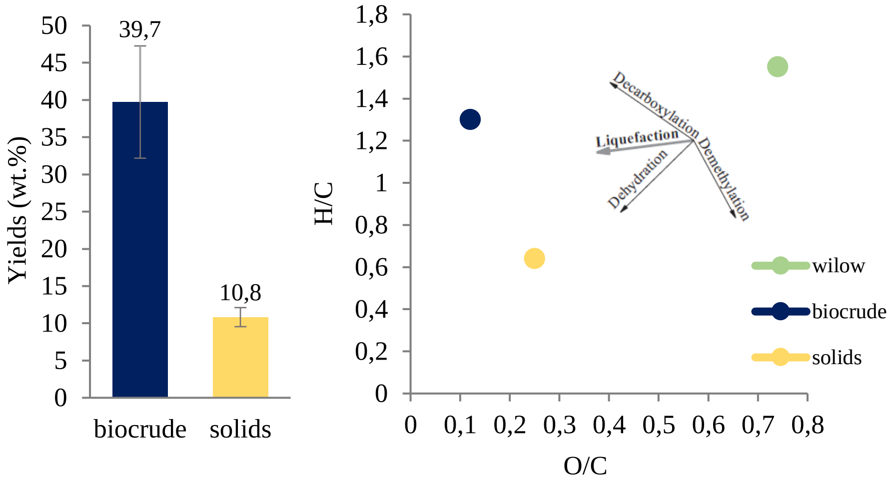


Figure 21: Biocrude and solids yields after HTL conversion of wastewater irrigated willow at supercritical conditions (diagram to the left). Van Krevelen diagram showing H/C and O/C atomic ratios relative to willow, biocrude, and solids (diagram to the right).

The TG analysis showed that the biocrude was constituted of both low and high boiling point compounds (see Figure 2 in Paper [B]). The volatile fraction (i.e. the fraction with boiling points below 300 °C) corresponded to about 50% of the total mass. This portion of biocrude was qualitatively investigated by GC-MS, which showed that the most abundant compounds were ketones and phenols. Ketones are produced from carbohydrates degradation, while phenols derive from lignin degradation [33]. Similar findings on the composition of biocrude produced from SRC willow were previously reported, where the most abundant compounds were ketones, phenols, and alcohols [81]. The elemental analysis of the biocrude showed the presence of nitrogen, however limited to the 0.95%. Among the compounds identified by GC-MS, only one was a N-containing compound (9-Octadecenamide, see Table 2 in Paper [B]). Therefore, N-containing compounds are expected to be primarily recovered in the heavy fraction of the biocrude, whose composition could not be determined by GC-MS. The concentration of N-heteroatoms in the heavy fraction of the biocrude rather than in the volatile fraction results advantageous in prospective of utilizing the biocrude for biofuels. Overall, the biocrude produced from the HTL of wastewater irrigated willow holds great potential for the production of fuels: prior to its upgrading, around 60% of the biocrude is made of compounds whose boiling range is in the same range as gasoline, jet fuel, and diesel (see Figure 2 in Paper [B]).

4.4 Recovery of the inorganics through HTL

Similarly as for the willow biomass, the presence of inorganic elements in the HTL products (i.e. in the solids, in the aqueous phase, and in the biocrude) was investigated by ICP analysis in order to determine in which phase the inorganics are transferred after the hydrothermal processing of the biomass. The ICP analysis provided information on the concentrations of the investigated elements in the HTL product phases; however, for a clearer overview of where the inorganics tended to transfer, the concentrations of the inorganics in the phases were combined with the yields of the product phases. The result was a normalized distribution of the inorganics among the HTL phases, presented in Figure 22, where the elements are reported by decreasing value of recoveries in the solids.

After supercritical HTL of the willow biomass, it appears that most of the investigated elements tended to concentrate in the solids, with recoveries above 70% by weight. A different trend was observed for sodium and potassium, which were primarily recovered in the aqueous phase, with recoveries above 88%. A third different behavior was found for sulphur: primarily recovered in the biocrude (47.7%), with the remaining part distributed among the aqueous phase (41.3%) and the solids (11.0%) [B].

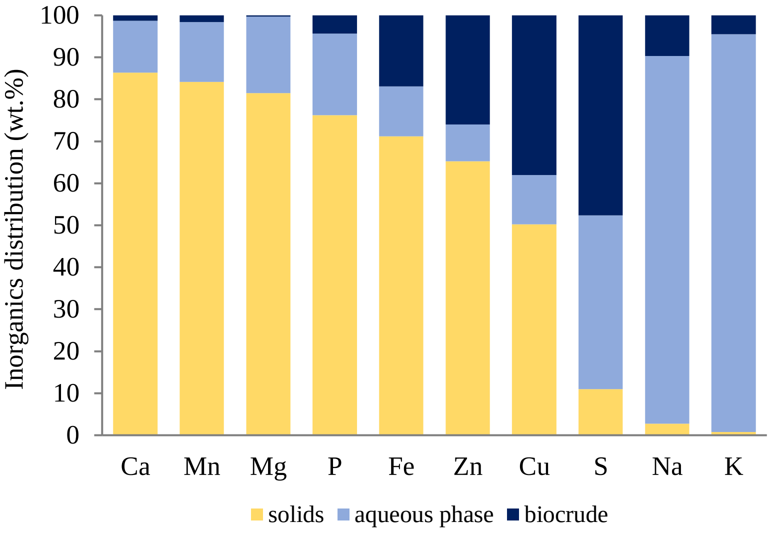


Figure 22: Normalized distribution of the inorganic elements among the products (solids, aqueous phase, and biocrude) after supercritical HTL of wastewater irrigated willow [B].

The different trends found for the distribution of the inorganics among the HTL products may be related to the different forms in which the inorganics are present in the biomass. For example, calcium, magnesium, and phosphorus are usually bound to the biomass, while potassium and sodium are frequently in the form of soluble salts [82]. This would explain why, after the hydrothermal processing of the willow biomass conducted in the present study, calcium, magnesium, and phosphorus were primarily recovered in the solids (with recoveries of 86.3%, 81.5%, and 76.3%, respectively), while potassium and sodium were almost exclusively recovered in the aqueous phase (with recoveries of 94.7% and 87.6%, respectively).

The recovery of the inorganics in the HTL products is also dependent on the process conditions used during the hydrothermal processing of the biomass. In fact, the solubility of the inorganic elements varies with the dielectric constant, which in turn changes with the temperature. For example, phosphates are soluble at low temperatures (below 200 °C), and insoluble at higher temperatures, especially in the region around the critical point of water [83]. Therefore, in Study 2, the use of supercritical conditions have favored the recovery of phosphorus in the solids, though part of it may be solubilized again in the aqueous phase, since the products were collected at room temperature due to the batch processing. In prospective of continuous HTL processing of the biomass, it is therefore advised to separate out the solids at higher temperatures (at least above 200 °C) to enhance the recovery of phosphorus in the solids.

The results on the inorganics redistribution among HTL products showed that, although heavy metals were primarily recovered in the solids, they also transferred to the biocrude to a minor extent. In case heavily contaminated biomass is processed, the presence of heavy metals in the solids might limit the direct application of the hydrochars to the soil, since the disposal of heavy metals is strictly regulated by law. On the other hand, the presence of heavy metals in the biocrude may represent a concern in its upgrading: for example, heavy metals may cause the deactivation of the catalyst used for the hydrotreating of the biocrude. The tendency of sulphur to concentrate in the biocrude implies that, when the biocrude is upgraded, hydrodesulfurization will be required along with hydrodenitrogenation and hydrodeoxygenation. Finally, as potassium and sodium were found primarily dissolved in the aqueous phase, it is proposed to use the aqueous stream as a source for irrigation in agriculture or, alternatively, it could be recirculated, reducing the need for fresh catalyst at continuous larger scale.

All in all, HTL allowed to valorize even the inorganic fraction of the willow biomass, as most of the inorganics were recovered in the solids, which were easily separated from the other products. As a result, valuable elements (i.e. P, Ca, Mg), which are fundamental nutrients in agriculture, may be recovered and re-used as fertilizers if they are in their bioavailable forms: nitrogen in the form of ammonia ($NH4^+$) or nitrate ($NO3^-$), phosphorus in the form of phosphate ($PO_4{}^{3-}$), and potassium in its ionic form (K^+) associated to an anion as sulfate or nitrate [84]. Therefore, future investigations will have focus on the forms of the inorganics in the solids and on the bioavailability of the nutrients.

Chapter 5

HTL of organic wastes

5.1 Organic waste fractions

The rapid growth in the global population and the urbanization, together with the increase in intensive farming activities to satisfy larger food demands, have resulted in a production of wastes, both of human and animal origin, greater than ever before cattle manure, swine manure, poultry manure, or fish sludge) are all examples of organic waste fractions produced from our society and whose disposal represent a great concern.

SS is the residual product from the processing of industrial or municipal wastewater in treatment plants. Landfilling of SS has been prohibited in many EU countries, while its disposal on fields has become strictly regulated by laws to prevent soil and water contamination due to the presence of pathogens, to limit the release of heavy metals, and to avoid that micro-plastics could enter in the food chain [85]. In Europe the disposal of sludge is regulated by the Directive 86/278/EEC, which sets limits on the concentration of heavy metals in sludge for application to agricultural fields and in the soil for sludge disposal on non-agricultural fields. Several EU countries have additionally established more strict limitations on the heavy metals concentration in sludge and set a maximum annual average load of heavy metals for the soil [86]. Table 6 presents the limit values for heavy metals in sludge set by EU and by some national legislations. The presence of residual plastics in SS or MSW represents an additional concern when these waste streams are treated in anaerobic digesters, as methane production is inhibited and the solid product – the digestate – cannot be applied to the soil as a source of fertilizers, if it still contains microplastics [88]. Moreover, the reduced temperatures used in anaerobic digestion do not always allow a total disruption of the pathogens [89]. Incineration with energy recovery is also practiced for effectively reducing the volume of the wastes; however, it is highly energy demanding due to the large amount of moisture contained in such type of wastes.

Table 6: Limit values for heavy metals in sludge (mg kg^{-1} DM) for application to agricultural fields. Red shaded cells indicate that national legislations have set more restrictive limits than the EU Directive [87].

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Directive 86/278/EEC	20-40	-	1000-1750	16-25	300-400	750-1200	2500-4000
Denmark	0.8	100	1000	0.8	30	120	4000
France	10	1000	1000	10	200	800	3000
Germany	10	900	800	8	200	900	2500
Ireland	20	-	1000	16	300	750	2500
Italy	20	-	1000	10	300	750	2500
Netherlands	1.25	75	75	0.75	30	100	300
Sweden	2	100	600	2.5	50	100	800

Animal manure from farming activities presents similar waste management issues as SS due to the presence of bioactive chemicals (BACs) (e.g. pathogens, pharmaceuticals, hormones, and antibiotics), which represent an increasing concern to human health and agricultural activities [90, 91]. In fact, most of the antibiotics administrated to animals are excreted in an unaltered state [92]; therefore, when manure is applied to the fields, antibiotics are released to the environment and microorganism that enter into contact with these substances develop resistance to them [93]. Similarly, estrogenic hormones excreted from human and animals may contaminate surface and ground water [94], and in this case, very low concentrations (10-100 ng/L) can have adverse effect on the reproductive system of vertebrates [95]. Hydrothermal processing represents a safe and efficient solution for the handling of biowastes, since the majority of the BACs is fully removed thanks to the high temperatures used in hydrothermal carbonization and liquefaction [96-100].

Though the disposal of human and animal wastes represents a pronounced concern, these waste fractions are also great sources of carbon and of valuable inorganic elements (e.g. N, P, K), largely used in agriculture. Particular attention is nowadays set on the recovery and the circular economy of phosphorus; this element is in fact among the fundamental macronutrients required in agriculture, and its availability is finite and limited to its extraction from rocks [101]. SS production in EU is estimated to account for 13 million dry tons in 2020 [102]; every year, this corresponds potentially to 300,000 ton of phosphorus that could be recovered from this waste fraction (assuming phosphorus represents the 2.3 % in weight of SS [103]). Similarly, swine and cow manure production in EU accounts respectively for 14 and 295 million tons of dried material [104], from which 125,000 tons and 175,000 tons of phosphorus could be extracted and reintroduced on the market (assuming phosphorus accounts for the 0.9% in weight in swine manure [105] and for the 0.6% in weight in cow manure [106]). The use of phosphorus in the agricultural sector was reported being 1.17 million tons in 2017 in EU [107]; therefore, based on the above calculations, an appropriate recovery of the phosphorus from animal and human wastes would significantly contribute to supply the phosphorus agricultural demand in Europe.

In Study 3 of the present PhD project we propose to treat organic wastes of animal and human origin through HTL. Among the advantages, HTL allows avoiding the expensive drying step required in other thermochemical processes and it excludes all the health risks associated to the presence of pathogens, as the efficient removal of these compounds is granted after processing at high temperatures (>300 °C) [108]. Additionally, the conversion through HTL allows valorizing both the organic fraction producing biocrude oil and the inorganic fraction by recovering the inorganics in the HTL products, as visualized in Figure 23. The objectives of Study 3 were to assess the effect of sub- and supercritical conditions and of the addition of K_2CO_3 catalyst on the liquefaction of organic wastes with focus on the biocrude. Furthermore, the study aimed to investigate the inorganic fraction and the elements redistribution after HTL to evaluate the recovery potentials.

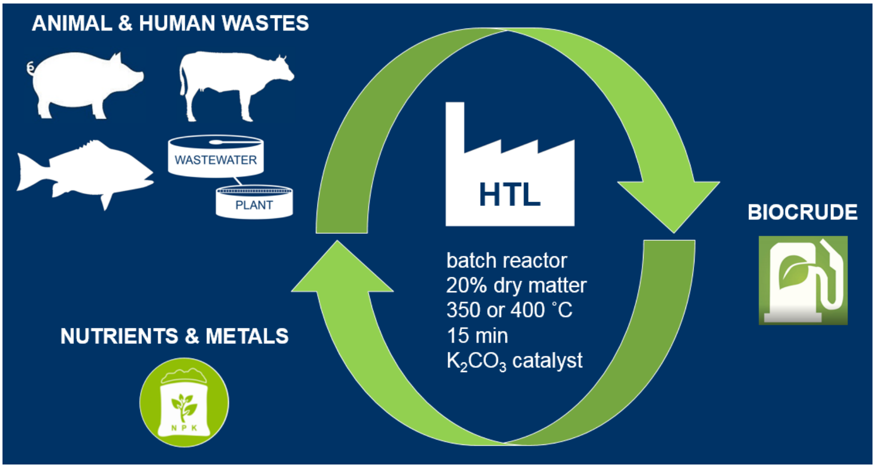
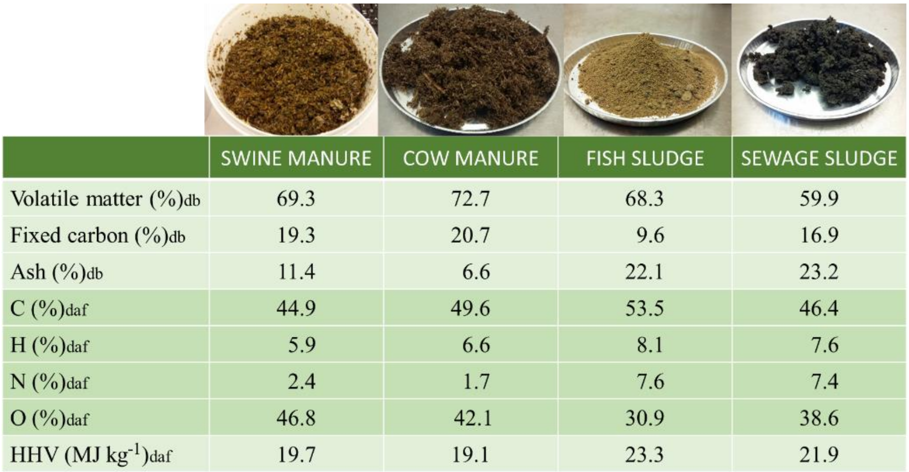


Figure 23: Conceptual overview of how animal and human waste fractions are valorized through HTL processing with the simultaneous production of biocrude for the production of advanced biofuels and the recovery of valuable inorganic elements.

5.2 Characterization of the organic wastes

The organic waste fractions, investigated in Study 3 of the present PhD project, were swine manure (SM), cow manure (CM), fish sludge (FS), and secondary sewage sludge (SS) (see the pictures above Table 7). Before being processed through HTL, the waste fractions were characterized in order to be able to establish how their chemical composition and structure would affect biocrude production and its quality.

Table 7: Proximate and ultimate analysis of the organic waste fractions investigated in Study 3 (adapted from Table 1 in [C]).



	SWINE MANURE	COW MANURE	FISH SLUDGE	SEWAGE SLUDGE
Volatile matter (%)$_{db}$	69.3	72.7	68.3	59.9
Fixed carbon (%)$_{db}$	19.3	20.7	9.6	16.9
Ash (%)$_{db}$	11.4	6.6	22.1	23.2
C (%)$_{daf}$	44.9	49.6	53.5	46.4
H (%)$_{daf}$	5.9	6.6	8.1	7.6
N (%)$_{daf}$	2.4	1.7	7.6	7.4
O (%)$_{daf}$	46.8	42.1	30.9	38.6
HHV (MJ kg^{-1})$_{daf}$	19.7	19.1	23.3	21.9

The volatile matter represented about 70% in weight of the dried biomasses (see Table 7), except for SS, for which a lower percentage (60%) was measured. The inorganic fraction accounted for about 20% of the dried weight for the sludges (22.08% for FS and 23.19% for SS), while lower ash contents were measured in the manures (11.40% in SM and 6.59% in CM). The fixed carbon was calculated being among 10% and 20%, with increasing values in the following order: FS<SS<SM<CM [C].

The elemental analysis of the feedstocks highlighted that the nitrogen content in the sludges was significantly higher than in the manures: 7.55% for FS and 7.37% for SS, as compared to 2.39% for SM and 1.68% for CM [C]. Higher levels of nitrogen in the biomass could potentially result in biocrudes containing more N-heteroatoms compounds, and consequently requiring a more severe upgrading in terms of H_2 supply and process conditions to reach the required denitrogenation extent.

As for the inorganics content and for the nitrogen content, similarities among the two typologies of manure and among fish and human sludge were found when exploring the main constituents of the feedstocks. In fact, the manures were predominantly made of lignocellulosics (84.40% for SM and 88.70% for CM), with only minor percentages of crude proteins (14.94% for SM and 10.50% for CM) and traces of lipids (<1%) (see Figure 24). The composition of the sludges differed from that of the manures, as the main constituents were both lignocellulosics (39.77% for FS and 48.09% for SS) and proteins (47.19% for FS and 46.06% for SS), with minor percentages of lipids (13.06% for FS and 5.86% for SS) [C]. When hydrothermally processing biomass, the trend for conversion efficiency is generally the following: lipids > protein > carbohydrates [109]; therefore higher conversions were expected from the liquefaction of the sludges as compared to the manures.

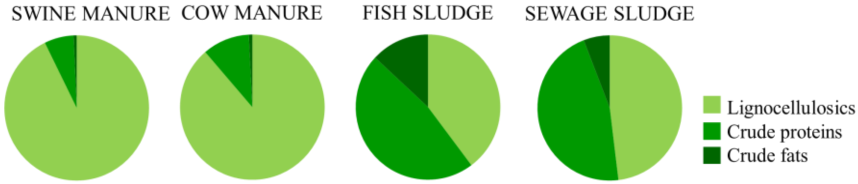
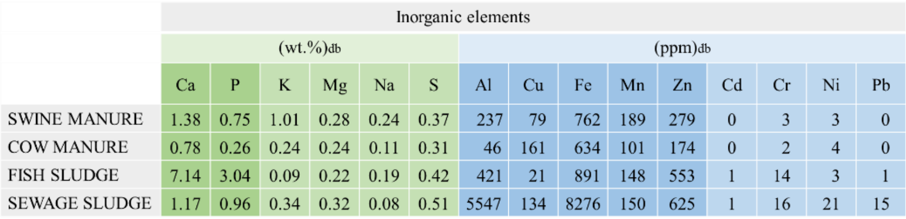


Figure 24: Composition of swine manure, cow manure, fish sludge, and sewage sludge in terms of lignocellulosics, crude proteins, and crude fats (data from Table 1 in [C]).

The composition of the inorganic fraction of the four feedstocks was investigated by ICP, and the results are presented in Table 8, where the elements are arranged in two groups depending on their concentration in the feedstocks. The main elements are highlighted in green and reported in weight percent of the dried biomass; the minor elements are highlighted in light blue and expressed in ppm.

Table 8: Inorganic elements in the waste fractions. The results of the most abundant elements are expressed in weight percent (in green), while for less abundant elements are expressed in ppm (in light blue) (data elaborated from Table S1 in [C]).



	Inorganic elements														
	(wt.%)db						(ppm)db								
	Ca	P	K	Mg	Na	S	Al	Cu	Fe	Mn	Zn	Cd	Cr	Ni	Pb
SWINE MANURE	1.38	0.75	1.01	0.28	0.24	0.37	237	79	762	189	279	0	3	3	0
COW MANURE	0.78	0.26	0.24	0.24	0.11	0.31	46	161	634	101	174	0	2	4	0
FISH SLUDGE	7.14	3.04	0.09	0.22	0.19	0.42	421	21	891	148	553	1	14	3	1
SEWAGE SLUDGE	1.17	0.96	0.34	0.32	0.08	0.51	5547	134	8276	150	625	1	16	21	15

For all feedstocks, the most abundant inorganic element was calcium, with a particularly high level registered in fish sludge (7.14%). Other abundant elements were phosphorus, potassium, magnesium, sodium, and sulfur – all essential macronutrients. The inorganics detected in lower concentrations were instead aluminum, copper, iron, manganese, and zinc. Finally, the inorganics in trace levels (below 20 ppm) were cadmium, chromo, nickel, and lead; these are instead the heavy metals whose concentration is strictly regulated by laws. Higher concentrations of aluminum and iron were detected in the SS as respect to the other feedstock (Al accounted for the 0.55% and Fe for the 0.83%) [C]. High levels of Al and Fe in sewage sludge may be explained by the addition of these elements in the wastewater treatment plant for the chemical precipitation of phosphorus [110]. The significant quantities of iron in the sewage sludge explains why the ash obtained from sewage sludge had a red color, which differed from the grey color of the ash obtained from the other feedstocks (see Figure 25).

Figure 25: Ash from fish sludge (left) and from sewage sludge (right) after 3h at 775°C.

5.3 Biocrude production

After sub- and supercritical HTL of the organic waste fractions, from one to two thirds of the biomass fed into the reactors was converted into biocrude. Particularly high yields were obtained from the conversion of FS (47.2-59.1%) and SS (35.7-44.5%), while the production of biocrude from the liquefaction of the manures resulted more moderate (34.8-41.0% for SM and 32.3-41.0% for CM) [C]. This outcome resulted in line with our hypothesis based on the composition of the biomasses: lower yields were expected from the liquefaction of the manures, mainly constituted of lignocellulosics, as respect to the sludges, made of lignocellulosics, proteins, and lower percentages of lipids. Moreover, a correlation was found among biocrude yields and fixed carbon in the feedstock: the lower the level of fixed carbon in the feedstock, the higher the production of biocrude. The results on the biocrude yields for the four feedstocks at the different process conditions are reported in Figure 26; the elemental compositions of the biocrudes, together with HHV, carbon and energy recoveries are instead presented in Table 9.

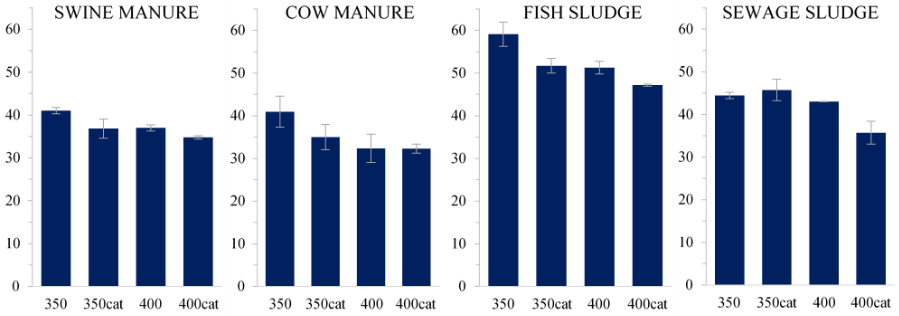
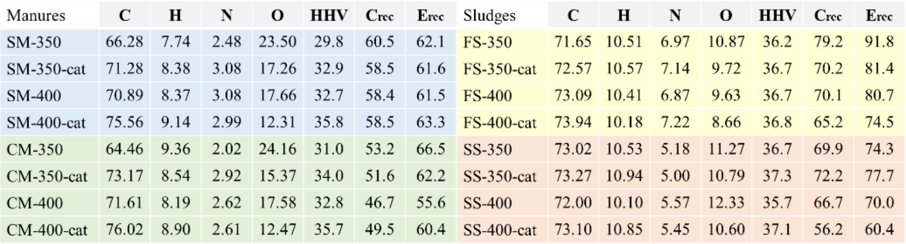


Figure 26: Yields in biocrude (on a dry ash-free basis) obtained from the HTL of swine manure, cow manure, fish sludge, and sewage sludge at the different process conditions (from [C]).

The use of supercritical conditions (400 °C), with respect to subcritical ones (350 °C) produced a significant decrease in the biocrude yield of 10%, 21%, and 13% for SM, CM, and FS, respectively [C]. This may be explained by the fact that at higher temperatures, the formation of gaseous products is favored respect to the production of oily or solid products [111]. On the other hand, the use of supercritical conditions remarkably improved the quality of the biocrudes obtained from the manures. For example, with reference to the non-catalytic runs, the carbon mass fraction increased from 66.28% to 70.89% and the oxygen mass fraction decreased from 23.50% to 17.66% for SM; while the carbon mass fraction increased from 64.46% to 71.61% and the oxygen mass fraction decreased from 24.16% to 17.58% for CM (see Table 9). Therefore, for the manure-derived biocrudes, the decrease in the yields obtained at supercritical conditions can be explained also with the increased deoxygenation extent achieved.

The addition of K_2CO_3 catalyst produced in most of the cases (with the exception for CM400 and SS350) a decrease in the biocrude yield. However, the quality of the biocrudes derived from manures noticeably improved with the addition of the catalyst both at sub- and supercritical conditions. The oxygen mass fraction in the biocrude originated from SM decreased from 23.50% to 17.26% at subcritical conditions and from 17.66% to 12.31% at supercritical conditions, while for the biocrude originated from CM it decreased from 24.16% to 15.37% at subcritical conditions and from 17.58% to 12.47 at supercritical conditions (see Table 9). The increased deoxygenation obtained from the addition of K_2CO_3 may be explained with an increase in decarboxylation reactions, usually produced by alkali catalysts [22]. An increased deoxygenation was also observed after catalytic conversion of the sludges, however in this case the decrease in the oxygen content only accounted for about 1% point (see Table 9).

Table 9: Elemental compositions (wt.%), high heating values (MJ kg^{-1}), carbon and energy recoveries of the biocrudes obtained from the HTL of swine manure (SM), cow manure (CM), fish sludge (FS), and sewage sludge (SS) at the different process conditions. Results are reported on dry ash-free basis (elaborated from Table 2 in [C]).



Manures	C	H	N	O	HHV	C_{rec}	E_{rec}	Sludges	C	H	N	O	HHV	C_{rec}	E_{rec}
SM-350	66.28	7.74	2.48	23.50	29.8	60.5	62.1	FS-350	71.65	10.51	6.97	10.87	36.2	79.2	91.8
SM-350-cat	71.28	8.38	3.08	17.26	32.9	58.5	61.6	FS-350-cat	72.57	10.57	7.14	9.72	36.7	70.2	81.4
SM-400	70.89	8.37	3.08	17.66	32.7	58.4	61.5	FS-400	73.09	10.41	6.87	9.63	36.7	70.1	80.7
SM-400-cat	75.56	9.14	2.99	12.31	35.8	58.5	63.3	FS-400-cat	73.94	10.18	7.22	8.66	36.8	65.2	74.5
CM-350	64.46	9.36	2.02	24.16	31.0	53.2	66.5	SS-350	73.02	10.53	5.18	11.27	36.7	69.9	74.3
CM-350-cat	73.17	8.54	2.92	15.37	34.0	51.6	62.2	SS-350-cat	73.27	10.94	5.00	10.79	37.3	72.2	77.7
CM-400	71.61	8.19	2.62	17.58	32.8	46.7	55.6	SS-400	72.00	10.10	5.57	12.33	35.7	66.7	70.0
CM-400-cat	76.02	8.90	2.61	12.47	35.7	49.5	60.4	SS-400-cat	73.10	10.85	5.45	10.60	37.1	56.2	60.4

With HTL, we assist to a densification of the biomass energy into the biocrude with the removal of the oxygen heteroatoms by decarboxylation, producing CO_2, and by dehydration, producing H_2O. Enhanced decarboxylation and reduced dehydration (i.e. decrease in the O/C ratio rather than in the H/C ratio) are preferred for an optimal biocrude quality and in prospective to its upgrading to fuel [112]. The Van Krevelen diagram with H/C and O/C atomic ratios of the feedstock and of the biocrudes allows visualizing the effect of HTL (see Figure 27). In the liquefaction of the manures, the oxygen removal occurred by both dehydration and decarboxylation reactions, with the latter particularly enhanced in the catalytic runs. In the liquefaction of fish sludge the oxygen was almost exclusively removed by decarboxylation. Finally, a decrease in both H/C and O/C values was observed when converting sewage sludge with decarboxylation prevailing on dehydration.

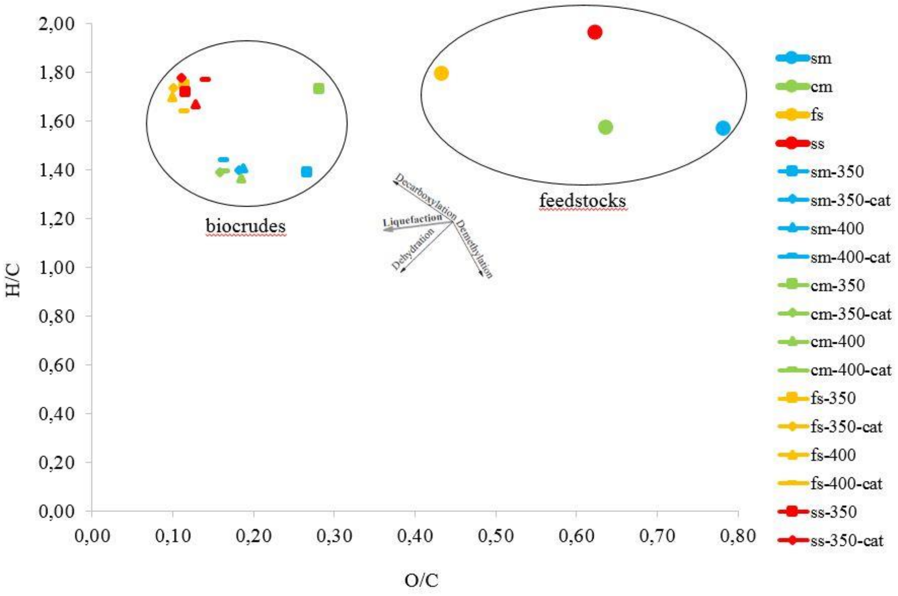


Figure 27: Van Krevelen diagram with H/C and O/C atomic ratios relative to the organic wastes used as feedstock (sm: swine manure, cm: cow manure, fs: fish sludge, and ss: sewage sludge) and to the biocrudes obtained from the HTL at the different process conditions (data from [C]).

The elemental composition of the biocrudes (see Table 9) revealed higher nitrogen contents in sludge-derived biocrudes (N: 5-7%) compared with manure-derived biocrudes (N: 2-3%). This finding was in line with the fact that the elemental composition of the feedstock (see Table 7 in Paragraph 5.2) had previously highlighted higher nitrogen content in the sludges (7.55% for FS and 7.37% for SS) as respect to its level in the manures (2.39% for SM and 1.68% for CM). The direct consequence of higher nitrogen levels in the biocrude is that sludge-derived biocrudes will require a more intense upgrading to reduce the N-heteroatoms content to the required level. The nitrogen balance revealed that about 50% of the nitrogen in the manures and in fish sludge was transferred to the biocrude, while only about 30% for sewage sludge (see Figure 6 in Paper [C]).

In order to establish which process conditions are more favorable for each biomass, it is not sufficient to look at the yields, but it is also necessary to consider the quality of the biocrudes (e.g. deoxygenation extent achieved that is reflected in the HHV). Other parameters contributing to the determination of the optimal conditions are the carbon recovery (C_{rec}) and energy recovery (E_{rec}). The carbon balance showed that, after liquefaction of the organic wastes, carbon was primarily transferred to the biocrudes with higher recoveries for the sludges (65.2-79.2% for FS and 56.2-72.2% for SS) as respect to the manures (58.4-60.5% for SM and 46.7-53.2% for CM). C_{rec} resulted almost unvaried for the manures, regardless of the process conditions, while higher C_{rec} were obtained at subcritical conditions for the sludges. Conversely, the highest HHV of manure-derived biocrudes was obtained at supercritical conditions in the presence of the catalyst (35.8 MJ kg^{-1} for SM and 35.7 MJ kg^{-1} for CM), while similar values resulted from all the process conditions for sludge-derived biocrudes (36.2-36.8 MJ kg^{-1} for FS and 35.7-37.3 MJ kg^{-1} for SS). Finally, the energy recoveries, which take into account both HHV and biocrude yields, were found to be notably higher at subcritical conditions only for the sludges (91.8% for FS and 74.3% for SS).

In conclusion, for the lignocellulosics-rich manures, the combined use of supercritical conditions and the catalyst improved the quality of the biocrudes, overcoming the loss in biocrude production. For the sludges, the use of the catalyst may be avoided with a consequent saving on its cost, crucial when operating at larger scale; on the other hand, the use of subcritical conditions may be preferable, as both higher carbon and energy recoveries can be achieved (see Table 9).

5.4 Recovery of the inorganics through HTL

In order to understand how the inorganic elements contained in the animal and human waste fractions tended to redistribute among the HTL products after liquefaction, the concentrations of the inorganics in each phase were investigated through ICP analysis. The concentrations were successively multiplied with the weight of the corresponding phase, and finally normalized to 100. The outcomes are normalized distributions of the inorganics among the HTL products after liquefaction of SM, CM, FS, and SS, and they are presented in Figure 28, Figure 29, Figure 30, and Figure 31, respectively.

Most of the investigated inorganics (Al, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Zn) were primarily recovered in the solids with recoveries above 70% in most of the cases. The remaining fraction of these elements was transferred to the aqueous phase, while only residual amounts were detected in the biocrudes. Only for the heavy metals (i.e. Cu, Ni, and Pb), higher recoveries in the biocrudes (10-30 wt.%) were registered under specific process conditions (as highlighted in Table S2 in the supplementary material of Paper [C]). Potassium and sodium showed a different behavior, with higher recoveries in the aqueous phase respect to the other inorganics. More specifically, after the hydrothermal processing of the manures, K and Na were mainly recovered in the aqueous phase with recoveries in the range 50.1-82.8 % (see Table S2 in [C]). Similarly, higher recoveries of K and Na in the aqueous phase were observed after HTL of wastewater irrigated willow in Study 2. After HTL of the sludges, K and Na were instead distributed among both the solids and the aqueous phase; nevertheless, they still exhibit a higher degree of solubility in the aqueous phase as respect to the other inorganics. Finally, S was more homogenously distributed among the different phases and, consequently, higher recoveries of S in the biocrude (among 33.5% and 66.0%, see Table S2 in [C]) were obtained as respect to the other inorganics. More specifically, the mass fraction of S detected in the manure-derived biocrudes was 0.37-0.58 wt.%, while in sludge-derived biocrudes was 0.27-1.00 wt.%. The higher S content of sludge-derived biocrudes reflects the higher S mass fraction detected in fish sludge and sewage sludge as respect to manures. In both cases, S-heteroatoms removal by desulphurization will be required for utilization as fuel. To some extent, the presence of S in the biocrude is required for an efficient upgrading, as conventional catalyst developed for crude oil upgrading are sulphided (i.e. they are activated and work in the presence of sulfur) and, therefore, low level of S in the biocrudes can negatively impact their activity [113, 114].

The use of different process conditions (sub- and supercritical and the addition of K_2CO_3 catalyst) did not affect the tendency of the inorganics to redistribute among the HTL products. However, a significant increase in the concentration of potassium in the biocrudes obtained from the catalytic runs was observed. This may suggest avoiding the use of K_2CO_3 catalyst, unless its contribution in enhancing biocrude quality (i.e. deoxygenation extent) is marked. Alkali metals have in fact a detrimental effect on the activity of the catalyst used in hydrocracking [115, 116].

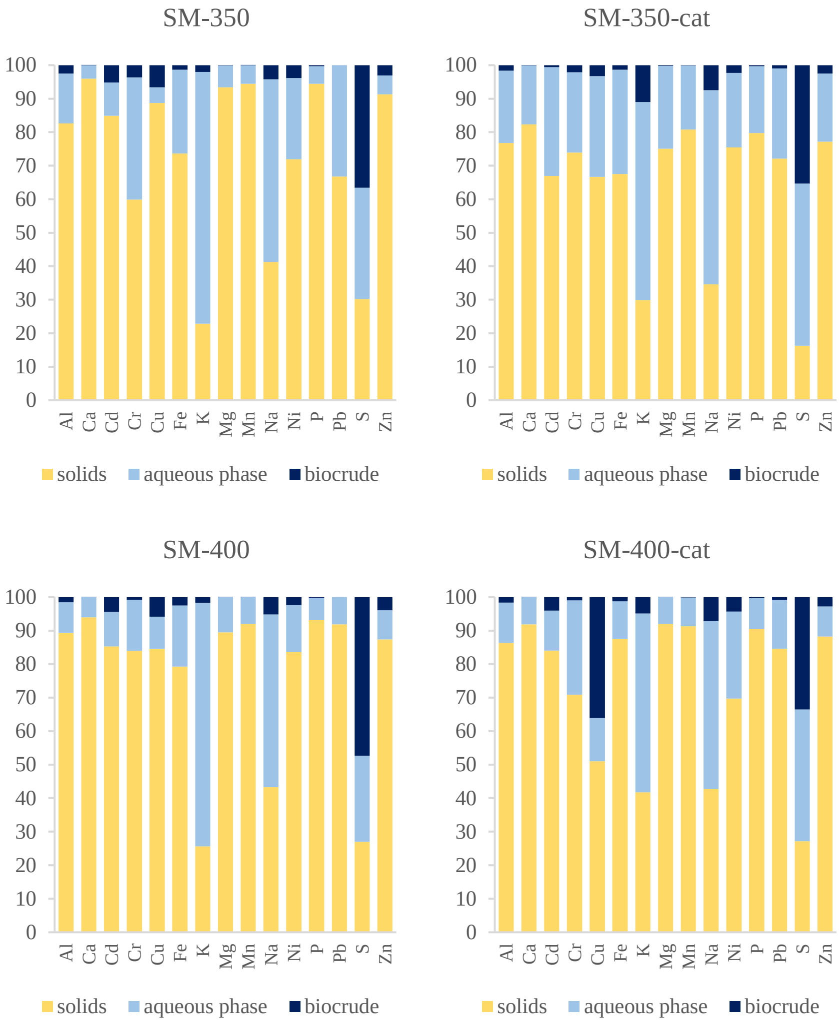


Figure 28: Normalized distribution of the inorganic elements among the products (solids, aqueous phase, and biocrude) after subcritical HTL of swine manure (SM) at the four different process conditions (350 °C without catalyst, 350 °C with catalyst, 400 °C without catalyst, 400 °C with catalyst).

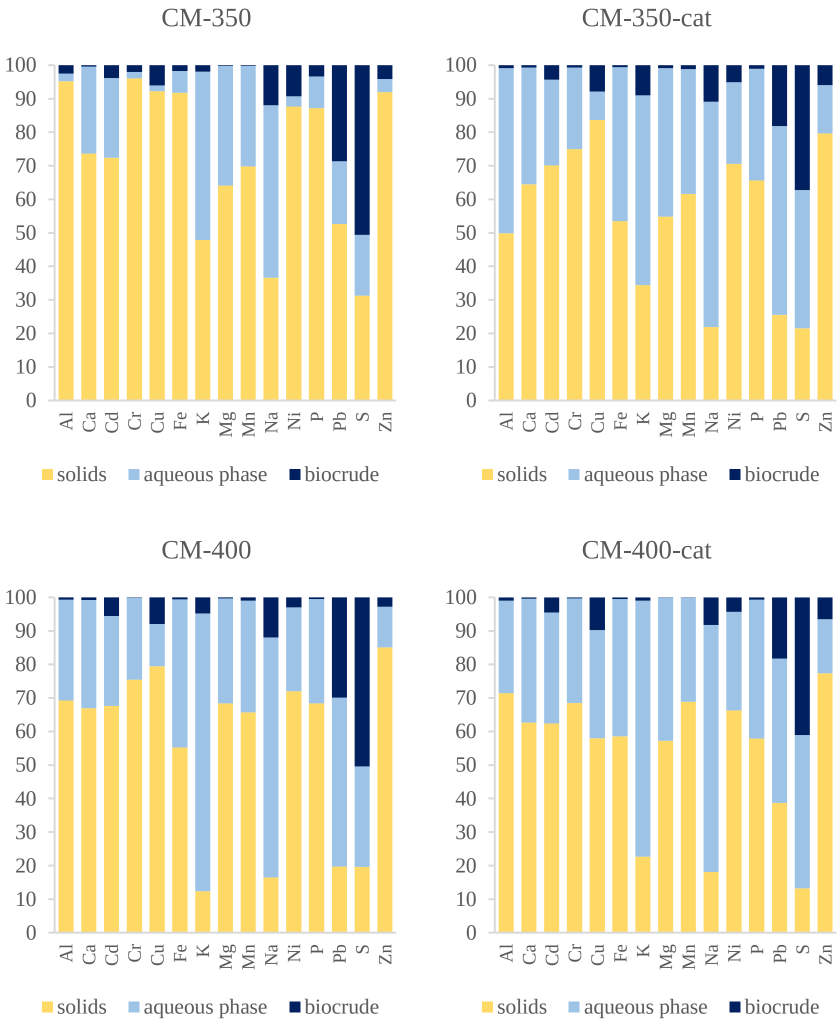


Figure 29: Normalized distribution of the inorganic elements among the products (solids, aqueous phase, and biocrude) after subcritical HTL of cow manure (CM) at the four different process conditions (350 °C without catalyst, 350 °C with catalyst, 400 °C without catalyst, 400 °C with catalyst).

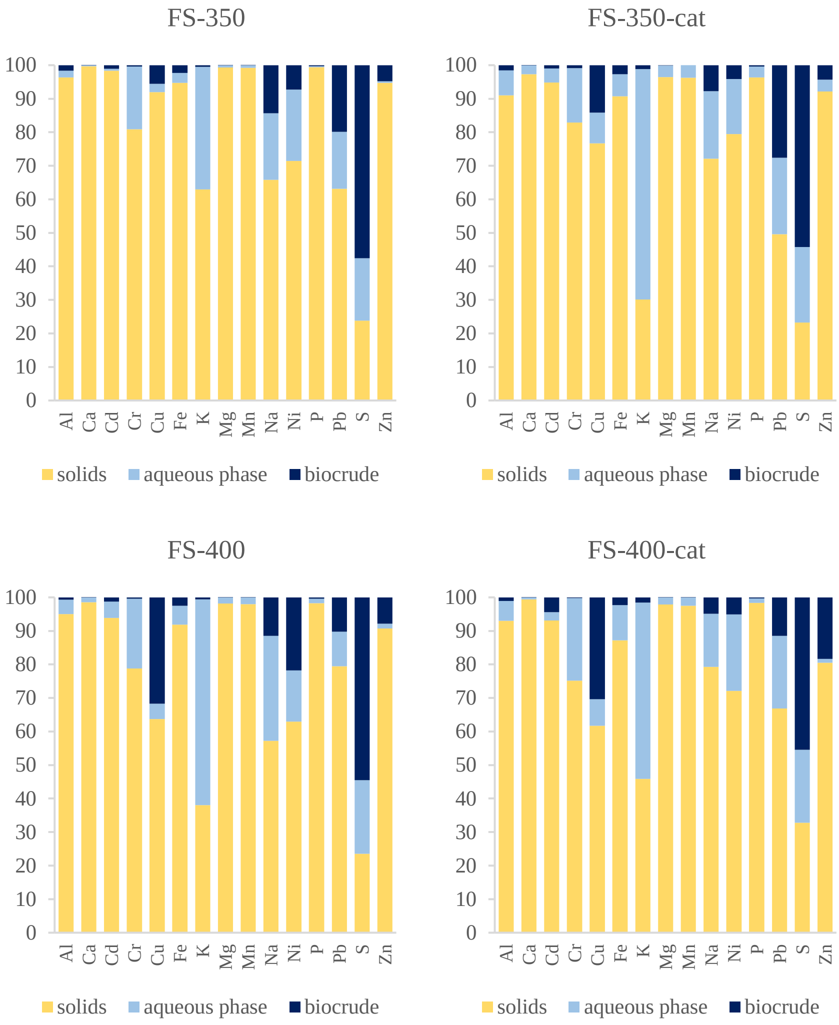


Figure 30: Normalized distribution of the inorganic elements among the products (solids, aqueous phase, and biocrude) after subcritical HTL of fish sludge (FS) at the four different process conditions (350 °C without catalyst, 350 °C with catalyst, 400 °C without catalyst, 400 °C with catalyst).

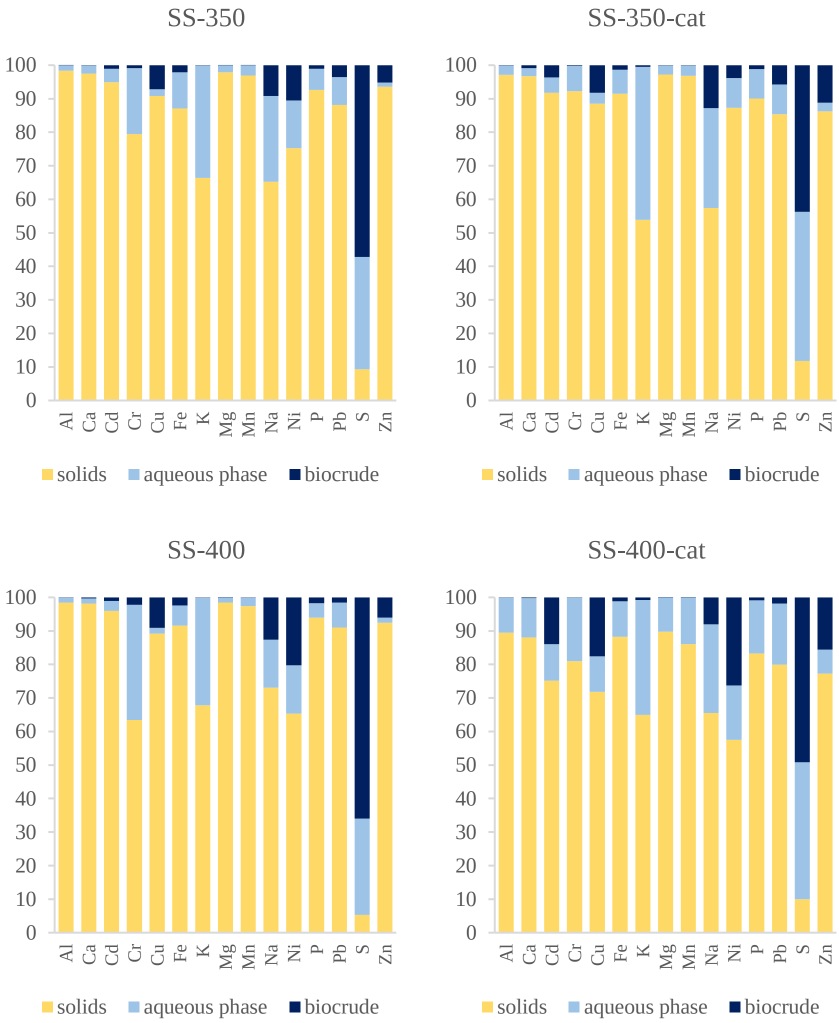


Figure 31: Normalized distribution of the inorganic elements among the products (solids, aqueous phase, and biocrude) after subcritical HTL of sewage sludge (SS) at the four different process conditions (350 °C without catalyst, 350 °C with catalyst, 400 °C without catalyst, 400 °C with catalyst).

The general trend for the redistribution of the inorganics among HTL products observed in Study 3 (on organic wastes) is in line with the findings from Study 2 (on willow biomass): multivalent metal ions (e.g. Al^{3+}, $Fe^{2+/3+}$, Ca^{2+}, Mg^{2+}) are primarily recovered in the HTL solids, while monovalent ions (i.e. K^+, Na^+) tend to dissolve in the HTL aqueous phase. The concentration of the inorganics in the HTL solids – rather than in the other phases – eases their recovery, as the solids can be effectively separated from the other HTL products regardless of the batch or the continuous processing of the feedstock. In fact, after batch processing, the solids are precipitated with the addition of the solvent and they can successively be separated from the products with the aid of filters, as performed in the present investigation. After continuous processing, a filter can be installed after the reaction system to collect the solids, as in the PNNL continuous HTL set-up [117].

In case of direct application of the HTL solids to the land as source of nutrients, there are upper limits on the heavy metals load. As previously introduced, there are legislations both at national and European level on the maximum concentration of heavy metals allowed in sludge (or, in this case, on products derived from sludge processing) for its application to agricultural fields. The limits set by EU Directive 86/278/EEC and the national limits for Denmark and Germany are reported in Table 10, together with the concentrations of the heavy metals detected in the HTL solids. As Danish limits for Cd, Cr, Ni, and Pb are considerably more restrictive when compared to those set by EU or Germany, the HTL solids produced from this study could be potentially applied to agricultural fields in many EU countries, but they would be subjected to some restrictions by the Danish authorities (see shaded values in Table 10). Nevertheless, it has to be noticed that the limits should be seen in relation to the extraction method used: in Denmark, it is usually used nitric acid, weaker than *aqua regia*, which is frequently used in other European countries [86].

Table 10: Limit values for heavy metals in sludge (mg kg^{-1} DM) for its application to the European, Danish, and German agricultural fields (first, second, and third row, respectively) [86, 87]. In the section below the limits, concentrations (mg kg^{-1}) of heavy metals in the HTL solids obtained from swine manure (SM), cow manure (CM), fish sludge (FS), and sewage sludge (SS) at the different process conditions. Orange shaded cells indicate that the concentration in the HTL solids is above the most restrictive limit.

	Cd	Cr	Cu	Ni	Pb	Zn
EU Directive 86/278/EEC	20-40	-	1000-1750	300-400	750-1200	2500-4000
Denmark	0.8	100	1000	30	120	4000
Germany	10	900	800	200	900	2500
SM-350	0.6	71.0	435.6	109.9	3.0	1892.5
SM-350cat	0.4	116.9	279.1	110.2	3.4	1973.3
SM-400	0.5	169.5	423.8	145.4	8.9	2240.5
SM-400cat	0.4	74.4	197.0	60.1	6.1	1388.6
CM-350	0.8	182.2	585.9	176.8	8.6	1651.5
CM-350cat	0.6	230.6	576.7	206.6	4.6	1168.5
CM-400	0.5	270.1	582.2	211.5	3.4	1605.3
CM-400cat	0.4	220.8	405.2	186.8	9.7	1551.5
FS-350	3.6	77.9	66.1	44.0	5.0	1817.3
FS-350cat	3.1	158.5	49.1	116.1	3.7	1724.2
FS-400	3.8	126.4	51.2	129.3	17.2	1990.2
FS-400cat	2.9	186.8	42.4	137.8	4.3	1560.4
SS-350	2.4	78.1	388.1	94.5	46.3	2959.8
SS-350cat	1.8	165.8	291.1	147.1	36.5	1718.3
SS-400	2.2	86.5	368.1	171.0	47.2	2007.4
SS-400cat	1.7	197.5	281.1	138.9	40.3	2100.3

The ICP analysis could only provide information on the concentrations of the inorganics in the product phases but not on their forms. However, the results on the concentrations were used to investigate whether some of the inorganics were correlated. The analysis highlighted that Ca and P were highly correlated (R=0.99; see Table S3 in [C]). From the slope of P-Ca curve, the molar ratio was found to be 0.42 g/g; suggesting that P is primarily present as apatite or hydroxyapatite ($Ca_5(PO_4)_3(OH)$), which has a molar ratio of 3P : 5Ca (0.46 gP/gCa). In support of this finding, the majority of P in hydrochar produced from HTC of cow manure and from HTL of primary sewage sludge was identified as apatite: 88.8% in the first study [118] and 96.7% in the second one [119]. Hydroxyapatite is a mineral and its main application is for the production of fertilizers [120]. Phosphorus precipitation as struvite, a slow-release fertilizer, is commonly performed in wastewater treatment plants [121], and its potential application to HTL solids for the extraction of phosphorus has been recently reported in literature [122]. Hence, the conversion of organic wastes through HTL results a prospective solution to further guarantee an improved circularity of phosphorus.

Chapter 6

Conclusions

This work proposes HydroThermal Liquefaction as an alternative process to treat three diverse category of wastes: plastics, lignocellulosic material, and organic wastes of animal and human origin.

In the first study, nine high-density plastics (PBT, PC, PET, PLA, PMMA, POM, PPO, PVA, and SB) were processed under supercritical HTL conditions (400 °C), obtaining in most of the cases high yields of synthetic crude oil. Particularly high biocrude yields were obtained from the liquefaction of PC (99.8%), SB (80.8%), and PPO (78.9%). These synthetic crude oils of aromatic structure have a simple product slate as compared to biomass-derived biocrudes and therefore hold great potential for the production of fuels or chemicals (e.g. for a targeted production of BTX compounds). Moreover, the oil derived from PC and SB conversion could be additionally used for the production of new plastics, since the monomers BPA and styrene were respectively identified among the oils constituents. The liquefaction of PET and PBT did not produce any synthetic crude oil; however, their conversion in supercritical water resulted in high yields of terephtalic acid (68.5% and 50.8%, respectively), which is one of the monomers used for the production of these plastics. Overall, HTL is a prospective technology for chemical recycling of unrecyclable high-density plastics, allowing to achieve the simultaneous production of high value chemicals and the recovery of monomers, ensuring an improved circular economy.

In the second study, HTL efficiently converted willow biomass ($Y_{biocrude}$= 40%), which had been subjected to irrigation with wastewater for absorbance of nutrients and metals, into an energy-dense biocrude (HHV = 36 MJ kg^{-1}). The biocrude was a mixture of ketones, phenols, and alcohols, which formed as a result of the lignocellulsic biomass decomposition. The investigation on the inorganics showed that most of elements (e.g. Ca, P, and Mg) were primarily (>70%) distributed in the HTL solids after the processing of the biomass. For this reason, the quality of the biocrude was not compromised by the load of the inorganics contained in the feedstock. A standard upgrading of the biocrude is expected being sufficient to reduce the oxygen, nitrogen, and sulphur heteroatoms contents. Thus, HTL allows producing a renewable crude oil, from which fuels can be derived, while the inorganics are filtered out from the biomass and concentrated in a reduced volume in the hydrochars. The outcomes from this work result highly prospective for the treatment of lignocellulosic material with high loads of heavy metals (e.g. impregnated wood).

In the third study, swine manure, cow manure, fish sludge, and sewage sludge were hydrothermally processed at both sub- and supercritical conditions. The organic fraction of these wastes was efficiently converted into biocrude with energy recoveries of up to 67%, 78%, and 92% for the manures, sewage sludge, and fish sludge, respectively. The chemical composition of the feedstocks had impact on the biocrude production: the liquefaction of lignocellulosics-based biomass, such as the manures, resulted in lower biocrude yields (36%) as respect to the sludges (42% for sewage sludge and 52% for fish sludge), whose constituents include also proteins and lipids. Supercritical conditions produced a decrease in the biocrude yields respect to subcritical ones; however, at the same time, the deoxygenation extent was significantly enhanced for manure-derived biocrudes. The combined use of supercritical conditions with K_2CO_3 catalyst is recommended to process manure in HTL, since biocrudes had reduced oxygen content. After hydrothermal processing of the animal and human wastes, most of the inorganic elements (Al, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Zn) were primarily collected in the HTL solids (>70%); this results advantageous in prospective of an effective separation of the valuable nutrients. In particular, being these organic waste feedstocks an abundant source of phosphorus, HTL provides an alternative way for the recovery of this finite element, which is largely required in agriculture. Overall, this work demonstrates that HTL offers a prospective solution for the management of wet ash-containing wastes, as these are efficiently converted into biocrude, from which advanced biofuels may be derived; moreover, the inorganics are concentrated into the hydrochars, from which heavy metals may be safely disposed and valuable nutrients may be reclaimed.

Chapter 7

Future prospective

Additional investigations, which could be performed as a natural continuation of the present PhD project, are proposed below:

- To hydrothermally process mixtures of plastics representative of un-recyclable waste streams and to assess the recovery of the monomeric compounds in the presence of dyes or pigments, such as colorants or other additives;
- To co-process plastic along with biomass (e.g. waste plastics contaminated with residual food) through HTL, exploring potential synergies towards biocrude production;
- To explore additional strategies to ease the decomposition of thermally resistant plastic polymers (e.g. PE and PP);
- To process lignocellulosic biomass with high heavy metals loading (e.g. construction wood) in HTL for a simultaneous production of biocrude and separation of the heavy metals;
- To identify the nature of the inorganics after being recovered in the HTL solids, and to establish the bioavailability of the nutrients (i.e. if they are in the forms accessible to plants so that biological uptake can take place).

References:

[1] NASA, “World of Change: Global Temperatures”, https://earthobservatory.nasa.gov/world-of-change/DecadalTemp, accessed: October 15, 2019

[2] NASA, “The Effects of Climate Change”, https://climate.nasa.gov/effects/, accessed: October 15, 2019

[3] IPCC, (2014): Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change

[4] United Nation, (2015): Paris Agreement. https://unfccc.int/files/essential_background/convention/application/pdf/english_paris_agreement.pdf

[5] IEA, “Energy Technology Perspectives 2017, Catalysing Energy Technology Transformations”

[6] IEA, “CO_2 emissions from fuel combustion: Overview 2019”

[7] IEA, “CO2 emissions from fuel combustion: Highlights 2019”

[8] European Environment Agency, “Greenhouse gas emissions from transport in Europe”, (2018)

[9] IEA, Renewables 2018 Market analysis and forecast from 2018 to 2023, https://www.iea.org/renewables2018/ accessed: October 20, 2019

[10] Eurostat, Energy for transport: 7.6% from renewable sources, https://ec.europa.eu/eurostat/web/products-eurostat-news/-/DDN-20190222-1 accessed: October 20, 2019

[11] IEA, Chapter 2 of "Perspectives for the energy transition – investment needs for a low-carbon energy system" ©OECD/IEA (2017)

[12] IEA, Transport Biofuels, Tracking Clean Energy Progress, https://www.iea.org/tcep/transport/biofuels/ accessed: October 17, 2019

[13] S. Karatzos, J. D. McMillan, J. N. Saddler, "The Potential and Challenges of Drop-in Biofuels", IEA Bioenergy, (2014), ISBN: 978-1-910154-07-6

[14] EU, Renewable Energy – Recast to 2030 (RED II), https://ec.europa.eu/jrc/en/jec/renewable-energy-recast-2030-red-ii accessed: October 17, 2019

[15] A. A. Peterson, F. Vogel, R. P. Lachance, M. Fröling, M. J. Antal, Jr. and J. W. Tester, "Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies", Energy Environ. Sci., 1 (2008) 32–65

[16] D. Castello, T. H. Pedersen, L. A. Rosendahl, "Continuous Hydrothermal Liquefaction of Biomass: A Critical Review", Energies 11 (11) (2018), 1-35 doi:10.3390/en11113165

[17] S. S. Toor, L. Rosendahl, A. Rudolf, "Hydrothermal liquefaction of biomass: A review of subcritical water technologies", Energy 36 (2011) 2328-2342

[18] J. Yang, Q. He, L. Yang, "A review on hydrothermal co-liquefaction of biomass", Applied Energy 250 (2019) 926–945

[19] S.S. Toor, L. Rosendahl, I. Sintamarean, "Recipe-based co-HTL of biomass and organic waste", in Direct Thermochemical Liquefaction for Energy Applications. Edited by L. Rosendahl. Woodhead Publishing. (2018) 169-189 ISBN 9780081010297 https://doi.org/10.1016/B978-0-08-101029-7.00005-9

[20] A. Dimitriadis, S. Bezergianni, "Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review" Renewable and Sustainable Energy Reviews 68 (2017) 113–125

[21] https://phyllis.nl/Browse/Standard/ECN-Phyllis accessed: April 23, 2020

[22] C. U. Jensen, J. K. Rodriguez Guerrero, S. Karatzos, G. Olofsson, S. B. Iversen, "Hydrofaction^{TM} of Forestry Residues to Drop-in Renewable Transportation Fuels", Chapter 10 in Direct Thermochemical Liquefaction for Energy

Applications edited by Lasse A. Rosendahl, ISBN: 9780081010259, pp. 319-345, 2018

[23] D. R. Vardon, B.K. Sharma, J. Scott, G. Yu, Z. Wang, L. Schideman, Y. Zhang, T. J. Strathmann, “Chemical properties of biocrude oil from the hydrothermal liquefaction of Spirulina algae, swine manure, and digested anaerobic sludge”, Bioresource Technology 102 (2011) 8295–8303

[24] P.A. Marrone, D.C. Elliott, J.M. Billing, R.T. Hallen, T.R. Hart, P. Kadota, J.C. Moeller, M.A. Randel, A.J. Schmidt. “Bench-scale evaluation of hydrothermal processing technology for conversion of wastewater solids to fuels”, Water Environment Research 90 (2018) 329–342

[25] D. Castello, M. S. Haider, L. A. Rosendahl, “Catalytic upgrading of hydrothermal liquefaction biocrudes: Different challenges for different feedstocks”, Renewable Energy 141 (2019) 420-430

[26] J. M. Jarvis, J. M. Billing, R. T. Hallen, A. J. Schmidt, T. M. Schaub, “Hydrothermal Liquefaction Biocrude Compositions Compared to Petroleum Crude and Shale Oil”, Energy Fuels 31 (2017) 2896−2906

[27] C. U. Jensen, J. Hoffmann, L. A. Rosendahl, “Co-processing potential of HTL bio-crude at petroleum refineries. Part 2: A parametric hydrotreating study”, Fuel 165 (2016) 536–543

[28] T. H. Pedersen, N. H. Hansen, O. M. Pérez, D. E. Villamar Cabezas, L. A. Rosendahl, “Renewable hydrocarbon fuels from hydrothermal liquefaction: A techno-economic analysis”, Biofuels, Bioproducts and Biorefining (2017)

[29] S. De Jong, R. Hoefnagels, A. Faaij, R. Slade, B. Mawhood, M. Junginger (2015). “The feasibility of short-term production strategies for renewable jet fuels – A comprehensive techno-economic comparison”, BioFPR (2015)

[30] H.J. Huang, X.Z. Yuan, H.N. Zhu, H. Li, Y. Liu, X.L. Wang, G.M. Zeng, “Comparative studies of thermochemical liquefaction characteristics of microalgae, lignocellulosic biomass and sewage sludge”, Energy 56 (2013) 52-60

[31] S. Leow, J. R. Witter, D. R. Vardon, B. K. Sharma, J. S. Guesta, T. J. Strathmann, “Prediction of microalgae hydrothermal liquefaction products from feedstock biochemical composition”, Green Chem. 17 (2015) 3584-3599

[32] T. H. Pedersen, (2016). HydroThermal Liquefaction of Biomass and Model Compounds. Aalborg Universitetsforlag. (Ph.d.-serien for Det Teknisk-Naturvidenskabelige Fakultet, Aalborg Universitet). ISBN 9788771124972 DOI: 10.5278/vbn.phd.engsci.00050

[33] T.H. Pedersen, L.A. Rosendahl, Production of fuel range oxygenates by supercritical hydrothermal liquefaction of lignocellulosic model systems, Biomass Bioenergy 83 (2015) 206–215

[34] F. Vogel, Hydrothermal conversion of biomass, in: R.A. Meyers (Ed.), Encyclopedia of Sustainability Science and Technology, Springer Science+Business Media LLC, 2017

[35] N. Akiya, P. E. Savage, “Kinetics and Mechanism of Cyclohexanol Dehydration in High-Temperature Water”, Industrial & Engineering Chemistry Research 40 (2001) 1822-1831

[36] M. Akizuki, N. Fujioka, Y. Oshima, “Catalytic Effect of the SUS316 Reactor Surface on the Hydrolysis of Benzamide in Sub- and Supercritical Water”, Industrial & Engineering Chemistry Research 55 (2016) 10243−10250

[37] P. E. Savage, “Organic Chemical Reactions in Supercritical Water”, Chem. Rev. 99 (1999) 603–622

[38] W. Wagner, A. Pruß, The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. J. Phys. Chem. Ref. Data 31 (2002) 387–535

[39] Z. Zhu, L. Rosendahl, S. S. Toor, D. Yu, G. Chen, “Hydrothermal liquefaction of barley straw to bio-crude oil: Effects of reaction temperature and aqueous phase recirculation”, Applied Energy 137 (2015) 183–192

[40] T.H. Pedersen, I.F. Grigoras, J. Hoffmann, S.S. Toor, I.M. Daraban, C.U. Jensen, S.B. Iversen, R.B. Madsen, M. Glasius, K.R. Arturi, R.P. Nielsen, E.G. Søgaard, L.A. Rosendahl, “Continuous hydrothermal co-liquefaction of aspen wood and glycerol with water phase recirculation”, Applied Energy 162 (2016) 1034–1041

[41] C. U. Jensen, J. K. Rodriguez Guerrero, S. Karatzos, G. Olofsson, S. B. Iversen, “Fundamentals of Hydrofaction™: Renewable crude oil from woody biomass”, Biomass Conv. Bioref. 7 (2017) 495-509 DOI 10.1007/s13399-017-0248-8

[42] O. Bobleter, “Hydrothermal degradation of polymers derived from plants,” Progress in Polymer Science

[43] Z. Zhu, S.S. Toor, L. Rosendahl, D. Yu, G. Chen, Influence of alkali catalyst on product yield and properties via hydrothermal liquefaction of barley straw, Energy 80 (2015) 284–292

[44] I-M. Sintamarean, (2016). Feedstock preparation and physico-chemical characterization. Optimization of feedstocks for continuous HTL and optimum yield. Aalborg Universitetsforlag. Ph.d.-serien for Det Ingeniør- og Naturvidenskabelige Fakultet, Aalborg Universitet

[45] S.A. Channiwala, P.P. Parikh, "A unified correlation for estimating HHV of solid, liquid and gaseous fuels", Fuel 81 (2002) 1051–1063

[46] P. Bharath, V. G.Sridhar, M. Senthil kumar, "Optimization of 316 Stainless Steel Weld Joint Characteristics using Taguchi Technique", Procedia Engineering 97 (2014) 881-891

[47] World Economic Forum, "The New Plastics Economy: Rethinking the future of plastics", January 2016

[48] PlasticsEurope Association of Plastics Manufacturers and EPRO (the European Association of Plastics Recycling and Recovery Organisations) "Plastics – the Facts 2019: An analysis of European plastics production, demand and waste data"

[49] M. R. Gent, M. Menendez, J. Toraño, I. Diego, "Recycling of plastic waste by density separation: prospects for optimization", Waste Management and Research 27 (2) (2009) 175-187

[50] PlasticsEurope Association of Plastics Manufacturers, "The unknown life of plastics", January 2016

[51] Eurostat, "Environment in the EU", 54, 26 March 2015

[52] The Danish Government, "Denmark without waste: Recycle more- incinerate less", November 2013

[53] https://www.licella.com.au/global-jv-armstrong-chemicals/ accessed: Maj 18th 2020

[54] https://renewelp.co.uk/about-us/ accessed: Maj 18th 2020

[55] https://muratechnology.com/sites-projects/ accessed: Maj 18th 2020

[56] https://www.basf.com/global/en/media/news-releases/2019/10/p-19-356.html accessed: Maj 18th 2020

[57] https://www.basf.com/global/en/who-we-are/sustainability/we-drive-sustainable-solutions/circular-economy/mass-balance-approach/chemcycling.html accessed: Maj 18th 2020

[58] Y. Zhang, W.-T. Chen, “Hydrothermal liquefaction of protein-containing feedstocks”, Chapter 5 in Direct Thermochemical Liquefaction for Energy Applications (2018) https://doi.org/10.1016/B978-0-08-101029-7.00004-7

[59] S. E. Hunter, C. A. Felczak, P. E. Savage, “Synthesis of p-isopropenylphenol in high-temperature water”, Green Chemistry 6 (2004) 222–226

[60] T. Adschiri, R. Shibata, K. Arai, “Phenol recovery by BPA tar hydrolysis in supercritical water”, Journal of the Japan Petroleum Institute 40 (1997) 291–297

[61] R. B. Madsen, , M. M Jensen, A. Mørup, K. Houlberg, P. S. Christensen, M. Klemmer, J. Becker, B. B Iversen, M. Glasius, “Using design of experiments to optimize derivatization with methyl chloroformate for quantitative analysis of the aqueous phase from hydrothermal liquefaction of biomass”, Analytical and Bioanalytical Chemistry 408 (2016) 2171–2183

[62] O. Sato, K. Arai, M. Shirai, “Hydrolysis of poly(ethylene terephthalate) and poly(ethylene 2, 6-naphthalene dicarboxylate) using water at high temperature: Effect of proton on low ethylene glycol yield”, Catalysis Today 111 (2006) 297–301

[63] C. L. Beyler, M. M. Hirschler, ”Thermal decomposition of polymers”, SFPE Handbook of Fire Protection Engineering 2, Section 1, C7, (2002) 110–131

[64] N. Matubayasi, S. Morooka, M. Nakahara, H. Takahashi, “Chemical equilibrium of formaldehyde and methanediol in hot water: Free-energy analysis of the solvent effect”, Journal of Molecular Liquids 134 (2007) 58–63

[65] PlasticsEurope Association of Plastics Manufacturers, “Plastics - the Facts 2015: An analysis of European plastics production, demand and waste data”, November 2015

[66] T. Moriya, H. Enomoto, “Characteristics of polyethylene cracking in supercritical water compared to thermal cracking”, Polymer Degradation and Stability 65 (1999) 373-386

[67] B. Singh, N. Sharma, “Mechanistic implications of plastic degradation”, Polymer Degradation and Stability 93 (3) (2008) 561-584

[68] M. Watanabe, S. Sawamoto, T. Adschiri, K. Arai, “Polyethylene conversion by partial oxidation in supercritical water”, Journal of Material Cycles and Waste Management 3 (2001) 99–102

[69] M.J. Aylott, E. Casella, I. Tubby, N.R. Street, P. Smith, G. Taylor, “Yield and spatial supply of bioenergy poplar and willow short-rotation coppice in the UK”, New Phytologist 178 (2) (2008) 358–370

[70] I.D. Pulford, C. Watson, “Phytoremediation of heavy metal-contaminated land by trees—a review”, Environment International 29 (4) (2003) 529–540

[71] P. Vervaeke, S. Luyssaert, J. Mertens, E. Meers, F.M. Tack, N. Lust, “Phytoremediation prospects of willow stands on contaminated sediment: a field trial”, Environmental Pollution 126 (2) (2003) 275–282

[72] W. Rosselli, C. Keller, K. Boschi, “Phytoextraction capacity of trees growing on a metal contaminated soil”, Plant Soil 256 (2) (2003) 265–272

[73] K.L. Perttu, P.J. Kowalik, Salix vegetation filters for purification of waters and solids, Biomass and Bioenergy 12 (1) (1997) 9–19

[74] http://www.pilerensning.dk/english/ accessed: May 1st 2020

[75] A. Nzihou, B. Stanmore, “The fate of heavy metals during combustion and gasification of contaminated biomass—a brief review”, Journal of Hazardous Materials 256-257 (2013) 56–66

[76] A. J. Pedersen, L. M. Ottosen, A. Villumsen, “Electrodialytic removal of heavy metals from different fly ashes, Influence of heavy metal speciation in the ashes”, Journal of Hazardous Materials 100 (1–3) (2003) 65–78

[77] M. Atienza-Martínez, G. Gea, J. Arauzo, S. R. A. Kersten, A. M. J. Kootstra, “Phosphorus recovery from sewage sludge char ash”, Biomass and Bioenergy 65 (2014) 42-50

[78] C.C. Evans, S.E. Allen, “Nutrient losses in smoke produced during heather burning”, Oikos 22 (2) (1971) 149–154

[79] S. van Loo and J. Koppejan, The Handbook of Biomass Combustion and Co-firing (2008) ISBN: 978-1-84407-249-1

[80] https://phyllis.nl/Browse/Standard/ECN-Phyllis#willow accessed: December 15, 2019

[81] I. F. Grigoras, R. E. Stroe, I. M. Sintamarean, L. A. Rosendahl, “Effect of biomass pretreatment on the product distribution and composition resulting from the hydrothermal liquefaction of short rotation coppice willow”, Bioresource. Technology 231 (2017) 116–123

[82] A.M. Smith, S. Singh, A.B. Ross, “Fate of inorganic material during hydrothermal carbonisation of biomass: influence of feedstock on combustion behaviour of hydrochar”, Fuel 169 (2016) 135–145

[83] T. Voisin, A. Erriguible, D. Ballenghien, D. Mateos, A. Kunegel, F. Cansell, C. Aymonier, “Solubility of inorganic salts in sub- and supercritical hydrothermal environment: application to SCWO processes”, Journal of Supercritical Fluids 120 (1) (2017) 18–31

[84] United Nations Industrial Development Organization, “Fertilizer Manual”, United Nations, (1980)

[85] FAO, “The future of food and agriculture – Trends and challenges”, (2017) Rome, ISBN 978-92-5-109551-5

[86] European Commission, “Disposal and recycling routes for sewage sludge Part 2 – Regulatory report”, October 2001 ISBN 92-894-1799-4

[87] H. Hudcová, J. Vymazal, M. Rozkošný, “Present restrictions of sewage sludge application in agriculture within the European Union”, Soil and Water Research, 14 (2) 2019 104–120

[88] L. Li, S. Geng, Z. Li, K. Song, “Effect of microplastic on anaerobic digestion of wasted activated sludge”, Chemosphere 247 (2020) 125874

[89] Q. Zhao, Y. Liu, “Is anaerobic digestion a reliable barrier for deactivation of pathogens in biosludge?”, Science of The Total Environment 668 (2019) 893-902

[90] S. D. Costanzo, J. Murby, J. Bates, “Ecosystem response to antibiotics entering the aquatic environment”, Marine Pollution Bulletin 51 (1) (2005) 218-223

[91] J. P. Graham, J. J. Boland, E. Silbergeld, “Growth promoting antibiotics in food animal production: an economic analysis”, Public Health Reports 122 (1) (2007) 79

[92] A. K. Sarmah, M. T. Meyer, A. B. A. Boxall, “A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment”. Chemosphere 65 (5) (2006) 725-759

[93] G. G. Khachatourians, “Agricultural use of antibiotics and the evolution and transfer of antibiotic-resistant bacteria”. Canadian Medical Association Journal 159 (9) (1998) 1129-1136

[94] T. A. Hanselman, D. A. Graetz, A. C. Wilkie, “Comparison of three enzyme immunoassays for measuring 17 beta-estradiol in flushed dairy manure wastewater”, Journal of Environmental Quality 33 (5) (2004) 1919-1923

[95] E. J. Routledge, D. Sheahan, C. Desbrow, G. C. Brighty, M. Waldock, J. P. Sumpter, “Identification of estrogenic chemicals in STW effluent. 2. In vivo responses in trout and roach”. Environmental Science & Technology 32 (11) (1998) 1559-1565

[96] M. T. V. Pham, “Characterizing the effects of hydrothermal processes on bioactive compounds in wastewater bioenergy systems”, PhD Dissertation, University of Illinois at Urbana-Champaign, (2013)

[97] Y. H. Shin, L. Schideman, M. J. Plewa, P. Zhang, J. Scott, Y. Zhang, “Fate and transport of estrogenic compounds in an integrated swine manure treatment systems combining algal-bacterial bioreactor and hydrothermal processes for improved water quality”, Environmental Science and Pollution Research 26 (2019) 16800–16813

[98] R. L. Morais, M. F. Santiago, J. W .Zang, W. A. Fonseca-Zang, F. Schimidt, “Removal of synthetic sex hormones by hydrothermal carbonization”, Anais da Academia Brasileira de Ciências 90(2) (2018) 1327-1336

[99] T. F. Ducey, J C. Collins, K. S. Ro, B. L. Woodbury, D. Dee Griffin, “Hydrothermal carbonization of livestock mortality for the reduction of pathogens and microbially-derived DNA”, Front. Environmental Science and Engineering 11 (3) (2017) 9

[100] C. vom Eyser, K. Palmuc, T.C. Schmidt, J. Tuerk, “Pharmaceutical load in sewage sludge and biochar produced by hydrothermal carbonization”, Science of the Total Environment 537 (2015) 180–186

[101] R. W. Scholz, A. E. Ulrich, M. Eilittä, A. Roy, “Sustainable use of phosphorus: A finite resource”, Science of The Total Environment 461–462 (2013) 799-803

[102] A. Kelessidis and A. S. Stasinakis, “Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries.” Waste Management 32(6), (2012) 1186–1195

[103] https://phyllis.nl/Browse/Standard/ECN-Phyllis#sewage%20sludge accessed: January 21, 2020

[104] Technical Report No. I to the European Commission, Directorate-General Environment, “Manure Processing Activities in Europe” - Project reference: ENV.B.1/ETU/2010/0007

[105] https://phyllis.nl/Browse/Standard/ECN-Phyllis#swine%20manure accessed: January 21, 2020

[106] https://phyllis.nl/Browse/Standard/ECN-Phyllis#swine%20manure accessed: January 21, 2020

[107] http://www.fao.org/faostat/en/#data/RFN accessed: January 21, 2020

[108] Y. H. Shin, L. Schideman, M. J. Plewa, P. Zhang, J. Scott, Y. Zhang, “Fate and transport of estrogenic compounds in an integrated swine manure treatment systems combining algal-bacterial bioreactor and hydrothermal processes for improved water quality”, Environmental Science and Pollution Research 26 (2019) 16800–16813

[109] P. Biller, A. B. Ross, “Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content”, Bioresource Technology 102 (2011) 215–225

[110] J. T. Novak, C. M. Park “The effect of iron and aluminium for phosphorus removal on anaerobic digestion and organic sulfur generation”, Water Science & Technology 62 (2) (2010) 419-426

[111] L. Qian, S. Wang, P. E. Savage, “Hydrothermal liquefaction of sewage sludge under isothermal and fast conditions”, Bioresource Technology 232 (2017) 27–34

[112] R. Posmanik, C. M. Martinez, B. Cantero-Tubilla, D. A. Cantero, D. L. Sills, M. J. Cocero, J. W. Tester, “Acid and alkali catalyzed hydrothermal liquefaction of dairy manure digestate and food waste”, ACS Sustainable Chemistry & Engineering 6 (2) (2018) 2724-2732

[113] C. U. Jensen, ”PIUS—Hydrofaction(TM) Platform with Integrated Upgrading Step”, Ph.d.-serien for Det Ingeniør- og Naturvidenskabelige Fakultet. Ph.D. Thesis, Aalborg Universitet, Aalborg, Denmark, (2018)

[114] D. Kubička, J. Horáček, “Deactivation of HDS catalysts in deoxygenation of vegetable oils”, Applied Catalysis A 394 (2011) 9–17

[115] E. Furimsky, “Hydroprocessing challenges in biofuels production,” Catalysis Today 217 (2013) 13–56

[116] E. Furimsky and F. E. Massoth, “Deactivation of hydroprocessing catalysts,” Catalysis Today vol. 52 (4) (1999) 381–495

[117] P. A. Marrone, “Genifuel Hydrothermal Processing Bench-Scale Technology Evaluation Report”, Water Environment and Reuse Foundation: Alexandria, VA, USA, (2016); ISBN 9781780408408 https://doi.org/10.2166/9781780408408

[118] L. Dai, F. Tan, B. Wu, M. He, W. Wang, X. Tang, et al., “Immobilization of phosphorus in cow manure during hydrothermal carbonization”, Journal of Environmental Management 157 (2015) 49–53

[119] E. Ovsyannikova, A. Kruse, G. C. Becker, “Feedstock-Dependent Phosphate Recovery in a Pilot-Scale Hydrothermal Liquefaction Bio-Crude Production”, Energies 13 (2020) 379

[120] J. Lucas, P. Lucas, T. Le Mercier, A. Rollat, W. Davenport, “Chapter 4 – Extracting Rare Earth Elements from Concentrates”, Science, Technology, Production and Use (2015) 47-67

[121] L. Peng, H. Dai, Y. Wu, Y. Peng, X. Lu, “A comprehensive review of phosphorus recovery from wastewater by crystallization processes. Chemosphere” 197 (2018) 768–781

Part II: Publications

Paper A

Improving the circular economy via hydrothermal processing of high density waste plastics

T. H. Pedersen and F. Conti

The manuscript has been published in:
Waste Management 68 (2017) 24–31

The layout has been revised.

Waste Management 68 (2017) 24–31

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Improving the circular economy via hydrothermal processing of high-density waste plastics

Thomas Helmer Pedersen *, Federica Conti

Department of Energy Technology, Aalborg University, Pontoppidanstæde 111, 9220 Aalborg, Denmark

ARTICLE INFO

Article history:
Received 18 February 2017
Revised 19 May 2017
Accepted 1 June 2017
Available online 13 June 2017

Keywords:
Hydrothermal liquefaction
Plastic monomers
Synthetic crude oil
Value added chemicals
Waste unrecyclable plastics

ABSTRACT

Rising environmental concerns on climate changes are causing an increasing attention on circular economies. The plastic economy, in particular, is in focus due to the accelerating consumption of plastics, mainly derived from virgin feedstock, combined with the lack of plastic recycling strategies. This work presents a novel outlook on the potential of using supercritical hydrothermal processing of waste plastic fractions for tertiary recycling. The study investigates hydrothermal processing of nine different, high-density types of plastics into original resin monomers and other value-added chemical compounds. The outlook presents conversion yields, carbon balances, and chemical details on the products obtained. It is found that all the investigated resins are prone to hydrothermal treatment, and that high yields of monomers and high value compounds (up to nearly 100%), suitable for chemicals and fuels applications, can be obtained. For instance, for polycarbonate, styrene-butadiene, poly(lactic acid), poly(ethylene terephthalate), and poly(butylene terephthalate), original monomeric compounds can be reclaimed for manufacturing new resins. The promising results presented demonstrate that hydrothermal processing of high-density plastics is a prospective technology for increasing the circularity of the plastic economy.

1. Introduction

Plastic production and consumption have increased dramatically over recent years, and with more than 300 million tons produced every year, plastic has become a global environmental concern. Striving for primary closed-loop recycling of plastics is ultimate, but has only been achieved for a very narrow plastic segment, such as clear PET bottles, for which dedicated collection schemes already exist [World Economic Forum, 2016]. The lack of primary recycling of plastics is challenged by many aspects, such as colors (dyes) and other contaminants, qualities, blends of different plastics, etc., and is manifested by the fact that only approximately 2% of all plastics is closed-loop recycled [World Economic Forum, 2016]. Secondary recycling of plastics into products of inferior qualities includes for example uni-coloring of mixed colored plastic, typically in black, but is limited mainly to fractions containing only a single type of plastic. Tertiary recycling, involving decomposition or depolymerization of the polymers for recovering of monomeric constituents or other valuable chemicals, is prospective for fractions of plastics were primary and secondary recycling is unviable [Al-Salem et al., 2009]. Tertiary recycling includes chemical depolymerization, solvolysis, catalytic and thermal cracking, pyrolysis, gasification, hydrogenation, etc. [Curlee and Das, 1998]. Whereas some types of polymers like polyesters, polyethers, polycarbonates, polyamides, are prone to solvolysis, such as hydrolysis (thermal and/or catalytic), others are more chemically resistant and require severe thermal conditions in order to decompose. For such polymers, including polyethylene and polypropylene, pyrolysis is suitable for converting the resins into basic chemicals and oils [Bockhorn et al., 1998; Onwudili et al., 2009]. Hydrothermal treatment is another thermochemical process identified as a highly cost competitive process for converting organic matter, e.g. wood, straw and sewage sludge, into value-added chemicals [De Jong, 2015; Zhu et al., 2014]. Hydrothermal processing of plastics at near and supercritical water conditions is an advanced tertiary technology, which has only scarcely been investigated [Sugano et al., 2009; Park et al., 2001; Watanabe et al., 1998]. Hydrolysis of Nylon 6 and Nylon 66 at near and supercritical conditions, without any added catalysts, was successfully applied for recovering high yields of monomers, such as caprolactam (85%) and apidic acid (>40%) [Meng et al., 2004; Iwaya et al., 2006]. Due to the bifunctionalities (thermal and chemical properties), a near or supercritical water environment is potentially useful for processing technically difficult waste, i.e. mixed types of plastics, and plastics contaminated with e.g. organic waste, which are otherwise incinerated. In fact, mixed fractions of plastics and plastics contaminated with organics are main challenges in plastic

---

* Corresponding author.
E-mail addresses: thp@et.aau.dk (T. Helmer Pedersen), fco@et.aau.dk (F. Conti).

http://dx.doi.org/10.1016/j.wasman.2017.06.002
0956-053X/

waste management as they cannot be sorted and cleaned to their pure forms, which are requested aspects for their primary or secondary recycling [Gent et al., 2009].

As an alternative solution to incineration, we propose to processwaste plastic streams under supercritical water conditions and to recycle the plastic monomers for the production of new plastics along extraction of value added chemicals for usage in the chemical industry (Fig. 1). The flexibility of this hydrothermal process would allow the processing of different plastics regardless of color, sizes, purity, physical properties etc. within the same process.

In this paper, we demonstrate the usefulness of supercritical water for processing various types of high-density plastics. The objective is to screen hydrothermal processing of different types of pure plastics, individually, in order to obtain novel insight into decomposition trends and chemical recoveries for the various types of plastics. Ultimately, the expansion of the fundamental understanding, presented by this study, of how pure plastics decompose will improve the understanding and prediction of how undifferentiated plastic waste can be processed under supercritical water conditions.

2. Materials and methods

2.1. Materials

The high-density plastics used as feedstock in this study were: Poly(butylene terephthalate) (PBT), Polycarbonate (PC), Poly(ethylene terephthalate) (PET), Poly(lactic acid) (PLA), Poly(methyl methacrylate) (PMMA), Poly(oxymethylene) (POM), Poly(*p*-phenylene oxide) (PPO), Poly(vinyl alcohol) (PVA), Styrene-butadiene (SB). The plastics were purchased from major polymer producers: BASF, Chevron Phillips Chemical, LanXess, SABIC and Total Petrochemicals. All plastics were supplied in granular form, approximate size 3 mm, and then used as received without performing any pretreatment.

2.2. Experimental procedure

All pure plastics were processed, in duplicates, under hydrothermal process conditions. The experiments were carried out in micro-batch reactors (12 mL) submerged in a preheated fluidized sand bath (Techne SBL-2D). For each experiment, distilled water (5 g) and plastic (0.5 g, about 10 wt.%) were added to the reactor. None catalyst was necessary for the conversion. Reactors were sealed, purged with N_2 to remove residual O_2 and for leaking test, and then rapidly heated to 400 °C, developing a corresponding pressure of about 250 bar. The retention time was set to 15 min, including the heating period. During the reaction, temperature and pressure were both monitored and an agitation system provided the mechanical mixing inside the reactors. After 15 min, reactors were instantly cooled to room temperature in a water bucket.

2.3. Products recovery

The importance of the products recovery technique lies in the fact that products yields and quality are strictly dependent on the separation procedure and the solvents involved.

Once reactors were at ambient temperature, any eventual overpressure was vented through a top mounted valve. In some cases, such as for PLA processing, gases were collected for analysis. Reactors were then opened, and an aqueous phase containing soluble organics was collected and named as aqueous phase (AP). Acetone ($\geq$95%, Cab Dan) was used to rinse reactors and to recover an oily phase. The collected mixture was vacuum filtrated and the solids (S) were dried in an oven (105 °C, 24 h) before being weighed. Then acetone was evaporated (40 °C, 556 mbar) in a rotary evaporator. Diethyl ether (DEE, ACS reagent, anhydrous, $\geq$99.0%, Sigma Aldrich) was added to extract the oily phase and then evaporated (40 °C, 990 mbar); the remaining oily phase was weighed and defined as synthetic crude oil (Fig. 2).

2.4. Products characterization

For some experiments, the gas phase composition was determined using a Gas Chromatograph (GC - Shimadzu, Tracera GC-2010 Plus). The GC was equipped with a micropacked column (Restek, length 2.0 m, I.D. 0.53 mm) and a BID detector. The oven was held at constant temperature of 85 °C. The total flow was 803 ml/min, split ratio was 1:200 and pressure was set to be the flow control mode (400 kPa). The injected volume was 0.1 mL.

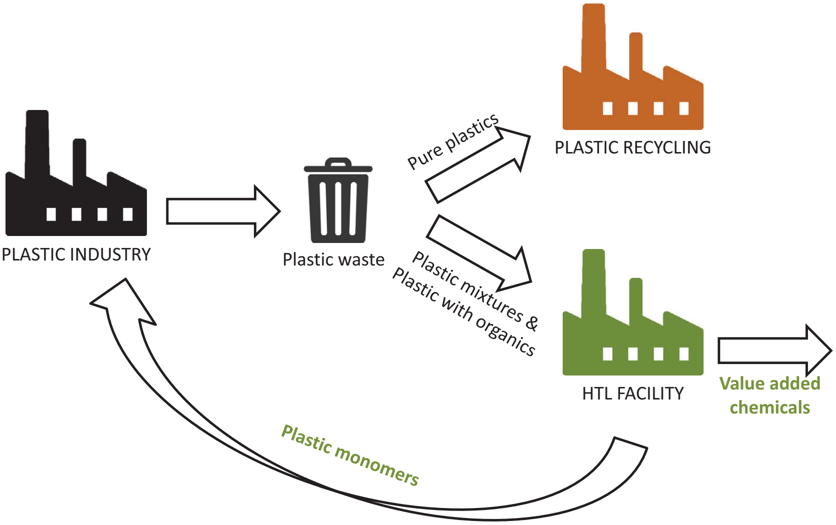


Fig. 1. Conceptual scheme for improving plastic economy via hydrothermal processing of unrecyclable plastics.

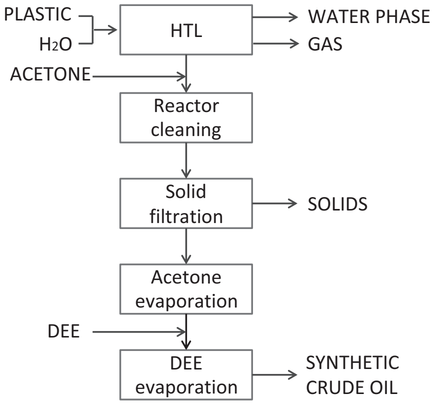


Fig. 2. Steps involved in the products recovery.

The aqueous phases were characterized by determining the pH (WTW, pH meter 3210) and the Total Organic Carbon (TOC) with a proper kit (LCK386) and a spectrophotometer (Hach & Lange DR3900).

Elemental composition of the solids and of the synthetic crudes was determined with an elemental analyzer (Perkin Elmer, 2400 Series II CHNS/O).

Functional groups in the synthetic crudes were detected through FT-IR spectroscopy (Thermo Scientific, Nicolet 380 spectrometer).

Crude oils and some solids were also qualitatively characterized by Gas Chromatography Mass Spectroscopy (GC–MS). Analyses were performed in a Thermo Scientific Gas Chromatograph (Trace 1300) equipped with a capillary column (Agilent Technologies, length 30 m, I.D. 0.25 mm, film thickness 0.25 μm) and coupled with a Mass Spectrometer (ISQ QD). Flow rate of the carrier gas (Helium) was set to 1 mL/min and 1 μL of sample was injected each time with a split ratio of 1:20. MS ion source was heated to 300 °C while the oven had the following temperature profile: 40 °C held for 1 min and then ramped to 300 °C (10 °C/min). Prior to analysis, oil samples were diluted in 2 mL of DEE and filtered with 0.45 μm syringe filters. In some cases, samples were also derivatized: few drops of N,O-Bis(trimethylsilyl)-trifluoroacetamide with trimethylchlorosilane (TMCS 1%, Sigma Aldrich) were added; the sample was then heated to 60 °C in a water bath for 1 h, and finally the excess derivatizing agent was removed with a gas stream.

GC–MS analysis was also used to trace the organic compounds in the aqueous phase obtained from PLA plastic. Before the analysis, the aqueous phase was treated to extract the organics using the method developed by [Madsen et al., 2016].In this case the temperature profile for the oven was: 40 °C hold for 1 min, ramped to 100 °C (4 °C/min) and held for 1 min, and finally ramped to 300 °C (15 °C/min).

The decomposition extent of oil samples was determined by Thermogravimetrical Analysis (TGA) in a TA Discovery. Starting from room temperature, samples were subjected to an increase in temperature up to 900 °C, with a temperature rate of 10 °C/min.

3. Results and discussion

3.1. Yields and properties of product phases

The plastics included in this study showed to be easily degraded via hydrothermal processing. The polymers converted to different extent into synthetic crude oils and solids. For each type of plastic, average yield in oil (Y_{oil}) and in solid (Y_{solid}) are reported in Table 1, together with the elemental composition of the two respective phases. Carbon and hydrogen content were determined from the analysis of products, while oxygen was calculated by difference. Nitrogen was not detected by the elemental analyzer and therefore not reported.

For some plastics, like PC, SB and PPO, the synthetic crude oil represents the main product, accounting for 99.8%, 80.8%, and 78.9%, respectively. A different tendency was observed when processing PBT and PET under the same hydrothermal conditions. The latter, in fact, were primarily recovered into solid products, which accounted for 50.8% and 68.5%, respectively, while synthetic oil was not detected. A more varied product distribution across the different phases was observed in the case of PMMA, PVA and POM; whose products were recovered in the form of oils, solids, organics dissolved in the aqueous phase and some gases. Neither oil nor solids were detected from PLA conversion; while the high TOC value (19.1 g/L) clearly reflects the presence of organics in the aqueous phase. An evolvement of gas was registered when processing PLA.

TOC analysis was performed in order to determine the amount of organics dissolved in the aqueous phase; results are summarized in Table 1 together with measured pH values. All aqueous phases were found to be acidic with values in the range 2.8–4.7. For most plastics, a correspondence between pH and TOC values was found: when pH is highly acidic, carbon content is also high, which could suggest that more organic acids are dissolved in the aqueous phase. The low TOC value (0.4 g/L) of SB aqueous phase is strictly dependent on the different products recovery method that was used. This involved the addition of DEE to the aqueous phase to extract residual oil and led to a cleaner aqueous phase.

Carbon balance was elaborated, comparing the carbon content in the plastic used as feedstock with the quantity of carbon detected in the different product phases. Results are presented in Fig. 3, which highlights the carbon distribution across the different phases for each plastic type involved in the study.

Synthetic crude oils were qualitatively analyzed by GC–MS, using temperatures up to 300 °C. Therefore it was relevant to establish the tendency of the oils to evaporate, below and above this temperature, in order to define up to which extent oils were characterized with GC–MS. For this reason, the oils were analyzed with TGA up to 900 °C, and decomposition curves by temperature are presented in Fig. 4.

A similar trend was observed for PC and PMMA: at 300 °C, more than 80% of the oil was evaporated, revealing that PC and PMMA oils contain compounds with relatively low-boiling points. From these results, it is suggested that PC and PMMA oils are fully characterized by GC–MS.

SB and PPO oils, instead, were found to contain more high-boiling point compounds: the evaporation extent accounted for only 40% and 30%. Only less than half of the compounds were therefore detected by GC–MS.

3.2. Decomposition and chemical recovery from the resins

3.2.1. Polycarbonate (PC)

Polycarbonate showed to be extremely susceptible to hydrothermal treatment, with nearly 100% conversion, where the vast majority was turned into volatile liquid products. Ether bonds (within the carbonates) are known to undergo hydrolysis in hot-compressed water, which was also the case for the polycarbonate polymer. Hydrolysis of the polymer was evident due to the formation of the Bisphenol A (BPA) monomer, which was confirmed by GC–MS. The GC–MS result is illustrated in Fig. 5.

It is observed that only four compounds were formed, including the BPA. The other compounds appeared to be phenol (1),

Table 1
Yield and composition of oils and solids, and analysis of aqueous phases.

	Yoil	Ysolid	Oils [wt.%]			Solids [wt.%]			pH	TOC
	[wt.%]	[wt.%]	C	H	O[a]	C	H	O[a]	[–]	[g/l]
PBT	nd[b]	50.8	–[c]	–[c]	–[c]	57.6	3.4	39.0	3.3	8.1
PC	99.8	nd[b]	75.0	8.0	17.0	–[c]	–[c]	–[c]	3.8	10.3
PET	nd[b]	68.5	–[c]	–[c]	–[c]	34.9	1.4	63.7	3.7	5.4
PLA	nd[b]	nd[b]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	3.6	19.1
PMMA	48.0	nd[b]	63.6	9.0	27.4	–[c]	–[c]	–[c]	2.8	23.4
POM	13.7	8.1	78.7	7.7	13.6	64.3	4.3	31.3	4.7	25.0
PPO	78.9	8.8	85.7	8.2	6.1	83.8	7.1	9.1	3.5	1.6
PVA	35.4	2.9	81.5	9.0	9.5	29.3	3.5	67.3	3.5	12.2
SB	80.8	1.2	90.5	8.6	0.9	–[c]	–[c]	–[c]	4.3	0.4

[a] Oxygen calculated by difference.
[b] Product not detected.
[c] Analysis could not be performed as the product was not detected or was not enough for analysis.

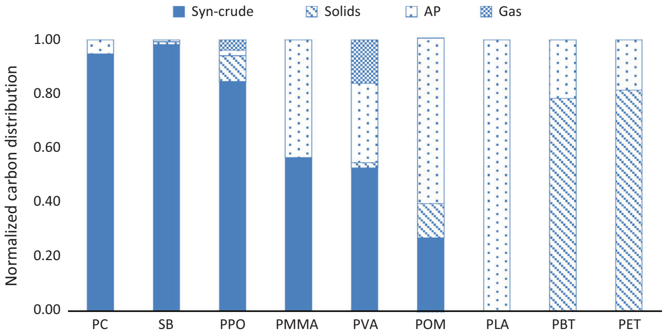


Fig. 3. Normalized carbon balance for the product phases obtained.

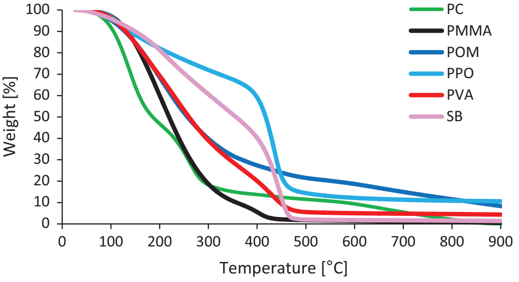


Fig. 4. Mass loss (TGA) curves of the syn-crudes.

isopropylphenol (2), and isopropenylphenol (3), and were all a clear result of BPA (4) cleavage. Hunter et al. demonstrated that these compounds can be synthesized from BPA in hot-compressed water, but clearly the present results show that similar products can be obtained by processing PC [Hunter et al., 2004]. The elemental analysis of the liquid product, which is nearly identical to that of the original resin, also confirms the fact that only these four main compounds are formed.

$$Polycarbonate \xrightarrow{hydrolysis} BPA \xrightarrow{cracking} phenolics \quad (1)$$

The simplicity of the product slate is a great advantage in further processing and product separation, and is in shape contrast to e.g. hydrothermal processing of biomass, where the product slate consists of hundreds of different compounds [Peterson et al., 2008].

From these results, it is evident that hydrothermal processing for tertiary recycling of PC is prospective. A significant portion of the BPA monomers can be obtained, which can be directly recycled to PC manufactures for new identical resins. Furthermore, the isopropylphenol, isopropenylphenol, and phenol are already valuable commodity chemicals [Hunter et al., 2004], and potential fuel candidates when further processed. It is expected, though, that the process severity can be tuned in order to obtain either a higher yield of BPA or more cracking products, in particular by temperature and reaction time, depending on the preferences [Adschiri et al., 1997].

3.2.2. Styrene-butadiene (SB)

Like for the PC, SB is also mainly converted into liquid, oily products. The TGA results of the SB derived syncrude, however, show that only approximately 40% of the liquid fraction is considered as volatile. The thermal decomposition of polystyrene and polybutadiene are well-known and occur generally through end-chain and random scission, and for which high levels of monomer recovery can be achieved [Beyler and Hirschler, 2002]. The initial temperature for thermal decomposition of polystyrene (~600 K) and polybutadiene (~500 K) are both well below the critical temperature of water (~647 K), and therefore it is expected that SB decomposes at a high degree. Through liquid product analysis, it is observed that the volatile fraction of the product slate from SB processing consists of a broad range of hydrocarbons, primarily of aromatics in the C_8-C_{16} range, including monomeric styrene (Fig. 6).

With more than 80% conversion into syncrude, hydrothermal processing of SB has been demonstrated successfully for tertiary recycling. The product slate of substituted monoaromatics and

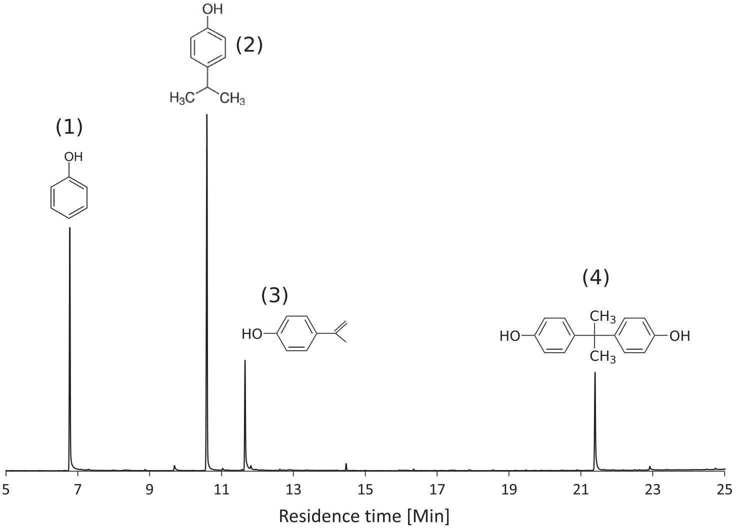


Fig. 5. Chromatogram of the syn-crude obtained for PC hydrothermal processing. (1) phenol, (2) isopropylphenol, (3) isopropenylphenol, and (4) bisphenol A.

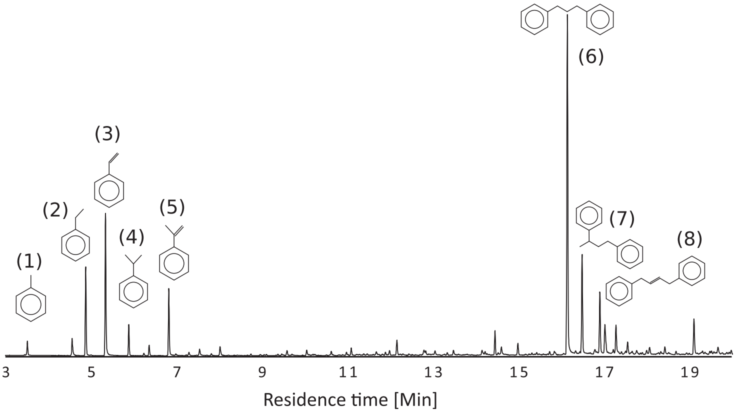


Fig. 6. Chromatogram of the syn-crude obtained for SB hydrothermal processing. (1) toluene; (2) ethylbenzene; (3) styrene; (4) benzene, (1-methylethyl)-; (5) a-methylstyrene; (6) benzene, 1,1′-(1,3-propanediyl)bis-; (7) benzene, 1,1′-(1-methyl-1,3-propanediyl)bis-; (8) benzene, 1,1′-(2-butene-1,4-diyl)bis- .

biphenyls is a potential feedstock for new plastics, e.g. as a BTX pool, and as a pool of gasoline compounds which can be processed by standard refinery technology. The formation of, primarily, hydrocarbons also simplifies the product separation after processing, since it spontaneously separates from the aqueous phase. Although monomeric butadiene was not detected, which will likely be present in the gas phase due to its volatility, the high yield of oily products reveals that butadiene has been synthesized into syncrude compounds. Thermal aromatization of butadiene or condensation reactions with other aromatic derivatives for substituted compounds would indeed both increase the yield of syncrude. These results show that SB is also highly susceptible to hydrothermal processing, although the product slate needs to be further characterized, especially the non-volatile fraction of the syncrude, in order to identify the full potential.

3.2.3. Poly(p-phenylene oxide) (PPO)

PPO is a polyether of aromatic monomers, and like PC and SB it converts into mainly liquid products. Nearly 80% of the PPO is turned into liquids, but of which the majority is considered non-volatile. Of all the investigated resins, PPO appears to be the least volatile, which also complicates the product analysis. With an elemental H/C ratio of the liquid product of 1.15, it is expected that the majority is of aromatic structure. FT-IR analysis shows strong absorptions in the 1720 cm^{-1}, and in the 1600–1400 cm^{-1} band, indicating carbonyl functionalities, including carboxylic acids, see Fig. 7. GC–MS analysis shows only various, methyl-, ethyl-, and propyl- substituted benzenes, and hardly no oxygenated compounds, despite the fact that approximately 6% oxygen is detected through elemental analysis. Therefore, it is assumed that the volatile fraction consists mostly of aromatic hydrocarbons, similar to

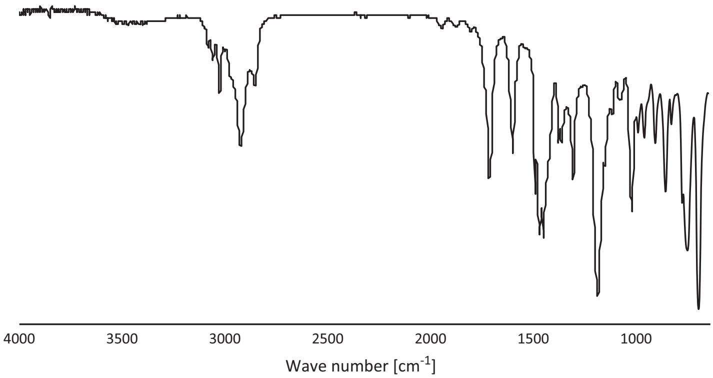


Fig. 7. FTIR spectrum of the PPO derived syncrude.

those obtained from PC and SB processing, and that the non-volatile fraction consists of higher molecular weight compounds containing the oxygenated functionalities. Due to the lack of liquid product analysis, it is hard at this point to determine the potential of hydrothermal processing of PPO. It is a fact that high yield of liquid products can be obtained, but it remains unclear to which extent this product can be used for manufacturing new resins.

3.2.4. Poly(methyl methacrylate) (PMMA)

Hydrothermal processing of PMMA primarily produced an oily phase, which nearly represented 50% of the recovered products. The elemental analysis shows that PMMA derived syncrude has the lowest carbon and the highest oxygen contents among all the syncrudes, which in fact reflect the elemental composition of PMMA itself and of its monomer. The TGA results show that PMMA derived syncrude, similarly to PC syncrude, consists of mainly volatile compounds: in fact, at 300 °C more than 80% is vaporized.

It is known that PMMA molecular scission is favored by thermal degradation at temperatures above 300 °C, which leads to the production of the monomer, methyl methacrylate (MMA), together with many other products [Manring, 1991].

The GC–MS analysis of the syncrude shows that many different compounds, mainly in the C_6-C_9 range, were obtained from PMMA degradation. The main identified products were found to be: cyclohexanecarboxylic acid, methyl ester, pentanoic acid, 4-methyl, methyl ester; pentanedioic acid, 2,4-dimethyl-, dimethyl ester; and 4,4-dimethyl mono-methylglutarate, methyl ester, all clearly derived from PMMA thermal decomposition and by cyclization reactions. The monomer MMA was instead not detected in the pool of these low boiling point compounds. In addition, several carboxylic acid compounds were identified, indicating hydrolysis reactions of derived esters. From the carbon balance it is observed that the rest of the carbon was collected in the aqueous phase. In agreement with the observation of the carboxylic acids formation, the AP appeared highly acidic with a pH value of 2.8, and furthermore its TOC was found among the highest (23.4 g/L). Such high value could be explained by the presence of the monomer MMA in the aqueous phase. Therefore further qualitative investigation on the AP is required. Hydrothermal processing of PMMA, alone or mixed in a blend with other polymers, is considered a valuable alternative for unrecyclable waste plastic handling with chemicals recovering.

$$PMMA \overset{cracking/}{\underset{}{\overset{cyclization}{\rightarrow}}} esters \overset{hydrolysis}{\rightarrow} carboxylicacids \tag{2}$$

3.2.5. Poly(vinyl alcohol) (PVA)

According to Table 1 it is evident that PVA also produces a significant amount of syncrude (~35%), and only to a minor extent a solid phase, when processed hydrothermally. Thermal decomposition of PVA via pyrolysis has previously been studied [Gilman et al., 1994]. It has been found that thermal decomposition is initiated well below 300 °C and terminates around 475 °C. The thermal decomposition of PVA involves H_2O chain stripping resulting in the formation of polyenes. These may then undergo cyclization, aromatization, condensation etc. forming substituted compounds, cyclic and aromatic compounds.

TGA of the PVA derived syncrude shows that approximately 60% is volatile. Of the volatiles, GC–MS analysis showed that mainly aromatic compounds are obtained, e.g. phenol, benzyl alcohol, benzoic acid, cumenol. This observation is in accordance with the elemental composition of the PVA derived syncrude, which shows a H/C ratio of 1.32 and an oxygen content of 9%, which indicates predominately aromatic oxygenated compounds. This reflects that PVA also undergo dehydration, cracking and to a great extent aromatization of intermediates when processed in supercritical water.

$$PVA \overset{-H_2O}{\rightarrow} polyenes \overset{cracking/}{\underset{}{\overset{cyclization}{\rightarrow}}} oxygenatedaromatics \tag{3}$$

In a plastics co-processing context, the formation of aromatic compounds from PVA has synergetic potential. For instance, if processed together with e.g. PC, SB, or PPO, the majority of compounds will still be an aromatic pool of compounds for which the extent of oxygenates can be tuned be varying the ratio of the different resins.

3.2.6. Poly(oxymethylene) (POM)

POM hydrothermal conversion led, in a smaller extent, to the production of syncrude (~14%) and solids (~8%); while the majority of the carbon was recovered in the aqueous phase, whose TOC content is in fact the highest among the aqueous phases, reaching a concentration of 25 g/L.

It is known that the thermal decomposition of POM yields formaldehyde by end-chain initiation followed by depolymerization [Beyler and Hirschler, 2002]. Formaldehyde is highly soluble in water, and below 200 °C it tends to react producing methanediol by hydration [Matubayasi et al., 2007]. The high carbon content of the aqueous phase could therefore be related to the presence of e.g. formaldehyde and methanediol. From the TGA it can be noted that the POM derived syncrude is both made of low and high boing point compounds: at 300 °C, 40% of the syncrude is not volatilized yet. In the pool of the low boiling point compounds, phenols (dimethyl, trimethyl and tetramethyl) together with ketones, such as 2-pentanone (4-hydroxy-4methyl) and 2-cyclopenten-1-one (2,3,4-trimethyl-), were identified as the main compounds by GC–MS analysis. This indicates that intermediates form POM decomposition may undergo more complex condensation reactions, ultimately leading to the formation of higher boiling and even non-volatile compounds. A great interest would be related to further investigate the formation mechanism of phenolic and ketonic compounds, and furthermore the recovery of the compounds due to their high added value, as they are not just commonly involved in the plastic production, but also used in the pharmaceutical industry.

3.2.7. Poly(lactic acid) (PLA)

From Table 1 it is evident that the vast majority of compounds, formed from PLA degradation, were obtained in the aqueous phase. In order to investigate the compounds formed, the aqueous phase was extracted using the method developed by Madsen et al. which is capable of extracting a broad range of different chemical compounds [Madsen et al., 2016]. A broad range of compounds were identified including several carboxylic acids accounting e.g. acetic acid, propanoic acid, butyric acid, lactic acid, valeric acid and 2-methyl butyric acid etc. In addition, several alcohols and ketones, mainly in the C_5 and C_6 range, were identified.

Through previous studies it is known that lactic acid chemically converts along several reaction pathways when subjected to supercritical water [Mok et al., 1989]. Decarbonylation, decarboxylation, and dehydration are known reactions in lactic acid conversion, which lead to a variety of different compounds, such as acetaldehyde and acrylic acid [Szedlacsek, 2013]. Serrano-Riuz and Dumesic showed that especially acetaldehyde, but also lactic itself, can be intermediate compounds for the formation of C_4-C_7 ketones and alcohols [Serrano-Ruiz and Dumesic, 2009].

The fact that lactic acid is detected in the aqueous is prospective from a circular plastic economy perspective. Moreover, the presence of a broad range of commodity chemicals, obtained mainly from the aqueous phase, might be a process advantage when considered in a plastic blending context. For instance, in PLA/PPO or PLA/PVA blends a straight forward separation scheme is expected since the majority of PLA degradation compounds will be obtained in the aqueous phase, whereas the PPO or PVA derived compounds will be obtained primarily in the water-insoluble synthetic crude phase.

3.2.8. Poly(butylene terephthalate) (PBT) and Poly(ethylene terephthalate) (PET)

For the PBT only aqueous phase and solid products were obtained, where approximately 80% of the carbon was recovered in the solid phase. PBT is known for its intolerance to hot water, and present results showed that full degradation can be achieved within short residence times [Beyler and Hirschler, 2002]. GC–MS analysis showed that the solid phase consisted almost exclusively of terephtalic acid (TPA), one of the two monomers of PBT (the other one being butanediol). This indicates that the esters groups underwent hydrolysis under the applied hydrothermal conditions forming TPA and butanediol. Furthermore, the results also show that TPA is thermally stable under the severe conditions, and that char formation reactions are retarded. The insolubility of TPA in water resulted in a benign chemical recovery, which could be performed simply by decanting or filtration. Moreover, in blend products, like PC/PBT blends, chemical recovery is expected to be simple since PC forms mainly supernatant syncrude, whereas the TPA will precipitate and be recovered as solids. According to Fig. 2, it is observed that the remaining carbon is obtained in the aqueous phase, but it still remains to be investigated if butanediol is in fact recovered in the aqueous phase.

PET is also, like PBT, known to be intolerant to hot water [Beyler and Hirschler, 2002]. Structurally, PET and PBT are very similar and therefore it is expected that these polymers will behave similarly when exposed to supercritical water. Just like it was observed for PBT, the majority of carbon (~80%) was obtained in a solid fraction, of which TPA was found as the dominating compound. The simplicity in these observations can easily be identified in blend products like PC/PET (same as for PC/PBT) and for PBT/PET blends. As in the case of PBT, it remains to be investigated if ethylene glycol can be recovered in the aqueous phase. The fate of ethylene glycerol in supercritical water, but under alkaline conditions, was investigated by [Pedersen and Rosendahl, 2015]. Under these conditions, it was found that ethylene glycerol is also synthesized into a syncrude, although in low yields.

3.3. Applications and challenges

Results have shown that high yields of synthetic crude oil can be achieved when processing plastic polymers individually under supercritical water conditions. For the majority of the polymers in the present study, more than 50% of the plastic fed into the reactor is in fact decomposed to synthetic crude oil.

The synthetic crude oil constitutes a variety of chemical compounds that makes it usable as source for extraction of valuable chemicals or as a fuel. It is envisioned that the postprocessing of the synthetic crudes, e.g. separated, purified, and upgraded can be handled by business-as-usual refinery operations. Furthermore, the analyses of the products have highlighted the presence of monomers, which if properly extracted can be reintroduced into the market for the production of new plastic materials. Both aspects, the production of the synthetic-crude oil and the presence of monomers in the products, show that hydrothermal processing can be considered as a potential technology for increasing the circularity of the plastic economy.

The recovery of monomers and other value added chemicals from the bulk synthetic crude must however be examined in the light of actual plastic waste processing. Dies, additives, and impurities etc. may likely challenge the separation since they will mixed with the synthetic crude product. For instance, if carbon blacks or titanium oxides are used for pigmentation, such additives will likely be obtained in the product precipitate. Processing colored PET or PBT could therefore be challenging since TPA monomers will mix with precipitated additives. Hydrothermal treatment of undifferentiated mixtures of plastics with and without additives is therefore a necessary consequential study needed to evaluate the technology potential. Co-processing of plastic materials with other organic feedstock, e.g. household waste and sewage sludge containing micro-plastics resembles other relevant plastics waste streams. Recovery of the plastics from these streams may turn out challenging, where direct co-processing, without any pre-separation, seems attractive. In conclusion, the results of the present study are promising and future studies focussing on handling real waste streams under hydrothermal conditions should be undertaken.

4. Conclusions

In this study nine different types of high-density plastics are processed in supercritical water. Results show that all the plastics are susceptible to hydrothermal treatment, which converts them into synthetic crude oil, water soluble organics, gases and solids. The yield of synthetic crude oil ranges from 0%, for e.g. PET, PBT, and PLA, to nearly a 100% for PC. For PC, the synthetic oil is a simple mixture of only few compounds included BPA, the original PC monomer. PPO, SB, and PVA, all demonstrate high yields of synthetic oils but of more complex nature, nonetheless all of aromatic structures. For PET and PBT it was observed that the obtained solid fractions contained almost exclusively terephalic acid, one of the original monomeric compounds. In conclusion, the study demonstrates that hydrothermal processing of high-density plastics is a prospective technology for tertiary recycling, in order to produce high value chemical compounds and to recover, at the same time, monomeric constituents.

AKNOWLEDGEMENTS

The Danish Council for Strategic Research financially supported this research (Grant No. 1305-00030B).

References

Adschiri, T., Shibata, R., Arai, K., 1997. Phenol recovery by BPA tar hydrolysis in supercritical water. J. Jpn. Pet. Inst. 40, 291–297.

Al-Salem, S.M., Lettieri, P., Baeyens, J., 2009. Recycling and recovery routes of plastic solid waste (PSW): a review. Waste Manage. 29, 2625–2643.

Beyler, C.L., Hirschler, M.M., 2002. Thermal decomposition of polymers, SFPE Handbook of Fire Protection Engineering 2, Section 1, C7, pp. 110–131.

Bockhorn, H., Hornung, A., Hornung, U., 1998. Stepwise pyrolysis for recycling of plastic mixtures. Macromol. Symp. 135, 35–41.

Curlee, T.R., Das, S., 1998. Viability of recycling plastics by tertiary processes. Solid Waste Technol., 50–57

De Jong, S., 2015. The feasibility of short-term production strategies for renewable jet fuels – a comprehensive techno-economic comparison. Biofuels Bioprod. Bioref. 9 (6), 778–800.

Gent, M.R., Menendez, M., Toraño, J., Diego, I., 2009. Recycling of plastic waste by density separation: prospects for optimization. Waste Manage. Res. 27, 175–187.

Gilman, J.W., VanderHart, D.L., Kashiwagi, T., 1994. Thermal decomposition chemistry of poly(vinyl alcohol), Fire and Polymers II: Materials and Tests for Hazard Prevention, pp. 161–185.

Hunter, S.E., Felczak, C.A., Savage, P.E., 2004. Synthesis of *p*-isopropenylphenol in high-temperature water. Green Chem. 6, 222–226.

Iwaya, T., Sasaki, M., Goto, M., 2006. Kinetic analysis for hydrothermal depolymerization of nylon 6. Polym. Degrad. Stab. 91, 1989–1995.

Madsen, R.B., Jensen, M.M., Mørup, A., Houlberg, K., Christensen, P.S., Klemmer, M., Becker, J., Iversen, B.B., Glasius, M., 2016. Using design of experiments to optimize derivatization with methyl chloroformate for quantitative analysis of the aqueous phase from hydrothermal liquefaction of biomass. Anal. Bioanal. Chem. 408, 2171–2183.

Manring, L.E., 1991. Thermal degradation of poly(methyl methacrylate) random side-group scission. Macromolecules 24, 3304–3309.

Matubayasi, N., Morooka, S., Nakahara, M., Takahashi, H., 2007. Chemical equilibrium of formaldehyde and methanediol in hot water: Free-energy analysis of the solvent effect. J. Mol. Liq. 134, 58–63.

Meng, L., Zhang, Y., Huang, Y., Shibata, M., Yosomiya, R., 2004. Studies on the decomposition behavior of nylon-66 in supercritical water. Polym. Degrad. Stab. 83, 389–393.

Mok, W.S.L., Antal, M.J., Jones, M., 1989. Formation of acylic acid from lactic acid in supercritical water. J. Org. Chem. 54, 4596–4602.

Onwudili, J.A., Insura, N., Williams, P.T., 2009. J Anal. Appl. Pyrol. 86, 293–303.

Park, Y., Hool, J.N., Curtis, C.W., Roberts, C.B., 2001. Depolymerization of styrene-butadiene copolymer in near-critical and supercritical water. Ind. Eng. Chem. Res. 40, 756–767.

Pedersen, T.H., Rosendahl, L.A., 2015. Production of fuel range oxygenates by supercritical hydrothermal liquefaction of lignocellulosic model systems. Biomass Bioenerg. 83, 206–215.

Peterson, A.A., Vogel, F., Lachance, R.P., Fröling, M., Antal, M.J., Tester, J.W., 2008. Thermochemical biofuel production in hydrothermal media: a review of sub- and supercritical water technologies. Energy Environ Sci. 1, 32–65.

Serrano-Ruiz, J.C., Dumesic, J.A., 2009. Catalytic upgrading of lactic acid to fuels and chemicals by dehydration/hydrogenation and C-C coupling reactions. Green Chem. 11, 1101–1104.

Sugano, M., Komatsu, A., Yamamoto, M., Kumagai, M., Shimizu, T., Hirano, K., Mashimo, K., 2009. Liquefaction process for a hydrothermally treated waste mixture containing plastics. J. Mater. Cycles Waster Manage. 11, 27–31.

Szedlacsek, H., 2013. On the dehydration of lactic acid in near- and supercritical water. Doctoral dissertation, Technische Universität, Damstadt.

Watanabe, M., Hirakoso, H., Sawamoto, S., Adschiri, T., Arai, K., 1998. Polyethylene conversion in supercritical water. J. Supercrit. Fluids 13, 247–252.

World Economic Forum, 2016. The New Plastics Economy Rethinking the Future of Plastics.

Zhu, Y., Biddy, M.J., Jones, S.B., Elliott, D.C., Schmidt, A.J., 2014. Techno-economic analysis of liquid fuel production from woody biomass via hydrothermal liquefaction (HTL) and upgrading. Appl. Energy, vol. 129, 384–394. Table 1. Yield and composition of oils and solids, and analysis of aqueous phases.

Paper B

Biocrude production and nutrients recovery through hydrothermal liquefaction of wastewater irrigated willow

F. Conti, S. S. Toor, T. H. Pedersen, A. H. Nielsen,
L. A. Rosendahl

The manuscript has been published in:
Biomass and Bioenergy 118 (2018) 24–31

The layout has been revised.

Biomass and Bioenergy 118 (2018) 24–31

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: www.elsevier.com/locate/biombioe

Research paper

Biocrude production and nutrients recovery through hydrothermal liquefaction of wastewater irrigated willow

Federica Conti[a,*], Saqib S. Toor[a], Thomas H. Pedersen[a], Asbjørn H. Nielsen[b], Lasse A. Rosendahl[a]

[a] Department of Energy Technology, Aalborg University, Pontoppidanstræde 111, Aalborg, 9220, Denmark
[b] Department of Civil Engineering, Aalborg University, Thomas Manns Vej 23, Aalborg, 9220, Denmark

ARTICLE INFO

Keywords:
SRC for wastewater cleaning
Supercritical HTL
Biocrude oil
Inorganics distribution
NPK recovery
Metals recovery

ABSTRACT

Willows are increasingly used as natural filters to treat nutrient-rich wastewater. Their natural tendency to absorb minerals is exploited both for the nutrients and the metals, which are contained in the wastewater. This application allows addressing environmental concerns related to wastewater management and, at the same time, achieving higher biomass yields. However, the end-use of this biomass is often a simple incineration for production of heat and power.

The present study proposes, alternatively, to use willow biomass, grown on wastewater irrigated fields, as feedstock for the hydrothermal liquefaction process. The thermochemical conversion route allows the valorization of the organic fraction of the biomass into a biocrude oil, and simultaneously collecting and preserving the inorganic elements in the effluent products.

The willow was converted at supercritical water conditions (400 °C) for 15 min in a micro-batch reactor (10 cm^3), and high mass yields (39.7%) of energy dense (38.6 $MJ\ kg^{-1}$) biocrude oil were obtained. It was found that most inorganics, including phosphorus (76% of total P on a mass basis), are mainly transferred to the solid products. The concentration of the elements in the solids eases their recovery and re-use for soil amendment. A different tendency was observed for potassium and sodium, which were almost exclusively collected in the aqueous phase (above 88% for both K and Na on a mass basis). Significant quantities of nitrogen and sulfur, and some metals, were transferred to the biocrude oil, however its quality resulted overall unaffected.

1. Introduction

The use of renewable energy sources for the production of fuels and chemicals is increasingly required as fossil reserves are depleting, and because of environmental concerns arising from fossil fuels usage [1]. Lignocellulosic biomasses (i.e. poplar and willow) are commonly grown in Short Rotation Coppice (SRC) as renewable carbon source to produce heat and power. In particular, willow is a fast growing plant, easily adaptable to various climates and soils, and can lead to high biomass yields per hectare of cultivation [2]. Willow plants find application also in the phytoremediation of metal polluted soils, where their natural capacity of up-taking elements through their roots is exploited for remediation of heavily contaminated lands [3–5]. Using willow as vegetation filter, for cleaning of wastewater, has been demonstrated to be a good alternative for waste management and to have an increased biomass production with no further costs for fertilizers [6]. Studies have investigated different wastewater streams: groundwater [7], municipal wastewater [8], or agricultural drainage water [9].

Every two to four years SRC willow crops are cut, and the biomass is mainly used for heat and power production. Heavy metals, absorbed by willow biomass during phytoremediation processes, are primarily recovered in the ashes after combustion [10], and some technologies have also been developed for their separation [11]; in contrast, a great portion of nitrogen and sulfur is irreversibly lost during combustion [12].

Willow biomass can also be used as lignocellulosic feedstock for biofuel production in thermochemical processes like Hydrothermal Liquefaction (HTL). HTL is a high pressure, medium temperature process, where various biomasses or organic waste sources are processed in the presence of water to produce an energy dense oily product, named biocrude, along with an aqueous phase, some solids, and gases [13]. HTL is an energy-efficient technology (85% of the energy in the feedstock is recovered in the biocrude). In continuous HTL processing, the feedstock can be efficiently converted into biocrude (45%, mass fraction of the dry ash free feedstock) [14]. In some studies, willow wood has already been investigated as a raw material for hydrothermal

---

[*] Corresponding author.
E-mail address: fco@et.aau.dk (F. Conti).

https://doi.org/10.1016/j.biombioe.2018.07.012
Received 8 October 2017; Received in revised form 14 July 2018; Accepted 16 July 2018

processing, for example with focus on the dissolution mechanism [15] or its application in a continuous bench scale reaction unit [16].

A new concept is proposed in this work, where the wastewater is used to grow willow trees, which are then converted by HTL to biocrude while nutrients are recovered simultaneously from the aqueous and solid by-products. Biocrude oil can be upgraded to meet drop-in fuels properties, while the nutrients could be re-utilized as fertilizers for agricultural lands.

Recycling of nutrients for cultivation of algae by recirculation of the aqueous phase produced from HTL [17,18] or hydrothermal gasification [19] of algae has been previously studied in literature. Moreover, few other studies were found on the fate of nitrogen [20] and other inorganics [21] in hydrothermal carbonization. Ekpo et al. [22] have investigated the inorganics in the solid residues and the nutrients in the water phases from hydrothermal processing of microalgae, manure and digestate at various temperatures. Lu et al. [23] have similarly looked into the inorganic content of aqueous and solid residues after HTL of human feces in subcritical water conditions. Carrier et al. [24], studied the effect of temperature on the inorganics redistribution after sub- and supercritical hydrothermal liquefaction of uncontaminated and As-contaminated fern biomass.

The aim of the present study was to understand the fate of nutrients and metals after HTL of willow, grown with wastewater, in supercritical water conditions; and ultimately to define the distribution of the inorganic elements among the different product phases from HTL, including the biocrude. Furthermore, it was investigated whether the quality of the oil was eventually affected by the presence of inorganics.

2. Materials and methods

2.1. Feedstock characterization

The raw material used in the HTL experiments is willow wood, clone variety Björn (Salix schwerinii x Salix viminalis), which has been developed in particular to get high biomass-yields and a high nutrient-uptake. The biomass was grown at Center for Recirkulering (Denmark, 55.831485, 8.635960), and it was irrigated with untreated household wastewater and sewage from local houses for two years. Two-year-old stems of fifteen-year-old roots were provided for the experiments. Stems were 25–30 cm long, with a diameter of 1–2 cm, and with bark. In order to ease the reactor loading, the willow stems including bark were chopped and further ground to sawdust with a particle size below 0.5 mm, in a cyclone mill (Foss, Cyclotec 1093). After the milling, the willow was characterized in terms of moisture content, ash content, and elemental composition, and the average results from the measurements are reported in Table 1. The moisture mass fraction of the willow sawdust was measured in a moisture analyzer (Kern, MLS) at 120 °C. The ash mass fraction was instead determined after holding pre-dried samples isothermally at 775 °C for 3 h in an electric muffle furnace (Protherm Furnaces). The TG curve of the willow biomass obtained by Thermo-Gravimetrical Analysis, confirmed both the moisture mass fraction (~5%, at 100 °C) and the ash mass fraction (< 1%, see Fig. 1).

Inductively Coupled Plasma (ICP) analysis was used to investigate the presence of nutrients and heavy metals in the willow biomass, and the average concentrations of the investigated inorganics are reported in Table 2. Calcium and potassium are the most abundant inorganic source, while the presence of phosphorus, sulfur, magnesium, and iron is significant as well. The mass fraction of inorganics investigated by ICP sums up to 0.38%, therefore the rest of the inorganics should be attributed to the elements as aluminum, lead or nickel, which are highly abundant in wastewater [25].

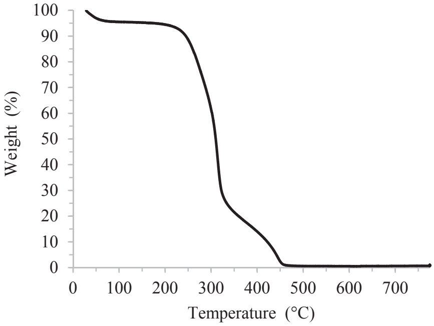


Fig. 1. Thermogravimetric curve of the willow wood.

2.2. Experimental procedure for HTL experiments

HTL experiments were carried out in stainless steel micro-batch reactors with 10 cm^3 volume. A total of three experiments were carried out under the same process conditions, and the average results are reported together with the standard deviations. A homogeneous slurry (7 g) was prepared by adding distilled water to the willow sawdust. The high biomass loading into the feed, corresponding to a mass fraction of 20% on a dry basis, is expected to additionally cause a relatively high biocrude yield. At the same time it will enable a smooth pumpability of the slurry when operating in a continuous system.

Potassium carbonate (K_2CO_3) was added to the feed mixture (2.5% in weight of the water-biomass mixture), as alkaline conditions promote biocrude oil production, reduce coke formation [26], and enhance the de-oxygenation of lignocellulosic biomass leading to biocrudes with lower oxygen content [27].

Reactors were sealed, purged with nitrogen to remove residual air, and then pre-pressurized to 2 MPa to push the slurry down into the reactor volume. Without pre-pressurizing, accumulation of the slurry in the upper capillary section of the reaction system [28] was observed, causing undesirable, unconverted material to appear in the products.

The biomass was converted at supercritical conditions; in this region, the thermo-physical properties of water are enhanced. The dielectric constant is significantly reduced and consequently water becomes a non-polar solvent in which organics can easily dissolve. At higher temperatures, taking advantage of the increased reaction rates, a higher degree of depolymerization can be achieved leading to biocrude oil with an improved quality (e.g. lower oxygen content, lower viscosity, higher HHV) [14,29]. Reactors were submerged in a pre-heated sand bath (Techne, SBL-2D), which provided the necessary heating to reach the reaction temperature, set to 400 °C, in about 1 min (heating

Table 1
Characterization of the willow sawdust used as the HTL feedstock material. The values measured are mass fractions.

Moisture	Ash[a]	C[a]	H[a]	N[a]	O[a b]	H/C	O/C
(%)	(%)	(%)	(%)	(%)	(%)	(−)	(−)
5.54 ± 0.42	0.70 ± 0.07	46.92 ± 0.23	6.10 ± 0.08	0.30 ± 0.11	45.98 ± 0.04	1.55	0.84

[a] Dry basis.
[b] Oxygen calculated by difference (O = 100-C-H-N-ash).

Table 2
Concentrations of inorganic elements in the pre-dried willow sawdust.

		Ca	Cu	Fe	K	Mg	Mn	Na	P	S	Zn
willow	(mg kg^{-1})	1688 ± 901	5 ± 2	234 ± 57	891 ± 297	240 ± 56	66 ± 17	87 ± 52	308 ± 70	211 ± 31	56 ± 15

rate: 250–450 K min^{-1} [30]). A rapid heating suppresses the formation of char by repolymerization of the intermediates, which frequently occurs at lower heating rate [26]. According to previous studies [30], reactors were kept in the bath for 15 min (including the heating period), while agitation was provided by a motor system. Both temperature and pressure were monitored during the entire reaction time. Pressures of about 35–38 MPa were achieved at supercritical water conditions. After the reaction time, the reactors were quenched to room temperature (cooling rate: 1000 K min^{-1} [30]) in a water bucket.

2.3. Products separation and recovery

The gas, produced during the hydrothermal conversion of the willow biomass, was released from a valve, placed on top of the reactors, into a gas collecting system for being analyzed qualitatively. Reactors were turned upside down and the aqueous phase was collected, without adding any solvents to preserve its quality and composition for analysis.

Reactors were unsealed and rinsed with acetone (Cab Dan, acetone > 95%) to collect the oil phase and the solids. The recovered mixture was vacuum filtered to separate the solids. The solids were collected on a filter paper (VWR, particle retention: 5–13 µm), rinsed with distilled water to wash away the catalyst, dried in the oven overnight at 105 °C, and finally weighted to determine their yield. The acetone was evaporated in a rotary evaporator (40 °C, 56 kPa), while Diethyl Ether (DEE, Sigma Aldrich, ACS reagent, anhydrous, > 99.0%) was added to recover the oil from the flask in the rotary, and to allow removing of any residual water. As DEE is immiscible in water, it formed a top phase with the oil, while the residual water was recovered at the bottom. DEE was finally evaporated (40 °C, 99 kPa) and the remaining biocrude oil was weighted to report the yield. The combined use of acetone and DEE was here adapted from the method used by Pedersen et al. for the recovery of oil products after HTL of lignocellulosic model compounds [30].

Although the use of micro-batch reactors enables a fast screening of the biomass, simulating what happens in continuous processing, there are some challenges related to working at such small scale. Each step in the recovery of the products includes an additional risk of losses. Therefore, the less steps involved the better it is. In the present work the aqueous phase was collected in two steps: first without adding any solvent to preserve its quality, and then after the addition of the DEE. It should be noticed also that a small amount of aqueous phase could get lost upon evaporating the acetone.

2.4. Products characterization

The elemental composition of the biocrude and solids was determined by an elemental analyzer (Perkin Elmer, 2400 Series II CHNS/O), operated in CHN mode. Acetanilide (Sigma Aldrich, puriss. p. a., ≥9.5%) was used as standard to calibrate the instrument. The instrument provided information on the C, H, and N mass fraction in the products, while O was calculated by difference however without accounting for the ashes. Ash determination was impossible because the product samples were too small for that. The volatility of the biocrude was assessed by Thermogravimetrical Analysis (TGA, TA Instrument, Discovery). Samples were heated from room temperature to 1000 °C (20 K min^{-1}) in a nitrogen atmosphere.

Qualitative analysis of the volatile fraction of the bio-crude was performed in a GC-MS system: a Gas Chromatograph (Thermo Scientific, Trace 1300) coupled with a Mass Spectrometer (ISQ QD). The GC oven was equipped with a capillary column (Agilent Technologies, length: 30 m, I.D.: 0.25 mm, film thickness: 0.25 mm), whose temperature was increased up to 300 °C (10 K min^{-1}) during the measurements. The MS ion source was kept at a constant temperature of 300 °C. Before injecting 1 mm^3 of bio-crude oil in the GC-MS inlet (injector temperature 300 °C), samples were diluted in DEE and filtered using 0.45 µm syringe filters.

The pH of the aqueous phase was measured with a WTW pH meter 3210. Total organic carbon, total nitrogen, chloride, phosphate, and sulphate concentrations of the water phase were instead determined using reagent vials (LCK: 386, 138, 311, 349, 153, respectively) and a spectrophotometer unit (Hach & Lange, DE3900).

The composition of the reaction gas was determined in a Gas Chromatograph (Shimadzu, Tracera, GC-2010 Plus). 0.1 mm^3 were injected into a micropacked column (Restek, length: 2.0 m, I.D.: 0.53 mm), whose temperature was set to 85 °C, while the signal was elaborated by a Barrier Ionization Discharge (BID) detector. Helium was the carrier gas (total flow: 803 cm^3 min^{-1}; split ration: 1:200; flow control mode: pressure 400 kPa). The GC had previously been calibrated for measuring of H_2, CH_4, CO and CO_2.

2.5. Analytical method for measuring inorganics

The concentration of inorganics in the solids, in the aqueous phase and in the biocrude was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). In order to extract the elements of interest, samples were digested by microwave assisted acid digestion according to EPA method 3051A (US. EPA., 2007). The microwave reaction system was an Anton Paar Multiwave 3000 equipped with a HF-16 high-pressure rotor and Teflon® lined ceramic digestion vessels. Approximately 0.2 g of material was weighed into each digestion vessel and 9 cm^3 concentrated nitric acid (HNO_3) and 3 cm^3 hydrochloric acid (HCl) were added. All acids were of suprapure quality (PlasmaPure, SCP Science). In accordance with the method, the digested samples were transferred into Polypropylene vials and diluted to 50 cm^3 with Type I ultrapure water (Elga LabWater). The ICP instrument was a Thermo iCap 6300 Duo view ICP-AES operated in axial view mode (Thermo Scientific). The forward power of the radio frequency (RF) generator was 1150 W and the plasma and auxiliary gas flows were set at 12 L min^{-1} and 1.0 L min^{-1}, respectively. The introduction system for samples was a cyclonic spray chamber equipped with a concentric glass nebulizer operated at sample uptake rate of 2 cm^3 min^{-1} and a nebulization gas pressure of 200 kPa. The ICP-AES was calibrated using matrix matched multi-element external standards. The standards were prepared from single element standards of 1 g L^{-1} (PlasmaCAL, SCP Science). Each element was quantified using several emission lines, measured in triplicate. When more than one emission line was used, the concentration was calculated based on the average concentration reported. The integration time was 5 s for emission lines above 243 nm, and 15 s for emission lines with shorter wavelengths. Internal standardization using yttrium (Y) was used for compensation of possible matrix effects; i.e. all samples and standards were spiked with Y to a final concentration of 1 mg L^{-1}. For quality control, Certified Reference Material (CRM) was digested and analyzed along with the samples. The CRM was lyophilized and homogenized sewage sludge of type EnviroMAT BE-1 (SCP Science). The method yielded results within the specified confidence interval of the CRM.

Table 3
Mass yield of solids and biocrude after HTL of willow, and characterization of solids (on dry basis) and biocrude in terms of elemental mass fractions and HHV.

Product	Yield[a,d]	C[d]	H[d]	N[d]	O[b,d]	H/C	O/C	HHV[c]
	(%)	(%)	(%)	(%)	(%)	(−)	(−)	(MJ kg^{-1})
solids	10.83 ± 1.28	71.64 ± 3.08	3.82 ± 0.06	0.43 ± 0.01	24.11 ± 3.13	0.64	0.29	32.00
biocrude	39.72 ± 7.54	78.15 ± 1.24	8.50 ± 0.43	0.95 ± 0.15	12.40 ± 0.96	1.30	0.14	38.57

[a] Dry basis.
[b] Oxygen calculated by difference (O = 100-C-H-N).
[c] HHV calculated using Channiwala and Parikh correlation [32].
[d] ± numbers refers to the standard deviations of the average values.

3. Results and discussion

3.1. Solid residues and biocrude oil

The catalytic thermochemical conversion of willow, grown on wastewater irrigated fields, in supercritical water produced a high yield of biocrude oil (mass fraction of the dried feedstock 39.7 ± 7.5%), and some solid residues (mass fraction of the dried feedstock 10.8 ± 1.3%). The rest of the carbon contained in the feedstock was recovered in the aqueous phase, as soluble organics, and in the reaction gas. Biocrude yields were higher than those (31% and 28.5 ± 1.0% in mass, dry basis) reported in previous studies [16,31]. Possible causes include the rapid heating provided by the present reaction set-up, the pre-pressurization of the reactors leading to higher pressure during the hydrothermal conversion, the choice of the catalyst, and the solvents used to collect the oil and the other products. The elemental composition of the solids and of the biocrude oil are shown in Table 3, where the average values from different experiments, each sample repeated twice, are reported. The high carbon mass fraction (78%) and the low oxygen mass fraction (12%) of the biocrude are reflected in its high HHV (38.6 MJ kg^{-1}). The carbon mass recovered in the biocrude corresponds to 66.16% of the carbon contained in the original biomass. The reduced oxygen content in the biocrude, with respect to the biomass, is explained by the reactions that take place during HTL processing. Oxygen was removed through decarboxylation and dehydration reactions, and carbon dioxide and water were formed as products. From the elemental analysis, it appeared also that a great portion of the nitrogen was transferred to the biocrude, and therefore an upgrading (e.g. catalytic hydrotreating) of the oil for reducing nitrogen heteroatoms will be needed to use it as fuel precursor.

TG analysis showed that the biocrude is a mixture of low and high boiling point compounds. The weight loss of the oil occurred in a single step. More than half of the mass of the biocrude (60%) consisted of low (< 180 °C) and medium (180–350 °C) boiling point compounds, which represent the gasoline, jet fuel, and diesel fractions. About 20% of the mass of the biocrude was volatilized in the boiling range of lubricants and maritime fuels (350–575 °C). The remaining non-volatile fraction accounted for 20% of the mass of the biocrude, and it represents the asphalts and residue (see Fig. 2).

The biocrude was analyzed qualitatively by GC-MS, which enabled the identification of compounds with a boiling point below 300 °C; this volatile fraction corresponds to half of the total composition, as visible from the TG analysis (Fig. 2). The volatile fraction of the biocrude appeared to be primarily composed of oxygenated cyclic compounds with carbon in the range C_6-C_{18}. In Table 4, the main identified compounds are reported, together with their chemical formula, peak area, and retention time. As compounds are grouped into chemical classes, it clearly appears that the most abundant compounds are ketones and phenols. Overall, the chemical composition of the biocrude obtained from willow irrigated with wastewater does not differ from the one of the biocrude obtained from normally irrigated willow, where ketones, phenols, and alcohols were also identified as the most abundant compounds [33]. Among the first 30 compounds by peak area, only one was a N-containing compound; the same one was also detected in the previous study [33]. Therefore, the quality of the biocrude appears to remain unaffected when using willow irrigated with wastewater instead of normally irrigated willow.

3.2. Aqueous phase

The aqueous phase appeared to be slightly acidic, despite the use of an alkaline catalyst (see Table 5). This is probably due to the dissolution in the water phase of organic acids and phenols, produced during HTL. The presence of organic compounds in the aqueous phase was in fact confirmed by TOC measurement, which revealed a high carbon concentration (25.09 g L^{-1}). On the other hand, total nitrogen (TN) appeared to be low (0.23 g L^{-1}); this confirmed the fact that most of the nitrogen was transferred to the biocrude, as observed by elemental composition of the oil.

Previous studies on HTL of algae at subcritical temperatures have found that most of the nitrogen was recovered in the aqueous phase [17–19,34,35]. The nitrogen abundance in the aqueous phase was sufficient for recycling and reutilization of HTL water for cultivation of new algae biomass [17,18]. However, they likewise all observed nitrogen in the biocrude. Biller et al. [18] have observed that at higher temperatures (350 °C) more proteins are broken down, resulting in an increased nitrogen content in the biocrude. Both higher temperatures and longer residence times resulted in an increased accumulation of the nitrogen in the biocrude oil in a study conducted by Yu et al. [34].

It should be noted that, in all the studies mentioned above, the nitrogen in the raw biomass was considerably higher than in the willow used in the current study; to some extent, this can explain the different trend in the distribution among HTL products. Considering the outcomes of the above mentioned studies, an aspect that had certainly played an important role in favoring nitrogen concentration in the biocrude is the more severe temperature and pressure used in the present study.

From the measurements reported in Table 5 it appears that the concentration of sulphate (SO_4^{2-}) in the aqueous phase is 200 times larger than the concentration of phosphate (PO_4^{3-}) in the same product phase. These higher concentrations of sulfur in the aqueous phase are also confirmed by ICP analysis (Table 6).

3.3. Reaction gases

The most abundant gas produced in supercritical HTL of willow is CO_2 (volume fraction 75.2%). The volume fraction of H_2 accounted for 19.0%, while only minor volume fractions of CH_4 (3.6%) and CO (2.2%) were detected in the gas mixture. The proportion of the various gas components is in line with results from HTL processing of lignocellulosic biomass, which usually results in slightly higher concentrations of CO_2 at the expense of H_2 [36]. Water gas shift equilibrium (at 400 °C and 30 MPa) would result in the following volume fractions: 78% CO_2, 17% H_2, 4.8% CH_4, and almost no CO. As the measured volume fractions are very close to the calculated ones, the reaction was close to equilibrium.

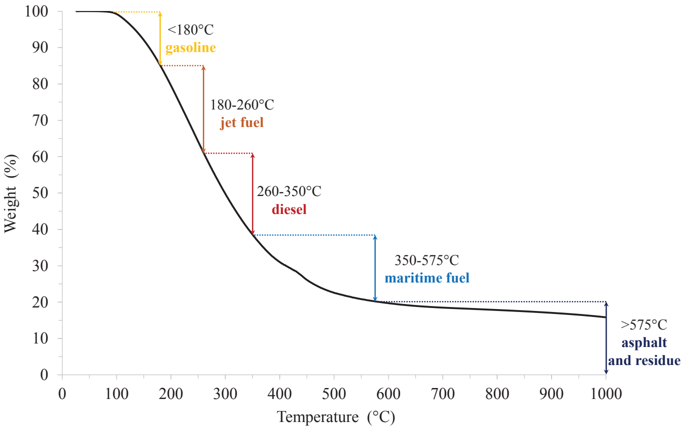


Fig. 2. Thermogravimetric curve of the biocrude and boiling point ranges of petroleum fractions.

3.4. Distribution of the inorganic elements among HTL products

When biomass is converted hydrothermally, the inorganic elements are transferred from the raw feedstock to the products. Therefore, the presence of inorganics in the solid residues, in the biocrude, and in the aqueous phase from HTL of willow, was investigated by ICP-AES analysis.

High concentrations of the inorganics in the solids were found as compared to the concentrations of the same elements in the biocrude and in the aqueous phase (see Table 6). This suggests that most inorganics tend to concentrate in the solid residue after HTL. A different behavior was observed for potassium (K) and sodium (Na): K and Na were mainly distributed in the aqueous phase.

Previous investigations, conducted at subcritical conditions, also reported that alkaline and earth metal elements are primarily recovered in the solid products regardless from the feedstock used: algae [17,22,35], digestate [22], animal manure [22], and human feces [23]. Furthermore, these studies confirmed the tendency of K and Na to concentrate in the water phase, as observed in the present study.

The various pathways followed by the inorganic elements while being distributed over the HTL products may be caused by the way they were included in the raw biomass. Within biomass, calcium, magnesium, and phosphorus bound frequently to the organic matter, which explains why they are primarily retained in the solid products. Instead,

Table 4
Main chemical compounds detected in the biocrude by GC-MS.

Chemical class	Identified compound	Chemical formula	Peak area (%)	Retention time (min)
Ketones	4-Hydroxy-4-methyl-pentan-2-one	$C_6H_{12}O_2$	5.30	7.75
	2,3-Dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	4.62	11.73
	2,3,4-Trimethyl-2-cyclopenten-1-one	$C_8H_{12}O$	3.90	12.15
	3,4,4-Trimethyl-2-cyclopenten-1-one	$C_8H_{12}O$	3.74	12.61
	4-Ethyl-4-methyl-2-cyclohexen-1-one	$C_9H_{14}O$	2.89	14.2
	2-Ethylidenecyclohexanone	$C_8H_{12}O$	1.73	13.32
	3-(1-Methylethyl)-2-cyclopenten-1-one	$C_8H_{12}O$	1.52	12.83
	2,3,4,5-Tetramethyl-2-cyclopenten-1-one	$C_9H_{14}O$	1.39	12.90
	3,4-Dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	0.97	11.44
Phenols	2,6-Dimethyl-phenol	$C_8H_{10}O$	2.82	13.52
	2-Methyl-phenol	C_7H_8O	2.29	12.02
	2,4,6-Trimethyl-phenol	$C_9H_{12}O$	1.94	14.41
	2,3,4,6-Tetramethyl-phenol	$C_{10}H_{14}O$	1.46	16.66
	2-(2-Penten-4-yl)-4-methyl-phenol	$C_{12}H_{16}O$	1.18	19.36
	5-Methyl-2-(1-methylethyl)-phenol	$C_{10}H_{14}O$	1.03	17.57
	3,4,5-Trimethyl-phenol	$C_9H_{12}O$	1.00	15.32
	3,5-Bis(1-methylethyl)-phenol	$C_{12}H_{18}O$	0.97	20.83
	2,3,5-Trimethyl-phenol	$C_9H_{12}O$	0.87	15.38
	2-Ethyl-6-methyl-phenol	$C_9H_{12}O$	0.83	14.72
Hydrocarbons	3-Ethyl-2,5-dimethyl-1,3-hexadiene	$C_{10}H_{18}$	2.56	13.61
(saturated & unsaturated)	Hexadecane	$C_{16}H_{34}$	1.10	18.34
Aromatic	1-(2-Methoxymethyl-3,5,6-trimethylphenyl)ethanol	$C_{13}H_{20}O_2$	1.46	18.92
alcohols	(6-Hydroxymethyl-2,3-dimethylphenyl)methanol	$C_{10}H_{14}O_2$	1.13	17.64
Aromatics	3-Ethyl-1,2,4,5-tetramethyl-benzene	$C_{12}H_{18}$	1.18	19.01
	1,2,4,5-Tetraethyl-benzene	$C_{14}H_{22}$	0.97	20.28
Aldehydes	2,4,6-Trimethyl-3-cyclohexene-1-carboxaldehyde	$C_{10}H_{16}O$	1.08	13.98
	1,3,4-Trimethyl-3-cyclohexene-1-carboxaldehyde	$C_{10}H_{16}O$	0.91	14.95
Esters	Butanoic acid, 3-methyl-, 3,7-dimethyl-2,6-octadienyl ester	$C_{15}H_{26}O_2$	1.31	15.48
Alcohols	5-Methyl-6-Hepten-1-ol	$C_8H_{16}O$	1.23	9.84
Amides	9-Octadecenamide	$C_{18}H_{35}NO$	0.91	27.08
		Total area	54.28%	

Table 5
Characterization of the aqueous phase from HTL.

pH (−)	TOC (g L^{-1})	TN (g L^{-1})	SO$_4$ $^{2-}$(g L^{-1})	PO$_4$ $^{3-}$(g L^{-1})	Cl^{-}(g L^{-1})
6.83 ± 0.68	25.09 ± 1.67	0.23 ± 0.02	14.34 ± 2.72	0.07 ± 0.03	1.34 ± 0.22

sodium and potassium are more frequently present as soluble ionic salts, which eases their recovery in the aqueous phase [21]. In the present study, the potassium in the aqueous product is mainly due to the addition of the potassium carbonate catalyst, which still is a salt soluble in water. Carrier et al. also related the inorganics redistribution among the HTL product phases to the nature and properties of the elements and to the pH rather than to the sub- or supercritical temperatures used. In particular, they highlighted that Al, Fe, and Zn, which are all amphoteric, were mostly recovered in the solids [24]. Similarly, in the present study, most of the Fe and Zn were found in the solid products.

Fig. 3 shows the distribution of the inorganics among the different HTL products, obtained by taking into account both the concentration of the inorganics in each phase and the amount of product for each of the phases. For each inorganic element, the distribution is normalized with respect to the total amount of inorganic recovered in the solids, biocrude and aqueous phase.

For most inorganics, the mass recovery in the solids was more than 50%: Ca (86%), Mn (84%), Mg (81%), P (76%), Fe (71%), Zn (65%), Cu (50%). Na and K were almost exclusively recovered in the aqueous phase (88% and 95%, respectively). Nearly half of the S was recovered in the biocrude, while the remaining was distributed over the aqueous phase and solids. Heavy metals (i.e.: Fe, Zn, and Cu) were also found in the biocrude. The amount of heavy metals in the willow biomass used in the present study did not have negative impact on the quality of the biocrude. However, the fact that heavy metals and sulfur also end up in the biocrude oil should be considered, if heavily polluted feedstock are processed (i.e. impregnated wood); this would in fact be a drawback for further use in combustion applications or as fuel precursor. The application of severe processing conditions could be beneficial in a way that it enhances the recovery of heavy metals (as Cu, Fe and Zn) in the solids rather than in the biocrude. This was in fact observed by Jiang and Savage, who investigated the influence of various processing conditions on inorganics redistribution after HTL of microalgae. On the other hand the distribution of Cu, Fe, and Zn distribution over the product phases appeared to be insensitive to different biomass and water loading [37].

Spectrophotometric analysis of the aqueous phase showed low concentrations of inorganic P, whereas ICP analysis revealed high concentration of P in the solids. Phosphates, as well as many other inorganic materials, are highly soluble in water at temperatures below 200 °C, while they become insoluble at sub and especially at super critical conditions. The insolubility at higher temperatures is explained by the fact that solubility is strictly dependent on the dielectric constant, which drops with increasing temperature [38]. Contrary to common understanding, however, the sharp drop around the critical temperature normally associated with supercritical conditions is not present at pressure above 30 MPa and thus solubility of phosphates at the conditions of this work is very similar to those of most subcritical HTL works. In order to maximize the recovery of P, continuous processing of biomass with continuous recovery of solid products at reaction temperature (or, at least, above 200 °C) and pressure is therefore required; batch processing instead implies the cooling down of the products with consequent re-dissolution of part of the P in the aqueous phase [39]. Ekpo et al. [22] observed that the recovery of P in the solids or in the aqueous phase depends on two parameters: the severity of the process and the concentration of Ca, Mg, and Fe in the feedstock. They registered a reduced extraction of the P in the aqueous phase at higher temperatures (corresponding to hydrothermal liquefaction and gasification) rather than at lower (corresponding to thermal hydrolysis and hydrothermal carbonization). They also noticed as feedstock with higher Ca:P ratio led to an increased recovery of P in the solid products. This was previously explained by Heilemann et al. [40], who identified multivalent metal ions (Al, Ca, Mg, Fe) as responsible for the formation of insoluble phosphates, which were detected after hydrothermal carbonization.

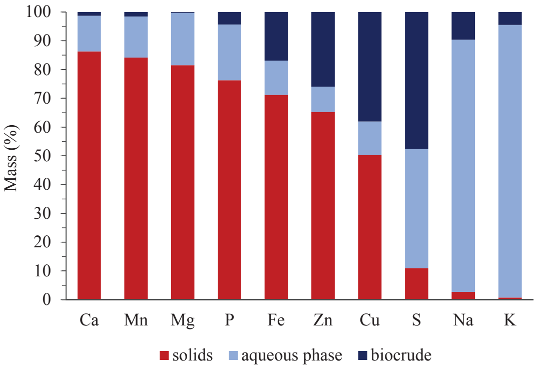


Fig. 3. Normalized mass distribution of the inorganic elements over the HTL product phases.

3.5. Potentials and challenges for the recovery of nutrients through HTL

The recovery of nutrients and metals after hydrothermal conversion of biomass is facilitated by the fact that most inorganics concentrate in the solid product. Macronutrients (i.e. P), secondary macronutrients (i.e. Ca, Mg, Mn), and micronutrients (i.e. Cu, Fe, Zn) are in fact recovered primarily in the solid product, also named hydrochar. Once solids are separated from the HTL products mixture, hydrochar can be used for example for soil amendment [41,42]. In order to use hydrochar as fertilizers, nutrients should be bioavailable, which means that they should be in the forms accessible to plants so that biological uptake can take place [43]. Therefore, future studies should also investigate in which forms nutrients exist in hydrochar residues from HTL of biomass in order to assess their bioavailability. Heavy metals (i.e. Cd, Cr, Ni, Pb) also tend to concentrate in the solids after HTL [44–46]. To be able to apply hydrochar to the soil, the concentration of heavy metals in the

Table 6
Concentrations of inorganics in solid, biocrude, and aqueous products from HTL.

		Ca	Cu	Fe	K	Mg	Mn	Na	P	S	Zn
solids	(mg kg^{-1})	8892 ± 1583	46 ± 1	3867 ± 1581	3089 ± 832	2353 ± 176	508 ± 86	44 ± 8	3009 ± 55	293 ± 6	692 ± 80
biocrude	(mg kg^{-1})	37 ± 53	9 ± 1	250 ± 114	4922 ± 3053	2 ± 3	3 ± 1	42 ± 2	47 ± 66	345 ± 6	75 ± 26
aqueous phase	(mg L^{-1})	45 ± 3	0 ± 0	23 ± 2	13339 ± 2229	18 ± 3	3 ± 0	50 ± 21	27 ± 7	39 ± 9	3 ± 0

solids should not exceed the limits established by law. Restrictions might vary from country to country, and differ depending on the land use (e.g. agricultural or non-agricultural destination of use). If the concentration of heavy metals in the solids is above the permitted limits, then the solids should be further treated to extract the heavy metals (e.g. by acid leaching) to guarantee a safe disposal. In order to avoid an overestimation on the risk posed by the presence of heavy metals, the concentration of element species, rather than the total concentration, should be considered. A few studies [44–46] have investigated the chemical speciation of heavy metals for HTL solid residues by using BCR or Tessier sequential extraction methods and concluded that though liquefaction process significantly reduce the mobility/leachability of heavy metals, still some organic bound heavy metals could be degraded under oxidizing conditions leading to the release of heavy metals. Therefore, more investigations will be required when processing heavily polluted biomass in order to assess the risk associate with the presence of heavy metals in the products. Nevertheless, HTL offers at least a method to concentrate the elements in the solid products, which would allow for containing the problem.

Potassium is another macronutrient, whose presence in plants is fundamental and which facilitates strong stem growth, movement of water in plants, and promotion of flowering and fruiting. After HTL, potassium, as well as sodium, are almost exclusively recovered in the aqueous phase. This product phase, rich also in K and Na, has a potential use as irrigation in agriculture or alternatively to be recycled in continuous HTL systems. The latter case would result in a reduced consumption of catalyst due to the presence of potassium in the recirculated water, and in an increased amount of oil due as the presence of soluble organics in the process water that limits the dissolution of more organics in the aqueous phase [14].

4. Conclusions

The hydrothermal liquefaction process offers a value-adding alternative for treating wastewater irrigated willow. The thermochemical conversion of the woody biomass in supercritical water simultaneously produces an energy-dense biocrude oil, while most nutrients and metals are concentrated from the willow biomass into a smaller volume, represented by the solid hydrochars. The results of the present work show that there are no adverse indications for the HTL process using wastewater irrigated willow, as the oil, hydrochar and gas yields are in the range expected for SRC, and the biocrude oil properties and element contamination are also in the expected range. A standard upgrading of the biocrude is required to reduce O, N and S content to meet drop-in fuel quality. Phosphorus is recovered in high yield in the solid char phase, potassium is instead mainly in the aqueous phase, while nitrogen is to a great extent transferred to the biocrude. The concentration of most of the inorganics (Ca, Cu, Fe, Mg, Mn, P, and Zn) in the solids eases their recovery for reutilization in soil amendment.

Acknowledgements

The research was financially supported by Innovation Fund Denmark (Grant no. 1305 -00030B) and INBIOM – Innovation Network for Biomass (Grant no.1363-00025B). The authors would also like to acknowledge Center for Recirkulering (Denmark), who kindly provided the biomass used in the study.

References

[1] P. McKendry, Energy production from biomass (part 1): overview of biomass, Bioresour. Technol. 83 (1) (2002) 37–46.

[2] M.J. Aylott, E. Casella, I. Tubby, N.R. Street, P. Smith, G. Taylor, Yield and spatial supply of bioenergy poplar and willow short-rotation coppice in the UK, New Phytol. 178 (2) (2008) 358–370.

[3] I.D. Pulford, C. Watson, Phytoremediation of heavy metal-contaminated land by trees—a review, Environ. Int. 29 (4) (2003) 529–540.

[4] P. Vervaeke, S. Luyssaert, J. Mertens, E. Meers, F.M. Tack, N. Lust, Phytoremediation prospects of willow stands on contaminated sediment: a field trial, Environ. Pollut. 126 (2) (2003) 275–282.

[5] W. Rosselli, C. Keller, K. Boschi, Phytoextraction capacity of trees growing on a metal contaminated soil, Plant Soil 256 (2) (2003) 265–272.

[6] P. Börjesson, G. Berndes, The prospects for willow plantations for wastewater treatment in Sweden, Biomass Bioenergy 30 (5) (2006) 428–438.

[7] W.G. Nissim, A. Voicu, M. Labrecque, Willow short-rotation coppice for treatment of polluted groundwater, Ecol. Eng. 62 (2014) 102–114.

[8] K.L. Perttu, P.J. Kowalik, Salix vegetation filters for purification of waters and solids, Biomass Bioenergy 12 (1) (1997) 9–19.

[9] S. Elowson, Willow as a vegetation filter for cleaning of polluted drainage water from agricultural land, Biomass Bioenergy 16 (4) (1999) 281–290.

[10] A. Nzihou, B. Stanmore, The fate of heavy metals during combustion and gasification of contaminated biomass—a brief review, J. Hazard Mater. 256-257 (2013) 56–66.

[11] A.J. Pedersen, L.M. Ottosen, A. Villumsen, Electrodialytic removal of heavy metals from different fly ashes, Influence of heavy metal speciation in the ashes, J. Hazard Mater. 100 (1–3) (2003) 65–78.

[12] C.C. Evans, S.E. Allen, Nutrient losses in smoke produced during heather burning, Oikos 22 (2) (1971) 149–154.

[13] S.S. Toor, L. Rosendahl, A. Rudolf, Hydrothermal liquefaction of biomass: a review of subcritical water technologies, Energy 36 (5) (2011) 2328–2342.

[14] C.U. Jensen, J.K. Rodriguez Guerrero, S. Karatzos, G. Olofsson, S. Brummerstedt, Fundamentals of Hydrofaction™: renewable crude oil from woody biomass, Biomass Convers. Biorefin 7 (2017).

[15] R. Hashaikeh, Z. Fang, I.S. Butler, J. Hawari, J.A. Kozinski, Hydrothermal dissolution of willow in hot compressed water as a model for biomass conversion, Fuel 86 (2007) 1614–1622.

[16] I.M. Sintamarean, I.F. Grigoras, C.U. Jensen, S.S. Toor, T.H. Pedersen, L.A. Rosendahl, Two-stage alkaline hydrothermal liquefaction of wood to biocrude in a continuous bench-scale system, Biomass Convers. Biorefin. 7 (4) (2017) 425–435.

[17] D. López Barreiro, M. Bauer, U. Hornung, C. Posten, A. Kruse, W. Prins, Cultivation of microalgae with recovered nutrients after hydrothermal liquefaction, Algal Research 9 (2015) 99–106.

[18] P. Biller, A.B. Ross, S.C. Skill, A. Lea-Langton, B. Balasundaram, C. Hall, R. Riley, C.A. Llewellyn, Nutrient recycling of aqueous phase for microalgae cultivation from the hydrothermal liquefaction process, Algal Research 1 (1) (2012) 70–76.

[19] D.J. Patzelt, S. Hindersin, S. Elsayed, N. Boukis, M. Kerner, D. Hanelt, Microalgal growth and fatty acid productivity on recovered nutrients from hydrothermal gasification of Acutodesmus obliquus, Algal Research 10 (2015) 164–171.

[20] A. Kruse, F. Koch, K. Stelzl, D. Wüst, M. Zeller, Fate of nitrogen during hydrothermal carbonization, Energy Fuels 30 (10) (2016) 8037–8042.

[21] A.M. Smith, S. Singh, A.B. Ross, Fate of inorganic material during hydrothermal carbonisation of biomass: influence of feedstock on combustion behaviour of hydrochar, Fuel 169 (2016) 135–145.

[22] U. Ekpo, A.B. Ross, M.A. Camargo-Valero, P.T. Williams, A comparison of product yields and inorganic content in process streams following thermal hydrolysis and hydrothermal processing of microalgae, manure and digestate, Bioresour. Technol. 200 (2016) 951–960.

[23] J. Lu, J. Zhang, Z. Zhu, Y. Zhang, Y. Zhao, R. Li, J. Watson, B. Li, Z. Liu, Simultaneous production of biocrude oil and recovery of nutrients and metals from human feces via hydrothermal liquefaction, Energy Convers. Manag. 134 (2017) 340–346.

[24] M. Carrier, A. Loppinet-Serani, C. Absalon, F. Marias, C. Aymonier, M. Mench, Conversion of fern (Pteris vittata L.) biomass from a phytoremediation trial in sub- and supercritical water conditions, Biomass Bioenergy 35 (2011) 872–883.

[25] M. Henze, P. Harremoes, J. la Cour Jansen, E. Arvin, Wastewater Treatment: Biological and Chemical Processes, Springer-Verlag Berlin Heidelberg, 1997.

[26] F. Vogel, Hydrothermal conversion of biomass, in: R.A. Meyers (Ed.), Encyclopedia of Sustainability Science and Technology, Springer Science + Business Media LLC, 2017.

[27] Z. Zhu, S.S. Toor, L. Rosendahl, D. Yu, G. Chen, Influence of alkali catalyst on product yield and properties via hydrothermal liquefaction of barley straw, Energy 80 (2015) 284–292.

[28] T.H. Pedersen, HydroThermal Liquefaction of Biomass and Model Compounds, Aalborg Universitet, 2016, https://doi.org/10.5278/vbn.phd.engsci.00050 Aalborg Universitetsforlag, Ph.d.-serien for Det Teknisk-naturvidenskabelige Fakultet.

[29] A.A. Peterson, F. Vogel, R.P. Lachance, M. Fröling, M.J. Antal Jr., J.W. Tester, Thermochemical biofuel production in hydrothermal media: a review of sub- and supercritical water technologies, Energy Environ. Sci. 1 (2008) 32–65.

[30] T.H. Pedersen, L.A. Rosendahl, Production of fuel range oxygenates by supercritical hydrothermal liquefaction of lignocellulosic model systems, Biomass Bioenergy 83 (2015) 206–215.

[31] I.M. Sintamarean, T.H. Pedersen, X. Zhao, A. Kruse, L.A. Rosendahl, Application of algae as cosubstrate to enhance the processability of willow wood for continuous hydrothermal liquefaction, Ind. Eng. Chem. Res. 56 (15) (2017) 4562–4571.

[32] S.A. Channiwala, P.P. Parikh, A unified correlation for estimating HHV of solid, liquid and gaseous fuels, Fuel 81 (2002) 1051–1063.

[33] I.F. Grigoras, R.E. Stroe, I.M. Sintamarean, L.A. Rosendahl, Effect of biomass pretreatment on the product distribution and composition resulting from the hydrothermal liquefaction of short rotation coppice willow, Bioresour. Technol. 231 (2017) 116–123.

[34] G. Yu, Y. Zhang, L. Schideman, T. Funk, Z. Wang, Distributions of carbon and nitrogen in the products from hydrothermal liquefaction of low-lipid microalgae,

Energy Environ. Sci. 4 (2011) 4587–4595.

[35] K. Anastasakis, A.B. Ross, Hydrothermal liquefaction of the brown macro-alga Laminaria Saccharina: effect of reaction conditions on product distribution and composition, Bioresour. Technol. 102 (7) (2011) 4876–4883.

[36] T.H. Pedersen, I.F. Grigoras, J. Hoffmann, S.S. Toor, I.M. Daraban, C.U. Jensen, S.B. Iversen, R.B. Madsen, M. Glasius, K.R. Arturi, R.P. Nielsen, E.G. Søgaard, L.A. Rosendahl, Continuous hydrothermal co-liquefaction of aspen wood and glycerol with water phase recirculation, Appl. Energy 162 (2016) 1034–1041.

[37] J. Jiang and P. E. Savage, Metals and other elements in biocrude from fast and isothermal hydrothermal liquefaction of microalgae, Energy Fuel. 32(4) 4118–4126.

[38] T. Voisin, A. Erriguible, D. Ballenghien, D. Mateos, A. Kunegel, F. Cansell, C. Aymonier, Solubility of inorganic salts in sub- and supercritical hydrothermal environment: application to SCWO processes, J. Supercrit. Fluids 120 (1) (2017) 18–31.

[39] S. Edmundson, M. Huesemann, R. Kruk, T. Lemmon, J. Billing, A. Schmidt, D. Anderson, Phosphorus and nitrogen recycle following algal bio-crude production via continuous hydrothermal liquefaction, Algal Research 26 (2017) 415–421.

[40] S.M. Heilmann, J.S. Molde, J.G. Timler, B.M. Wood, A.L. Mikula, G.V. Vozhdayev, E.C. Colosky, K.A. Spokas, K.J. Valentas, Phosphorus reclamation through hydrothermal carbonization of animal manures, Environ. Sci. Technol. 48 (17) (2014) 10323–10329.

[41] H.S. Kambo, A. Dutta, A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications, Renew. Sustain. Energy Rev. 45 (2015) 359–378.

[42] J. Fang, L. Zhan, Y.S. Ok, B. Gao, Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass, J. Ind. Eng. Chem. 57 (2018) 15–21.

[43] S.A. Barber, Soil Nutrient Bioavailability: a Mechanistic Approach, second ed., John Wiley & Sons, 1995.

[44] H. Huang, X. Yuan, G. Zeng, H. Zhu, H. Li, Z. Liu, H. Jiang, L. Leng, W. Bi, Quantitative evaluation of heavy metals' pollution hazards in liquefaction residues of sewage sludge, Bioresour. Technol. 102 (2011) 10346–10351.

[45] X. Yuan, H. Huang, G. Zeng, H. Li, J. Wang, C. Zhou, H. Zhu, X. Pei, Z. Liu, Z. Liu, Total concentrations and chemical speciation of heavy metals in liquefaction residues of sewage sludge, Bioresour. Technol. 102 (2011) 4104–4110.

[46] H. Huang, X. Yuan, The migration and transformation behaviors of heavy metals during the hydrothermal treatment of sewage sludge, Bioresour. Technol. 200 (2016) 991–998.

Paper C

Valorization of animal and human wastes through hydrothermal liquefaction for biocrude production and simultaneous recovery of nutrients

F. Conti, S. S. Toor, T. H. Pedersen, T. H. Seehar,
A. H. Nielsen, L. A. Rosendahl

The manuscript has been published in:
Energy Conversion and Management 216 (2020) 112925

The layout has been revised.

Energy Conversion and Management 216 (2020) 112925

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Valorization of animal and human wastes through hydrothermal liquefaction for biocrude production and simultaneous recovery of nutrients

Federica Conti[a], Saqib S. Toor[a], Thomas H. Pedersen[a], Tahir H. Seehar[a], Asbjørn H. Nielsen[b], Lasse A. Rosendahl[a,*]

[a] *Department of Energy Technology, Aalborg University, Pontoppidanstræde 111, 9220 Aalborg, Denmark*
[b] *Department of Civil Engineering, Aalborg University, Thomas Manns Vej 23, 9220 Aalborg, Denmark*

ARTICLE INFO

Keywords:
Cow manure
Swine manure
Fish sludge
Sewage sludge
sub-supercritical HTL
Inorganics

ABSTRACT

Intense farming activities and the growth of the population produce increasing amounts of wastes, which represent an environmental concern and require an adequate disposal. Animal manure, fish sludge, and sewage sludge are all wet wastes consisting of organic, but also inorganic material. Hydrothermal liquefaction is proposed to treat these wastes as wet feedstocks can be processed without any drying. The organic fraction is valorized, being converted into biocrude oil, while the inorganics are recovered primarily in the solid products. The decomposition of these wastes is investigated under sub- (350 °C) and supercritical (400 °C) conditions, and with and without the addition of K_2CO_3 catalyst with focus on the biocrude yield and quality. High yields of biocrude are obtained from the liquefaction of all the feedstocks, especially from fish sludge (ca. 50% d.a.f.) and sewage sludge (ca. 45% d.a.f.). A reduction in biocrude production is observed at supercritical conditions for animal wastes, however, the quality of manure-derived biocrudes is improved when using supercritical conditions and by the addition of the catalyst. Carbon is primarily recovered in the biocrude: 50–60% for swine and cow manure, 55–80% for fish and sewage sludge. Considerable quantities of nitrogen and sulfur are transferred to the biocrude, respectively 26–60% and 33–66%. Most of the inorganics (e.g. Ca, Mg, P) are recovered in the solids (above 70%), except for potassium and sodium, which show a higher degree of solubility in the aqueous phase.

1. Introduction

The depletion of conventional fossil resources, the increase in greenhouse gas concentrations, and waste management issues are the main reasons behind an urgent need for renewable resources. Population growth and the gap between world's energy demand and supply are other key factors that contribute to predicting a significant depletion of fossil fuels by 2050 [1]. The transportation sector is the greatest contributor to climate emissions, having produced 27% of total EU-28 greenhouse gas emissions in 2016 [2]. Increasing the use of biofuels is, therefore, necessary to reduce CO_2 emissions in the transportation sector. Advanced biofuels, obtained from inedible biomass and wastes, represent a promising solution, being able to overcome some limitations of plant-based biofuels: shortage of raw materials, low CO_2 mitigation effect, blending wall, and poor cost competitiveness [3].

Hydrothermal liquefaction (HTL) is a promising technology producing advanced biofuels directly from biomass and wastes. HTL is a thermochemical process capable of converting dry or wet biomass, as water is the reaction medium. This results in wide feedstock flexibility and reduces the expensive costs associated with the drying, essential in other thermochemical processes. In HTL, the biomass can be processed at sub- or supercritical water conditions (temperatures 280–400 °C, pressure 10–35 MPa), and with or without the addition of a catalyst to the feed mixture [4]. The main product of interest of biomass liquefaction is the biocrude, a product similar to crude oil except oxygenated, which can be further upgraded to achieve drop-in fuel qualities. Techno-economic assessments have shown that the production of renewable fuels via HTL and upgrading can be highly cost competitive to other alternative fuel processes [5,6]. Together with the biocrude yield, the price of the feedstock is among the key factors affecting the production costs [6,7]. For this reason, the use of waste resources as feedstocks in HTL would reduce the final price of the fuel and simultaneously improve the circular economy. Treating the animal and human wastes through HTL would valorize their organic fraction by converting them into an energy-dense product, and, at the same time, allowing the recovery of the inorganics, including phosphorus.

---

[*] Corresponding author.
E-mail address: lar@et.aau.dk (L.A. Rosendahl).

https://doi.org/10.1016/j.enconman.2020.112925
Received 9 February 2020; Received in revised form 28 April 2020; Accepted 29 April 2020

Phosphorus is an essential nutrient for the human diet and in agricultural activities. Its current major source, phosphate rock, is a finite, non-renewable resource. Therefore, recycling and closing phosphate loops are essentials both to avoid environmental pollution and to secure fertilizers supply [8].

As a result of intense farming activities, pig and cattle manure production in Europe accounts for 14 and 295 million tons of dried material, respectively [9]. Animal manure is commonly applied to farm lands as fertilizers or is treated by anaerobic digestion and then the digestate is applied to the land. However, the presence of pathogens, hormones, and antibiotics represent an increasing concern for human health and the environment [10]. Another source of animal sludge is coming from fish farming activities; the largest of these farms in Europe are located in Norway. Here the estimated annual production of dry matter in smolt sludge is 11 thousand tons, which corresponds to 225 tons of phosphorus [11]. Similarly to manure, a portion of the fish sludge is spread on agricultural fields; alternatively, it is treated for biogas production, with the remaining fraction used as soil enhancer with strict regulations on the concentration of heavy metals [12]. Finally, sewage sludge production in EU26 is expected to grow to 13 million tons of dry solids in 2020 [13]. However, only around one third of sewage sludge is currently recycled in agriculture, leading to a loss of 300,000 tons of phosphorus every year [14].

Some parametric studies on HTL of manure, principally from pigs, were found in literature: He et al. investigated swine manure liquefaction, using CO as reducing agent, and suggested 295–305 °C and 15–30 min as the optimal temperature range and retention times, respectively [15]. They additionally found that reducing gases (i.e., CO and H_2) produce more oil and favor its solubility in benzene [16]. Furthermore, high pH values (pH ~ 10) increased oil production, though its solubility in benzene decreased with respect to neutral and acidic pH [17]. Posmanik et al. studied the effect of acid (H_3PO_4) and basic (NaOH) catalysts on HTL of manure digestate, and reported higher biocrude yields in both cases, particularly when using H_3PO_4, which also enhanced dehydration reactions [18]. Other investigations suggested 15 min as the optimal retention time for the HTL of swine and cattle manure, while different temperatures were indicated to achieve maximum biocrude yields: 340 °C for swine manure [19] and 310 °C for cattle manure [20]. In all the studies mentioned above, optimal temperatures refer to maximum biocrude yield, however, information is missing on how the temperature affected the biocrude quality (e.g. deoxygenation extent). Therefore, the effect of the temperature on the biocrude quality is among the objectives of the present work.

Quian et al. investigated isothermal (400 °C, 60 min) and fast (500 °C, 1 min) HTL of sewage sludge, reporting that biocrudes with higher H/C and O/C ratios and lower N/C ratio were obtained from fast HTL [21]. They suggested the use of dichloromethane for biocrude recovery, while the addition of additives (K_2CO_3, Na_2CO_3, MoO_3-CoO/γ-Al_2O_3, and Ru/C) decreased biocrude yield. Wang et al. registered the highest biocrude yield (39.7 wt%) from sewage sludge conversion at 375 °C with 0 min retention time [22]. Ma et al. similarly suggested the use of supercritical temperatures (385 °C) and a moisture content of 85 wt% for maximum biocrude production (37.23 wt%) [23]. The effect of Ni-Tm/TiO_2 catalyst on sewage sludge liquefaction was investigated at various subcritical temperatures (250–350 °C) and the largest increase in the biocrude yield was reported at 330 °C with 30 min retention time [24]. Biocrude production via co-HTL of wastewater treatment derived microalgae and domestic sewage sludge was explored in the subcritical range reporting higher biocrude yields (39.6 wt%) at 325 °C with 45 min residence time. Additionally, the co-liquefaction significantly improved the production of low-boiling biocrude fractions [25]. A synergistic effect on the biocrude yield (+4.7 wt%) and quality was also observed in another recent work where co-HTL of microalgae and SS (1:1) was investigated at 340 °C with 0.3 MPa of initial H_2 addition. The authors reported an increase in the low boiling points compounds (50–250 °C) and a reduction in the fraction of compounds with boiling points in the range 250–450 °C [26].

The behavior of different biomasses in HTL and how the feedstocks composition is reflected in the biocrude were investigated in [27-29]. Ekpo et al. [29] explored the conversion of microalgae, digestate, and swine and chicken manure under a wide temperature range (170–500 °C) and the fate of N, P, and K at increasing process severity. They found that P is immobilized in the residue after processing at higher temperatures due to precipitation of P salts and they linked its extraction to the presence of inorganics, such as Ca, Mg and Fe. Few other publications investigated both the fate of inorganics and the subcritical HTL of a single waste fraction: swine manure [30], sewage sludge [31], and human feces [32]. Lu et al. reported that most of the heavy and alkaline-earth metal elements including Ca (89%), Mg (81%), Al (88%), Fe (72%), and Zn (94%) were distributed in the solid residue, whereas K (89%) and Na (73%) were mainly dissolved into the aqueous phase [32].

The present study investigates the use of four different organic waste fractions of animal and human origin in the HTL process: swine manure, cow manure, fish sludge, and sewage sludge. To the best of our knowledge, no previous work has been done processing fish sludge through HTL; thus, we present the first results in the scientific literature. The feedstocks are individually processed using batch reactors at four different process conditions. Most batch HTL studies are conducted at subcritical conditions; instead, the present work investigates the liquefaction under both subcritical (350 °C) and supercritical (400 °C) conditions, and with or without the addition of K_2CO_3 catalyst to the feed mixture. The influence of the process conditions on the biocrude yield and quality is assessed with respect to the degree of de-oxygenation. The recovery of C and N in the HTL products and their balances are presented. Finally, the redistribution of the inorganic elements (Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, and Zn) among HTL product phases is assessed to establish the potential for their recovery. HTL is investigated and proposed to improve the circular economy of animal and human waste streams, since it allows valorizing the organic fraction producing biocrude and recovering valuable inorganics for being re-utilized. The outcomes of the present study are also intended to establish the knowledge necessary to proceed to continuous HTL processing as well as the following step: upgrading the biocrude to drop-in fuels.

2. Materials and methods

2.1. Feedstocks characterization

Four different waste fractions were used as feedstock for the HTL experiments: swine manure (SM), dairy cow manure (CM), fish sludge (FS), and secondary sewage sludge (SS). Before delivery, the dry matter of the feedstocks was increased either by mechanical pretreatment with a screw press for SM and CM, or with the addition of polymer flocculants for FS and SS. Once received, SM and CM were preserved at room temperature, while FS and SS were stored in a refrigerator before analysis and their use in the experiments. All feedstocks were characterized by proximate and ultimate analysis. The moisture mass fraction was measured with a moisture analyzer (Kern, MLS) at 120 °C. The ash mass fraction was determined with an electric muffle furnace (Protherm Furnaces), where pre-dried samples were held isothermally at 775 °C for 3 h in air. The volatile matter (VM) was calculated as the difference in weight percent heating up the feedstocks from 105 °C to 775 °C under nitrogen, with a DSC/TGA system (TA Instrument, Discovery SDT 650). The fixed carbon (FC), on dry basis, was calculated as in Eq. (1):

$$\mathrm{FC}(\%) = 100(\%) - \mathrm{ash}(\%) - \mathrm{VM}(\%) \tag{1}$$

The crude fats (CF), or lipids, were determined after Soxhlet extraction for 24 h using petroleum ether as solvent. Crude proteins (CP) were estimated by multiplying the nitrogen mass fraction (from

Table 1

Proximate and ultimate analysis of the feedstocks used in the HTL experiments.

		Swine manure	Cow manure	Fish sludge	Sewage sludge
Moisture	(%)	75.46 ± 0.14	63.04 ± 0.63	5.58 ± 0.97	78.64 ± 0.51
Volatile matter	(%) $_{db}$ *	69.26	72.67	68.33	59.88
Fixed carbon	(%) $_{db}$	19.34	20.74	9.59	16.93
Ash	(%) $_{db}$	11.40 ± 0.04	6.59 ± 1.08	22.08 ± 0.29	23.19 ± 0.37
Lignocellulosics	(%) $_{daf}$ *	84.40	88.70	39.77	48.09
Crude proteins	(%) $_{daf}$	14.94	10.50	47.19	46.06
Crude fats	(%) $_{daf}$	0.68	0.79	13.06	5.86
C	(%) $_{daf}$	44.89 ± 1.92	49.63 ± 0.67	53.49 ± 0.22	46.43 ± 0.99
H	(%) $_{daf}$	5.91 ± 0.28	6.55 ± 0.05	8.05 ± 0.02	7.62 ± 0.32
N	(%) $_{daf}$	2.39 ± 0.02	1.68 ± 0.38	7.55 ± 0.18	7.37 ± 0.22
O**	(%) $_{daf}$	46.81 ± 2.23	42.14 ± 0.23	30.91 ± 0.02	38.58 ± 1.54
H/C	(-)	1.57	1.57	1.79	1.96
O/C	(-)	0.78	0.64	0.43	0.62
HHV	(MJ kg^{-1}) $_{daf}$	19.68 ± 0.05	19.10 ± 0.07	23.30 ± 0.05	21.93 ± 0.07

* db = dry basis; daf = dry ash-free basis.

** Oxygen calculated by difference.

elemental analysis) by 6.25 factor [33]. The lignocellulosic fraction was calculated based on an equation previously described in literature [28] and here reported in Eq. (2):

$$\text{lignocellulosics}(\%) = \text{combustibles}(\%) - (\text{CF} + \text{CP})(\%) \tag{2}$$

where combustibles are intended as the sum of VM and FC.

The elemental composition was determined with an elemental analyzer (Perkin Elmer, 2400 Series II CHNS/O), operated in CHN mode. Acetanilide (Sigma Aldrich, puriss. p. a., ≥99.5%) was used as standard to calibrate the instrument. The higher heating values (HHV) were determined with an oxygen bomb calorimeter (IKA, C2000). The results from the proximate and ultimate analysis of the feedstocks are presented in Table 1. The average with standard deviations are reported for the analysis performed in duplicates or triplicates. By looking at the lignocellulosics, crude proteins, crude fats, and ash contents, it appears that SM and CM have similar compositions, and likewise the compositions of FS and SS can be compared. SM and CM are mainly constituted of lignocellulosics (84.40% and 88.70%), while for FS and SS the main constituents are both lignocellulosics (39.77% and 48.09%) and proteins (47.19% and 46.06%). Crude fats in SM and CM are almost negligible (< 1%), while they account for some percentages in FS and SS (13.06% and 5.86%). FS and SS also show high inorganic contents (> 20%).

The composition of the inorganic fraction of the feedstocks was investigated by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using a Thermo iCap 6300 Duo view (Thermo Scientific). To extract the elements, the samples were first digested by microwave assisted acid digestion according to the EPA method 3051A (US. EPA., 2007). The microwave reaction system was an Anton Paar Multiwave 7000 equipped with 18 digestion vials made from modified polytetrafluoroethylene (PTFE-TFM). Each digestion vial had a volume of 18 mL and was loaded with approximately 0.2 g of sample material and 9 cm^3 concentrated nitric acid (HNO_3). The vials were inserted into a PTFE-TFM rack and placed in the pressurized digestion cavity of the reaction system. The cavity was pressurized with high purity nitrogen gas (N_2) before the microwave energy was applied. After the digestion, 3 mL of hydrochloric acid (HCl) was added for stabilization of certain elements (particularly Fe). All acids were of suprapune quality (PlasmaPure, SCP Science). After digestion, the samples were analyzed by ICP-AES following the procedure previously described in [34]. 15 elements (Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Zn) were investigated and the concentrations of each element in each feedstock are reported in the supplementary material (Table S1). Ca was the most abundant inorganic element in all feedstocks, as clearly visible from Fig. 1. The other main constituents of the inorganic fraction were then K, P, S, and Mg. Some elements were detected only at trace level: Cd, Cr, Ni, Pb < 20 ppm, while Cu and Mn < 200 ppm. The inorganic fraction of FS was almost exclusively represented by Ca and P which together account for 90% of the investigated elements. In SS, among the most abundant inorganics there were also Fe and Al, which respectively account for 17% and 11.4%. Considerable quantities of iron in SS explain the red color of the ash from SS, which strongly differed from the grey color of the ash obtained from all the other feedstocks.

2.2. HTL experiments

Each feedstock was individually converted under four different process conditions: subcritical (350 °C), with and without the catalyst, and supercritical (400 °C), with and without the catalyst. In the catalytic runs, potassium carbonate (K_2CO_3) was added to the feed slurry (2.5% in weight of the water-biomass mixture) as catalyst and regulator of alkalinity, previously found being effective to prevent coke formation and to achieve a higher deoxygenation extent [35]. Each experiment was performed at least in duplicate to verify the consistency of the results, and the average values with their standard deviations are reported in the results section. The feed slurries were prepared by adjusting the dry matter content of the feedstocks to 20% with the addition of demineralized water. For SS, this step was not necessary as its dry matter content (21.36%) was already close to the desired value. The experiments were carried out in stainless steel micro-batch reactors (10 cm^3 volume), which were loaded with 7 g of feed slurry, sealed, purged with nitrogen to remove residual air, and then slightly pressurized (1.5–2.0 MPa) to push the slurry down into the reactor's volume. The heating was provided by a preheated sand bath (Techne, SBL-2D), in which the reactors were submerged for 15 min, based on the results from a previous investigation [36]. The mixing inside the reactors was provided by a mechanical agitator. Thermocouples and pressure transducers were connected to the reactors so that both temperature and pressure were monitored throughout the reaction time. Once the reaction time was reached, the reactors were cooled to room temperature by quenching in a water bucket.

2.3. Recovery of the products

The HTL products were separated according to the procedure already described in detail in [34]. The main steps involved in the recovery of the products are summarized in Fig. 2. The first product to be collected is the reaction gas, then the aqueous phase is collected from the top by turning reactors upside-down and without the addition of any solvents to preserve its quality for analysis. The solids are defined as the fraction, insoluble in acetone, which is collected on a filter paper (VWR, particle retention: 5–13 μm), and then dried overnight at 105 °C.

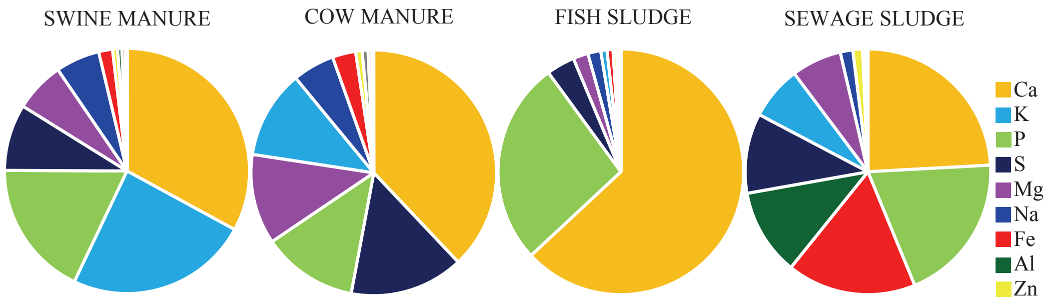


Fig. 1. Most abundant elements constituting the inorganic fraction of the feedstocks.

Two solvents are used in the recovery of the products: acetone and diethyl ether (DEE), as previously used [34] and adapted from [36]. In the first stage, acetone is used to recover the products and to clean the reactors with the aid of a brush: reactors are rinsed with acetone until clear solvent is collected. Successively DEE, which is immiscible in water, is used for removing the residual water from the biocrude. Biocrude weight and yield are calculated after the evaporation of the DEE solvent. We would like to highlight the fact that the recovery of the products and especially the results obtained for the biocrude yields are strictly dependent on the procedure adopted and the solvents used.

The use of micro-batch reactors is very practical for assessing the behavior of different feedstocks under various HTL processing conditions; however, working at such small scale can lead to losses of the products while recovering them. The most challenging steps of the method used in the present work are the recovery of the biocrude with DEE from the round evaporating flask after evaporation of acetone and the removal of residual water from the biocrude/DEE mixture. The latter step was performed with the aid of a syringe, after having centrifuged the samples obtaining the separation of the residual water to the bottom and the biocrude/DEE mixture at the top.

2.4. Analysis of the products

The elemental composition of the biocrudes and solids was determined with an elemental analyzer (Perkin Elmer, 2400 Series II CHNS/O), which directly measured C, H, and N mass fractions, while O mass fractions were calculated by difference. For the solids, mass fractions were calculated subtracting also the ash, measured by TGA. TGA highlighted that a significant portion of the solids was constituted of ash, while the ash content of the biocrudes was negligible. TGA was also used to assess the volatility of the biocrudes. All biocrudes and solids samples were investigated using a DSC/TGA system (TA Instrument, Discovery SDT 650) with the following program: ramp to 775 °C (10 K/min) in N_2, isothermal at 775 °C for 15 min in N_2, isothermal at 775 °C for 60 min in air.

The aqueous phase was characterized in terms of pH, total organic carbon (TOC) and total nitrogen (TN). The pH was measured with a pH meter (WTW 3210), while TOC and TN were determined using reagent vials (LCK386 and LCK138, respectively) and a spectrophotometer unit (Hach & Lange, DE3900). Similarly as for the feedstocks, the concentrations of inorganic elements in the biocrudes, solids, and aqueous phases were investigated by ICP analysis, after microwave assisted acid digestion of the samples.

3. Results and discussion

3.1. Biocrudes yields and quality

The average biocrude yields obtained from HTL of SM, CM, FS, SS are reported in Fig. 3. FS is the feedstock, whose conversion produced the greatest quantity of biocrude, with yields close to or above 50 wt%. Likewise, SS conversion resulted in high biocrude yields: about 45 wt%. About 35 wt% biocrude was produced from CM and SM conversion. A higher degree of liquefaction was achieved from HTL of biomass containing higher percentages of proteins and lipids (i.e. FS and SS) compared to lignocellulosic biomass (i.e. SM and CM). This is in line with the general trend for conversion efficiency: lipids > protein > carbohydrates [37]. Spirulina and SM conversion (300 °C, 30 min)

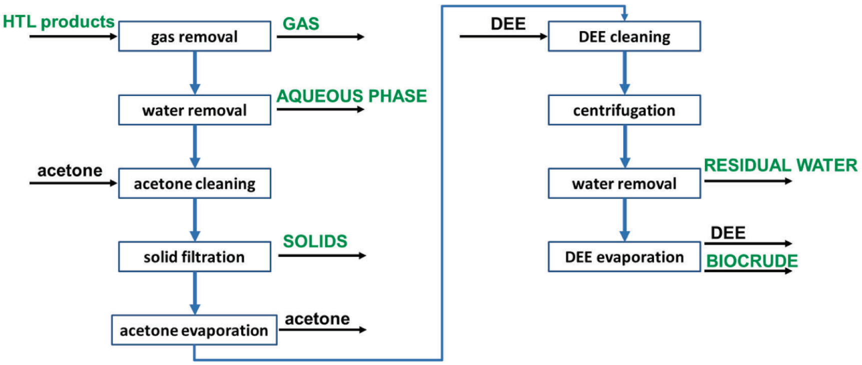


Fig. 2. Diagram of the steps involved in the recovery of the HTL products (highlighted in green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

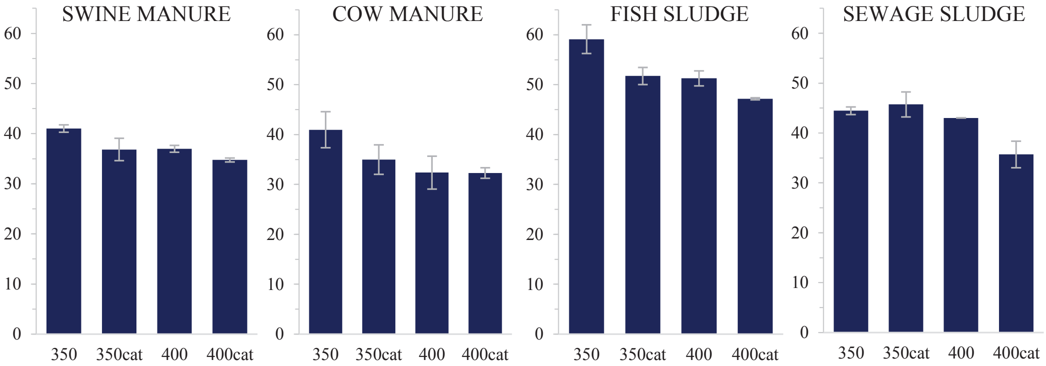


Fig. 3. Biocrude yields (on a dry ash-free basis) from the conversion of swine manure, cow manure, fish sludge, and sewage sludge at different HTL process conditions.

resulted in similar biocrude yields (32.6 wt% and 30.2 wt%, respectively), despite the higher lipids content of the algae [27]; the authors identified the higher carbohydrate content of manure as the reason for its lower conversion efficiency. Similarly, Huang et al. explained the lower biocrude yield obtained from rice straw (21.1 wt%) compared with Spirulina (34.5 wt%) and sewage sludge (33.6 wt%), with the larger carbohydrate content of the first [28].

Except for SS, the other three feedstocks showed a significant decrease in biocrude production at supercritical conditions (400 °C) compared with subcritical conditions (350 °C). The decrease corresponds to 10% for SM, 21% for CM, and 13% for FS and it may be explained with an increase in gasification reactions at supercritical conditions [21]. Similar biocrude yields among sub- and supercritical HTL of SS without catalyst were also obtained in a previous investigation [22]. In that study, the maximum biocrude yield was achieved at 375 °C (62.3 wt% on d.a.f. basis), while similar lower values were obtained among 350 °C and 400 °C (46.9 wt% and 47.1 wt%, respectively).

In the present study, both at sub- and supercritical conditions, the addition of K_2CO_3 catalyst did not affect positively the biocrude yields. In particular, the catalytic experiments showed a decrease by 10–15% for SM, CM, and FS at subcritical conditions, while a decrease by 17% was registered for SS at supercritical conditions. A decrease by 19% in the biocrude yield from the addition of K_2CO_3 (10 wt%) was reported in literature after isothermal HTL of SS at 400 °C [21]. Alkali catalyst are known having positive effect on biomass liquefaction since they enhance the degradation of macromolecules by hydrolysis, decarboxylation, and depolymerization [38]. Therefore, one reason for the decreased biocrude yields in the catalytic experiments may be the increased decarboxylation, which would lead to biocrudes having less oxygen compared to those obtained under non-catalytic conditions. This particularly applies to the biocrudes derived from manures for which the increase in the deoxigenation extent in the catalytic runs is significant, both at sub- and supercritical conditions, as shown by our elemental analysis reported in Table 2. However, the extended deoxygenation cannot entirely explain the substantial decrease in yield. Another effect could be the formation of water soluble salts from the reactions between acidic bio-crude compounds and the basic catalyst. In other published procedures [39,40] an acidification step is involved lowering the pH of the aqueous phase to 1–2. However, in this present study such acidification was not applied to keep the phases as pristine as possible.

Although yield is an important parameter for the process economics, it is as crucial to evaluate the quality of the biocrude and to establish how this is influenced by the different process conditions. The elemental compositions of the biocrudes obtained from the current HTL experiments are reported in Table 2. The results show that different process conditions influenced the elemental compositions – and consequently the quality – of the biocrudes obtained from SM and CM. For manure-derived biocrudes, the addition of the catalyst improved the quality, both at sub- and supercritical conditions. The content of C in the biocrude increased and simultaneously less O was transferred from the biomass to the biocrudes. For fish and sewage sludge-derived biocrudes, the addition of the catalyst did not affect the quality in the same manner: C and O contents were increased and decreased, respectively, by only 1%. Therefore, the use of K_2CO_3 catalyst can be avoided when processing sludges; this would also reduce process costs, especially at larger continuous scale.

A lower O content in the biocrude leads to a lower biocrude yield, because a greater amount of the O contained in the biomass has been transferred to the other HTL products (i.e. water solubles or gases). For the present investigation, this particularly applies for manure-derived biocrudes (see Table 2). The removal of O in HTL occurs by decarboxylation and by dehydration, respectively, in the form of carbon dioxide and water [40]. Therefore, a decrease in the O/C ratio is related to decarboxylation, while a decrease in the H/C ratio can be related to dehydration. Regarding manures, O was removed by both dehydration and decarboxylation, with strong decarboxylation at supercritical conditions in the presence of the catalyst. Regarding sludges, for FS the O was removed almost exclusively by decarboxylation and independently from the conditions adopted; while in the case of SS a decrease in both H/C and O/C values is observed. A decrease in the O/C ratio rather than in the H/C ratio (i.e., enhanced decarboxylation and reduced dehydration) is an advantage with respect to the biocrude quality and its consequent upgrading to fuel [18]. Higher nitrogen mass fractions were detected in the biocrudes obtained from SS (5 wt%) and FS (6–7 wt%) with respect to the biocrudes obtained from SM and CM (2–3 wt%). This diversity among the biocrudes is a direct consequence of the different nature of the feedstocks: the elemental composition of these waste fractions had, in fact, higher percentages of N in FS and SS (~7 wt%) as compared to manures (~1 wt%). As a result, the HHV of the manure-derived biocrudes have increasingly higher values for the experiments conducted at higher temperatures and in the presence of the catalyst, while the HHV of the sludge-derived biocrudes are constant for the different process conditions.

The volatility curves of the biocrudes, obtained from TGA (Fig. 4), show that FS and SS biocrudes are more volatile compared to manure-derived biocrudes: above 450 °C, only 10% of FS biocrude and 20% of SS biocrude are respectively left, while about 30% of manure-derived biocrude. The reduced volatility of manure-derived biocrudes may be linked to the larger contribution of lignocellulosic compounds in the manures respect to the sludges and, more specifically, to the presence of

Table 2

Yields, elemental compositions, H/C and O/C ratios, high heating values (HHV), carbon recovery (C_{rec}), and energy recovery (E_{rec}) of the biocrudes obtained from the waste feedstocks at the different process conditions. Results are reported on dry ash-free basis.

		$Y_{biocrude}$	C	H	N	O	H/C	O/C	HHV	C_{rec}	E_{rec}
		$(-)_{daf}$	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(-)	(-)	(MJ kg^{-1})	(-)	(-)
SM	350	41.01 ± 0.73	66.28 ± 2.54	7.74 ± 0.62	2.48 ± 0.30	23.50 ± 3.46	1.39	0.27	29.79	60.5	62.1
	350cat	36.82 ± 2.23	71.28 ± 1.94	8.38 ± 0.20	3.08 ± 0.53	17.26 ± 2.67	1.40	0.18	32.92	58.5	61.6
	400	36.97 ± 0.70	70.89 ± 0.80	8.37 ± 0.44	3.08 ± 0.14	17.66 ± 0.50	1.41	0.19	32.74	58.4	61.5
	400cat	34.76 ± 0.39	75.56 ± 0.73	9.14 ± 0.35	2.99 ± 0.08	12.31 ± 1.16	1.44	0.12	35.83	58.5	63.3
CM	350	40.96 ± 3.63	64.46 ± 0.47	9.36 ± 0.06	2.02 ± 0.02	24.16 ± 0.39	1.73	0.28	31.00	53.2	66.5
	350cat	34.98 ± 2.96	73.17 ± 0.54	8.54 ± 0.17	2.92 ± 0.02	15.37 ± 0.35	1.39	0.16	33.97	51.6	62.2
	400	32.37 ± 3.28	71.61 ± 1.03	8.19 ± 0.02	2.62 ± 0.39	17.58 ± 1.44	1.36	0.18	32.79	46.7	55.6
	400cat	32.29 ± 1.04	76.02 ± 2.17	8.90 ± 0.58	2.61 ± 0.28	12.47 ± 2.48	1.40	0.12	35.70	49.5	60.4
FS	350	59.11 ± 2.86	71.65 ± 1.27	10.51 ± 0.10	6.97 ± 0.06	10.87 ± 1.30	1.75	0.11	36.17	79.2	91.8
	350cat	51.74 ± 1.72	72.57 ± 0.76	10.57 ± 0.10	7.14 ± 0.19	9.72 ± 0.67	1.74	0.10	36.67	70.2	81.4
	400	51.27 ± 1.51	73.09 ± 0.65	10.41 ± 0.13	6.87 ± 0.04	9.63 ± 0.81	1.70	0.10	36.68	70.1	80.7
	400cat	47.17 ± 0.23	73.94 ± 0.21	10.18 ± 0.08	7.22 ± 0.54	8.66 ± 0.66	1.64	0.09	36.80	65.2	74.5
SS	350	44.46 ± 0.74	73.02 ± 1.81	10.53 ± 0.17	5.18 ± 0.46	11.27 ± 1.52	1.72	0.12	36.65	69.9	74.3
	350cat	45.73 ± 2.50	73.27 ± 0.95	10.94 ± 0.58	5.00 ± 0.21	10.79 ± 1.32	1.78	0.11	37.28	72.2	77.7
	400	43.02 ± 0.03	72.00 ± 0.11	10.10 ± 0.30	5.57 ± 0.18	12.33 ± 0.22	1.67	0.13	35.68	66.7	70.0
	400cat	35.70 ± 2.65	73.10 ± 1.82	10.85 ± 0.23	5.45 ± 0.88	10.60 ± 1.17	1.77	0.11	37.13	56.2	60.4

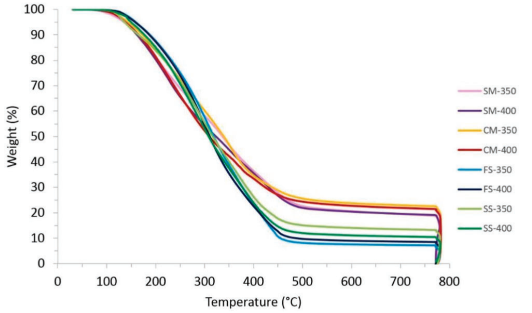


Fig. 4. Thermogravimetric curves of the biocrudes (at 775 °C the gas was switched from N_2 to air) obtained from the subcritical (350 °C) and supercritical (400 °C) liquefaction of swine manure (SM), cow manure (CM), fish sludge (FS) and sewage sludge (SS).

lignin, which leads to the production of heavier biocrudes [41]. After investigating the volatility under an inert nitrogen atmosphere, the biocrudes were burnt in air and this resulted in a drop of weight down to about 0%, meaning that most of the inorganics are not concentrated in the biocrude after HTL, and this is in line with the results obtained by ICP-AES. Negligible amounts of ash in the biocrude were observed in a previous study conducted on digested manure [18].

3.2. Solids yields and characterization

Solids yields were first calculated on a dry basis but, as the TGA showed that most of the solids are constituted of inorganics, they were calculated a second time on dry ash-free basis, in order to estimate the effective production of solid chars from HTL conversion of the waste feedstocks. These results are reported in Table 3, together with the elemental compositions of the solids, adjusted on dry ash-free basis. An increasing amount of ash was detected in the solids obtained from CM (23–40%), SM (48–57%), FS (74–80%) and SS (71–89%), and this reflects the increasing amounts of ash found in the raw materials (see Table 1 for comparison). The elemental analysis shows that more C is recovered in the solids obtained from manures as respect to solids obtained from the FS and SS. The increase in the solids yields (on dry basis) of the catalytic experiments respect to the non-catalytic ones may be related to the recovery procedure used in the present work: the addition of acetone to the reaction mixture might have caused the precipitation of the inorganics in the residual aqueous phase.

3.3. Aqueous phases characterization

The aqueous phases obtained from the conversion of the manures resulted being acidic (5.21–6.93 for SM and 3.85–6.41 for CM), except for the one derived from processing SM at 400 °C with catalyst, resulting slightly basic (pH 7.83). On the contrary, the aqueous phases from FS and SS were basic (8.54–8.76 for FS and 8.47–8.87 for SS). This difference in the pH values of the aqueous phases relates to the composition of the feedstock. In protein-rich biomass, protein hydrolysis and deamination produces ammonia, which in turn results in alkaline pH. The HTL aqueous phase obtained from the conversion of lignocellulosic biomass is instead often acidic due to the production of organic acids from the degradation of carbohydrates [42]. This explains why in the present study the aqueous phases obtained from the conversion of the sludges have alkaline pH while the aqueous phases obtained from the manures have values in the acidic range (see Table 4). The use of different process conditions did not have any effect on the pH of the aqueous phases from FS and SS, while increased basicity was measured for the aqueous phases obtained from the experiments at supercritical conditions for both SM and CM, and using the catalyst. Biocrude quality seems to be correlated to the pH of the aqueous phase. In fact, FS and SS biocrudes showed similar quality regardless of the process conditions and, for these feedstocks, the aqueous phases are all similarly in the basic range. For SM and CM, improved biocrude quality was obtained only under catalytic supercritical conditions, which is the only condition to which corresponds basic - or towards basic - pH of the aqueous phase. The results for the pH of the aqueous phases are reported in Table 4, together with the results for the total organic carbon and the total nitrogen, which were measured to establish how C and N, respectively, distribute among the HTL products.

3.4. Carbon and nitrogen recovery

The recovery of C and N in each product phase was calculated as the ratio between C or N wt.% in the product phase and C or N wt.% in the feedstock, times the yield of that phase. Regarding the biocrude and the solids, the C or N wt.% was obtained from the elemental analysis, while for the aqueous phase it was measured as TOC or TN. For each feedstock, the average yield of the aqueous phase (based on the four process conditions investigated) was determined as the mass ratio water out/water in: 69.23 for SM, 76.69 for CM, 77.31 for FS, and 66.55 for SS. The C and N recovery in the gas phase was instead calculated by difference. The results on C and N recovery for all phases are reported in Fig. 5 and in Fig. 6, respectively.

For all the feedstocks, most of the C was recovered in the biocrude,

Table 3

Yields, ash content, and elemental compositions (on dry ash-free basis) of the HTL solids.

		Y_{solids}	Ash	Y_{solids}	C	H	N	O
		$(-)_{db}$	(wt.%)	$(-)_{daf}$	(wt.%)	(wt.%)	(wt.%)	(wt.%)
SM	350	20.92 ± 0.92	52.61	11.19 ± 0.49	76.56 ± 1.92	4.39 ± 0.37	3.91 ± 0.17	15.14 ± 2.46
	350cat	22.65 ± 1.01	57.21	10.94 ± 0.49	70.13 ± 1.32	4.94 ± 0.27	3.04 ± 0.12	21.89 ± 1.71
	400	20.66 ± 1.50	52.49	11.08 ± 0.80	80.36 ± 5.51	3.83 ± 0.45	3.87 ± 0.25	11.94 ± 6.21
	400cat	27.10 ± 0.29	47.93	15.93 ± 0.17	72.58 ± 5.02	4.67 ± 0.16	1.34 ± 0.41	21.41 ± 5.59
CM	350	21.43 ± 3.12	22.78	17.72 ± 2.58	66.75 ± 0.32	5.78 ± 0.40	2.83 ± 0.13	24.64 ± 0.22
	350cat	22.82 ± 1.21	39.34	14.82 ± 0.79	73.81 ± 1.54	6.06 ± 0.34	2.87 ± 0.04	17.26 ± 1.92
	400	18.55 ± 0.23	27.29	14.44 ± 0.18	79.84 ± 1.29	4.85 ± 0.31	3.12 ± 0.10	12.19 ± 1.69
	400cat	20.05 ± 0.24	40.49	12.78 ± 0.15	73.97 ± 5.06	5.56 ± 0.90	2.57 ± 0.11	17.90 ± 6.07
FS	350	26.94 ± 1.00	77.71	7.71 ± 0.29	52.15 ± 0.06	4.62 ± 0.03	4.44 ± 0.19	38.78 ± 0.22
	350cat	29.03 ± 0.32	75.58	9.10 ± 0.10	45.54 ± 3.56	4.06 ± 0.33	3.20 ± 0.22	47.19 ± 4.11
	400	25.83 ± 0.18	80.12	6.59 ± 0.05	51.14 ± 6.46	3.03 ± 1.08	3.56 ± 0.84	42.27 ± 8.38
	400cat	32.89 ± 0.48	74.43	10.79 ± 0.16	55.40 ± 4.54	5.93 ± 0.84	2.96 ± 0.43	35.71 ± 5.81
SS	350	28.05 ± 1.72	70.51	10.77 ± 0.66	46.33 ± 6.68	2.24 ± 2.95	5.16 ± 2.07	46.27 ± 11.7
	350cat	34.81 ± 0.38	73.98	11.79 ± 0.13	53.91 ± 2.11	2.82 ± 1.32	5.05 ± 0.46	38.22 ± 3.89
	400	27.26 ± 0.82	85.28	5.22 ± 0.16	64.81 ± 0.82	1.99 ± 0.22	7.95 ± 0.29	25.25 ± 0.89
	400cat	29.35 ± 1.44	89.28	4.10 ± 0.20	53.19 ± 6.17	0.00 ± 0.00	0.93 ± 0.73	45.87 ± 5.44

in particular, 50–60% of C is recovered in the biocrude after HTL of SM (58.4–60.5%) and CM (46.7–53.2%), and higher recoveries are obtained after processing FS (65.2–79.2%) and SS (56.2–72.2%). On the other hand, a greater amount of C is recovered in the manure-derived solids (17.1–25.8%) as respect to the C recovered in the solids obtained from the sludges (4.7–13.7%). The recoveries of C in the aqueous phase show similar values (2.2–7.5%), independently from the feedstock and the process condition used. Fig. 6 shows that about half of the N is transferred to the biocrude, except for SS, where N recovery is lower (around 30%). Similar to the C recovery, N recovery in the solids is greater for the manure-derived biocrudes (around 15% for SM and 25% for CM) compared to the sludges (around 5% for FS and SS), while the recovery of N in the aqueous phases shows similar values for SM, CM, FS (4–9%) and slightly higher values for SS (around 15%).

In the study conducted by Lu et al., most of the nitrogen contained in the SM was instead released to the aqueous phase (> 42%) and lower percentages were transferred to the biocrude (17–30%) [30]. Similarly, 72% of the N was released to the aqueous phase after HTL (340 °C, 10 min, and 25% total solids) of human feces [32]. However, in the latter study, the particularly high value for the N in the aqueous phase might also be explained by the different approach adopted by the authors, who assumed the N in the gas phase negligible and calculated the N in the aqueous phase by difference.

3.5. Composition of the inorganic fraction of the HTL products

The concentrations of the inorganic elements in the HTL products, investigated by ICP-AES, are reported in the supplementary material (Table S1). Nevertheless, it is not enough to evaluate the concentrations of the inorganics to understand how they distribute among the products: the yield of each phase should be considered as well. The amount of each inorganic element recovered in each of the product phases, was calculated by multiplying the concentration of an element in a phase by the weight of that phase. The corresponding weight percent was calculated normalizing the total to 100. The weight percentage of each inorganic element in each of the product phases are provided in the supplementary material (Table S2). The results show that the majority of the inorganics investigated (Al, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, and Zn) concentrate in the solids after HTL, with weight percentages above 70% for most of the elements. The remaining fraction is primarily found in the aqueous phase (in most of the cases below 30 wt%), while only minor quantities are detected in the biocrudes (< 3 wt%), except for the heavy metals (i.e. Cu, Ni, and Pb), for which higher values are registered (wt.% also in the range 20–30%). K and Na show a higher degree of dissolution in the aqueous phase as respect to the other inorganics, being primarily recovered in the aqueous phase (50.1–82.8 wt %) after processing SM and CM. For FS and SS, K and Na are instead primarily recovered in the solids in most of the process conditions, but still higher recoveries in the aqueous phase are obtained compared with other inorganics. Finally, a further different trend is registered for S, which, besides being found in the solids and the aqueous phase, is also recovered in the biocrude for more than a third (33.5–66.0 wt%) that corresponds to 2260–9965 ppm.

Though the inorganics seem to have similar behavior when redistributing among HTL products, however, higher recoveries of the elements in the solids are registered after processing FS and SS at all the process conditions investigated, compared with SM and CM. The different temperatures investigated (350 °C and 400 °C) and the presence of the catalyst did not seem to have a significant influence in the redistribution of the inorganics in the product phases. Fig. 7 visualizes how the inorganics distribute among the products after processing the feedstocks at subcritical conditions.

The distribution of the inorganics found in the present study is also in line with our previous research on willow irrigated with wastewater [34], showing that K and Na were primarily recovered in the aqueous phase, as in the present study for SM and CM. Similarly, it was reported that over 70% of the heavy metal elements (Zn, Cu, As, Pb, and Cd) were accumulated in the solid residue after HTL of SM [30]. Xu et al.

Table 4

Characterization of the aqueous phases obtained from HTL of the waste feedstocks at the different process conditions.

	pH (-)				TOC (g L^{-1})				TN (g L^{-1})			
	SM	CM	FS	SS	SM	CM	FS	SS	SM	CM	FS	SS
350	5.21	3.85	8.59	8.69	48.52	27.74	15.43	37.70	3.14	1.28	6.74	10.99
350cat	6.93	5.36	8.76	8.87	33.63	44.46	19.52	45.25	2.95	1.63	7.41	11.56
400	5.35	4.25	8.54	8.47	29.18	45.48	23.06	32.47	2.98	1.74	5.49	11.06
400cat	7.83	6.41	8.76	8.86	35.46	37.89	22.55	49.64	3.18	1.95	6.40	11.34

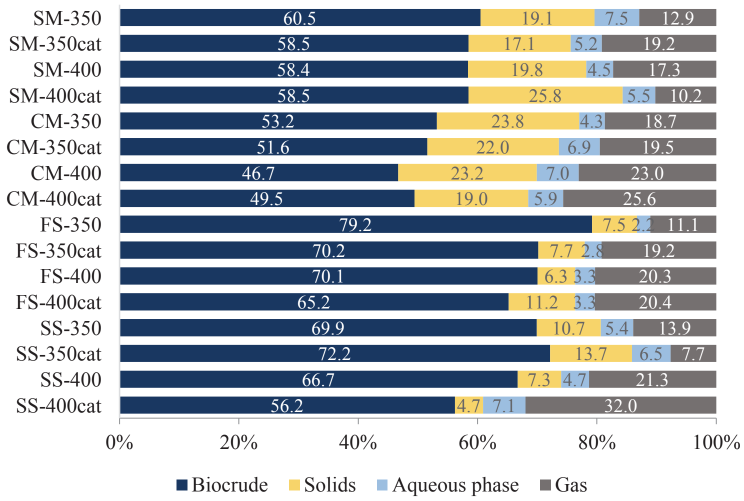


Fig. 5. Carbon recovery in the HTL product phases (biocrude, solids, aqueous phase, and gas) after processing the four feedstocks (swine manure (SM), cow manure (CM), fish sludge (FS), and sewage sludge (SS)) at the different process conditions (350 °C, 350 °C with catalyst (cat), 400 °C, 400 °C with catalyst (cat)).

also observed that over 93% of heavy metals (i.e., Cu, Zn, or Cr) were collected in the HTL solids, except for As, which was almost equally portioned among solids, aqueous phase, and biocrude [31]. K resulted almost entirely extracted into the aqueous phase after hydrothermal processing of chicken manure and swine manure [29].

The tendency of the inorganics to concentrate in the solids facilitates their recovery after HTL; on the contrary, the presence of inorganics in the biocrude is highly undesired for its final use as fuel and for the upgrading process, where the presence of metals can cause the deactivation of the catalyst.

Regarding the concentrations of the inorganics, Ca and P are strongly correlated in the solids with R = 0.99 (see Table S3, in the supplementary material). From the slope of P-Ca curve, the molar ratio is found to be 0.42 g/g; therefore, for every g of Ca in the sample, we find on average 0.42 g of P. This suggests that P is primarily present as apatite or hydroxyapatite ($Ca_5(PO_4)_3(OH)$), which has a molar ratio of 3P : 5Ca (0.46 gP/gCa). This finding is in line with the outcome of a previous study reporting that > 88.76% of the P in the hydrochar, obtained from hydrothermal carbonization (HTC) of cow manure, was apatite. The study reported an increase by > 85% in apatite P and consequently proposed HTC as a treatment to immobilize the P in the hydrochar and reduce the problem of P loss associated to cow manure [43].

3.6. Prospective for continuous HTL processing

The present study was conducted at laboratory scale, as this allows a practical screening of the feedstocks and exploring different process

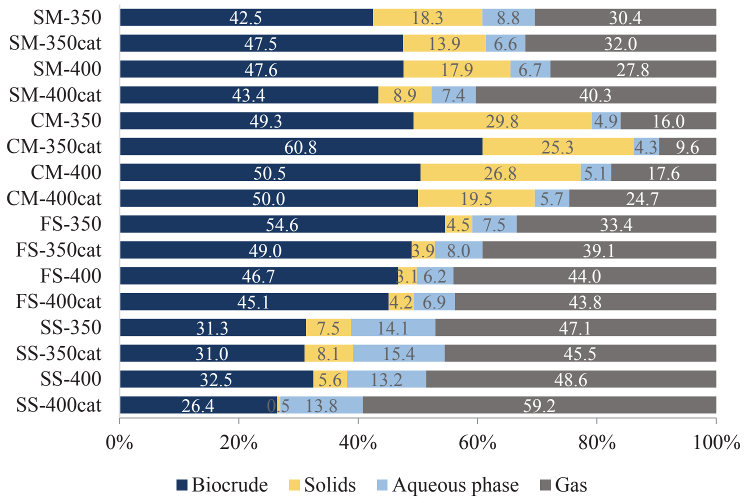


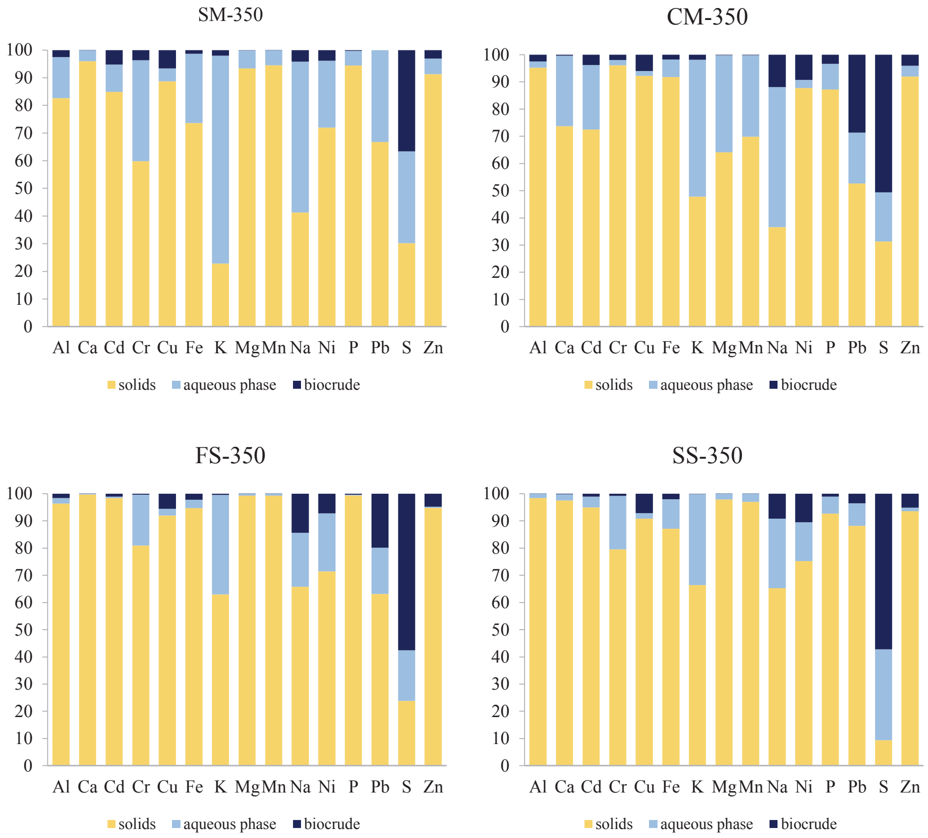
Fig. 6. Nitrogen recovery in the HTL product phases (biocrude, solids, aqueous phase, and gas) after processing the four feedstocks (swine manure (SM), cow manure (CM), fish sludge (FS), and sewage sludge (SS)) at the different process conditions (350 °C, 350 °C with catalyst (cat), 400 °C, 400 °C with catalyst (cat)).

Fig. 5 values (Biocrude / Solids / Aqueous phase / Gas):

	Biocrude	Solids	Aqueous phase	Gas
SM-350	60.5	19.1	7.5	12.9
SM-350cat	58.5	17.1	5.2	19.2
SM-400	58.4	19.8	4.5	17.3
SM-400cat	58.5	25.8	5.5	10.2
CM-350	53.2	23.8	4.3	18.7
CM-350cat	51.6	22.0	6.9	19.5
CM-400	46.7	23.2	7.0	23.0
CM-400cat	49.5	19.0	5.9	25.6
FS-350	79.2	7.5	2.2	11.1
FS-350cat	70.2	7.7	2.8	19.2
FS-400	70.1	6.3	3.3	20.3
FS-400cat	65.2	11.2	3.3	20.4
SS-350	69.9	10.7	5.4	13.9
SS-350cat	72.2	13.7	6.5	7.7
SS-400	66.7	7.3	4.7	21.3
SS-400cat	56.2	4.7	7.1	32.0

Fig. 6 values:

	Biocrude	Solids	Aqueous phase	Gas
SM-350	42.5	18.3	8.8	30.4
SM-350cat	47.5	13.9	6.6	32.0
SM-400	47.6	17.9	6.7	27.8
SM-400cat	43.4	8.9	7.4	40.3
CM-350	49.3	29.8	4.9	16.0
CM-350cat	60.8	25.3	4.3	9.6
CM-400	50.5	26.8	5.1	17.6
CM-400cat	50.0	19.5	5.7	24.7
FS-350	54.6	4.5	7.5	33.4
FS-350cat	49.0	3.9	8.0	39.1
FS-400	46.7	3.1	6.2	44.0
FS-400cat	45.1	4.2	6.9	43.8
SS-350	31.3	7.5	14.1	47.1
SS-350cat	31.0	8.1	15.4	45.5
SS-400	32.5	5.6	13.2	48.6
SS-400cat	26.4	0.5	13.8	59.2


SM-350

CM-350

FS-350

SS-350

Fig. 7. Normalized distribution of the inorganic elements among the products (solids, aqueous phase, and biocrude) after subcritical HTL of the waste feedstocks: swine manure (SM), cow manure (CM), fish sludge (FS) and sewage sludge (SS).

conditions. The results obtained are also intended to be used in support of the processing of the same feedstocks on a continuous larger scale. However, when a feedstock is processed in a continuous plant, there are some aspects, which require additional attention. For example, the high inorganic content of organic wastes could result in deposits and blockages of the system. The pumping of the feedstock into the reactor could also result highly challenging, especially when processing swine and cow manures which have a fibrous consistency. The mixing of various feedstocks with different dry matter contents and consistency could help in overcoming some issues related to the feeding. Furthermore, at larger scale the use of solvents is avoided, the solids including the inorganics would be recovered together with the biocrude in the downstream section of the plant. Nevertheless, this can be overcome, for example, by introducing a filter after the reaction system, as in the PNNL continuous HTL set-up [44]. An in-line filter is also placed in the downstream section of the CBS1 unit at Aalborg University, to ensure the collection of the solid hydrochars and inorganics.

With regards to the large amount of aqueous phase, in continuous processing, this can be recycled to reduce the use of fresh water and simultaneously decrease the production of a waste product, which requires treatment before disposal. Recycling the water phase would also result in a decreased consumption of K_2CO_3 catalysts, as K is dissolving in the aqueous phase. Moreover, the recycling of the aqueous phase produces its saturation, enhancing the production of insoluble compounds and increasing the production of biocrude [35,45,46]. Besides being a waste stream, HTL aqueous phase is a source of energy and nutrients and, for this reason, several technologies are still under investigation with the aim of maximizing its valorization. Value-added chemicals could be extracted and used as fuel additives, nutrients dissolved in the aqueous phase could be used for biomass cultivation or for fertilizers production. Other alternatives for the valorization of the aqueous stream consist in the hydrothermal gasification or the anaerobic fermentation of the HTL aqueous phase. A detailed investigation pointing out the advantages and challenges of the various approaches for the aqueous phase valorization in prospective of HTL commercialization is provided in [42].

4. Conclusions

Hydrothermal liquefaction represents a suitable alternative for handling organic wastes of animal and human origin as manure, fish sludge, or sewage sludge. These wet ash-containing waste fractions can be processed directly in the HTL process with high yields of energy dense biocrudes ranging from about 35% for manures, 45% for sewage sludge, and 50% for fish sludge. Supercritical conditions (400 °C) result in lower biocrude yields as compared to subcritical conditions (350 °C), however, for swine and cow manure, higher temperatures produce biocrudes with a better quality in terms of lower oxygen content. The quality of manure-derived biocrudes is also improved by the addition of K_2CO_3 to the feed mixture, while this catalyst does not affect the quality of biocrudes derived from sludges. As one to two thirds of N and S in the feedstocks are transferred to the biocrude, denitrogenation and desulfurization of the biocrude are necessary during biocrude upgrading. Most of the inorganics (e.g. P, Ca, Mg) are instead transferred to the solids after HTL, easing their separation for further reutilization as a fertilizer. In this way, the processing of waste products through HTL results simultaneously in the production of biocrude oil and in the recovery of valuable inorganics.

Fundings:

This work was supported by Innovation Fund Denmark under the project “WATERVALUE” -Integrated waste water treatment and resource valorization for reduced urban carbon footprint – [grant number 8087-00028B].

CRediT authorship contribution statement

Federica Conti: Conceptualization, Methodology, Investigation, Formal analysis, Validation, Visualization, Writing - original draft. **Saqib S. Toor:** Conceptualization, Investigation. **Thomas H. Pedersen:** Conceptualization, Methodology, Validation. **Tahir H. Seehar:** Investigation. **Asbjørn H. Nielsen:** Methodology, Investigation, Validation. **Lasse A. Rosendahl:** Conceptualization, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.enconman.2020.112925.

References

[1] Malins K, Kampars V, Brinks J, Neibolte I, Murnieks R, Kampare R. Bio-oil from thermo-chemical hydro-liquefaction of wet sewage sludge. Bioresour Technol 2015;187:23–9.

[2] European Environment Agency, Greenhouse gas emissions from transport. https://www.eea.europa.eu/data-and-maps/indicators/transport-emissions-of-greenhouse-gases/transport-emissions-of-greenhouse-gases-11; 2018.

[3] Oh Y-K, Hwang K-R, Kim C, Kim JR, Lee J-S. Recent developments and key barriers to advanced biofuels: A short review. Bioresour Technol 2018;257:320–33.

[4] Dimitriadis A, Bezergianni S. Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review. Renew Sustain Energy Rev 2017;68(1):113–25.

[5] Pedersen TH, Hansen NH, Pérez OM, Villamar Cabezas DE, Rosendahl LA. Renewable hydrocarbon fuels from hydrothermal liquefaction: A techno-economic analysis. Biofuels, Bioprod Biorefin 2018;12:213–23.

[6] De Jong S, Hoefnagels R, Faaij A, Slade R, Mawhood B, Junginger M. The feasibility of short-term production strategies for renewable jet fuels – A comprehensive techno-economic comparison. Biofuel Bioprod. Bioref. 2015;9:778–800.

[7] Zhu Y, Biddy MJ, Jones SB, Elliott DC, Schmidt AJ. Techno-economic analysis of liquid fuel production from woody biomass via hydrothermal liquefaction (HTL) and upgrading. Appl Energy 2014;129:384–94.

[8] Scholz RW, Ulrich AE, Eilittä M, Roy A. Sustainable use of phosphorus: A finite resource. Sci Total Environ 2013;461–462:799–803.

[9] Technical Report No. I to the European Commission, Directorate-General Environment, Manure Processing Activities in Europe - Project reference: ENV.B.1/ETU/2010/0007 http://balticsea2020.org/images/Bilagor/21010_future%20trends%20on%20manure%20processing%20activitieis%20in%20europe.pdf.

[10] Sims J.T. Maguire R.O. Manure management, in Hillel D. (ed) Encyclopedia of Soils in the Environment. 2005; Elsevier: Oxford. doi: 10.1016/B0-12-348530-4/00515-4 402 410.

[11] Aas T. S. Åsgård, T. Estimated content of nutrients and energy in feed spill and faeces in Norwegian salmon culture, Nofima Report 19, Published July; 2017 https://pdfs.semanticscholar.org/5290/8d3bdc5861e18571a82f918ffc9837e2f2f6.pdf.

[12] Brod E, Oppen J, Kristoffersen AØ, Haraldsen TK, Krogstad T. Drying or anaerobic digestion of fish sludge: Nitrogen fertilization effects and logistics. Ambio 2017;46(8):852–64.

[13] Kelessidis A, Stasinakis AS. Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries. Waste Manage 2012;32(6):1186–95.

[14] Kacprzak M, Neczaj E, Fijałkowski K, Grobelak A, Grosser A, Worwag M, et al. Sewage sludge disposal strategies for sustainable development. Environ Res 2017;156:39–46.

[15] He BJ, Zhang Y, Yin Y, Funk TL, Riskowski GL. Operating temperature and retention time effects on the thermochemical conversion process of swine manure, Transactions of the ASAE. Am Soc Agricult Eng 2000;43(6). pp. 1821–1825 10.13031/2013.3086.

[16] He BJ, Zhang Y, Yin Y, Funk TL, Riskowski GL. Effects of alternative process gases on the thermochemical conversion process of swine manure, Transactions of the ASAE. Am Soc Agricult Eng 2001;44(6). pp. 1873–1880 10.13031/2013.7026.

[17] He B, Zhang Y, Yin Y, Funk TL, Riskowski GL. Effects of feedstock ph, initial co addition, and total solids content on the thermochemical conversion process of swine manure. Trans ASAE, Am Soc Agricult Eng 2001;44(3). pp. 697–701 10.13031/2013.6108.

[18] Posmanik R, Martinez CM, Cantero-Tubilla B, Cantero D, Sills D, Jose Cocero M, et al. Acid and alkali catalyzed hydrothermal liquefaction of dairy manure digestate and food waste. ACS Sustainable Chem Eng 2018;6(2):2724–32.

[19] Xiu S, Shahbazi A, Shirley V, Cheng D. Hydrothermal pyrolysis of swine manure to bio-oil: Effects of operating parameters on products yield and characterization of bio-oil. J Anal Appl Pyrol 2010;88:73–9.

[20] Yin S, Dolan R, Harris M, Tan Z. Subcritical hydrothermal liquefaction of cattle manure to bio-oil: Effects of conversion parameters on bio-oil yield and characterization of bio-oil. Bioresour Technol 2010;101:3657–64.

[21] Qian L, Wang S, Savage PE. Hydrothermal liquefaction of sewage sludge under isothermal and fast conditions. Bioresour Technol 2017;232:27–34.

[22] Wang Y, Chen G, Li Y, Yan B, Pan D. Experimental study of the bio-oil production from sewage sludge by supercritical conversion process. Waste Manage 2013;33:2408–15.

[23] Ma W, Du G, Li J, Fang Y, Hou L, Chen G, et al. Supercritical water pyrolysis of sewage sludge. Waste Manage 2017;59:371–8.

[24] Wang W, Yang L, Yin Z, Kong S, Han W, Zhang J. Catalytic liquefaction of human feces over Ni-Tm/TiO2 catalyst and the influence of operating conditions on products. Energy Convers Manage 2018;157:239–45.

[25] Mishra S, Mohanty K. Co-HTL of domestic sewage sludge and wastewater treatment derived microalgal biomass – An integrated biorefinery approach for sustainable biocrude production. Energy Convers Manage 2020;204:112312.

[26] Xu D, Wang Y, Lin G, Guo S, Wang S, Wu Z. Co-hydrothermal liquefaction of microalgae and sewage sludge in subcritical water: Ash effects on bio-oil production. Renew Energy 2019;138:1143–51.

[27] Vardon DR, Sharma BK, Scott J, Yu G, Wang Z, Schideman L, et al. Chemical properties of biocrude oil from the hydrothermal liquefaction of Spirulina algae, swine manure, and digested anaerobic sludge. Bioresour Technol 2011;102:8295–303.

[28] Huang H, Yuan X, Zhu H, Li H, Liu Y, Wang X, et al. Comparative studies of thermochemical liquefaction characteristics of microalgae, lignocellulosic biomass and sewage sludge. Energy 2013;56:52–60.

[29] Ekpo U, Ross AB, Camargo-Valero MA, Williams PT. A comparison of product yields and inorganic content in process streams following thermal hydrolysis and hydrothermal processing of microalgae, manure and digestate. Bioresour Technol 2016;200:951–60.

[30] Lu J, Watson J, Zeng J, Li H, Zhu Z, Wang M, et al. Biocrude production and heavy metal migration during hydrothermal liquefaction of swine manure. Process Saf Environ Prot 2018;115:108–15.

[31] Xu D, Lin G, Liu L, Wang Y, Jing Z, Wang S. Comprehensive evaluation on product characteristics of fast hydrothermal liquefaction of sewage sludge at different temperatures. Energy 2018;159:686–95.

[32] Lu J, Zhang J, Zhu Z, Zhang Y, Zhao Y, Li R, et al. Simultaneous production of biocrude oil and recovery of nutrients and metals from human feces via hydrothermal liquefaction. Energy Convers Manage 2017;134:340–6.

[33] Leow S, Witter JR, Vardon DR, Sharma BK, Guesta JS, Strathmann TJ. Prediction of microalgae hydrothermal liquefaction products from feedstock biochemical composition. Green Chem 2015;17:3584–99.

[34] Conti F, Toor SS, Pedersen TH, Nielsen AH, Rosendahl LA. Biocrude production and nutrients recovery through hydrothermal liquefaction of wastewater irrigated willow. Biomass Bioenergy 2018;118:24–31.

[35] Zhu Z, Toor SS, Rosendahl LA, Yu D, Chen G. Hydrothermal liquefaction of barley straw to bio-crude oil: effects of reaction temperature and aqueous phase recirculation. Appl Energy 2015;137:183–92.

[36] Pedersen TH, Rosendahl LA. Production of fuel range oxygenates by supercritical hydrothermal liquefaction of lignocellulosic model systems. Biomass Bioenergy 2015;83:206–15.

[37] Biller P, Ross AB. Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content. Bioresour Technol 2011;102:215–25.

[38] Jensen, C. U. Rodriguez Guerrero, J. K. Karatzos, S. Olofsson, G. Iversen, S. B. Fundamentals of Hydrofaction™: Renewable crude oil from woody biomass, Biomass Conv Bioref (4); 2017. DOI: 10.1007/s13399-017-0248-8.

[39] Jensen MM, Djajadi DT, Torri C, Rasmussen HB, Madsen RB, Venturini E, et al. Hydrothermal Liquefaction of Enzymatic Hydrolysis Lignin: Biomass Pretreatment Severity Affects Lignin Valorization. ACS Sustainable Chem Eng 2018;6(5):5940–9.

[40] Zheng X, Ma X, Chen L, Huang L, Cao S, Nasrallah J. Lignin extraction and recovery

in hydrothermal pretreatment of bamboo. J Bioresour Bioprod 2016;1(3):145–51.

[41] Castellví Barnes M, de Visser MM, van Rossum G, Kersten SRA, Lange J-P. Liquefaction of wood and its model components. J Anal Appl Pyrol 2017;125:136–43.

[42] Watson J, Wang T, Si B, Chen W-T, Aierzhati A, Zhang Y. Valorization of hydrothermal liquefaction aqueous phase: pathways towards commercial viability. Prog Energy Combust Sci 2020;77:100819.

[43] Dai L, Tan F, Wu B, He M, Wang W, Tang X, et al. Immobilization of phosphorus in cow manure during hydrothermal carbonization. J Environ Manage 2015;157:49–53.

[44] Marrone P.A. Genifuel Hydrothermal Processing Bench-Scale Technology Evaluation Report; Water Environment and Reuse Foundation Alexandria: VA, USA. 2016 ISBN: 9781780408408 doi: 10.2166/9781780408408.

[45] Biller P, Madsen RB, Klemmer M, Becker J, Iversen BB, Glasius M. Effect of hydrothermal liquefaction aqueous phase recycling on bio-crude yields and composition. Bioresour Technol 2016;220:190–9.

[46] Pedersen TH, Grigoras IF, Hoffmann J, Toor SS, Daraban IM, Jensen CU, et al. Continuous hydrothermal co-liquefaction of aspen wood and glycerol with water phase recirculation. Appl Energy 2016;162:1034–41.

Supplementary material:

Table S1: Concentrations of inorganic elements in the feedstocks (swine manure (SM), cow manure (CM), fish sludge (FS) and sewage sludge (SS)) and in the HTL products (solids, aqueous phase, and biocrude) obtained at the different process conditions (350 °C, 350 °C with catalyst (cat), 400 °C, 400 °C with catalyst (cat)). Concentrations are expressed in (mg kg^{-1}) for the feedstocks, the solids, and the biocrudes, while in (mg L^{-1}) for the aqueous phases.

		Al	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Zn
Feedstock	SM	237.3	13772.3	0.2	2.5	79.4	762.1	10099.8	2764.2	189.4	2432.0	3.2	7531.9	0.4	3672.5	278.7
	CM	45.8	7816.5	0.1	1.9	160.5	633.8	2394.4	2445.1	100.9	1138.2	4.0	2591.9	0.0	3092.9	174.4
	FS	421.0	71370.0	1.1	13.9	21.1	890.9	926.5	2244.3	148.4	1921.5	2.8	30425.4	1.3	4223.3	553.3
	SS	5546.9	11744.6	0.7	16.1	133.5	8276.0	3433.1	3219.9	150.2	801.4	20.9	9560.6	14.6	5117.8	625.0
Solids	SM-350	1518.2	104955.8	0.6	71.0	435.6	4626.6	7983.3	17487.7	1356.7	3764.0	109.9	54612.4	3.0	6653.6	1892.5
	SM-350cat	1487.5	93190.7	0.4	116.9	279.1	3838.5	81653.7	13894.9	1173.5	3637.0	110.2	46965.0	3.4	3264.0	1973.3
	SM-400	1696.5	127295.7	0.5	169.5	423.8	3518.5	11798.7	19043.8	1559.0	4528.2	145.4	62973.9	8.9	5577.1	2240.5
	SM-400cat	969.0	73830.2	0.4	74.4	197.0	4100.5	108102.3	15030.3	967.9	4047.9	60.1	38544.2	6.1	4298.7	1388.6
	CM-350	1162.4	23325.2	0.8	182.2	585.9	3958.7	7007.3	6898.1	297.8	1724.3	176.8	9373.8	8.6	3937.4	1651.5
	CM-350cat	873.5	25274.0	0.6	230.6	576.7	4371.2	90616.4	6648.4	301.9	1515.5	206.6	10703.2	4.6	3032.9	1168.5
	CM-400	2097.4	25194.3	0.5	270.1	582.2	4297.3	2275.6	6890.5	305.3	895.8	211.5	10585.2	3.4	2647.5	1605.3
	CM-400cat	1509.1	23058.5	0.4	220.8	405.2	3411.3	54050.8	6582.0	314.9	1049.9	186.8	7526.4	9.7	1872.5	1551.5
	FS-350	1472.6	264808.4	3.6	77.9	66.1	3516.1	3402.9	7813.6	535.7	2419.4	44.0	115113.2	5.0	2651.1	1817.3
	FS-350cat	1265.6	233896.9	3.1	158.5	49.1	2968.3	53592.6	7079.5	475.9	4733.7	116.1	100000.0	3.7	2080.3	1724.2
	FS-400	1581.1	278428.7	3.8	126.4	51.2	3297.9	5252.0	8024.5	559.5	2463.7	129.3	118891.9	17.2	2588.3	1990.2

	FS-400cat	1429.7	216820.3	2.9	186.8	42.4	3130.9	69608.3	6557.6	461.8	4522.6	137.8	93456.2	4.3	2132.7	1560.4
	SS-350	19439.5	44585.4	2.4	78.1	388.1	11395.9	10689.5	11958.5	449.7	2358.3	94.5	24209.0	46.3	1528.3	2959.8
	SS-350cat	15909.1	34494.0	1.8	165.8	291.1	29103.8	80703.3	9133.8	364.5	1593.9	147.1	27697.3	36.5	1768.0	1718.3
	SS-400	20027.4	47556.9	2.2	86.5	368.1	21765.0	14113.3	11731.3	488.6	2119.2	171.0	27211.5	47.2	1000.0	2007.4
	SS-400cat	13963.9	37772.7	1.7	197.5	281.1	24614.1	107844.0	10079.7	670.7	2198.0	138.9	24513.4	40.3	1411.1	2100.3
Aqueous phase	SM-350	24.2	383.9	0.0	3.8	2.0	138.7	2314.3	107.6	6.9	438.5	3.3	267.4	0.1	646.4	10.3
	SM-350cat	32.1	1531.2	0.0	2.9	9.7	136.0	12355.4	350.7	21.3	468.8	2.5	901.5	0.1	743.2	39.8
	SM-400	14.8	697.6	0.0	2.6	4.1	69.4	2862.2	190.1	11.7	461.4	2.1	390.1	0.1	454.7	19.1
	SM-400cat	11.2	535.2	0.0	2.4	4.1	43.5	11385.0	107.5	7.6	391.1	1.8	323.1	0.1	511.1	11.7
	CM-350	2.7	803.5	0.0	0.4	1.1	27.5	719.9	375.3	12.5	237.1	0.6	99.0	0.3	222.5	6.9
	CM-350cat	51.5	815.5	0.0	4.5	3.5	223.4	8911.5	320.2	10.9	276.8	4.2	323.8	0.6	346.2	12.6
	CM-400	53.6	716.3	0.0	5.2	5.4	202.8	896.5	185.8	9.1	230.1	4.3	284.1	0.5	238.4	13.4
	CM-400cat	36.3	848.2	0.0	6.3	14.0	148.5	11324.6	306.3	8.8	266.7	5.2	335.7	0.7	404.4	20.2
	FS-350	3.6	79.9	0.0	2.1	0.2	13.1	232.0	6.2	0.5	85.6	1.5	37.5	0.2	242.5	1.0
	FS-350cat	9.0	547.9	0.0	2.7	0.5	18.7	10611.7	22.2	1.6	114.7	2.1	294.6	0.1	173.7	5.8
	FS-400	6.3	360.7	0.0	2.9	0.3	17.7	742.9	12.6	1.0	118.3	2.8	142.3	0.2	211.9	2.7
	FS-400cat	9.4	138.2	0.0	6.3	0.6	38.7	8223.3	14.4	1.2	93.2	4.5	131.3	0.1	145.3	2.3
	SS-350	34.7	120.0	0.0	2.2	1.0	160.7	611.5	29.1	1.6	104.6	2.0	186.1	0.5	619.1	4.6
	SS-350cat	66.1	125.3	0.0	2.0	1.6	327.7	9964.7	36.8	1.7	120.6	2.2	390.5	0.6	972.4	7.6
	SS-400	31.8	77.1	0.0	4.9	0.8	149.8	693.7	18.7	1.3	43.3	3.9	130.6	0.4	558.4	3.4
	SS-400cat	207.1	635.0	0.0	5.9	5.3	374.4	7196.5	144.8	13.7	111.9	5.0	589.0	1.2	727.4	24.5
Biocrude	SM-350	27.1	16.4	0.0	2.6	19.1	51.0	414.7	11.9	0.4	226.9	3.5	107.8	0.0	4725.2	37.1
	SM-350cat	21.1	55.3	0.0	2.2	8.8	48.8	19366.9	25.5	1.2	506.0	2.2	130.0	0.0	4560.8	42.0

SM-400	17.9	0.5	0.0	1.0	17.2	66.2	470.5	7.9	0.1	319.9	2.5	88.2	0.0	5774.6	60.2
SM-400cat	15.8	10.3	0.0	0.9	122.6	53.7	11088.7	8.2	0.7	599.9	3.3	124.8	0.1	4662.0	38.3
CM-350	18.0	68.9	0.0	2.2	22.4	44.2	162.9	14.6	0.4	326.3	10.9	211.8	2.7	3706.5	43.0
CM-350cat	11.1	181.5	0.0	1.5	38.6	35.0	16947.7	79.4	4.0	539.2	10.6	130.0	2.4	3741.2	62.1
CM-400	13.9	196.1	0.0	0.2	38.7	31.6	589.2	19.4	3.0	432.9	5.9	49.5	3.4	4543.9	35.4
CM-400cat	13.7	92.3	0.0	0.8	46.8	20.7	1533.5	7.4	0.4	329.9	8.4	59.5	3.2	3994.8	89.4
FS-350	15.7	82.2	0.0	0.2	2.5	52.5	15.4	3.3	0.0	328.3	2.8	251.0	1.0	3982.1	57.4
FS-350cat	15.5	124.3	0.0	1.3	6.7	63.4	1541.0	4.1	0.0	374.0	4.4	302.5	1.5	3548.3	59.1
FS-400	8.1	24.3	0.0	0.4	16.9	59.8	54.9	2.9	0.1	329.2	29.7	313.9	1.5	3980.6	114.2
FS-400cat	14.9	44.3	0.1	0.5	18.7	74.6	2098.2	2.8	0.2	249.4	8.7	298.3	0.7	2660.8	320.4
SS-350	8.8	66.2	0.0	0.7	26.5	237.4	18.6	3.1	0.1	289.3	11.5	243.7	1.6	8105.6	142.2
SS-350cat	13.4	329.4	0.1	0.4	27.6	454.0	726.3	11.8	0.6	363.0	6.7	382.7	2.5	6704.3	228.0
SS-400	15.3	107.8	0.0	2.4	30.3	463.5	25.9	4.4	0.5	296.2	42.8	407.1	0.7	9965.4	105.8
SS-400cat	12.2	96.4	0.3	0.2	72.5	338.3	1440.0	4.9	0.3	285.0	66.9	267.3	1.0	7283.2	445.8

Table S2: Inorganics distribution among HTL products expressed in terms of weight percent of each inorganic element in each HTL product (solids, aqueous phase, and biocrude) after the processing of the feedstocks (swine manure (SM), cow manure (CM), fish sludge (FS), and sewage sludge (SS)) at the different process conditions (350 °C, 350 °C with catalyst (cat), 400 °C, 400 °C with catalyst (cat)).

Legend:

50-70 wt.%	in the solids
70-100 wt.%	in the solids
30-50 wt.%	in the aqueous phase
>50 wt.%	in the aqueous phase
10-30 wt.%	in the biocrude
>30 wt.%	in the biocrude

		Al	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Zn
solids	SM-350	82.6	96.0	84.9	59.9	88.7	73.6	22.9	93.4	94.5	41.3	71.9	94.4	66.8	30.2	91.3
	SM-350cat	76.8	82.3	67.0	73.9	66.7	67.5	30.0	75.1	80.8	34.6	75.4	79.7	72.1	16.3	77.2
	SM-400	89.3	94.0	85.2	83.9	84.6	79.2	25.7	89.5	92.0	43.3	83.6	93.1	91.8	27.0	87.3
	SM-400cat	86.3	91.9	84.0	70.9	51.0	87.5	41.8	92.0	91.3	42.7	69.7	90.5	84.6	27.2	88.2
	CM-350	95.2	73.7	72.4	96.1	92.2	91.7	47.8	64.1	69.8	36.6	87.7	87.2	52.7	31.3	91.9
	CM-350cat	49.9	64.5	70.1	75.0	83.7	53.5	34.4	54.8	61.6	21.9	70.6	65.6	25.6	21.6	79.7
	CM-400	69.3	66.9	67.6	75.4	79.5	55.2	12.4	68.4	65.7	16.4	72.0	68.4	19.7	19.6	85.1
	CM-400cat	71.5	62.7	62.4	68.4	58.0	58.6	22.7	57.2	68.9	18.1	66.3	57.9	38.7	13.2	77.4
	FS-350	96.3	99.7	98.4	80.9	91.9	94.7	63.0	99.3	99.2	65.8	71.4	99.4	63.1	23.8	94.7
	FS-350cat	91.0	97.3	94.9	82.9	76.7	90.7	30.1	96.4	96.3	72.1	79.5	96.3	49.6	23.3	92.1
	FS-400	95.0	98.5	93.9	78.8	63.7	91.9	38.0	98.2	98.0	57.2	62.9	98.3	79.5	23.5	90.7
	FS-400cat	93.0	99.4	93.1	75.2	61.7	87.2	45.9	97.9	97.5	79.3	72.1	98.3	66.8	32.8	80.5
	SS-350	98.4	97.5	94.9	79.5	90.8	87.1	66.4	97.9	97.0	65.2	75.2	92.6	88.1	9.4	93.5
	SS-350cat	97.1	96.7	91.7	92.3	88.5	91.5	53.9	97.2	96.8	57.4	87.3	90.1	85.4	11.8	86.2
	SS-400	98.4	98.2	95.9	63.4	89.1	91.5	67.8	98.5	97.4	73.0	65.4	93.9	91.0	5.3	92.5
	SS-400cat	89.4	88.1	75.1	81.0	71.8	88.2	64.9	89.8	86.1	65.6	57.5	83.3	80.0	10.0	77.3
aqueous phase	SM-350	14.9	4.0	9.9	36.5	4.7	25.0	75.1	6.5	5.5	54.5	24.2	5.2	33.2	33.2	5.6
	SM-350cat	21.5	17.6	32.4	24.0	30.1	31.1	59.0	24.7	19.1	58.0	22.3	19.9	26.9	48.3	20.3
	SM-400	9.1	6.0	10.4	15.3	9.6	18.2	72.6	10.4	8.0	51.5	14.0	6.7	8.2	25.7	8.7
	SM-400cat	12.1	8.1	12.0	28.1	12.9	11.2	53.4	8.0	8.6	50.1	26.0	9.2	14.6	39.2	9.0
	CM-350	2.2	25.9	23.7	1.9	1.7	6.5	50.2	35.7	30.0	51.5	3.0	9.4	18.7	18.1	4.0

	CM-350cat	49.2	34.9	25.6	24.4	8.5	45.9	56.6	44.3	37.2	67.1	24.3	33.3	56.3	41.2	14.4
	CM-400	30.1	32.3	26.9	24.5	12.6	44.2	82.8	31.3	33.3	71.7	25.0	31.2	50.4	30.0	12.1
	CM-400cat	27.6	37.0	33.1	31.2	32.2	40.9	76.4	42.7	31.0	73.7	29.4	41.4	43.0	45.7	16.1
	FS-350	2.0	0.3	0.5	18.7	2.5	3.0	36.6	0.7	0.8	19.8	21.3	0.3	17.0	18.6	0.5
	FS-350cat	7.5	2.6	4.2	16.2	9.1	6.6	68.7	3.5	3.7	20.2	16.4	3.3	22.9	22.4	3.6
	FS-400	4.3	1.5	4.8	20.8	4.6	5.6	61.4	1.8	2.0	31.3	15.3	1.3	10.3	22.0	1.4
	FS-400cat	5.9	0.6	2.5	24.6	7.9	10.5	52.6	2.1	2.5	15.8	22.9	1.3	21.7	21.7	1.2
	SS-350	1.6	2.3	4.0	19.7	2.0	10.8	33.5	2.1	3.0	25.5	14.2	6.3	8.3	33.5	1.3
	SS-350cat	2.8	2.4	4.6	7.5	3.3	7.1	45.7	2.7	3.0	29.8	8.8	8.7	8.9	44.5	2.6
	SS-400	1.5	1.5	3.0	34.4	1.8	6.0	32.0	1.5	2.5	14.3	14.4	4.3	7.4	28.7	1.5
	SS-400cat	10.5	11.7	10.9	19.0	10.6	10.6	34.2	10.2	13.9	26.4	16.2	15.8	18.2	40.8	7.1
biocrude	SM-350	2.5	0.0	5.2	3.7	6.6	1.4	2.0	0.1	0.0	4.2	3.9	0.3	0.0	36.6	3.1
	SM-350cat	1.7	0.1	0.6	2.1	3.2	1.3	11.0	0.2	0.1	7.5	2.3	0.3	1.0	35.3	2.5
	SM-400	1.6	0.0	4.4	0.8	5.8	2.5	1.7	0.1	0.0	5.2	2.4	0.2	0.0	47.3	4.0
	SM-400cat	1.6	0.0	4.0	1.0	36.1	1.3	4.9	0.1	0.1	7.2	4.4	0.3	0.8	33.5	2.8
	CM-350	2.5	0.4	3.8	2.0	6.1	1.8	1.9	0.2	0.2	11.9	9.3	3.4	28.7	50.6	4.1
	CM-350cat	0.9	0.6	4.3	0.7	7.8	0.6	9.0	0.9	1.1	10.9	5.1	1.1	18.1	37.2	5.9
	CM-400	0.7	0.8	5.5	0.1	7.9	0.6	4.8	0.3	1.0	11.9	3.0	0.5	29.9	50.4	2.8
	CM-400cat	0.9	0.4	4.5	0.3	9.8	0.5	0.9	0.1	0.1	8.3	4.3	0.7	18.3	41.1	6.5
	FS-350	1.6	0.0	1.1	0.4	5.6	2.3	0.5	0.1	0.0	14.4	7.3	0.3	19.9	57.6	4.8
	FS-350cat	1.5	0.1	0.9	0.9	14.2	2.6	1.2	0.1	0.0	7.8	4.1	0.4	27.6	54.3	4.3
	FS-400	0.7	0.0	1.3	0.4	31.7	2.5	0.6	0.1	0.0	11.5	21.8	0.4	10.2	54.5	7.8
	FS-400cat	1.1	0.0	4.4	0.2	30.3	2.3	1.5	0.0	0.0	4.9	5.0	0.3	11.5	45.5	18.3
	SS-350	0.1	0.2	1.1	0.8	7.1	2.1	0.1	0.0	0.0	9.2	10.6	1.1	3.6	57.2	5.2
	SS-350cat	0.1	0.9	3.7	0.2	8.2	1.4	0.5	0.1	0.2	12.8	3.9	1.2	5.8	43.7	11.2
	SS-400	0.1	0.3	1.1	2.2	9.1	2.4	0.2	0.0	0.1	12.6	20.2	1.7	1.6	66.0	6.0
	SS-400cat	0.1	0.2	14.0	0.1	17.6	1.2	0.8	0.0	0.0	8.1	26.3	0.9	1.8	49.2	15.6

Table S3: Correlation among inorganics in the solids used to predict in which forms the inorganics are present. When the correlation among different inorganics is above 0.9, it is highlighted in orange.

	Al	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Zn
Al	1.00	-0.39	0.21	-0.24	0.08	0.86	0.01	0.08	-0.22	-0.30	0.02	-0.33	0.97	-0.57	0.58
Ca	-0.39	1.00	0.75	-0.32	-0.82	-0.41	-0.24	-0.10	0.14	0.55	-0.53	0.99	-0.34	0.05	0.04
Cd	0.21	0.75	1.00	-0.30	-0.75	0.10	-0.25	-0.39	-0.34	0.16	-0.38	0.75	0.26	-0.49	0.27
Cr	-0.24	-0.32	-0.30	1.00	0.40	-0.04	0.19	-0.54	-0.43	-0.42	0.81	-0.38	-0.22	-0.21	-0.44
Cu	0.08	-0.82	-0.75	0.40	1.00	0.05	-0.18	0.11	-0.04	-0.54	0.66	-0.84	0.04	0.26	-0.05
Fe	0.86	-0.41	0.10	-0.04	0.05	1.00	0.27	0.02	-0.19	-0.33	0.11	-0.34	0.85	-0.49	0.26
K	0.01	-0.24	-0.25	0.19	-0.18	0.27	1.00	-0.05	-0.01	0.14	-0.04	-0.22	0.01	-0.20	-0.40
Mg	0.08	-0.10	-0.39	-0.54	0.11	0.02	-0.05	1.00	0.92	0.51	-0.38	-0.01	0.06	0.65	0.42
Mn	-0.22	0.14	-0.34	-0.43	-0.04	-0.19	-0.01	0.92	1.00	0.66	-0.40	0.21	-0.23	0.75	0.27
Na	-0.30	0.55	0.16	-0.42	-0.54	-0.33	0.14	0.51	0.66	1.00	-0.55	0.59	-0.33	0.42	0.12
Ni	0.02	-0.53	-0.38	0.81	0.66	0.11	-0.04	-0.38	-0.40	-0.55	1.00	-0.58	0.03	-0.18	-0.32
P	-0.33	0.99	0.75	-0.38	-0.84	-0.34	-0.22	-0.01	0.21	0.59	-0.58	1.00	-0.29	0.08	0.08
Pb	0.97	-0.34	0.26	-0.22	0.04	0.85	0.01	0.06	-0.23	-0.33	0.03	-0.29	1.00	-0.58	0.60
S	-0.57	0.05	-0.49	-0.21	0.26	-0.49	-0.20	0.65	0.75	0.42	-0.18	0.08	-0.58	1.00	-0.11
Zn	0.58	0.04	0.27	-0.44	-0.05	0.26	-0.40	0.42	0.27	0.12	-0.32	0.08	0.60	-0.11	1.00

Paper D

Hydrothermal Liquefaction - A Sustainable Solution to the Sewage Sludge Disposal Problem

S. S. Toor, F. Conti, A. A. Shah, T. H. Seehar, L. A. Rosendahl

The manuscript has been published in:
Advances in Waste-to-Energy Technologies (2019), Chapter 9, 143-163 ISBN 978-1-138-39042-3

9 Hydrothermal Liquefaction

A Sustainable Solution to the Sewage Sludge Disposal Problem

Saqib Sohail Toor, Federica Conti, Ayaz Ali Shah, Tahir Hussain Seehar, and Lasse Aistrup Rosendahl*
Aalborg University

CONTENTS

9.1 INTRODUCTION

Sewage sludge (SS) is a product of modern society, as wastewater treatment has been implemented following a growing awareness of hygiene and water management issues. SS management has evolved from merely disposal of sludge in landfills

---

* Email address: sst@et.aau.dk

or on agricultural soil to become a key component in a circular economy for organic and inorganic materials. Highlighted by the increasing urbanization seen in Europe with more than 70% of the population living in urban areas and many other places in the world, aggregated SS is challenged not only by the sheer volumes of biohazardous sludge to treat, but also by the legislative requirements to reuse of fertilizer components (phosphates) as well as to disposal methods [1–3].

By 2020, European wastewater treatment plants will produce approx. 13 million dry tons of sludge per year. Even allowing for high levels of inorganics, this represents an enormous potential for circular valorization of the organic content for energy purposes, and there are efforts to implement various technologies to realize this potential, such as through anaerobic digestion. However, impurities such as plastics and endocrine disruptants make this challenging, as the potential for downstream pollution remains significant after such a process. Thus, approaches that can combine high energy and conversion efficiencies with high tolerance for input material variations, and provide full recovery of fertilizers without the risk of downstream pollution are required. One such approach is hydrothermal liquefaction (HTL).

9.2 SS IN THERMO-CHEMICAL CONTEXT

Due to the continuous and abundant production of SS, new challenges are arising, concerned with sustainable management of sludge disposal. Usually, most of SS has been used directly in agricultural sector as a fertilizer, but several factors make that exercise unfavorable due to the transfer of undesirable substances to the food chain through crops [4]. Incineration process is widely used for volume reduction of SS and simultaneous thermal energy production. However, incineration of SS involves environmental and economic concerns in the form of scrubbing costs of the product gases for air pollution control. Gases released from incineration are not environment-friendly and require filtrations, which imply additional costs [5]. Another conventional route for SS disposal is landfilling, which is restricted due to European Union (EU) legislation. Land area requirement and proper maintenance, the two main issues other than ground water pollution through leaching system, are associated with the landfill applications which make landfill unfit for managing the waste, i.e., SS [6].

Over the last decades of research, different thermo-chemical conversion technologies have received focus, and each has its own advantages and disadvantages. Conventional thermo-chemical treatment of SS is energy-intensive due to high moisture content in SS and therefore does not fit well into modern circular economies. Anaerobic digestion has become an alternative that serves to reduce the volumes of sludge before disposal and recycling of nutrients but with relatively small energy output and volume reduction. Pyrolysis also requires dewatering step for feedstock utilization, which incurs considerable cost for drying process.

Recently, HTL has positioned itself as an attractive and suitable process capable of converting a broad range of wet organic solids, like SS, with high efficiency and energy yield, and with recovery of nutrients as an attractive bonus. HTL, therefore, fits very well into the circular economy schemes and recycle-upcycle strategies for

TABLE 9.1
Comparison of HTL and Pyrolysis Processes [8–9]

	HTL Process	**Pyrolysis Process**
Drying	Unnecessary	Necessary
Temperature (°C)	200–400	370–526
Pressure (MPa)	5–20	0.1–0.5
Catalyst	Sometimes	No
C (wt%)	73	58
H (wt%)	8	6
O (wt%)	16	36
S (wt%)	<45	29
Moisture	5.1	24.8
HHV (MJ/kg)	35.7	22.6
Viscosity (cP)	15,000	59

handling urban waste streams. Being a wet process, the costs for drying are avoided, compared to pyrolysis and gasification. From the energy perspective, HTL is gaining significant attention due to its capability to produce sustainable drop-in biofuels as well as contributing to district heating. HTL reactions are carried out at elevated temperatures (250°C–450°C) and pressures (100–350 bars) in a hydrothermal water reaction medium for relatively short residence time (RT) to form a carbon-rich biocrude that, when refined, yields fuels such as gasoline, diesel, and jet fuels [7]. From the products of the HTL process, inorganics such as phosphates can be isolated for redistribution into agriculture. One of the important benefits of the HTL process, highlighted by Gollakota et al., is that HTL has the ability to recover 70% of the feedstock carbon content. Additionally, HTL is favorable due to the efficiency of consuming 10%–15% energy from feedstock which results in the output energy efficiency of up to 90% [8].

Both HTL and pyrolysis are presented in Table 9.1 in terms of process parameters, biocrude composition, and properties. In comparison with pyrolysis, HTL has a lower operating cost as the expensive procedure of drying the feedstock is avoided. Furthermore, HTL product has lower oxygen and moisture contents and higher heating value (HHV), which reduces both the fixed and operating costs of the equipment. The utilization of high-pressure operation equipment for HTL plant needs further investigations to reduce the cost of the HTL plant [8–9].

9.3 SS IN HTL CONTEXT

9.3.1 SS Composition

SS from Waste Water Treatment Plants (WWTP) shows high moisture content, usually in the range of 75–85 wt% (see Table 9.2). Drying SS would require intensive energy input, resulting in extremely high costs, which are avoided with HTL, as the reaction medium and reactant is water [10]. The presence of water additionally allows

TABLE 9.2
Proximate and Ultimate Analysis of Different Sewage Sludge

		[14]	[15]	[16]	[6]
Feedstock		**Primary and Activated Sludge**[a]	**Fresh Human Feces**[a]	**Dewatered Sewage Sludge**[b]	**Sewage Sludge**[b]
Moisture	(%)	83.0	85.1	5.6	97.8
Ash	(%)	N/A	11.5	39.2	10.3
Carbohydrates	(%)	57.0	34.2	33.3	N/A
Crude proteins	(%)	30.0	34.7	55.1	N/A
Crude fats	(%)	13.0	14.0	11.3	N/A
C	(%)	49.0	47.8	43.4	51.8
H	(%)	8.0	7.2	5.9	7.8
N	(%)	3.7	6.1	3.2	2.3
S	(%)	1.0	N/A	N/A	1.0
O[c]	(%)	38.3	38.9	47.5	37.1
H/C	(-)	1.9	1.8	1.6	1.8
O/C	(-)	0.6	0.5	0.8	0.5
HHV	(MJ/kg)	N/A	20.4	14.6	19.9

[a] On dry basis.
[b] On dry ash-free basis.
[c] By difference.

a smooth pumpability of the slurry into the reaction system, though dry matter (DM) contents above 15%–20% are recommended for better process economics [11].

The DM in SS consists of both organic and inorganic elements. The latter, often referred to as ash, can vary widely (10–40 wt%) depending on the collection point in the WWTP line, the geographical area where the sludge is produced, and the presence (or not) of industries. High ash content in the feedstock can result in an increased production of HTL solid residue [12], which can cause blockage in continuous processing units and in general reduces the capacity for organic loading. For this reason, in some cases, it is advised to pretreat the biomass to lower the inorganic content through acid leaching of the feedstock [13], or by other means. However, this typically incurs loss of carbon and must be considered from case to case. The main organic constituents of SS are carbohydrates (30–50 wt%) and proteins (30–50 wt%), while lipids account for about 13% of the dried biomass (see Table 9.2). The elemental compositions of different SS found in literature consistently show that half of the dried sludge is made of carbon, while about 8% of the weight corresponds to hydrogen (see Table 9.2). Above one third of the dried SS is instead constituted by oxygen (see Table 9.2), which will be partly removed during hydrothermal processing, and further deoxygenation will take place while upgrading the biocrude oil. The two other undesired heteroatoms are nitrogen and sulfur. Both are present in SS (3–6 wt% nitrogen and about 1.0 wt% sulfur), and they are primarily removed from the biocrude in the upgrading stage.

9.3.2 Effect of Process Parameters

In the HTL process, the organic matter is first hydrolyzed into its main components, sugars, amino acids, and fatty acids from carbohydrates, proteins, and lipids, respectively. These main components break into their intermediates, like acids, alcohols, aldehydes, phenols, nitrogen-containing compounds, and long chain hydrocarbons via different reactions such as dehydration, decarboxylation, deamination, and repolymerization. These compounds distribute into biocrude, solids, gases, and the aqueous phase as well.

Numerous studies have already been conducted on the energy enhancement from the liquefaction of SS. The majority of the research was carried out on subcritical state while only few were carried out on supercritical conditions. Some important studies related to the liquefaction of SS are listed in Table 9.3.

In HTL, the production of biocrude could also be affected from various process parameters, like temperature, RT, catalyst, solvent type, and water to SS ratio.

9.3.2.1 Effect of Temperature

Temperature is one of the dominant operating parameters in HTL and it strongly affects biocrude yield and properties. Li et al. liquefied SS at 300°C–380°C and found that the highest biocrude yield was achieved at 340°C as shown in Figure 9.1. It was due to the low dielectric constant of water, which promotes hydrolysis of the organic matter. The subcritical state decreases the density and polarity of water, which improves the solubility of hydrophobic organic fractions. However, the biocrude yield was decreased when temperature rose from 340°C to 380°C, it is because of supercritical state, where biocrude could be cracked into gaseous products and repolymerization might have occurred that exhibited higher amount of solids [18]. Another study also observed the same trend with reduction in biocrude yield while liquefying SS from subcritical to supercritical conditions [22].

TABLE 9.3
Production of Biocrude From Hydrothermal Liquefaction of Sewage Sludge

Temp (°C)	Solvent	Catalyst	Biocrude (wt%)	Solid Residue (wt%)	db/daf	HHV (MJ/kg)	References
340	Water	None	23.00	43.00	db	35.94	Xu et al. [17]
340	Water	None	37.10	16.70	daf	28.52	Li et al. [18]
340	MeOH-H_2O	None	39.40	12.10	daf	34.14	Li et al. [18]
300	Water	None	40.12	38.01	daf	31.42	Malins et al. [19]
300	Water	None	19.00	56.00	db	36.04	Liu et al. [13]
300	Water	None	9.40	—	db	32.01	Vardon et al. [20]
325	Water	None	27.00	15.00	daf	34.58	Prestigiacomo et al. [21]
350	Ethanol	None	40.00	46.00	db	36.14	Huang et al. [16]
400	Water	None	27.50	15.15	db	—	Qian et al. [6]

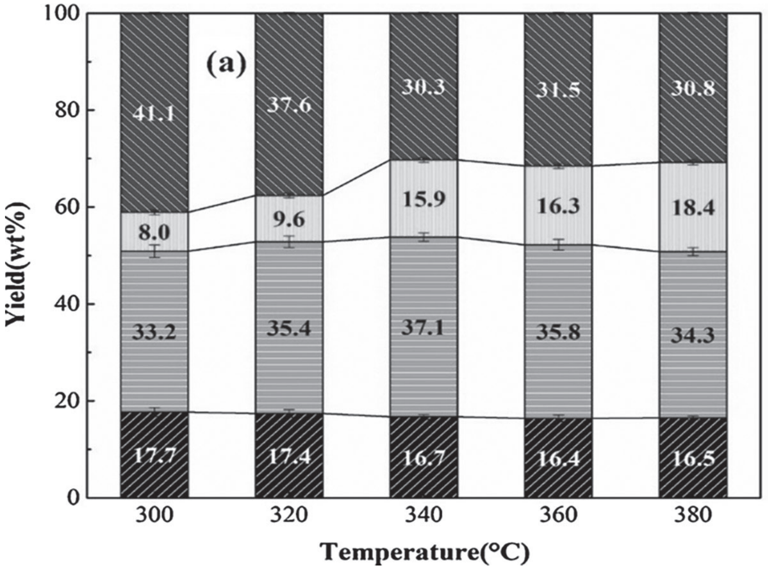


FIGURE 9.1 Effect of temperature on liquefied products yield daf (▧: Aqueous fraction; ▥: Gases; ▤: Bio-oil; ▨: Solid residue) obtained from HTL of sewage sludge. (Adapted from [18].)

Temperature also influences the elemental composition of biocrude, which is correlated with HHV. Xu et al. performed the liquefaction of SS from 260°C to 350°C and concluded that higher temperature increases the degree of deoxygenation via decarboxylation and dehydration. The maximum HHV 35.94 MJ/kg was measured at 350°C, although maximum biocrude yield was achieved at 340°C [17]. The justification of this would be the intensified thermal decomposition of SS at higher temperature, which converted organic matter into gaseous state and different char substances. This phenomenon decreases the biocrude yield but improves the HHV [19].

9.3.2.2 Effect of RT

RT is the second most significant parameter after temperature in the HTL process. Short RT increases biocrude yield, however beyond a certain level, further increase in RT has adverse results. The threshold of the RT depends on the biomass feed and catalyst type [9].

Li et al. treated SS under different retention times at 340°C to assess the influence of RT on the product yields. They concluded that biocrude yield significantly depends upon the RT, as the highest biocrude yield was obtained at 20 min, on the other hand, prolonged RT like 40 and 60 min decreases the biocrude yield as demonstrated in Figure 9.2. The apparent cause behind this would be the condensation, cyclization, and repolymerization reactions between intermediate products, which decreases the biocrude yield and increases the yield of solids.

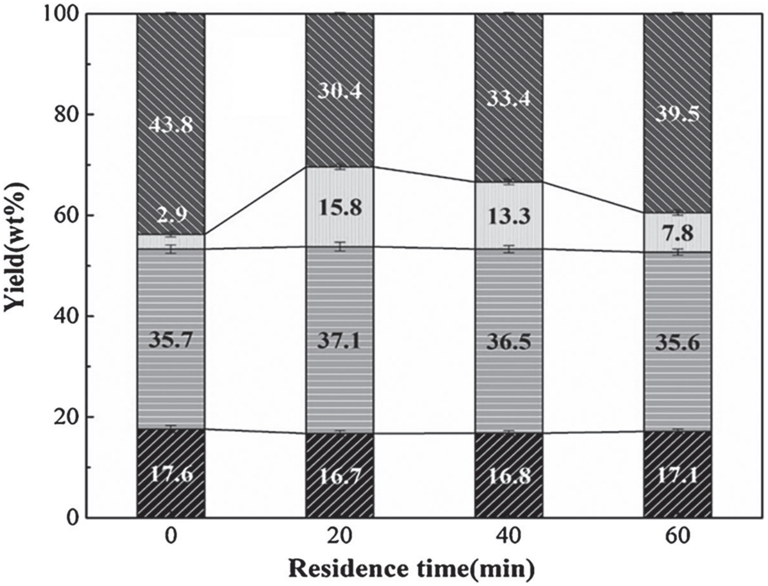


FIGURE 9.2 Effect of residence time on liquefied products yield daf (▧: Aqueous fraction; ▥: Gases; ▤: Bio-oil; ▨: Solid residue) obtained from HTL of sewage sludge. (Adapted from [18].)

Malin et al. mentioned that long RT is favorable for formation of gaseous product but undesirable for biocrude production. Approximately 44% of biocrude yield was observed at both 20 and 40 min, respectively.

9.3.2.3 Effect of Catalyst

Catalyst is another main constituent of biomass feed, which affects the overall economics and effectiveness of HTL processing. Mostly catalysts have been used in the liquefaction experiments for char reduction.

Several studies [6,19,21,23–24] reported the effect of catalyst on product yield distribution after HTL of SS. Malins et al. used four different catalysts with SS and achieved the highest biocrude yield (45.58% daf) with $FeSO_4$ as shown in Figure 9.3a, whereas maximum HHVs 33.90 and 35.74 MJ/kg were observed with Na_2CO_3 and $FeSO_4$, respectively. Biocrude has shown increased concentration of sulfur on utilization of $FeSO_4$ and MoS_2, this shows that some fractions of catalysts might be dispersed into biocrude [19], hindering downstream upgrading. Although biocrude yield is an important parameter, its quality needs to be taken into consideration as well. Prestigiacomo et al. also employed heterogeneous catalysts on SS and found that none of the catalysts resulted in increasing the biocrude yield as presented in Figure 9.3b [21].

Moreover, it has been highlighted from several studies that catalyst improves the biocrude quality as reported by Malins et al., that catalytic biocrude had higher HHVs as 33.90 and 35.76 MJ/kg with Na_2CO_3 and $FeSO_4$, respectively, as compared

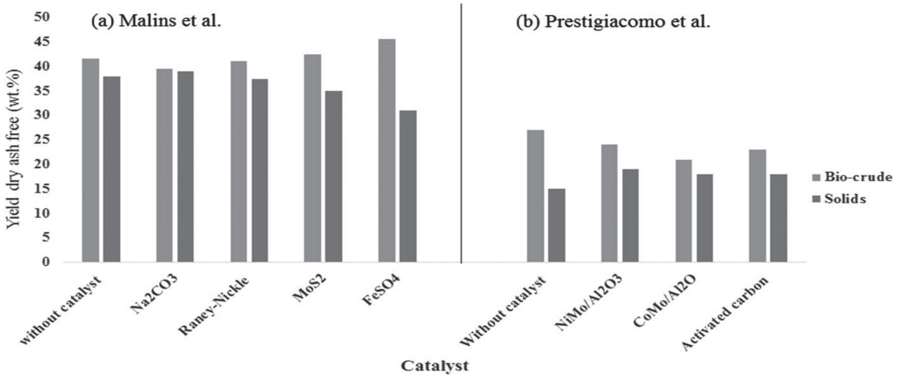


FIGURE 9.3 (a and b) Effect of different catalysts on HTL products from sewage sludge. (Adapted from (a) [19], (b) [21].)

to 31.42 MJ/kg without catalyst. Prestigiacomo et al. also noticed the higher carbon and hydrogen contents in catalytic biocrude.

9.3.2.4 Effect of Solvent

Solvent plays a crucial role in HTL of SS, as it was highlighted in many studies [7, 18, 25–28]. The liquefaction of biomass is greatly influenced by the type of solvent used, and the solvent does not only affect the product yields but also the chemical composition of the biocrude. In various studies, water has been used as a solvent due to its cheap, environmental benign nature, and as it is already present in the biomass [9].

Huang et al. investigated the effect of three solvents (methanol, ethanol, and acetone) with SS, at temperatures of 260°C–380°C and RT of 60 min. They reported that the highest biocrude yield was achieved with acetone, whereas methanol showed the highest conversion rate, as presented in Figure 9.4. The efficiency of the solvents in achieving higher biocrude yields was estimated to follow this order: acetone,

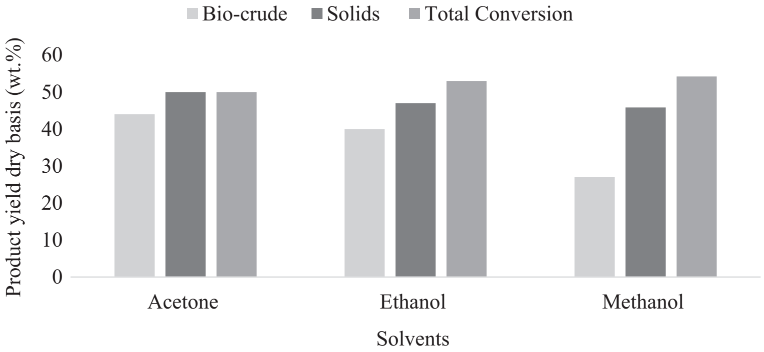


FIGURE 9.4 Effect of different solvents on HTL products obtained from sewage sludge. (Adapted from [25].)

ethanol, and methanol. The solvents serve as reaction substrates during the liquefaction process, which react with biomass intermediates fractions to form biocrude [26]. In light of this statement, the lower biocrude yield with methanol is due to its lower molecular weight with respect to acetone and ethanol [29].

The methanol gave a high conversion rate due to its high polarity and low dipole moment. The polarities are sequenced in a way as methanol (76.2) > ethanol (65.4) > acetone (35.5), whereas dipole moments of the three solvents are in the order of acetone (2.88 D) > methanol (1.69 D) > ethanol (1.67 D). Therefore, acetone gave a lower conversion rate corresponding to its high dipole moment and low polarity [26].

Looking at biocrude quality, the best biocrude, with maximum HHV (38.40 MJ/kg), was obtained using ethanol, followed by methanol and acetone. Ethanol and methanol could act as hydrogen contributors and promote dehydration reactions, which lead to the lower oxygen content in biocrude [26]. Li et al. also observed the similar findings with high HHVs where methanol and hexane were used as co-solvents with water [18].

Although organic solvents yield more biocrude and enhance the energy recovery, using these solvents in continuous HTL is not a viable option in terms of the process economics outlook. Therefore, researchers are very much keen to explore the synonymous of these solvents as with the recirculation of aqueous phase. In the recent past, recirculation has been discussed in many articles with other feedstocks like barley straw, algae, and aspen wood [57–59]. In this context, recirculation of aqueous phase from SS needs to be investigated to assess the overall efficiency of HTL processing based on SS.

9.3.2.5 Effect of Water to SS Ratio

The high moisture content of SS makes this feedstock easily pumpable. Malins et al. investigated different water to sludge ratios 1/0, 1/4, 1/5, 1/8, 1/12 and 1/15 at 300°C. They found that the biocrude yield, total conversion, and energy recovery increased with an increase in amount of water in SS. However, HHV decreased from 35.95 to 31.35 MJ/kg [19]. The presence of sufficient amount of water improves the hydrolysis of polysaccharides, lipids, and proteins, which leads to the formation of oxygen containing compounds [30].

In agreement with the above-mentioned studies, Qian et al. found maximum oil yield at 85% moisture content, as shown in Figure 9.5 [6]. High amount of water increases the density of water in the reactor, which favors the decomposition of organic matter [31]. Qian et al. also investigated the effect of pressure and reported that it did not influence the biocrude yield. Once the critical pressure ($P_c = 22.1$ MPa) of water is reached, pressure has no effect on the biocrude yield as shown in Figure 9.6. This outcome is consistent with the results obtained from HTL of *Nannochloropsis* [32].

9.3.3 PRODUCT COMPOSITION & UTILIZATION

9.3.3.1 Characterization of Biocrude

Biocrudes obtained from HTL of SS have heating values and H/C ratio in the following ranges 26.74–38.42 MJ/kg and 0.76–1.77, respectively (see Table 9.4).

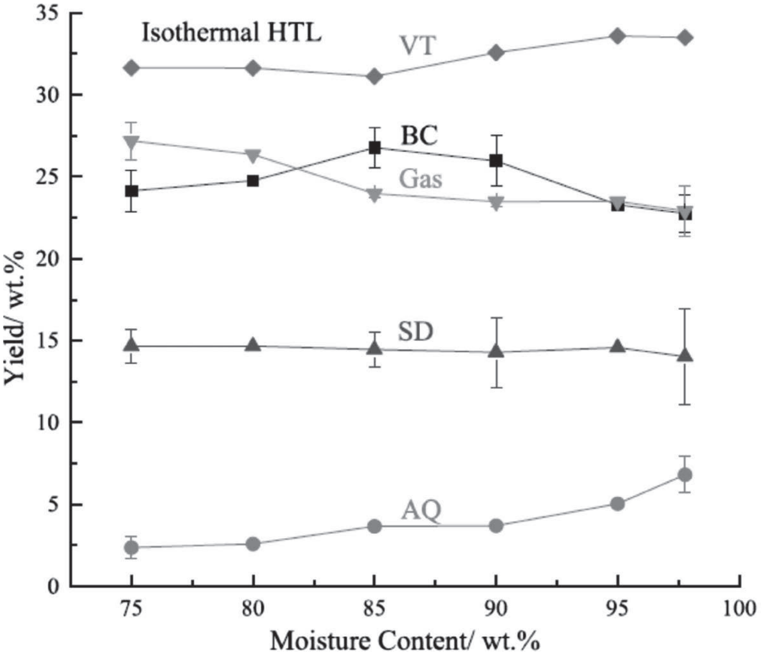


FIGURE 9.5 Effect of moisture content on product distribution after HTL of sewage sludge. (Adapted from [6].)

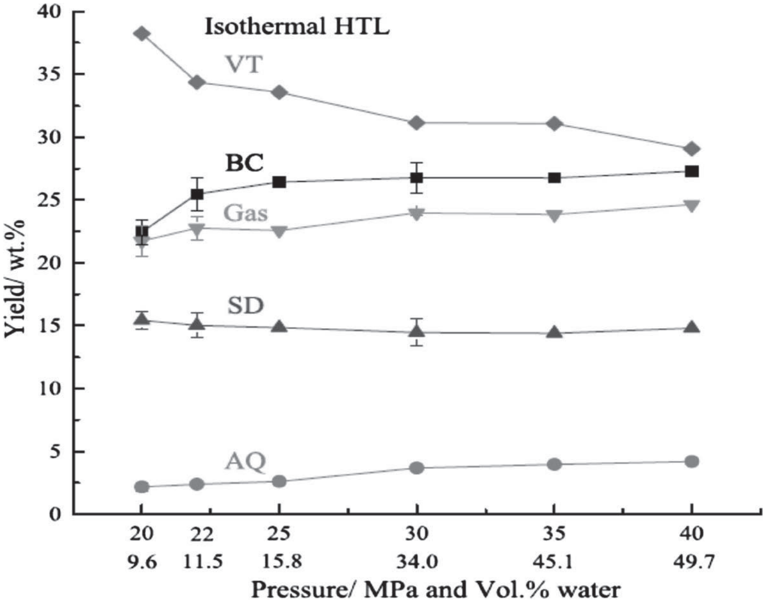


FIGURE 9.6 Effect of pressure on product distribution after HTL of sewage sludge. (Adapted from [6].)

TABLE 9.4
Elemental Analysis of Sewage Sludge Biocrudes From Different Liquefaction Studies

			Elemental Analysis (wt%)							HHV	
Temp (°C)	**Solvent**	**Catalyst**	**C**	**H**	**N**	**S**	**O**	**H/C**	**O/C**	**(MJ/kg)**	**References**
350	None	None	73.12	9.20	4.43	1.67	11.58	1.51	0.12	35.94	Xu et al. [17]
340	MeOH-H_2O	None	73.94	10.55	4.33	1.84	9.34	1.71	0.09	34.14	Li et al. [18]
360	MeOH	None	73.97	9.85	6.62	1.39	6.66	1.60	0.07	37.69	Huang et al. [25]
350	Acetone	None	70.21	4.42	5.56	1.05	18.76	0.76	0.20	26.74	Huang et al. [25]
360	Ethanol	None	75.12	9.85	6.98	1.05	18.76	1.57	0.19	38.42	Huang et al. [25]
300	None	$FeSO_4$	71.09	10.29	4.25	1.38	12.99	1.74	0.14	35.76	Malins et al. [19]
300	None	None	66.60	9.20	4.30	0.97	18.90	1.66	0.21	32.01	Vardon et al. [20]
300	None	Na_2CO_2	71.40	10.50	5.60	NR	12.50	1.77	0.13	34.77	Suzuki et al. [23]
340	None	Na_2CO_3	69.60	9.10	0.29	NR	21.01	1.57	0.23	32.70	Yokoyama et al. [24]
325	None	$NiMo/Al_2O_3$	77.46	9.06	1.43	0.87	11.18	1.40	0.11	37.34	Prestigiacomo et al. [21]
350	Ethanol	None	72.51	9.44	11.09	NR	11.09	1.56	0.11	36.14	Huang et al. [16]

Biocrude is often characterized through Fourier-transform infrared spectroscopy (FT-IR) and Gas chromatography mass spectrometry (GC-MS), as FT-IR only describes the functional groups of the compounds. Therefore, researchers firmly rely on GC-MS for identification of the compounds, which volatilizes up to temperatures of 300°C–350°C. The composition of biocrude depends upon the chemical constituents of the feedstock. SS-derived biocrude contains nitrogenous compounds (amides and heterocyclic) due to the presence of proteins, as well as ketones, esters, phenols, fatty acids, and long chain aliphatic hydrocarbons. These compounds are derived from the reactions like hydrolysis, C–C bond cleavage, decarboxylation, deamination, dehydration, cyclization, and repolymerization [17].

Heterocyclic compounds are formed by Maillard reaction between reducing sugars and amino acids. Branched chain amides are converted from the reaction of fatty acids with amines that are produced from amino acids [17]. Ketones are formed by hydrolysis and dehydration of sugars, or by decarboxylation of amino acids to form keto-acids and then ketones by further decarboxylation. Aldehydes are formed through the same route or via isomerization of ketones. Fatty acid esters are derived from the reactions between alcohols and fatty acids. It has been experienced from several studies that the esters tend to become dominant compounds, when solvents other than water, like methanol or ethanol, are used for degradation of organic matter [16]. Phenols and their associated derivatives are converted from hydrolysis, dehydration, and ring closure reactions of lignin and cellulose [13]. Fatty acids are produced by the hydrolysis of lipids, that later on converted into long hydrocarbons via decarboxylation [18].

9.3.3.2 Utilization of Biocrude

HTL biocrude cannot be directly used as transportation fuel due to its high viscosity, high water and ash contents, low heating value, instability, and corrosiveness (reflected in high total acid number (TAN)). In fact, it is an intermediate product, which requires to be upgraded, similar to petroleum crude. Different techniques have been used, and are under investigation, for biocrude upgrading; however, hydrotreating appears to be the most suitable technique [33]. Hydrotreating is a technology already well established at commercial scale, and it is commonly used in conventional refineries for crude oil upgrading. Hydrotreating consists of processing biocrude with hydrogen (30–200 bar) in the presence of a heterogeneous bimetallic catalyst at temperatures ranging from 300°C to 450°C [34]. Under these conditions, oxygen, nitrogen, and sulfur heteroatoms, which are contained in biocrude (O: 5–18 wt%, N: 0.5–1.0 wt%, S: 0.3–8.0 wt%), are removed in the form of H_2O, NH_3, and H_2S via hydrodeoxygenation (HDO), hydrodenitrogenation (HDN), and hydrodesulfurization (HDS) [35]. Once the biocrude is upgraded, it can be further refined via distillation into fractions, which correspond to gasoline, diesel, and jet fuel [36].

Various research groups have investigated the catalytic upgrading of HTL biocrude produced from lignocellulosic [37–39] and algae [40–44] biomass. However, very few investigations on catalytic hydrotreating of biocrude from SS are reported in the literature. At present, all the studies on SS upgrading refer to PNNL (Pacific Northwest National Laboratory, USA) [45–46]. Jarvis et al. [45] have recently assessed the hydrotreating of HTL biocrude, comparing the upgraded biocrude derived from primary SS with the upgraded biocrude from microalgae and pinewood. The three biocrudes obtained using a bench-scale continuous-flow process equipment, were individually hydrotreated in a continuous trickle-bed reactor at 400°C with 103–106 bar in the presence of a catalyst composed of cobalt oxide and molybdenum oxide on alumina. After hydrotreating, the bulk properties of all three biocrudes showed similar changes: density, viscosity, and moisture content of the hydrotreated biocrudes were lower than that of their respective biocrudes. A successful degree of HDN, HDO, and HDS was reported for all the biocrudes. In particular, for SS, oxygen decreased from 8.4 to 1.2 wt%, nitrogen from 4.3 to 0.05 wt%, and sulfur from 0.63 wt% to 23 ppm. The increase in carbon and hydrogen content corresponded to an increase in the H/C ratio from 1.6 of the biocrude to 2.0 of the upgraded biocrude. A greater concentration of n-alkanes was detected in hydrotreated SS and microalgae biocrudes (similar to shale oil), while a lower concentration of n-alkanes and a larger diversity of compounds was instead associated with the upgraded pine biocrude (similar to Gulf of Mexico crude oil).

Marrone et al. [46] have instead investigated the hydrotreating of primary sludge and digested solids using a 30 mL tubular fixed-bed reactor filled with a conventional catalyst (3.4%–4.5% CoO and 11.5%–14.5% MoO_2 on alumina). The changes in biocrudes and hydrotreated biocrudes characteristics can be observed in Table 9.5. The carbon and hydrogen content increased leading to H/C atomic ratios of 2.0 and 1.9, respectively, for hydrotreated biocrude from primary sludge and digested solids. The authors reported a low loss of carbon to byproduct gas (~6% on carbon basis) and a minimal loss of carbon into the aqueous phase. The reduction in N, O, S heteroatoms is of the same order of magnitude as in the above-described study conducted by Jarvis et al. The changes in the elemental composition are reflected in the changes in density and viscosity: both reduced. Dissolved water and TAN were instead reduced to zero.

TABLE 9.5
Characterization of Biocrudes, From Primary Sludge and Digested Solids, Before and After Hydrotreating [46]

		Primary Sludge		Secondary Sludge	
Analysis	**Units**	**Biocrude Feed**	**Hydrotreated (HT) Product**	**Biocrude Feed**	**Hydrotreated (HT) Product**
Carbon	wt%	76.5	84.7	82.3	85.2
Hydrogen	wt%	10.1	14.2	9.3	13.8
H:C atomic ratio	—	1.57	2.00	1.35	1.92
Nitrogen	wt%	4.3	0.03	4.7	0.06
Oxygen	wt%	8.43	1.10	2.6	0.96
Sulphur	ppm	6,300	22	11,400	24
Moisture	wt%	13.0	~0	14.2	~0
Density	g/cm^3	1.00	0.796	1.01	0.812
Kinematic viscosity	cSt.	571 @ 40°C	2.2 @ 20°C	1,090 @ 40°C	2.4 @ 20°C
TAN	mg KOH/g	55	<0.01	36	<0.01

9.3.3.3 Inorganics in SS & HTL Products

SS has high ash content (10–50 wt%), especially if compared with lignocellulosic biomass (1–3 wt%) [47]. The ash content is associated with the presence of inorganic elements, which consists of both nutrients (e.g., N, P, K) and heavy metals (e.g., Co, Cr, Cu, Ni, Pb, Zn). The first, if properly separated and extracted, can be utilized as fertilizers in agriculture, providing an overall benefit to the HTL process. Heavy metals, instead, can represent a concern as their concentrations are strictly regulated by law in case of land application or disposal. An example of concentrations of inorganics in primary SS, secondary SS, and digested solids is reported in Table 9.6. It appears that, regardless of the point of collection in the WWTP, the most abundant elements in SS are Al, Ca, Fe, P, and S. Table 9.6 also reports the concentrations of the inorganics in the HTL product phases (solids, aqueous phase, and biocrude). Finally, it should also be noted that these concentrations are not only strictly dependent on the concentrations of the corresponding elements in the feedstock, but also on the technology used for separating the HTL product phases. In this case, first the solids were separated by hot filtration, and then the biocrude and aqueous phase were separated gravimetrically.

When SS is hydrothermally treated, the inorganics are processed along with the biomass, and they are recovered in the products at the end of the process. A downside of biomass with high inorganic content is therefore the increased chance for deposits and blockages, especially in continuous HTL systems. For this reason, researches focused on acid leaching, as a pretreatment for reducing the inorganic loading of the biomass prior to HTL. Liu et al. [13] have investigated the use of organic (HCOOH, CH_3COOH, HOOCCOOH) and inorganic acids (HCl, HNO_3, H_2SO_4) on municipal secondary sludge, and have observed that, even if all the acids increase the biocrude yield, only the inorganic ones improve the biocrude quality in terms of HHV, energy recovery, and increased production of light oils. However, the use of strong acids often reduces the carbon content of biomass feedstock, and the costs and disposal of chemicals can become unfeasible when moving to continuous commercial scale. Another approach is to use wastewater sludge without any pretreatment and to remove the inorganics from HTL products. In lab-scale batch experiments, this is usually achieved by vacuum filtration of HTL products using a solvent. HTL solids, including most of the inorganics, are collected on the filter paper, while biocrude, water, and the solvent are recovered together in the filtrate.

Ekpo et al. [49] investigated the fate of inorganics after hydrothermal processing of digestate, reporting that K and Na are almost entirely extracted into the aqueous phase. N is also released in the water phase in the form of NH_3–N. On the other hand, Ca, Mg, Fe, and Al concentrate in the solid residue. P is also precipitated in the residue as phosphate salts, and its extraction is linked to the presence of inorganics such as Ca, Mg, and Fe. Similarly, Lu et al. [15] investigated how inorganics tend to distribute among HTL products after liquefaction of human feces. They concluded that most ash contents were collected in the solid residue. They observed that alkaline-earth metal elements (Al, Ca, Fe, Mg, and Zn) tend to concentrate in the solid residue, while K, Na, and N are mainly recovered in the aqueous phase.

TABLE 9.6
Concentrations (ppm) of Inorganic Elements in Sewage Sludge and HTL Product Phases: Solids, Aqueous Phase, and Biocrude [48]

	Feedstock			HTL Solids			HTL Aqueous Phase			HTL Biocrude		
	Primary Sludge	Secondary Sludge	Digested Solids	Primary Sludge	Secondary Sludge	Digested Solids	Primary Sludge	Secondary Sludge	Digested Solids	Primary Sludge	Secondary Sludge	Digested Solids
Al	2,220	3,330	7,850	17,500	13,600	20,000	2.7	1.7	<1	65	78	84
Ba	44	170	329	579	667	844						
Ca	4,890	9,030	23,400	48,100	46,000	66,000	2.8	1.6	<1	<30	<50	<25
Cr	82	50	38	847	1,070	309						
Cu	246	590	840	2,130	2,510	2,340						
Fe	6,020	26,200	38,800	34,200	34,700	58,400	1.1	<1	<1	59	79	225
K	785	4,280	1,770	1,700	1,700	3,030	71	275	117	77	134	63
Mg	984	2,920	6,600	10,200	12,400	18,100	3.1	1.3	1.3	<30	29	<25
Mn	53	250	373	624	1,060	979				<30	29	<25
Na	424	890	527	714	528	793	67	101	75	57	62	<25
P	6,880	33,300	29,900	55,400	60,600	59,200	12	290	33	<30	73	<25
S	4,130	6,420	17,600	3,870	4,840	15,900	102	157	280	1,900	2,600	9,770
Si	190	280	270	81	206	83	260	190	301	55	210	390
Sr	54	110	137	263	380	375	2.5	<1	<1			
Ti	36	94	162	<40	78	<25				<30	<50	<25
Zn	303	530	1,070	3,070	2,950	3,500						
Zr	<40	51	70	30	<50	<25						

In continuous HTL processing, the separation of the solids can also take place by filtration. In PNNL set-up, for example, a hot filter vessel, which operates at reaction conditions (350°C and 207 bar), is placed right after the PFR (plug flow reactor) HTL reactor. The low solubility of many inorganic salts in the near-critical and supercritical region is exploited to collect the inorganics apart from the main stream. Solids fall due to gravity to the bottom of the vessel, or the filter alternatively catches them as the flow leaves the top of the vessel. When and if necessary, the filter can be backflushed for cleaning. The removal of inorganics also minimizes the formation of emulsions, easing the separation of water and biocrude, which is the following step in the process [48]. A similar system is also installed at the pilot plant in Foulum, Aarhus University (Denmark). However, an additional demineralization step might be required, before hydrotreating biocrude oil to prevent catalyst deactivation and poisoning [34].

Different demineralization techniques, also used in petroleum refining, can be applied for removal of inorganics prior to hydrotreating [34]:

- flashing with further hydrotreating of the light fraction (used by Licella [50] and Biofuel B.V. [51]) or extraction with a polar solvent of the heavy fraction or of the entire product (used by Biofuel B.V. [51])
- filtration of the reactor effluents at process conditions to separate the inorganics by precipitation (used by PNNL [52])
- desalting or washing with water at 90°C–150°C in two or more stages, with or without the addition of a diluent (proposed in early HTL literature [53], and currently used by UOP [54])
- washing with carbonated water to remove organically bound metal ions from crude (ExxonMobil holds a patent [55]), which is of interest in the HTL context, as CO_2 is the main gas produced, and dissolved CO_2 acts as a pH reducing agent enhancing phase separation (Steeper has filed a patent in this regard [34]).

9.3.3.4 Utilization of an Aqueous Phase

When wet biomass is hydrothermally processed, an aqueous phase is also obtained as a product and this represents a large part of the HTL products. A substantial amount of total organic carbon (TOC) and total nitrogen (TN) are lost into the aqueous phase affecting the process effectiveness of HTL. Therefore, the recovery of TOC and TN is indispensable for improving the efficiency and economics of the HTL process. The aqueous phase contains TOC in the form of oxygenated compounds that preferably dissolve in water such as ketones, organic acids, phenols, and some nitrogen-containing compounds [7]. The concentration of TOC in the aqueous phase is highly reliant upon the type of biomass, solid loading, reaction conditions, and the recirculation of aqueous phase [56].

Previous studies demonstrated the beneficial effects of the recirculation of aqueous phase from feedstock like barley straw [57], microalgae [58], and co-liquefaction of aspen wood and glycerol [59]. All studies reported higher biocrude yield and decreasing loss of organics to the aqueous phase. The recirculation of aqueous phase during the HTL of SS has not been reported yet.

Various studies *detected the nutrients like K, Na, P, and N, etc. from the aqueous phase produced through HTL of SS* (see Table 9.6). It was deduced from the study that the aqueous phase could be used as a nutrient source for the cultivation of biomass, like microalgae, after the possible detoxification [17,48]. Catalytic hydrothermal gasification (CHG) is another alternative route to valorize the organic potential of the aqueous phase.

9.3.4 Economic and Environmental Assessment

The overall economic value of the HTL process depends upon several factors, among which the cost of the feedstock plays an important role [60]. Other factors, i.e., product yield, hydrogen price for fuel upgrading, high-pressure equipment cost, efficient pumps, and heat exchanger systems are also sensitive parameters, which have an impact on the minimum fuel selling price (MFSP) of biocrude production [7–9,60]. As compared to the other feedstocks, i.e., forestry, algal biomass, etc., SS does not need any cultivation and harvesting step due to unavoidable production from wastewater treatment plants, which results in a reduction of the HTL process costs. Furthermore, the average cost of different SS management strategies in EU, e.g., landfilling costs on an average 290 $/ton of DM, incineration 359 $/ton of DM, and for composting 353 $/ton of DM [61]. However, in connection with the wastewater treatment plants, small HTL plants seem to be a better alternative. The coupled system of HTL with other heat integration network can improve the biocrude yield, process efficiency, as well as overall economics [62].

SS is a product of the wastewater treatment plant, which deals with large flows of water constantly, through which solid concentration used to separate from effluent water for its environmentally friendly disposal pathway. Traditionally, SS from wastewater treatment plant is used in the anaerobic digestion process to reduce the amount of sludge. After that, it is disposed in rural fields or in landfill. A new process configuration, which recently gained attention, is to couple the WWTP facility with an HTL plant [63]. This process configuration can reduce the transportation cost of sludge, and also reduce the environmental burden of greenhouse gases. Additionally, the recovery of nutrients from HTL solids can contribute to meet the demand for fertilizers. To make the HTL process more efficient and economical, it is better to integrate the HTL system in a closed network loop to utilize all the phases of energy obtained by HTL process.

REFERENCES

1. European Commission, 2020 climate & energy package, 2018. Available: https://ec.europa.eu/clima/policies/strategies/2020 [Accessed: 05.12.18].
2. European Commission, Biofuels, 2018. Available: https://ec.europa.eu/energy/en/topics/renewable-energy/biofuels [Accessed: 05.12.18].
3. A. Kelessidis, A.S. Stasinakis. Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries, *Waste Management* 32(6) (2012), 1186–1195. doi: 10.1016/j.wasman.2012.01.012.
4. M.K. Jamali, T.G. Kazi, M.B. Arain, H.I. Afridi, N. Jalbani, A.R. Memon. Heavy metal contents of vegetables grown in soil, irrigated with mixtures of wastewater and sewage sludge in Pakistan, using ultrasonic-assisted pseudo-digestion, *Journal of Agronomy and Crop Science* 193 (2007), 218–228.

5. P. Manara, A. Zabaniotou. Towards sewage sludge based biofuels via thermochemical conversion – A review, *Renewable and Sustainable Energy Reviews* 16 (2012), 2566–2582.
6. L. Qian, S. Wang, P.E. Savage. Hydrothermal liquefaction of sewage sludge under isothermal and fast conditions, *Bioresource Technology* 232 (2017), 27–34.
7. D. Castello, T.H. Pedersen, L.A. Rosendahl. Continuous hydrothermal liquefaction of biomass: A critical review, *Energies* 11 (2018), 3165; doi:10.3390/en11113165.
8. A.R.K. Gollakota, N. Kishore, S. Gu. A review on hydrothermal liquefaction of biomass, *Renewable and Sustainable Energy Reviews* 81 (2018), 1378–1392.
9. A. Dimitriadis, S. Bezergianni. Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review, *Renewable and Sustainable Energy Reviews* 68 (2017), 113–125.
10. A. Kruse, E. Dinjus. Hot compressed water as reaction medium and reactant: Properties and synthesis reactions, *The Journal of Supercritical Fluids* 39 (2007), 362–380.
11. F. Vogel. *Hydrothermal Conversion of Biomass, Encyclopedia of Sustainability Science and Technology*, Springer Science+Business Media LLC, New York (2017).
12. S. S. Toor, L. Rosendahl, A. Rudolf. Hydrothermal liquefaction of biomass: A review of subcritical water technologies, *Energy* 36(5) (2011), 2328–2342.
13. R. Liu, W. Tian, S. Kong, Y. Meng, H. Wang, J. Zhang. Effects of inorganic and organic acid pretreatments on the hydrothermal liquefaction of municipal secondary sludge, *Energy Conversion and Management* 174 (2018), 661–667.
14. Y. Dote, T. Hayashi, A. Suzuki, T. Ogi. Analysis of oil derived from liquefaction of sewage sludge, *Fuel* 71 (1992), 1071–1073.
15. J. Lu, J. Zhang, Z. Zhu, Y. Zhang, Y. Zhao, R. Li, J. Watson, B. Li, Z. Liu. Simultaneous production of biocrude oil and recovery of nutrients and metals from human feces via hydrothermal liquefaction, *Energy Conversion and Management* 134 (2017), 340–346.
16. H. Huang, X. Yuan, H. Zhu, H. Li, Y. Liu, X. Wang, G. Zeng. Comparative studies of thermochemical liquefaction characteristics of microalgae, lignocellulosic biomass and sewage sludge, *Energy* 56 (2013), 52–60.
17. D. Xu, G. Lin, L. Liu, Y. Wang, Z. Jing, S. Wang. Comprehensive evaluation on product characteristics of fast hydrothermal liquefaction of Sewage sludge at different temperatures, *Energy* 159 (2018), 686–695.
18. R. Li, Z. Ma, T. Yang, B. Lib, L. Wei, Y. Sun. Sub–supercritical liquefaction of municipal wet sewage sludge to produce bio-oil: Effect of different organic–water mixed solvents, *Journal of Supercritical Fluids* 138 (2018), 115–123.
19. K. Malins, V. Kampars, J. Brinks, I. Neibolte, R. Murnieks, R. Kampare. Bio-oil from thermo-chemical hydro-liquefaction of wet sewage sludge, *Bioresource Technology* 187 (2015), 23–29.
20. D.R. Vardon, B.K. Sharma, J. Scott, G. Yu, Z. Wang, L. Schideman, Y. Zhang, T.J. Strathmann. Chemical properties of biocrude oil from the hydrothermal liquefaction of Spirulina algae, swine manure, and digested anaerobic sludge, *Bioresource Technology* 102(17) (2011), 8295–8303.
21. C. Prestigiacomo, P. Costa, F. Pinto, B. Schiavo, A. Siragusa, O. Scialdone, A. Galia. Sewage sludge as cheap alternative to microalgae as feedstock of catalytic hydrothermal liquefaction processes, *The Journal of Supercritical Fluids* 143 (2019), 251–258.
22. C. Xu, J. Lancaster. Conversion of secondary pulp/paper sludge powder to liquid oil products for energy recovery by direct liquefaction in hot-compressed water, *Water Research* 42 (2008), 1571–1582.
23. A. Suzuki, T. Nakamura, S.Y. Yokoyama, T. Ogi, K. Koguchi. Conversion of sewage sludge to heavy oil by direct thermochemical liquefaction, *Journal of Chemical Engineering of Japan* 21 (1988), 288–293.

24. S.Y. Yokoyama, A. Suzuki, M. Murakami, T. Ogi, K. Koguchi, E. Nakamura. Liquid fuel production from sewage sludge by catalytic conversion using sodium carbonate, *Fuel* 66 (1987), 1150–1155.
25. H.J. Huang, X.Z. Yuan, B.T. Li, Y.D. Xiao, G.M. Zeng. Thermochemical liquefaction characteristics of sewage sludge in different organic solvents, *Journal of Analytical and Applied Pyrolysis* 109 (2014), 176–184.
26. H.J. Huang, X.Z. Yuan, G.M. Zeng, H. Li, Q. You, M. Zhou. Thermochemical liquefaction characteristics of sewage sludge in the sub- and supercritical acetone, *China Environmental Science* 30 (2010), 197–203.
27. W.J. Wang, Q. Yu, H. Meng, W. Han, J. Li, J.L. Zhang. Catalytic liquefaction of municipal sewage sludge over transition metal catalysts in ethanol-water co-solvent, *Bioresource Technology* 249 (2018), 361–367.
28. L. Hui, Y. Xingzhong, Z. Guangming, H. Danlian, H. Huajun, T. Jingyi, Y. Qiao, Z. Jiachao, Z. Ming. The formation of bio-oil from sludge by deoxy-liquefaction in supercritical ethanol, *Bioresource Technology* 101 (2010), 2860–2866.
29. H. Li, X.Z. Yuan, G.M. Zeng, D.L. Huang, H.J. Huang, J.Y. Tong, Q. You, J.C. Jia, M. Zhou, Z. Liu, F.S. Zhang. Effects of various solvents on the liquefaction of biomass to produce fuels and chemical feedstocks, *Energy Conversion and Management* 49 (2008), 3498–3504.
30. A. Demirbas. Mechanism of liquefaction and pyrolysis reactions of biomass, *Energy Conversion and Management* 41(6) (2000), 633–646.
31. J. Akhtar, N.A.S. Amin. A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass, *Renewable and Sustainable Energy Reviews* 15(3) (2011), 1615–1624.
32. P.J. Valdez, M.C. Nelson, H.Y. Wang, X.N. Lin, P.E. Savage. Hydrothermal liquefaction of *Nannochloropsis* sp.: Systematic study of process variables and analysis of the product fractions, *Biomass Bioenergy* 46 (2012), 317–331.
33. S. Xiu, A. Shahbazi. Bio-oil production and upgrading research: A review, *Renewable and Sustainable Energy Reviews* 16 (2012), 4406–4414.
34. C.U. Jensen. PIUS - Hydrofaction$^{(TM)}$ platform with integrated upgrading step, Doctoral dissertation, Aalborg Universitetsforlag, 2018
35. D.C. Elliott, P. Biller, A.B. Ross, A.J. Schmidt, S.B. Jones. Hydrothermal liquefaction of biomass: Developments from batch to continuous process, *Bioresource Technology* 178 (2015), 147–156.
36. P. Biller, A. Roth. Hydrothermal liquefaction: A promising pathway towards renewable jet fuel. In Kaltschmitt M., Neuling U. (eds), *Biokerosene*, Springer-Verlag GmbH, Heidelberg Germany (2018).
37. C.U. Jensen, J. Hoffmann, L.A. Rosendahl. Co-processing potential of HTL bio-crude at petroleum refineries. Part 2: A parametric hydrotreating study, *Fuel* 165 (2016), 536–543.
38. Y. Yue, J. R. Kastner, S. Mani. Two-stage hydrothermal liquefaction of sweet sorghum biomass - Part II: Production of upgraded biocrude oil, *Energy Fuels* 32 (2018), 7620–7629.
39. J. Yu, P. Biller, A. Mamahkel, M. Klemmer, J. Becker, M. Glasius, B.B. Iversen. Catalytic hydrotreatment of bio-crude produced from the hydrothermal liquefaction of aspen wood: A catalyst screening and parameter optimization study, *Sustainable Energy Fuels* 1 (2017), 832–841.
40. P. Biller, B.K. Sharma, B. Kunwar, A.B. Ross. Hydroprocessing of bio-crude from continuous hydrothermal liquefaction of microalgae, *Fuel* 159 (2015), 197–205.
41. M.S. Haider, D. Castello, K.M. Michalski, T.H. Pedersen, L.A. Rosendahl. Catalytic hydrotreatment of microalgae biocrude from continuous hydrothermal liquefaction: Heteroatom removal and their distribution in distillation cuts, *Energies* 11 (2018), 3360.

42. D.C. Elliott, T.R. Hart, A.J. Schmidt, G.G. Neuenschwander, L.J. Rotness, M.V. Olarte, A.H. Zacher, K.O. Albrecht, R.T. Hallen, J.E. Holladay. Process development for hydrothermal liquefaction of algae feedstocks in a continuous-flow reactor, *Algal Researh* 2(4) (2013), 445–454.
43. R. Shakya, S. Adhikari, R. Mahadevan, E.B. Hassan, T.A. Dempster. Catalytic upgrading of bio-oil produced from hydrothermal liquefaction of *Nannochloropsis* sp., *Bioresource Technology* 252 (2018), 28–36.
44. Z. Li, P.E. Savage. Feedstocks for fuels and chemicals from algae: Treatment of crude bio-oil over HZSM-5, *Algal Research* 2(2) (2013), 154–163.
45. J.M. Jarvis, K.O. Albrecht, J.M. Billing, A.J. Schmidt, R.T. Hallen, T.M. Schaub. Assessment of hydrotreatment for hydrothermal liquefaction biocrudes from sewage sludge, microalgae, and pine feedstocks, *Energy Fuels* 32 (2018), 8483–8493.
46. P.A. Marrone, D.C. Elliott, J.M. Billing, R.T. Hallen, T.R. Hart, P. Kadota, J.C. Moeller, M.A. Randel, A.J. Schmidt. Bench-scale evaluation of hydrothermal processing technology for conversion of wastewater solids to fuels, *Water Environment Research* 90 (2018), 329–342.
47. S.S.A. Syed-Hassan, Y. Wang, S. Hu, S. Su, J. Xiang. Thermochemical processing of sewage sludge to energy and fuel: Fundamentals, challenges and considerations, *Renewable and Sustainable Energy Reviews* 80 (2017), 888–913.
48. P.A. Marrone. *Genifuel Hydrothermal Processing Bench-Scale Technology Evaluation Project*, Water Environment and Reuse Foundation, Alexandria, VA (2016); ISBN 9781780408408.
49. U. Ekpo, A.B. Ross, M.A. Camargo-Valero, P.T. Williams. Comparison of product yields and inorganic content in process streams following thermal hydrolysis and hydrothermal processing of microalgae, manure and digestate, *Bioresource Technology* 200 (2016), 951–960.
50. Y. Mathieu, L. Sauvanaud, L. Humphreys, W. Rowlands, T. Maschmeyer, A. Corma. Opportunities in upgrading biomass crudes, *Faraday Discussions* 197 (2017), 389–401.
51. L. Van de Beld, F.R. Boerefijn, G.M. Bos, F. Goudriaan, J.E. Naber, J.A. Zeevalkink. Process for the production of liquid fuels from biomass, Aug. 28 2007, US Patent 7262331 B2.
52. D.C. Elliott, T.R. Hart, G.G. Neuenschwander, J.R. Oyler, L.J. Rotness, A.J. Schmidt, A.H. Zacher. System and process for efficient separation of biocrudes and water in a hydrothermal liquefaction system, Aug. 2 2016, US Patent 9404063 B2.
53. B. Gevert, P. Andersson, S. Jaeras, S. Sandqvist. Hydroprocessing of desalted directly liquefied biomass, Preprints of Papers- American Chemical Society, Division of Fuel Chemistry, vol. 33, no. CONF-8809228, 1988.
54. F.S. Lupton, P. Edirisinghe. Methods for removing contaminants from oils using base washing and acid washing, Jun. 2 2015, US Patent 9045698.
55. S.C. Blum, G. Sartori, M.L. Gorbaty, D.W. Savage, D.C. Dalrymple, W.E. Wales. CO_2 treatment to remove organically bound metal ions from crude, Feb. 13 2001, US Patent 6187175.
56. R.B. Madsen, P. Biller, M.M. Jensen, J. Becker, B.B. Iversen, M. Glasius. Predicting the chemical composition of aqueous phase from hydrothermal liquefaction of model compounds and biomasses. *Energy Fuels* 30 (2016), 10470–10483.
57. Z. Zhu, L. Rosendahl, S.S. Toor, D. Yu, G. Chen. Hydrothermal liquefaction of barley straw to bio-crude oil: Effects of reaction temperature and aqueous phase recirculation. *Applied Energy* 137(0) (2015), 183–192.
58. P. Biller, R.B. Madsen, M. Klemmer, J. Becker, B.B. Iversen, M. Glasius. Effect of hydrothermal liquefaction aqueous phase recycling on bio-crude yields and composition. *Bioresource Technology* 220 (2016), 190–199.

59. T.H. Pedersen, I.F. Grigoras, J. Hoffmann, S.S. Toor, I.M. Daraban, C.U. Jensen, S.B. Iversen, R.B. Madsen, M. Glasius, K.R. Arturi, R.P. Nielsen. Continuous hydrothermal co-liquefaction of aspen wood and glycerol with water phase recirculation. *Applied Energy* 162 (2016), 1034–1041.
60. M. Kumar, A.O. Oyedun, M. Kumar. A review on the current status of various hydrothermal technologies on biomass feedstock. *Renewable and Sustainable Energy Reviews* 81 (2018), 1742–1770.
61. M. Kacprzak, E. Neczaj, K. Fijałkowski, A. Grobelak, A. Grosser, M. Worwag, A. Rorat, H. Brattebo, Å. Almås, B.R. Singh. Sewage sludge disposal strategies for sustainable development, *Environmental Research* 156 (2017), 39–46.
62. S. Jones, Y. Zhu, D. Anderson, R. Hallen, D.C. Elliott, A.J. Schmidt, K.O. Albrecht, T.R. Hart, M.G. Butcher, C. Drennan, L.J. Snowden-Swan. Process design and economics for the conversion of algal biomass to hydrocarbons: whole algae hydrothermal liquefaction and upgrading. US Department of Energy Bioenergy Technologies Office; 2014.
63. www.genifuel.com/process.html.

Paper E

Hydrothermal liquefaction of high ash containing sewage sludge at sub and supercritical conditions

A. A. Shah, S. S. Toor, F. Conti, A. H. Nielsen,
Lasse A. Rosendahl

The manuscript has been published in:
Biomass & Bioenergy 135 (2020) 105504

The layout has been revised.

Biomass and Bioenergy 135 (2020) 105504

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Research paper

Hydrothermal liquefaction of high ash containing sewage sludge at sub and supercritical conditions

Ayaz A. Shah[a,b], Saqib S. Toor[a], Federica Conti[a], Asbjørn H. Nielsen[c], Lasse A. Rosendahl[a,*]

[a] Department of Energy Technology, Aalborg University, Pontoppidanstræde 111, Aalborg, 9220, Denmark
[b] Department of Energy & Environment Engineering, Dawood University of Engineering & Technology, Karachi, Sindh, 74800, Pakistan
[c] Department of Civil Engineering, Aalborg University, Thomas Manns Vej 23, Aalborg, 9220, Denmark

ARTICLE INFO

Keywords:
Sewage sludge
Sub-supercritical HTL
Bio-crude
Catalyst (K_2CO_3)
Inorganic elements
Leaching

ABSTRACT

With the rapid growth in population and urbanization, sustainable disposal of sewage sludge has become a prominent problem worldwide. Therefore, an adequate treatment is required to reduce the environmental impacts created from traditional methods such as incineration, landfill, etc. In this context, sewage sludge was liquefied hydrothermally under sub-supercritical conditions with and without catalyst (K_2CO_3). The effect of temperature and alkali catalyst on product distribution was investigated. Obtained results showed that the temperature had a negligible influence, whereas catalyst slightly improved the bio-crude yield and quality for both sub-supercritical conditions (350 and 400 °C). Bio-crude contained N-containing compounds, ketones, phenols, acids, and long-chain hydrocarbons. Carbon and nitrogen recoveries revealed that 58–67% of the carbon went into bio-crude, while the majority of the nitrogen was transferred to the aqueous phase. ICP-AES analysis indicated that approximately 80% of the heavy metals were concentrated in the solid phase. The leaching action of citric acid with sewage sludge not only removed 40% of ash content but also reduced 38% of the fat content.

1. Introduction

Due to the rapid growth in population and urbanization, the energy demand increases persistently [1]. It has been forecasted that the available energy resources will be expressively depleted up to 2050 if the proportion of the world's energy consumption and population growth remains the same. Obtaining energy from fossil resources is the root cause of environmental pollution that can be associated with global warming, acid rain, etc. [2]. However, the utilization of renewable resources such as water, sun, wind, and biomass can reduce the dependence upon fossil resources. Among all, biomass is an easily accessible and cheap renewable energy resource, and it has been used as a fuel since early times. The biomass can be classified into many groups such as agricultural crops and their waste, wood, municipal sludge waste, animal wastes, aquatic plants, algae, and food processing waste [3].

Sewage sludge (SS) is produced from the disposal processes of wastewater, and it is classified as primary sludge, secondary sludge, and digested sludge according to the treatment process and wastewater source [4]. SS is comprised of a high amount of water, hazardous organic matter, and heavy metals [5]. The major constituents of SS are carbohydrates, proteins, and lipids; the ratio between these constituents can vary considerably depending upon its origin [6]. The higher heating value (HHV) for dry SS varies from 12 to 20 MJ kg $^{-1}$ that is comparable with other high-energy biomass [7]. Currently, SS has become a major issue due to its abundant production, environmental harm, and treatment difficulty [8]. It has been reported that by the implementation of Urban Waste Water Treatment (UWWT) Directive 91/271/EC (CEC, 1991), the total annual sludge production from the European Union (EU) will be exceeded from 13 million tons up to 2020 [9]. Hydrothermal liquefaction (HTL) is an attractive thermochemical process, that converts low-quality organic matter into high-quality bio-crude at temperatures around (280–450 °C) and pressures (10–35 MPa) [10]. HTL uses hot compressed water, which serves as a reactive medium, and accelerates many chemical reactions for the conversion of organic matter [11].

In literature, several studies are already available related to liquefaction of SS; few of them which are recently published are mentioned here. Qian et al. investigated the effect of moisture content on bio-crude yield under isothermal (400 °C, 60 min), and fast (500 °C, 1 min) HTL conditions, as the highest bio-crude yields (26.8% from isothermal HTL

---

[*] Corresponding author.
E-mail address: lar@et.aau.dk (L.A. Rosendahl).

https://doi.org/10.1016/j.biombioe.2020.105504
Received 31 July 2019; Received in revised form 26 January 2020; Accepted 10 February 2020

and 27.5% from fast HTL) produced with 85% moisture content from SS [12]. Yang et al. pretreated SS in subcritical water (SCW) at 160–200 °C with different surfactants, such as non-ionic fatty alcohol polyoxyethylene ether (AEO9), and cat-ionic surfactant cetyl trimethyl ammonium bromide (CTAB). It was observed that co-pretreatment with (CTAB–AEO9–SCW) increased bio-crude yield along with a 95% reduction of acids in bio-crude [13]. Li et al. studied the effects of mixed solvents (methanol-water-1:1), and (n-hexane-water-1:1) with SS at 340 °C, and achieved highest bio-crude yield with (methanol-water-1:1). Whereas maximum HHV (36.45 MJ kg^{-1}) was detected with (n-hexane-water-1:1) [14]. Liu et al. used different inorganic and organic acids for the ash reduction from SS and found the highest bio-crude yield (26.75%) from HCL. The order of bio-crude yield verses the pretreatment solvents was: HCl > HNO_3 > H_2SO_4 > HCOOH > CH_3COOH > HOOCCOOH [15]. In some publications, it was emphasized that bio-crude yield from SS could also be affected by the addition of a catalyst [16]. Suzuki et al. treated different kinds of sludge with Na_2CO_3 and experienced that the catalyst did not improve the heavy oil yield, except in few sludges with lower content of alkali metals [17]. Malins et al. tested SS with both the homogenous and heterogeneous catalysts (Na_2CO_3, Raney nickel, $FeSO_4$, and MoS_2), it was reported that the optimum temperature for maximum bio-crude yield (47.79% was 300 °C with 5% $FeSO_4$ [18]. The overall composition of SS often varies with respect to the location, therefore comparing these results with each other is quite a problematic task.

Besides the presence of organic matter, SS carries a high amount of valuable nutrients mainly: N, P, K, and Ca [19], and heavy metals like Zn, Cu, Pb, Ni, Cr, Cd, and Hg [20]. Xu et al. performed liquefaction and analyzed inorganic elements in the aqueous phase of SS, it is stated that the concentration of the water-soluble inorganic matter is highly dependent upon their original composition of the SS feedstock [21]. According to the published report of the European Commission in 2010, only 39% of SS was recycled into agriculture in the EU specially due to the existence of heavy metals [22]. Huang et al. reviewed the migration and transformation of heavy metals from SS via hydrothermal processing, but no clear idea was conceived due to limited information about the distribution of the heavy metals among HTL products at subcritical conditions [23]. Thus, the distribution of nutrients and heavy metals from SS at sub-supercritical conditions still remains a contradicting case in the HTL field.

Till now, the majority of the SS studies were published at subcritical conditions, but no comprehensive study was conducted in terms of detailed product analysis from SS in the context of sub and supercritical conditions. Therefore, this article aims to provide complete comparative information about the bio-crude properties, carbon/nitrogen recoveries in products, and aqueous phase characteristics at sub-supercritical conditions with and without catalyst (K_2CO_3). Furthermore, the fate of nutrients and heavy metals was investigated to explore the nutrient potential in product streams. The leaching effect of different agents on ash and organic matter was also discussed in the last part of this study.

2. Materials and methods

2.1. Feedstock characterization

A secondary SS sample was collected from Wastewater Treatment Plant, Aalborg Forsyning (Renseanlaeg Ost), Aalborg East, Denmark. The moisture content (MC) was calculated by a moisture analyzer (Kern, MLS) at 120 °C. The mass fraction of ash was determined by the weight difference via burning the SS in a muffle furnace at 775 °C for 4 h. Soxhlet extraction was performed to determine the concentration of Crude fat (CF) by using petroleum ether as a solvent. The Crude protein (CP) was obtained by multiplying the factor 6.25 by nitrogen (from elemental analyzer) [24]. The Higher Heating Value (HHV) for the SS was detected by a C2000 basic Calorimeter (IKA, Germany). Potassium carbonate (K_2CO_3) was used as a catalyst 2% by weight of the total 7g slurry.. The elemental composition was analyzed by an elemental analyzer (Perkin Elmer, 2400 Series II CHNS/O), operated in CHN mode. Volatile matter (VM) was determined through TGA (TA instrument Discovery) under the nitrogen atmosphere at 750 °C at the ramp of 10 °C min^{-1}. Inorganics in SS were estimated through Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Prior to ICP-AES analysis, the SS sample was digested in microwave-assisted acid digestion according to EPA method 3051A (US. EPA., 2007) by adopting an identical procedure as mentioned in Conti et al. [25].

2.2. Experimental procedure

The liquefaction experiments with and without catalyst were carried out in stainless steel reactors of 10 ml. 7 g of SS was loaded into the reactor corresponding to 27% dry matter, or water:solid ratio of 2.7:1. Potassium carbonate (K_2CO_3) was used as a catalyst (2% weight of the total slurry) for catalytic runs. The high moisture content in SS leads an amenable pumpability; thus, no extra water was added. The Reactors were sealed, purged with nitrogen to remove residual air and pre-pressurized at 10 MPa. The reactors were safely inserted into pre-heated sand bath at desired temperatures (350 and 400 °C) for a retention time of 15 min. Both temperature and pressure were assessed during the entire retention time. After the retention time, reactors were quenched to room temperature, and products were separated and collected. All experiments were performed in duplicates, and mean values were reported along with their standard deviations to minimize the possible risk of errors.

After the experiments, the SS sample was leached with two different agents, citric acid and aqueous phase produced from the HTL of SS at 350 °C in a separate autoclave. The citric acid (Sigma-Aldrich, 99.9%) was diluted to a 5% solution. 50 g of SS sample was soaked in 500 ml of 5% citric acid solution at 30 °C under the magnetical stirring of (1000 rpm) for 4 h. After the leaching, the SS was washed a couple of times to get rid of acid residuals. In last centrifugation was conducted to separate and collect the two phases. For the aqueous phase, same methodology was applied except the masses as 5g of SS in 50 ml of the aqueous phase. Treated SS samples were dried at 105 °C for 24 h. Later on, Soxhlet extraction was carried out to determine the fat content from the leached samples of SS.

2.3. Products separation and recovery

The produced gas was vented through opening the valves of the reactors. The aqueous phase was collected by turning the reactors upside down. Reactors were uncapped and rinsed with acetone to collect the mixture of bio-crude phase and solids. The solids were separated by vacuum filtration by filter paper (particle retention: 5–13 μm) and dried in the oven at 105 °C for 24 h. From the remaining mixture of bio-crude and acetone, the acetone was evaporated in a rotary evaporator at (60 °C, 56 KPa). While Diethyl ether (DEE, Sigma Aldrich, ACS reagent, anhydrous, >99.0%) was added to get the bio-crude from the rotary flask. Finally, DEE disappeared at (40 °C, 99 KPa) and leftover bio-crude was measured to the report the yield. The overall schematic diagram of the HTL process is given in Fig. 1.

2.4. Products characterization

The elemental composition of bio-crude was determined by the analyzer (Perkin Elmer. 2400 Series II CHNS/O) operated in CHN mode, while the concentration of oxygen was determined by difference. The volatility of the bio-crude was detected via TGA (TA instrument Discovery) by heating the bio-crude samples from room temperature to 775 °C under nitrogen atmosphere. The organic compounds in the bio-crude were identified by using GC-MS system: a Gas Chromatograph (Thermo Scientific, Trace 1300) coupled with a Mass Spectrometer (ISQ, QD). The GC oven was equipped with a capillary column (HP-5MS, Agilent

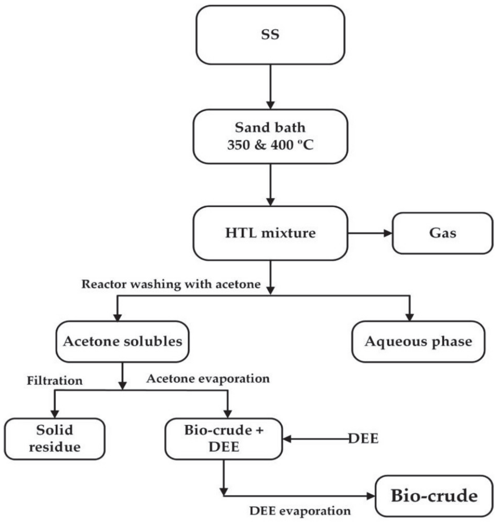


Fig. 1. Schematic description of hydrothermal liquefaction of SS.

Technologies, length: 30 m, I.D.: 0.25 mm, film thickness: 0.25 mm), whose temperature was raised to 300 °C (10 K min^{-1}). The MS ion source was kept at a constant temperature of 300 °C. The samples were diluted in DEE and filtered using syringe filters (0.45 μm) before being injected into GC-MS inlet.

The concentration of inorganic elements in the bio-crude, solids and aqueous phase was determined by ICP-AES. To extract the required elements, the samples were prepared for analysis by microwave-assisted acid digestion according to EPA method 3051A (US. EPA., 2007). The microwave reaction system was an Anton Paar Multiwave 3000 equipped with a HF-16 high-pressure rotor and Teflon® lined ceramic digestion vessels. Approximately 0.2 g of material was weighed into each digestion vessel, then 9 cm^3 concentrated nitric acid (HNO3), and 3 cm^3 hydrochloric acid (HCl) were added. All acids were of supra-pure quality (PlasmaPure, SCP Science). Following the method, the digested samples were shifted into Polypropylene vials and diluted to 50 cm^3 with Type I ultrapure water (Elga LabWater). The rest of the procedure for ICP-AES was in accordance with Conti et al. [25].

The concentration of Total Organic Carbon (TOC) and Total Nitrogen (TN) in the aqueous phase were determined by using reagent vials (LCK: 386, 138 respectively) and a spectrophotometer unit (Hach & Lange, DE3900). The aqueous phase pH was measured with a WTW pH meter 3210. The Higher Heating Value (HHV) for bio-crude calculated by using Channiwala and Parikh correlation [7]. The product yields on dry ash-free basis (daf), energy recovery (ER) and HHVs for bio-crudes were calculated by using the following formulae:

Bio-crude yield (%) = (weight of bio-crude/dried ash-free weight of SS) × 100 (1)

Solid yield (%) = (dried ash-free weight of solid/dried ash-free weight of SS) × 100 (2)

Energy recovery: ER (%) = (HHV of bio-crude/HHV of SS) × bio-crude yield (3)

HHV (MJ kg^{-1}) = (0.3419) C + (1.11783) H + (0.1005) O - (0.1034) N [7](4)

3. Results and discussion

3.1. Inorganic elements in SS

The concentration of inorganic elements in SS was measured through ICP-AES. It was noticed that ICP-AES analysis only detected around 24% of the total ash (40.63%) in the SS, as demonstrated in Fig. 2. However, the ICP-AES technique is only limited to the detection of metals; thus, the rest mass could be occupied by oxides, carbonates, and sulfates of their respective metals or other elements such as silicon, barium, etc., which are not reported in this study.

Among all inorganic elements, the calcium, phosphorus, sulfur, and magnesium were found to be the major inorganic elements in the range of 7–42%. The concentration of each element is given in (mg kg^{-1}) in the following Table 2. Here,the concentration in (weight.%) is calculated as the concentration of each element divided by the sum of the concentrations of all detected elements via ICP-AES.

3.2. Effect of temperature on product yield

The HTL experiments of SS were carried out at 350 and 400 °C with and without catalyst (K_2CO_3). Fig. 3 illustrates that the temperature did not influence the bio-crude yield, the maximum bio-crude yield (45.22%) was obtained at 350-Catalytic. In non-catalytic samples, the bio-crude yield was almost similar at both temperatures as 40.21 and 40.24% for 350-None and 400-None respectively. The temperatures around sub and near-critical region decrease the dielectric constant, density, and polarity of water, which accelerate hydrolysis reaction and improves the solubility of hydrophobic organic fractions. However, no significant increase in bio-crude yield was observed in the supercritical state; this might be due to exceeding the threshold temperature (critical point: 373.74 °C), which converts the bio-crude components into the aqueous or gaseous phase. In the previous study, Li et al. reported almost the same trend in bio-crude yield as 35.8 and 34.3% at 360 and 400 °C respectively [14]. At supercritical conditions, the lower solid yield was due to the conversion of heavier fragments into the lighter ones by cracking reactions [27].

3.3. Effect of catalyst on product yield

The overall effectiveness of the catalyst depends upon the chemical composition of the organic matter enriched in the form of carbohydrates, lipids, and proteins in the SS. The bio-crude yield was slightly increased by 5 and 3% on the action of catalyst for 350-Catalytic and 400- Catalytic respectively. Earlier studies reveal that the alkali catalyst is beneficial for the conversion of carbohydrates. In the alkaline

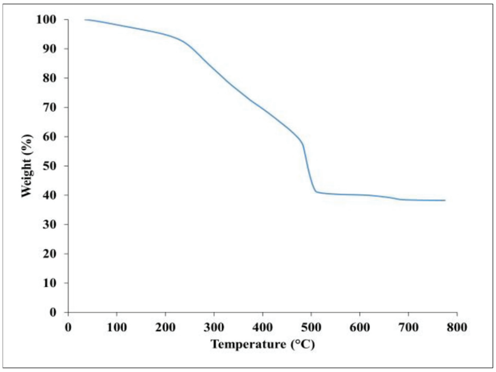


Fig. 2. Thermogravimetric curve of SS for ash content.

Table 1
Characterization of SS.

Proximate and ultimate analysis (wt. %)						
MC[a]	VM	FC[c]	Ash	Crude Protein[b]	Crude Fat[b]	Carbohydrate[b,d]
73.39	50.52	8.80	40.63	43.16	7.79	48.16
C[b]	H[b]	N[b]	O[e]	H/C	O/C	HHV (MJ kg $^{-1}$)[b]
50.95	7.36	6.91	34.78	1.73	0.51	22.15

[a] As received.
[b] Dry ash free.
[c] Fixed Carbon: FC = 100-VM-Ash.
[d] Carbohydrate = [(VM+FC)–(CP + CF)] [26].
[e] By Difference.

Table 2
Inorganics elements detected by ICP-AES in SS.

Inorganic elements	Concentration (mg/kg)	Concentration (weight.%)
Al	5721.90	5.93
Ca	41220.93	42.69
Cd	0.98	0.00
Cr	47.05	0.05
Cu	206.54	0.21
Fe	6162.79	6.38
K	3320.49	3.44
Mg	6855.62	7.10
Mn	278.63	0.29
Na	1274.47	1.32
Ni	35.48	0.04
P	22335.27	23.13
Pb	28.61	0.03
S	8086.24	8.38
Zn	975.05	1.01
Others	NR	–

NR: Not reported.

environment, the carbohydrates are readily converted into their intermediate components by cleavage of glycosidic bonds via depolymerization, decomposition, decarboxylation, and dehydration of sugars [28, 29]. For lipids, the alkali catalyst also enhances the decarboxylation of fatty acids and converts them into long-chain hydrocarbons [14].

Since protein is also an integral constituent of SS, however, some high protein contained algal studies. For example, Shakya et al. stated the negative effect of alkali catalyst due to inefficient cleavage of peptide linkages between amino acids present in protein [28]. In this study, the SS contained lower proteins as compared to carbohydrates in mass fraction (Table 1). The higher magnitude of carbohydrates than proteins could be the strong reason for the activation of the catalyst, which results in higher bio-crude yield. Owing to this perspective, we can conclude that using the alkali catalyst is a beneficial option for the SS containing high carbohydrates. With the good agreement of this observation, Yokoyama et al. witnessed an increase in bio-crude yield while using 2.5% sodium carbonate catalyst for the conversion of SS with 57% carbohydrates [16]. The solid yield was decreased with the addition of the catalyst because the alkali catalyst frequently suppresses the formation of char [11]. Alkali catalyst is an active promoter of water gas shift reaction, which forms more hydrogen that allows fragmented intermediates to stabilize and averts repolymerization, which ultimately reduces the solid yield [30].

3.4. *Elemental analysis of bio-crude*

The elemental composition, energy recoveries, and HHVs of bio-crudes are given in the following Table 3. Besides, the elemental composition of bio-crude, the properties of petroleum [31], are also listed to distinguish the quality of bio-crude. The elemental composition of bio-crude was not significantly affected by temperature; in contrast, the catalyst slightly improved the bio-crude quality. In all bio-crude samples, the carbon content was in the range of 73–76%, the hydrogen content was almost consistent around 10%, and nitrogen contributed 3–6% in the bio-crude.

Non-catalytic bio-crude had higher nitrogen content as compared to catalytic ones because carbonates readily react with ammonium ion that originates from the deamination of amino acids and forms ammonium carbonate which could be easily dissolved in the aqueous phase. This phenomenon subsequently inhibits the reaction of ammonium ion with bio-crude fractions to form amines and amides that results in lower nitrogen in catalytic bio-crude. The reaction of alkali catalyst with ammonium ion is given in the following equations:

$$K_2CO_3^{-2} + 2NH_4^+ \rightarrow (NH_4)_2CO_3 + 2K^+ \tag{5}$$

$$(NH_4)_2CO_3 \rightarrow NH_3 + CO_2 + H_2O \tag{6}$$

The lowest amount of nitrogen was detected in 400-Catalytic bio-crude, which may be due to higher temperatures and the presence of a catalyst. However, 350-Catalytic bio-crude showed the highest energy recovery (74.60%).

The H/C (1.62–1.68) and O/C (0.09–0.11) atomic ratios were also

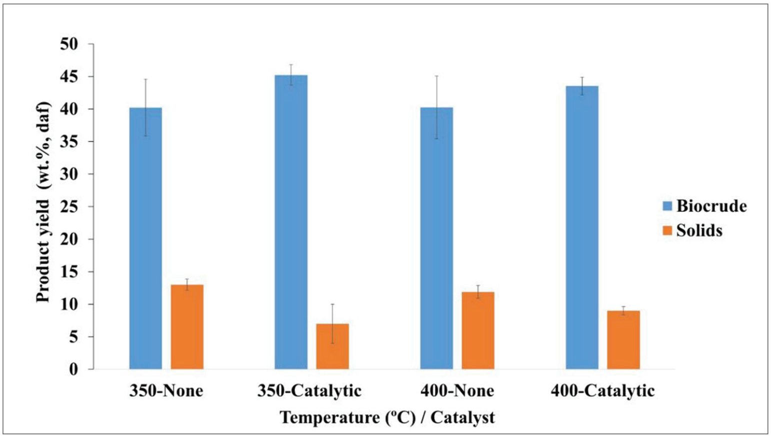


Fig. 3. Product yields at 350 and 400 °C with and without the catalyst.

Table 3
Elemental composition of bio-crude.

Samples	Elemental analysis (wt. %)				H/C	O/C	HHV (MJ kg^{-1})[b]	ER (%)
	C	H	N	O[a]				
SS	50.95	7.36	6.91	34.78	1.73	0.51	22.15	–
350-None	73.68	10.09	5.71	10.52	1.64	0.11	35.30	63.98
350-Catalytic	75.51	10.56	4.69	9.24	1.68	0.09	36.60	74.60
400-None	74.60	10.33	5.20	9.88	1.66	0.10	35.95	65.21
400-Catalytic	75.75	10.22	3.77	10.26	1.62	0.10	36.21	71.04
Petroleum crude	83–87	10–14	1–1.0	0.1–3.0	–	–	~42.75	–

[a] Oxygen calculated by difference (O = 100-C-H-N).
[b] HHV calculated by using Channiwala and Parikh correlation [6].

calculated. The lower O/C ratios in bio-crude as compared to original feedstock (SS) indicates the conversion of SS through dehydration and decarboxylation reactions, as shown in Van krevelen diagram in Fig. 4. Lower O/C ratio could improve the stability and viscosity of bio-crude, and less hydrogen would be required for the upgrading of the bio-crude. Nevertheless, the H/C ratios of the bio-crude were still lower as compared to petroleum crude, therefore, upgrading techniques are required to remove the heteroatoms, which further increases the bio-crude feasibility to be used as petroleum fuel.

3.5. *TGA of bio-crude*

The thermal behavior of bio-crude was determined through TGA. The volatility curves of all bio-crudes are illustrated in Fig. 5. Around 350 °C, almost 50% mass of all bio-crudes comprised of volatile components, which depicts the fractions of gasoline, diesel, and jet fuel. The bio-crude 350-None showed slightly higher volatile matter as compared to other catalytic bio-crudes. It could be hypothesized that in the presence of the catalyst, some repolymerization and cyclization might occur (particularly at supercritical conditions) between the reactive components of the bio-crudes, which formed heavier fragments. In addition, the Differential Thermogravimetric (DTG) weight loss was also calculated in Fig. 5 (b), it further supports the volatility analysis as more peaks of non-catalytic bio-crudes were displayed at 100–200 °C. At extreme temperatures, 6–11% of heavy residue was noticed after burning the bio-crudes at 950 °C under the nitrogen atmosphere.

3.6. *Compound composition in bio-crude*

The organic compounds of bio-crude were identified by using GCMS at 300 °C. The comprehensive information about the retention time (RT), compound names, and peak area percentage is provided in Table S1 (Supplementary material). From GCMS results, the bio-crude is categorized into N-containing compounds (N&O heterocyclic compounds and amides), Oxygenated compounds (ketones, aldehydes, alcohols, acids, and esters), and Hydrocarbons, as shown in Fig. 6. Oxygenated compounds were found to be the most abundant in all bio-crudes followed by the N-containing compounds and hydrocarbons.

One interesting finding was observed that at both temperatures, non-catalytic bio-crudes contained higher peaks of N&O heterocyclic compounds, especially [RT:13.06, 4-Piperidinone-2,2,6,6-tetramethyl]. Whereas more or less the same magnitude of amides were detected in the catalytic and non-catalytic bio-crudes. This confirms that the N&O heterocyclic compounds are responsible for the overall increase in nitrogen content in the non-catalytic bio-crudes. This is because the alkali catalyst readily converts the sugars into their secondary intermediates and does not allow polysaccharides to interact with amino-acids to form N&O heterocyclic compounds. In evidence, the chromatograms of all bio-crudes are provided in Fig. S1 (Supplementary material). Previously, Biller et al. already observed higher amides in his study while using sodium carbonate as a catalyst with algal feedstock [32]. The bio-crude produced at both supercritical conditions had lower hydrocarbons as compared to subcritical conditions. A reasonable explanation of this would be the cracking of the long-chain aliphatic compounds into short

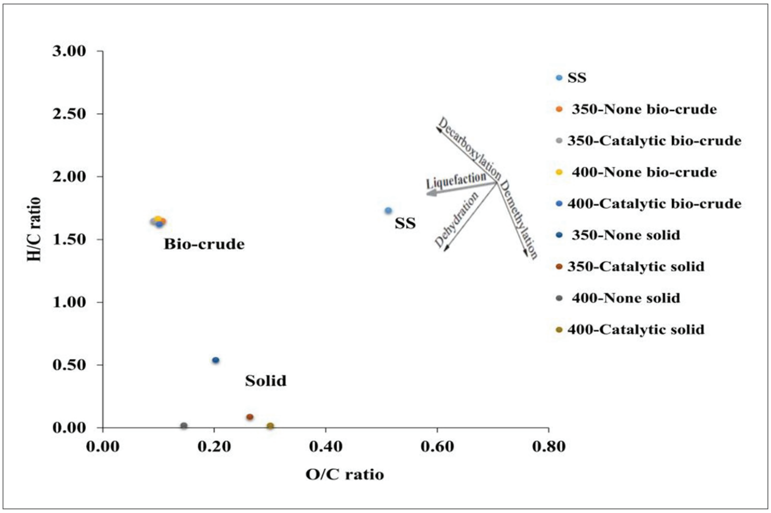
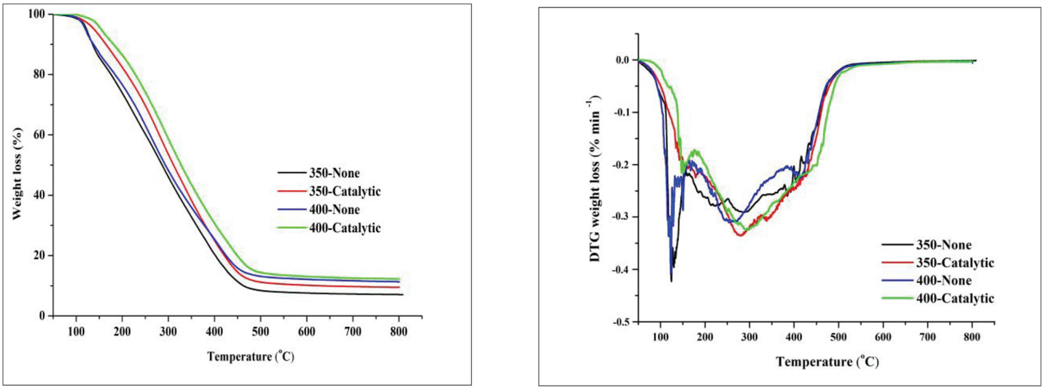


Fig. 4. Van krevelen diagram shows dehydration and decarboxylation reactions.



(a) (b)

Fig. 5. (a) Volatility curves of bio-crude, and (b) DTG curves of bio-crude.

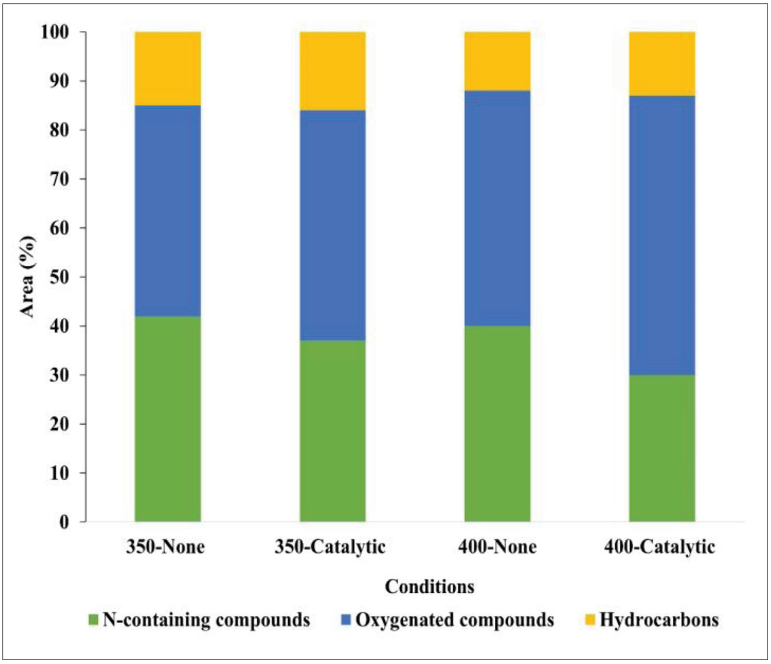


Fig. 6. Distribution of compounds in bio-crude.

ones and the formation of other kinds of compounds such as arenes and cyclic compounds at high temperatures [31].

Considering the complex nature of SS, it is difficult to explain the exact pathways of these compounds. From N-containing compounds, the amides [Dodecanamide, N-Methyldodecanamide, 9-Octadecenamide-(Z)], were formed by decarboxylation, deamination, dehydration, depolymerization, and decomposition reactions of proteins [32]. Zhang et al. reported another pathway for the formation of amides by the reaction of fatty acids with amines via acylation [33]. N-Heterocyclic compounds [Pyrimidine-2-methyl, 2(1H)-Pyridinone-1-propyl, Pyrazine-2-ethyl-3-methyl, Indole, and its derivatives] were produced by Maillard reaction between polysaccharides from carbohydrates, and amino acids from protein [34]. Phenolic compounds were mostly derived from hydrolysis, dehydration, and ring closure reaction from the cellulose [21,35].

The ketones such as [3-Penten-2-one- 4-methyl, 2-Nonadecanone, Cyclohexanone 2,6-diethyl, and Cyclohexanone, 2,6-diethyl] were derived from cellulose by hydrolysis, dehydration, and cyclization [29,36]. Peterson et al. mentioned another route for the formation of ketones from Keto-acids that primarily produced from amino acids via deamination and decarboxylation reactions [37]. Zhang et al. also observed the same kinds of ketones from secondary pulp and paper sludge in a supercritical atmosphere [38]. Only one aldehyde [5-Octadecenal] was found at 350-None, which be converted from isomerization of ketones.

Fatty acids such as [Hexadecanoic acid, 9 Hexadecanoic acid, and Dodecanoic acid-3-hydroxy], were derived from the hydrolysis of lipids. Fatty esters like, [7-Methyl-Z-tetradecen-1-ol acetate] were formed from the reaction between alcohols produced by cellulose and fatty acids [39]. Long-chain hydrocarbons including such as [Tetradecane, 1-Nonadecene, 5-Octadecene, (E)- etc.] produced from decarboxylation of fatty acids. The GCMS results represent that around 80% of bio-crude contained heteroatoms, thereby bio-crude needs to be upgraded to meet the standards of the drop-in fuels.

3.7. Analysis of solid residue

The elemental composition of solid residue is reported by excluding the amount of ash produced in the solids in Table 4. The ash content in the solids was detected by TGA. The lower H/C ratios in solids indicate that almost all hydrogen was consumed, which might form more unsaturated and aromatic compounds in solids [29]. The solids at 350-None with considerable higher H/C (0.54) is due to the lowest amount of ash detected, as shown in Fig. 7. The O/C were high due to the higher degree of deoxygenation via dehydration and decarboxylation reactions. The catalyst decreased the amount of carbon in solids, and this is quite understandable due to lower solid yields and a higher amount of carbon in bio-crudes at catalytic conditions.

3.8. Carbon and nitrogen recoveries (CR & NR)

The carbon or nitrogen recovery (CR/NR) was calculated as the ratio of the weight of carbon or nitrogen in the product to the weight of carbon or nitrogen in the original SS multiplied by the product yield. Whereas CR and NR in the aqueous phase were determined by the measurements of TOC and TN. For gases, the mass balance of carbon and nitrogen was estimated by difference. Almost 58% of carbon was recovered in bio-crude at non-catalytic conditions. Whereas catalyst brought 64–67% carbon into the bio-crude. Ma et al. also found 64% CR in bio-crude from the supercritical pyrolysis of SS [27]. The CR in the solids was 7–19%. The higher amount of CR was detected in the catalytic aqueous phases. However, catalyst assists in the hydrolysis of organic matter in water and resulting in a higher amount of TOC in the aqueous phases [17,28]. For gases, no trend was observed, at both conditions, approximately 5–8% carbon went into the gaseous phase as illustrated in Fig. 8.

The SS is a high protein-containing feedstock; hence, the distribution of nitrogen in products is a crucial part of the discussion. Fig. 9 represents that the majority of nitrogen transferred to the aqueous phase. Whereas bio-crude and solid-phase contained 23–35% and 5–12% of NR respectively. The higher NR in the aqueous phase is further satisfied by Chen et al., who observed almost 60% of the nitrogen in the aqueous phase in the subcritical environment from co-liquefaction of swine manure and mixed algal biomass [40].

The lower NR was found in catalytic bio-crudes because the catalyst has promoted the denitrogenation in bio-crude and transferred the majority of nitrogen probably in the form of ammonium in the aqueous phase. Earlier, Chen et al. reported in his other study that NR in the bio-crude is inversely correlated with the concentration of calcium carbonate ($CaCO_3$) [40]. However, how exactly the alkali carbonates react with N-containing compounds within HTL requires further research. The NR in the gas phase was very negligible in the range of 0.4–2.3%.

Table 4
Elemental analysis of solid residue.

Samples	Elemental analysis (wt. %)[a]				Ash (%)	H/C	O/C
	C	H	N	O[b]			
350-None	70.80	3.17	6.86	19.17	77.62	0.54	0.20
350-Catalytic	69.57	0.50	5.42	24.52	85.97	0.09	0.26
400-None	77.57	0.11	7.21	15.11	86.76	0.02	0.15
400-Catalytic	67.65	0.10	5.11	27.14	84.25	0.02	0.30

[a] Dry ash free basis.
[b] Oxygen calculated by difference (O = 100-C-H-N).

3.9. Aqueous phase analysis

The characteristics of the aqueous phase were determined through TOC and TN. In the non-catalytic aqueous phase, the TOC values were detected as 18 and 20 g L^{-1} for 350-None, and 400-None respectively. On the other hand, higher values for TOCs were obtained by the addition of the catalyst, as illustrated in Fig. 10. However, the catalyst raises the pH level and assists in the degradation of organic matter. Suzuki et al. observed in his study that catalytic samples had two times the TOC as compared to the non-catalytic aqueous phase from SS [17]. The organic carbon in the aqueous phase is associated with other oxygenates, especially in the form of acids, alcohols, etc., which imparts toxicity to the aqueous phase. In order to ensure safe disposal of the aqueous phase, it must be treated before being discharged into the ambient environment. This treatment requires an additional cost and energy, which makes the HTL as an expensive process in a broader outlook. Therefore, nowadays, researchers are strongly recommending the valorization of the aqueous phase either by recirculation back to the HTL unit or via Catalytic Hydrothermal Gasification (CHG) [30,41,42].

Biller et al. proposed that the aqueous phase containing 15–50 g L^{-1} of TOC could be used for recycling in HTL, and beyond this range, the CHG would become thermally efficient [42]. In this respect, some quantity of aqueous phase can be recirculated back to the HTL (by controlling the dry matter content in the original feed) to improve the bio-crude productivity and overall efficiency of the HTL system [43]. The concentration of TN was more consistent, but again slightly higher in the catalytic aqueous phase. Catalytic bio-crude had lower nitrogen, as discussed earlier in the previous section 3.4.

3.10. Distribution of the inorganic elements in products

To observe the effect of temperature on the concentration of inorganic elements in products, the (ICP-AES) analysis was performed on non-catalytic samples. The distribution of inorganic elements was obtained by considering the concentration of each inorganic element in the product phase and the weight of the product for each phase. For an individual element, the distribution is standardized with regard to the total amount of inorganics recovered in each phase. The inorganics were primarily distributed among bio-crude, solids, and aqueous phase. More than 70% of inorganic elements were concentrated into the solids, except K, Na, and Fe, as represented in Fig. 11.

Besides the transference of the majority of heavy metals to the solid phase, yet bio-crude at both conditions contained 3–21% of heavy metals like Cr, Cu, Mn, Pb, Zn, and Ni. The concentrations of all inorganic elements in (mg kg^{-1}) are listed in Table S2. Almost all the phosphorus (98%) was found in the solids, and it was evident because of the high concentration of phosphorus (23%) in the original SS feedstock, as listed in Table 2. This phosphorus might be present in the form of phosphates with other alkali and alkaline earth metals like potassium, sodium, calcium, and magnesium, which were also present in higher concentrations at both temperatures. Owing to the availability of these valuable nutrients, the solid phase can also be utilized as a fertilizer for the cultivation of biomass or soil amendment [44].

At supercritical condition, the higher amount of sodium and potassium were dissolved in the aqueous phase (Fig. 12). This may be attributed to a higher pressure (350 bar) at a supercritical state, which slightly increases the ionic product of the water, and exhibits a higher degree of solubilization [45]. Moreover, higher reaction temperature enhances the extraction of heavy metals as more Zn and Fe were dissolved into the aqueous phase [23]. At subcritical condition, sulfur was

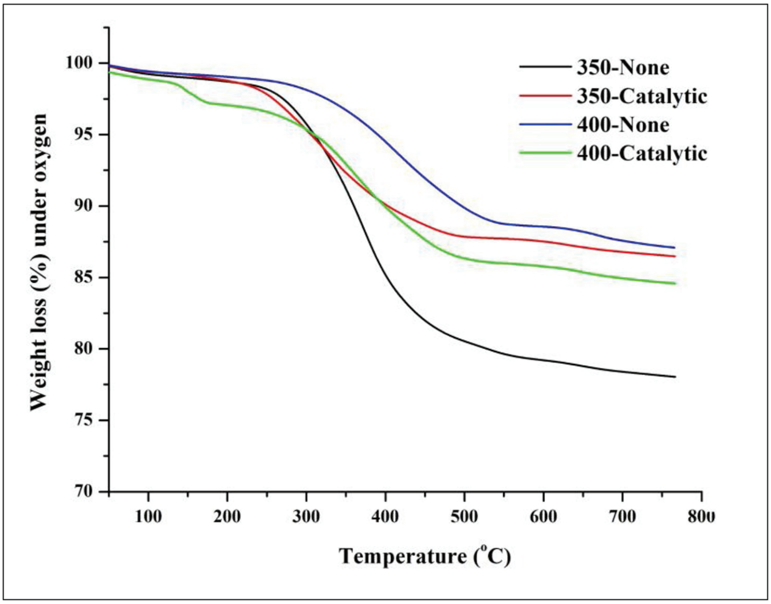


Fig. 7. Thermogravimetric curves of solids under oxygen environment.

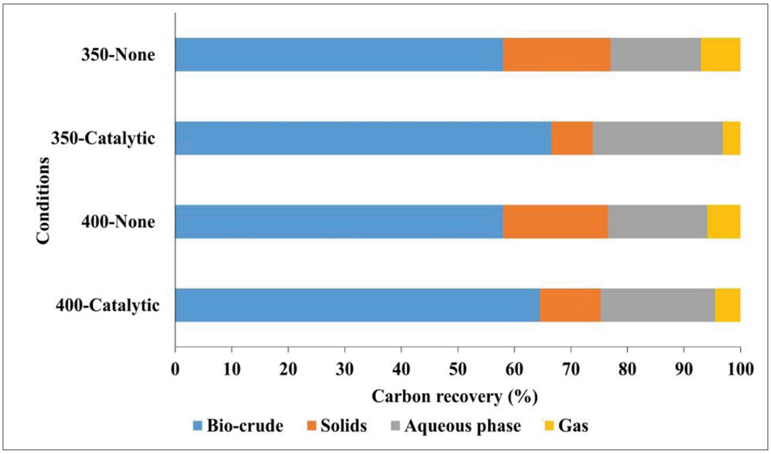


Fig. 8. Carbon recovery in products.

equally distributed among the three phases, while it was exceeded up to 80% in the bio-crude at supercritical state. The higher amount of sulfur in bio-crude at supercritical condition may be due to the cleavage of polysaccharides containing sulfur in the ring structure, or precipitation of metal sulfates at higher temperatures. Conti et al. observed a similar trend of inorganic elements and high sulfur content while liquefying willow in supercritical water [28]. From the above findings, the fate of nutrients and heavy metals is significantly important in designing and operation of large-scale HTL facility to tackle the economic and environmental challenges related to the utilization of SS as feedstock.

3.11. Leaching of SS

To examine the leaching effect of different agents on the composition of SS. The SS samples were leached with citric acid and aqueous phase. Here the aqueous phase was selected to investigate its leaching effect, minimize the cost of acids, and to make pretreatment process viable for the large scale HTL plant. Fig. 13 shows that ash content was decreased from 40.63 to 24.52%, which means that almost 39% of the ash mass lost in the acid-water soluble fractions mainly in the form of nitrates, phosphates, chlorides, and carbonates. This finding is consistent with the study Toor et al., who leached Spent Mushroom Compost (SMC) with a 5% citric acid solution and found 66% ash reduction [46]. Here,

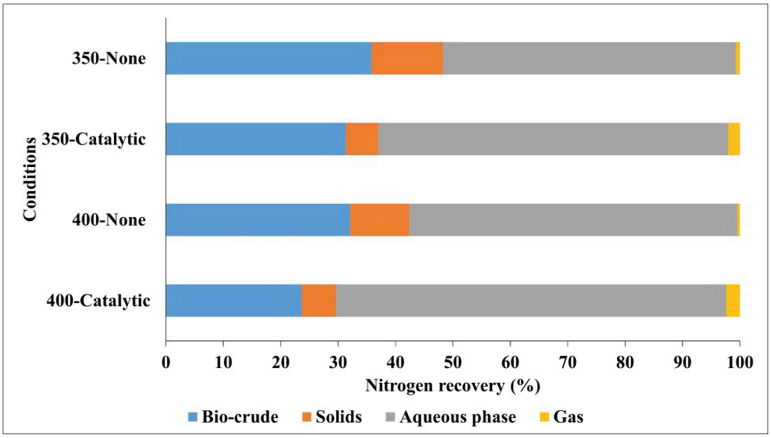


Fig. 9. Nitrogen recovery in products.

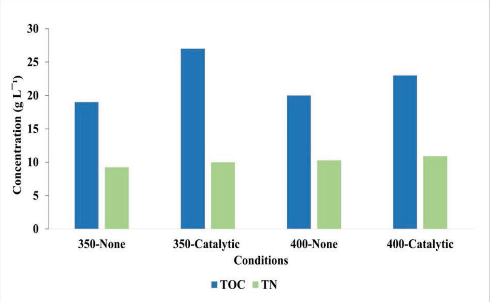


Fig. 10. TOC and TN in the aqueous phase of SS.

besides the reduction of inorganics, the fat content was highly impacted by citric acid and decreased from 7.7 to 4.76%. Earlier, many studies reported that fat or lipid is an essential constituent for the production of bio-crude, and it has a higher conversion rate with respect to proteins and carbohydrates [32]. From this observation, it can be summarized that organic acids are beneficial for the ash reduction but simultaneously these acids leach out some significant organic fractions from the biomass.

Leaching with aqueous phase showed a negligible reduction in ash content up to 1%. This lower leaching efficiency may be due to the lower concentration of acids and more N-containing compounds in the aqueous phase, which is relatively understandable due to its alkaline pH (8.92). Biller et al. also observed the alkaline pH due to the accumulation of N-containing compounds in the aqueous phase from high protein contained biomass Dried Distillers Grains with Solubles (DDGS) [30].

4. Conclusion

Hydrothermal liquefaction of SS has been investigated with and without catalyst (K_2CO_3) in sub-supercritical conditions. Obtained results showed that the temperature did not influence bio-crude yield, whereas catalyst slightly improved the bio-crude yield and quality. The addition of the catalyst reduced the nitrogen content in the bio-crude, particularly at the supercritical conditions. However, 350-Catalytic bio-crude expressed the highest energy recovery (74.60%). Moreover, ICP-AES analysis has shown more intrusion of heavy metals in bio-crude at supercritical conditions. In last, the leaching experiments showed that the ash content was decreased up to 40%, while 38% of the fat was lost on the action of citric acid.

Based on these outcomes, subcritical HTL seems to be a relatively viable option due to lower temperatures; while supercritical HTL promotes denitrogenation in bio-crude. Thereby it is quite challenging to choose an optimal condition for the production of bio-crude from SS

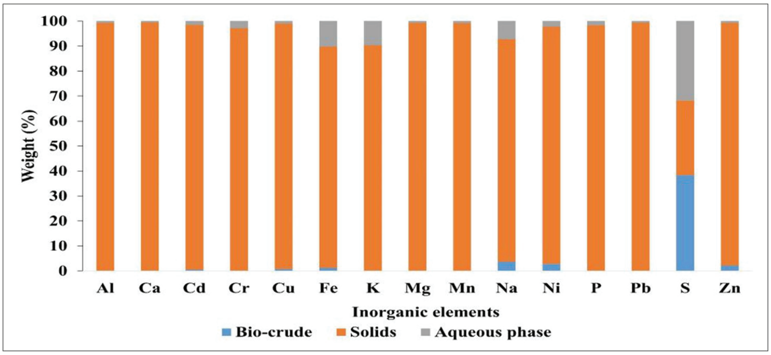


Fig. 11. Normalized mass distribution of inorganic elements at 350 °C.

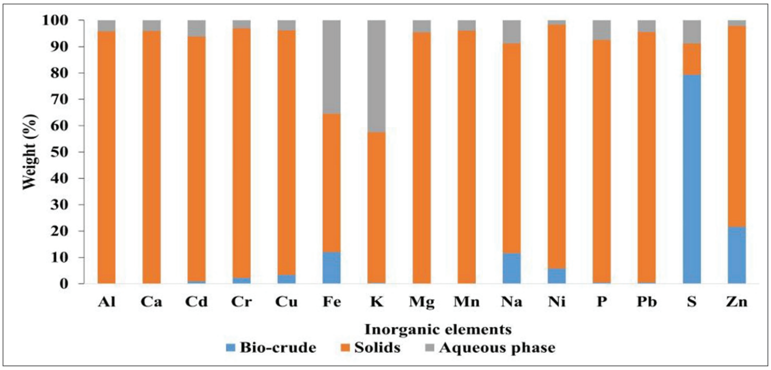


Fig. 12. Normalized mass distribution of inorganic elements at 400 °C.

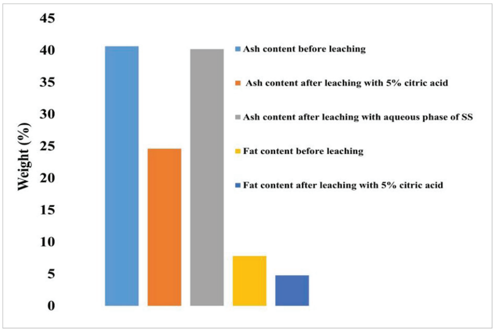


Fig. 13. Effect of leaching on the composition of SS.

concerning the complexities of continuous HTL plant and cost estimation related to the removal of heteroatoms.

Funding

This research work was funded by the Higher Education Commission (HEC) of Pakistan under the program “Strengthening of Dawood University of Engineering and Technology, Karachi”.

Declaration of competing interest

The authors declare no conflict of interest. The funding agency had no role in the design of the study, writing manuscript, and in the decision to publish results.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biombioe.2020.105504.

References

[1] H.B. Goyal, D. Seal, R.C. Saxena, Bio-fuels from thermochemical conversion of renewable resources: a review, Renew. Sustain. Energy Rev. 12 (2008) 504–517, https://doi.org/10.1016/j.rser.2006.07.014.

[2] A. Demirbaş, Biomass resource facilities and biomass conversion processing for fuels and chemicals, Energy Convers. Manag. 42 (2001) 1357–1378, https://doi.org/10.1016/S0196-8904(00)00137-0.

[3] A. Demirbaş, Mechanisms of liquefaction and pyrolysis reactions of biomass, Energy Convers. Manag. 41 (2000) 633–646, https://doi.org/10.1016/S0196-8904(99)00130-2.

[4] L. Wang, Y. Chang, A. Li, Hydrothermal carbonization for energy-efficient processing of sewage sludge: a review, Renew. Sustain. Energy Rev. 108 (2019) 423–440, https://doi.org/10.1016/j.rser.2019.04.011.

[5] H. Huang, X. Yuan, B. Li, Y. Xiao, Thermochemical liquefaction characteristics of sewage sludge in different organic solvents, J. Anal. Appl. Pyrolysis 109 (2014) 176–184, https://doi.org/10.1016/j.jaap.2014.06.015.

[6] P. Manara, A. Zabaniotou, Towards sewage sludge based biofuels via thermochemical conversion - a review, Renew. Sustain. Energy Rev. 16 (2012) 2566–2582, https://doi.org/10.1016/j.rser.2012.01.074.

[7] J. Parikh, S. Channiwala, G. Ghosal, A correlation for calculating HHV from proximate analysis of solid fuels, Fuel 84 (2005) 487–494, https://doi.org/10.1016/j.fuel.2004.10.010.

[8] B.M. Cieślik, J. Namieśnik, P. Konieczka, Review of sewage sludge management: standards, regulations and analytical methods, J. Clean. Prod. 90 (2015) 1–15, https://doi.org/10.1016/j.jclepro.2014.11.031.

[9] A. Kelessidis, A.S. Stasinakis, Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries, Waste Manag. 32 (2012) 1186–1195, https://doi.org/10.1016/j.wasman.2012.01.012.

[10] D. Castello, T.H. Pedersen, L.A. Rosendahl, Continuous hydrothermal liquefaction of biomass: a critical review, Energies 11 (2018), https://doi.org/10.3390/en11113165.

[11] S.S. Toor, L. Rosendahl, A. Rudolf, Hydrothermal liquefaction of biomass: a review of subcritical water technologies, Energy 36 (2011) 2328–2342, https://doi.org/10.1016/j.energy.2011.03.013.

[12] L. Qian, S. Wang, P.E. Savage, Hydrothermal liquefaction of sewage sludge under isothermal and fast conditions, Bioresour. Technol. 232 (2017) 27–34, https://doi.org/10.1016/j.biortech.2017.02.017.

[13] T. Yang, X. Liu, R. Li, B. Li, X. Kai, Hydrothermal liquefaction of sewage sludge to produce bio-oil: effect of co-pretreatment with subcritical water and mixed surfactants, J. Supercrit. Fluids 144 (2019) 28–38, https://doi.org/10.1016/j.supflu.2018.10.005.

[14] R. Li, Z. Ma, T. Yang, B. Li, L. Wei, Y. Sun, Sub–supercritical liquefaction of municipal wet sewage sludge to produce bio-oil: effect of different organic–water mixed solvents, J. Supercrit. Fluids 138 (2018) 115–123, https://doi.org/10.1016/j.supflu.2018.04.011.

[15] T. Yang, X. Liu, R. Li, B. Li, X. Kai, Hydrothermal liquefaction of sewage sludge to produce bio-oil: effect of co-pretreatment with subcritical water and mixed surfactants, J. Supercrit. Fluids 144 (2019) 28–38, https://doi.org/10.1016/j.supflu.2018.10.005.

[16] S. ya Yokoyama, A. Suzuki, M. Murakami, T. Ogi, K. Koguchi, E. Nakamura, Liquid fuel production from sewage sludge by catalytic conversion using sodium carbonate, Fuel 66 (1987) 1150–1155, https://doi.org/10.1016/0016-2361(87)90315-2.

[17] A. Suzuki, T. Nakamura, S. Yokoyama, T. Ogi, K. Koguchi, Conversion of sewage sludge to heavy oil by direct thermochemical liquefaction, J. Chem. Eng. Jpn. 21 (1988) 288–293, https://doi.org/10.1252/jcej.21.288.

[18] K. Malins, V. Kampars, J. Brinks, I. Neibolte, R. Murnieks, R. Kampare, Bio-oil from thermo-chemical hydro-liquefaction of wet sewage sludge, Bioresour. Technol. 187 (2015) 23–29, https://doi.org/10.1016/j.biortech.2015.03.093.

[19] U. Jena, N. Vaidyanathan, S. Chinnasamy, K.C. Das, Evaluation of microalgae cultivation using recovered aqueous co-product from thermochemical liquefaction of algal biomass, Bioresour. Technol. 102 (2011) 3380–3387, https://doi.org/10.1016/j.biortech.2010.09.111.

[20] W.D. Chanaka Udayanga, A. Veksha, A. Giannis, G. Lisak, V.W.C. Chang, T.T. Lim, Fate and distribution of heavy metals during thermal processing of sewage sludge, Fuel 226 (2018) 721–744, https://doi.org/10.1016/j.fuel.2018.04.045.

[21] D. Xu, G. Lin, L. Liu, Y. Wang, Z. Jing, S. Wang, Comprehensive evaluation on product characteristics of fast hydrothermal liquefaction of sewage sludge at

different temperatures, Energy 159 (2018) 686–695, https://doi.org/10.1016/j.energy.2018.06.191.

[22] K. Fijalkowski, A. Rorat, A. Grobelak, M.J. Kacprzak, The presence of contaminations in sewage sludge – the current situation, J. Environ. Manag. 203 (2017) 1126–1136, https://doi.org/10.1016/j.jenvman.2017.05.068.

[23] H.J. Huang, X.Z. Yuan, The migration and transformation behaviors of heavy metals during the hydrothermal treatment of sewage sludge, Bioresour. Technol. 200 (2016) 991–998, https://doi.org/10.1016/j.biortech.2015.10.099.

[24] S. Leow, J.R. Witter, D.R. Vardon, B.K. Sharma, J.S. Guest, T.J. Strathmann, Prediction of microalgae hydrothermal liquefaction products from feedstock biochemical composition, Green Chem. 17 (2015) 3584–3599, https://doi.org/10.1039/c5gc00574d.

[25] F. Conti, S.S. Toor, T.H. Pedersen, A.H. Nielsen, L.A. Rosendahl, Biocrude production and nutrients recovery through hydrothermal liquefaction of wastewater irrigated willow, Biomass Bioenergy 118 (2018) 24–31, https://doi.org/10.1016/j.biombioe.2018.07.012.

[26] H. jun Huang, X. zhong Yuan, H. na Zhu, H. Li, Y. Liu, X. li Wang, G. ming Zeng, Comparative studies of thermochemical liquefaction characteristics of microalgae, lignocellulosic biomass and sewage sludge, Energy 56 (2013) 52–60, https://doi.org/10.1016/j.energy.2013.04.065.

[27] W. Ma, G. Du, J. Li, Y. Fang, L. Hou, G. Chen, D. Ma, Supercritical water pyrolysis of sewage sludge, Waste Manag. 59 (2017) 371–378, https://doi.org/10.1016/j.wasman.2016.10.053.

[28] R. Shakya, J. Whelen, S. Adhikari, R. Mahadevan, S. Neupane, Effect of temperature and Na2CO3 catalyst on hydrothermal liquefaction of algae, Algal Res. 12 (2015) 80–90, https://doi.org/10.1016/j.algal.2015.08.006.

[29] Z. Zhu, S.S. Toor, L. Rosendahl, D. Yu, G. Chen, Influence of alkali catalyst on product yield and properties via hydrothermal liquefaction of barley straw, Energy 80 (2015) 284–292, https://doi.org/10.1016/j.energy.2014.11.071.

[30] P. Biller, R.B. Madsen, M. Klemmer, J. Becker, B.B. Iversen, M. Glasius, Effect of hydrothermal liquefaction aqueous phase recycling on bio-crude yields and composition, Bioresour. Technol. 220 (2016) 190–199, https://doi.org/10.1016/j.biortech.2016.08.053.

[31] Z. Zhu, S.S. Toor, L. Rosendahl, G. Chen, Analysis of product distribution and characteristics in hydrothermal liquefaction of barley straw in subcritical and supercritical water, Environ. Prog. Sustain. Energy 33 (2014) 737–743, https://doi.org/10.1002/ep.11977.

[32] P. Biller, A.B. Ross, Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content, Bioresour. Technol. 102 (2011) 215–225, https://doi.org/10.1016/j.biortech.2010.06.028.

[33] J. Zhang, W.T. Chen, P. Zhang, Z. Luo, Y. Zhang, Hydrothermal liquefaction of Chlorella pyrenoidosa in sub- and supercritical ethanol with heterogeneous catalysts, Bioresour. Technol. 133 (2013) 389–397, https://doi.org/10.1016/j.biortech.2013.01.076.

[34] A. Kruse, P. Maniam, F. Spieler, Influence of proteins on the hydrothermal gasification and liquefaction of biomass. 2. Model compounds, Ind. Eng. Chem. Res. 46 (2007) 87–96, https://doi.org/10.1021/ie061047h.

[35] A. Kruse, A. Gawlik, Biomass conversion in water at 330-410 °C and 30-50 MPa. Identification of key compounds for indicating different chemical reaction pathways, Ind. Eng. Chem. Res. 42 (2003) 267–279, https://doi.org/10.1021/ie0202773.

[36] L. Zhang, C.(Charles) Xu, P. Champagne, Energy recovery from secondary pulp/paper-mill sludge and sewage sludge with supercritical water treatment, Bioresour. Technol. 101 (2010) 2713–2721, https://doi.org/10.1016/j.biortech.2009.11.106.

[37] A.A. Peterson, F. Vogel, R.P. Lachance, M. Fröling, M.J. Antal, J.W. Tester, Thermochemical biofuel production in hydrothermal media: a review of sub- and supercritical water technologies, Energy Environ. Sci. 1 (2008) 32–65, https://doi.org/10.1039/b810100k.

[38] D. Zhou, L. Zhang, S. Zhang, H. Fu, J. Chen, Hydrothermal liquefaction of macroalgae enteromorpha prolifera to bio-oil, Energy Fuels 24 (2010) 4054–4061, https://doi.org/10.1021/ef100151h.

[39] A.A. Peterson, R.P. Lachance, J.W. Tester, Kinetic evidence of the maillard reaction in hydrothermal biomass processing: glucose−Glycine interactions in high-temperature, high-pressure water, Ind. Eng. Chem. Res. 49 (2010) 2107–2117, https://doi.org/10.1021/ie9014809.

[40] W.T. Chen, Y. Zhang, J. Zhang, G. Yu, L.C. Schideman, P. Zhang, M. Minarick, Hydrothermal liquefaction of mixed-culture algal biomass from wastewater treatment system into bio-crude oil, Bioresour. Technol. 152 (2014) 130–139, https://doi.org/10.1016/j.biortech.2013.10.111.

[41] T.H. Pedersen, I.F. Grigoras, J. Hoffmann, S.S. Toor, I.M. Daraban, C.U. Jensen, S. B. Iversen, R.B. Madsen, M. Glasius, K.R. Arturi, R.P. Nielsen, E.G. Søgaard, L. A. Rosendahl, Continuous hydrothermal co-liquefaction of aspen wood and glycerol with water phase recirculation, Appl. Energy 162 (2016) 1034–1041, https://doi.org/10.1016/j.apenergy.2015.10.165.

[42] P. Biller, A. Roth, Hydrothermal Liquefaction: A Promising Pathway towards Renewable Jet Fuel, 2018, pp. 607–635, https://doi.org/10.1007/978-3-662-53065-8_23.

[43] A.A. Shah, S.S. Toor, T.H. Seehar, R.S. Nielsen, A.H. Nielsen, T.H. Pedersen, L. A. Rosendahl, Bio-crude production through aqueous phase recycling of hydrothermal liquefaction of sewage sludge, Energies 13 (2020) 493, https://doi.org/10.3390/en13020493.

[44] D. López Barreiro, M. Bauer, U. Hornung, C. Posten, A. Kruse, W. Prins, Cultivation of microalgae with recovered nutrients after hydrothermal liquefaction, Algal Res. 9 (2015) 99–106, https://doi.org/10.1016/j.algal.2015.03.007.

[45] C.U. Jensen, J.K. Rodriguez Guerrero, S. Karatzos, G. Olofsson, S.B. Iversen, Fundamentals of Hydrofaction^{TM}: renewable crude oil from woody biomass, Biomass Convers. Biorefinery 7 (2017) 495–509, https://doi.org/10.1007/s13399-017-0248-8.

[46] S.S. Toor, L. Jasiunas, C.(Charles) Xu, I.M. Sintamarean, D. Yu, A.H. Nielsen, L. A. Rosendahl, Reduction of inorganics from macroalgae Laminaria digitata and spent mushroom compost (SMC) by acid leaching and selective hydrothermal liquefaction, Biomass Convers. Biorefinery 8 (2018) 369–377, https://doi.org/10.1007/s13399-017-0290-6.

ISSN (online): 2446-1636
ISBN (online): 978-87-7210-646-5

AALBORG UNIVERSITY PRESS