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HYDROTHERMAL LIQUEFACTION OF SEWAGE SLUDGE

INVESTIGATION OF THE EFFECTS OF PROCESS PARAMETERS, RECYCLING OF AQUEOUS PHASE, AND CO-LIQUEFACTION ON BIO-CRUDE PROPERTIES

BY
AYAZ ALI SHAH

DISSERTATION SUBMITTED 2021

AALBORG UNIVERSITY
DENMARK

Hydrothermal liquefaction of sewage sludge.

Investigation of the effects of process parameters, recycling of aqueous phase, and co-liquefaction on bio-crude properties

A SUBTITLE

by

Ayaz Ali Shah

AALBORG UNIVERSITY
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Dissertation submitted

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Preface

This PhD thesis is compiled as an accomplishment of the PhD project that I have conducted in the Advanced Biofuels research group at the Faculty of Engineering and Science, Aalborg University, Denmark.

I would present my sincere gratitude to my supervisor, Associate Prof. Saqib Sohail Toor for his guidance and motivation during the entire period of this PhD project. I enjoyed this three-year journey of my PhD within your group.

Furthermore, I would like to acknowledge Prof. Lasse Aistrup Rosendahl for providing laboratory facilities and sharing his deep knowledge about the field of HTL. With this, I would also appreciate the services of Associate Prof. Asbjørn H. Nielsen for his productive collaboration and key contribution for ICP-AES analysis.

Additionally, I would like to say thank you to all my past and present colleagues of the Advanced Biofuel research group, and to the technicians from the workshop, who played a very little but important role in the accomplishment of this PhD project.

In last, I would like to thank my family, especially my parents and my wife who prayed and supported me morally throughout this irregular and adventurous journey of my PhD project.

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Nomenclature

Abbreviations, Units, and Acronyms

CH_4	Methane
CF	Crude fats
CP	Crude proteins
CO	Carbon monoxide
CO_2	Carbon dioxide
CR	Carbon recovery
daf	Dry ash-free
db	Dry basis
DEE	Diethyl ether
ER	Energy recovery
EU	European Union
FC	Fixed carbon
GC	Gas chromatograph
GC-MS	Gas chromatography-mass spectrometry
GHG	Greenhouse gas
H_2	Hydrogen
HPLC	High-pressure liquid chromatography
HHV	Higher heating value
HTL	Hydrothermal liquefaction
ICP-AES	Inductively coupled plasma-atomic emission spectroscopy
NR	Nitrogen recovery
ppm	Parts per million
SEM	Scanning electron microscopy
SM	Swine manure
SS	Sewage sludge
Tc	Critical temperature
TEA	Techno-economic analysis
TGA	Thermogravimetric analysis
TN	Total nitrogen
TOC	Total organic carbon
VM	Volatile matter

Thesis details

Thesis Title: Hydrothermal liquefaction of sewage sludge. Investigation of the effects of Process parameters, recycling of aqueous phase, and co-liquefaction on bio-crude properties.

Ph.D. Student: Ayaz Ali Shah

Supervisor: Associate Prof. Saqib Sohail Toor, Aalborg University, Denmark.

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

[A]   Shah AA, Toor SS, Conti F, Nielsen AH, Rosendahl LA. Hydrothermal liquefaction of high ash containing sewage sludge at sub and supercritical conditions. Biomass and Bioenergy. 135 (2020) 105504. https://doi.org/10.1016/j.biombioe.2020.105504.

[B]   Shah AA, Toor SS, Seehar TH, Nielsen RS, H. Nielsen A, Pedersen TH, et al. Bio-Crude Production through Aqueous Phase Recycling of Hydrothermal Liquefaction of Sewage Sludge. Energies. 13**, (2020**), 493. https://doi.org/10.3390/en13020493.

[C]   Shah AA, Toor SS, Seehar TH, Sadetmahaleh KK, Pedersen TH, Nielsen AH, et al. Bio-crude production through co-hydrothermal processing of swine manure with sewage sludge to enhance pumpability. Fuel. 288, (2021), 119407. https://doi.org/10.1016/j.fuel.2020.119407.

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

Publications

[D]   Seehar TH, Toor SS, Shah AA, Pedersen TH, Rosendahl LA. Biocrude Production from Wheat Straw at Sub and Supercritical Hydrothermal Liquefaction. Energies 13, (2020), 3114. https://doi.org/10.3390/en13123114.

[E]   Seehar TH, Toor SS, Shah AA, Nielsen AH, Pedersen TH, Rosendahl LA. Catalytic hydrothermal liquefaction of contaminated construction wood waste for biocrude production and investigation of fate of heavy metals. Fuel Process Technol. 212, (2021), 106621. https://doi.org/10.1016/j.fuproc.2020.106621.

[F]   Toor SS, Conti F, Shah AA, Seehar TH, Rosendahl LA. "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.

Contribution to conferences

- Shah AA, Toor SS, Conti F, Pedersen TH, Rosendahl LA."Hydrothermal liquefaction of high ash containing sewage sludge at sub and supercritical condition", Poster presentation at EUBCE 2019, Lisbon (Portugal), 27-30th May 2019.

- Shah AA, Toor SS, Seehar TH, Pedersen TH, Rosendahl LA. "Bio-crude production through co-hydrothermal processing of swine manure with sewage sludge to enhance pumpability". Thermal & Catalytic Sciences (TCS-2020), (Washington State, USA), 3-7th October 2020.

- Shah AA, Toor SS, Seehar TH, Pedersen TH, Rosendahl LA."Hydrothermal Liquefaction of Sewage Sludge with Recirculation of Pretreated Aqueous Phase from Activated Carbon". 2nd Bioenergy Sustainability Conference, AIChE-group of conferences (Newyork, USA), 13-15th October-2020.

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 visible changes in climate change lead the world towards the usage of renewable fuels, particularly in the transport sector to control GHG emissions and counter the dependence on fossil fuels.

Hydrothermal liquefaction (HTL) is an efficient technology that thermochemically converts a variety of feedstocks into high-energy bio-crude. Nowadays, sewage sludge is considered to be a suitable candidate for renewable fuel production due to its cheap cost and abundant production. Thus, HTL is proposed as alternative disposal and simultaneous energy extraction process in the form of bio-crude from sewage sludge in promoting the principle of the circular economy. This PhD project investigated the three aspects of the valorization of the sewage sludge through HTL, its processibility at different temperatures, the impact of aqueous phase recycling on bio-crude properties, and its compatibility of co-liquefaction with other biomass like swine manure.

In the first study, the effects of process conditions (temperature and catalyst) on the conversion of sewage sludge via HTL were deeply investigated. Four experiments were conducted at the sub and supercritical conditions 350 and 400°C, with and without alkali catalyst K_2CO_3. The results showed that in all the experiments, sufficient bio-crude yields (40%) were obtained. Whereas alkali catalyst slightly increased the bio-crude yield with reduction of solid residue at both temperature conditions. Moreover, the addition of the catalyst resulted in lower nitrogen content in the bio-crude with the average HHVs of 35 to 36 MJ/kg. The TGA analysis showed that almost 60% mass of all the bio-crudes was converted into gasoline, diesel, and jet fuel fractions. The bio-crude was composed of mostly N-heterocyclics, amides, ketones, acids, alcohols, and some fatty acids. During experiments, a substantial amount of organic carbon (19 to 27 g/l) was dissolved in the aqueous phase, particularly at supercritical conditions. The majority of the ash elements (Al, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Zn) were recovered in the solid phase. While potassium and sodium showed a different trend as they were accumulated 30 to 50% in the aqueous phase.

As the first study led to the higher carbon loss to the aqueous phase. In this context, a sustainable approach of aqueous phase recycling was adopted in the second study to recover that dissolved carbon from the aqueous phase. Eight experiments of sewage sludge were conducted at subcritical temperature 350°C with the recycling of the aqueous phase. The results revealed that aqueous phase recycling increased the bio-crude yield and energy recovery by 50% after eight rounds of recycling. However, the quality of the bio-crude was affected by higher nitrogen content (double with respect to the baseline experiment). The aqueous phase was comprised of mostly N-heterocyclic, short-chain acids (acetic acid, etc), alcohols, and ketones. Therefore, acetic acid (2.5% of the total slurry) was also employed as a catalyst to explore its catalytic effect, but no significant effect on bio-crude yield and quality was noticed.

Aqueous phase recycling did not impact the distribution of the inorganic elements, as more than 80% of the elements were shifted to the solids phase.
Phosphorus was mainly recovered in the solid phase, this implies that the solid phase has a good potential to be used as an extracting material for phosphorus recovery in the form of struvites.

The third study explored the co-liquefaction of swine manure and sewage sludge-based upon their pumpability analysis (wet received basis). The syringe test demonstrated that swine manure was not pumpable due to its fibrous nature but it was efficiently pumped by the addition of sewage sludge as a co-substrate. For the detailed examination, SEM analysis was conducted to unfold the morphology of both of the feedstocks. A maximum of 80% swine manure was pumped with sewage sludge. Subsequently, five co-liquefaction experiments were performed on samples SM, SS, SM/SS (50:50), SM/SS (80:20), and SM/SS (20:80). The higher bio-crude yield was obtained from mixed samples. The bio-crudes from sewage sludge containing samples had higher carbon and HHVs as compared to Swine manure alone. Almost 65% of the bio-crude was formed of volatile components within the range of 350° C. The aqueous phase analysis showed the values of TOC in the range of (26 to 40 g/l) and TN (3 to 14 g/l), and half of the TN was comprised of inorganic nitrogen. ICP-AES measurements indicated that the transference of inorganic elements was not highly affected by different mixing ratios of the feedstocks. A similar pattern of the migration of inorganic elements in the solid phase was observed as in the first and second studies.

Resume in Danish

De synlige ændringer i klimaet fører verden mod brugen af vedvarende brændstoffer, især i transportsektoren, for at kontrollere udledningen af drivhusgasser og mindske afhængigheden af fossile brændstoffer.

Hydrothermal Liquefaction (HTL) er en effektiv teknologi der termokemisk konverterer forskellige råmaterialer til bio-råolie. Spildevandsslam bliver betragtet som en egnet kandidat til vedvarende brændstofproduktion på grund af billig pris og rigelig produktion. Derfor foreslås HTL som alternativ måde til at afskaffe spildevandsslam samtidig med at energi kan udvindes i processen i form a bio-råolie fra spildevandsslammet, hvilket fremmer den cirkulære økonomi. I dette PhD projekt er tre aspekter af valorissering af spildevandsslam gennem HTL undersøgt, spildevandsslammets bearbejdelighed ved forskellige temperaturer, indflydelsen af genanvendelse af vandfasen i processen på bio-råoliens egenskaber, og kompatibilitet ved co-liquefaction med andet biomasse som svinegylle.

Det første studie undersøger grundigt procesbetingelsernes (temperatur og katalysator) indflydelse på konverteringen af spildevandsslam gennem HTL. Fire eksperimenter blev udført ved sub- og superkritiske betingelser 350 og 400°C, med og uden alkalisk katalysator K_2CO_3. Resultaterne viste at der blev opnået tilstrækkelig udbytte af bio-råolie. Desuden øgede den alkaliske katalysator udbyttet af bio-råolie en smule med reduktion af fast rest ved begge temperaturbetingelser. Tilføjelsen af katalysator medførte også et lavere indhold af nitrogen i bio-råolien som havde en gennemsnitlig øvre brændværdi på 35 til 36 MJ/kg. TGA analysen viste at næsten 60% af massen af bio-råolie blev omdannet til benzin-, diesel- og flybrændstof-fraktioner. Bio-råolien var sammensat af overvejende N-heterocyclics, amider, ketoner, syrer, alkoholer, og nogle fedtsyrer. Under eksperimenterne, blev en betydelig mængde organisk kulstof (19 til 27 g/l) opløst i vandfasen, især ved superkritiske betingelser. Hoveddelen af grundstofferne i asken (Al, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Zn) blev genfundet i den faste fraktion. Mens kalium og natrium viste en anden tendens da 30-50% af det samlede sig i vandfasen.

I det første studie blev der identificeret et betydeligt tab af kulstof i vandfasen. I den sammenhæng blev en bæredygtig fremgangsmåde til genanvendelse af vandfasen taget i brug i andet studie for at genvinde det opløste kulstof fra vandfasen. Otte eksperimenter med spildevandsslam blev udført ved en subkristisk temperatur på 350°C med genanvendelse af vandfasen. Resultaterne viste at genanvendelse af vandfasen øgede udbyttet af bio-råolie og energigenvindingen med 50% efter otte runder af genanvendelse. Dog blev kvaliteten af bio-råolien påvirket af et højere indhold af nitrogen (dobbelt sammenlignet med udgangspunktet). Vandfasen bestod hovedsageligt af N-heterocyclics, kortkædede syrer (acetylsyre osv.), alkoholer og ketoner. Derfor blev acetylsyre (2.5% af den samlede opløsning) også anvendt som

katalysator for at undersøge dens katalytiske effekt, men der blev ikke observeret en signifikant effekt på udbyttet af bio-råolie og kvalitet. Genanvendelsen af vandfasen påvirkede ikke udbredelsen af uorganiske grundstoffer, da mere end 80% af grundstofferne migrerede til den faste fraktion. Fosfor blev hovedsageligt fundet i den faste fraktion. Dette tyder på at den faste fraktion har et potentiale som materiale til udvinding af fosfor i form af struvit.

Det tredje studie undersøger co-liquefaction af svinegylle og spildevandsslam (SS) baseret på en analyse af pumpbarhed (fugtigt som modtaget). Sprøjte testen demonstrerede at det ikke var muligt at pumpe svinegylle (SG) på grund af gyllens fibrøse natur, men det blev effektivt pumpet efter tilføjelse af spildevandsslam som co-substrat. En SEM analyse blev udført for en mere detaljeret undersøgelse af opbygningen af begge råmaterialer. Et maksimum på 80% svinegylle blev pumpet med spildevandsslam. Efterfølgende blev fem co-liquefaction eksperimenter udført på prøver af SG, SS, SG/SS (50:50), SG/SS (80:20), og SG/SS (20:80). Det højeste udbytte af bio-råolie blev opnået ved de blandede prøver. Bio-råolien fra prøverne med spildevandsslam havde en højere øvre brændværdi sammenlignet med bio-råolien fra prøverne med svinegylle alene. Næste 65% af bio-råolien bestod af flygtige bestanddele ved en temperatur på 350°C. Analysen af vandfasen viste at værdierne af TOC i intervallet (26 til 40 g/l) og TN (3 til 14 g/l), og halvdelen af TN blev udgjort af uorganisk nitrogen. ICP-AES målinger indikerede at overførslen af uorganiske grundstoffer ikke blev påvirket i særlig høj grad af forskellige blandingsforhold af råmaterialerne. Migrationen af uorganiske elementer i den faste fraktion mindede om hvad der blev observeret i første og andet studie.

Extended Summary

Chapter 1

1. Introduction

1.1. Climate change and CO_2 emissions

The global rise in population has created serious environmental issues over the years. Since 1880, the average Earth´s temperature has raised by 0.8°C, of which two-thirds of the temperature rise has been taken place since 1975 [1]. The threatening effects of climate change are perceptible and becoming more alarming in the form of global warming, the rise in sea levels, and the increasing rate of extreme events, like heavy rains, hurricanes, and heat waves [2].

The increasing rate of anthropogenic greenhouse gas emissions has been noticed as a dominant cause of global warming. Over the last 150 years, the CO_2 level in the atmosphere has rapidly incased from 280 to 400 ppm. It is reported that from only fossil fuel combustion and industrialization sector; the CO_2 emissions contributed 78% of the total increase in GHG from 1970 to 2010. It is predicted that, without controlling or adopting the mitigation measures, the average global surface temperature will rise by 3.7-4.8°C [3]. To cope up with climate change issues, more than 190 countries signed the Paris Agreement in 2015, which includes the restrictions and mitigation measures to control the increase in global average temperature below 2°C and to limit this ultimately to 1.5°C in the near future [4]. The generation of electricity and heat, and automobile transport sectors are the main sources of CO_2 emissions that cover almost 66% of the total emissions. In 2016, the total GHG emissions from European Union countries EU-28, the transport sector lonely produced 27% of the CO_2 emissions, which is 1145 times higher than 1990 [5]. From the transport sector, the road transport sector is sharing the maximum percentage of 74% followed by the aviation and maritime sectors [6], as illustrated in Figure 1.

1.2. Renewable fuel in the transport sector

It is stated that renewable energy only contributes 3.4% in the transport sector, much lower than electricity 24%, and heat generation 10.3% in 2017 [7]. The higher portion of the renewables in the transport sector 7.6% is noticed in a similar year, while more efforts need to be taken to reach the target of 10% for upcoming years [8].

Recently, both biofuels and electric-vehicles have played a key role in terms of decarbonization of the transport sector. Renewable electricity particularly runs the rail system. Whereas electrification is only suitable for light vehicles, and it is currently limited. Until now, Electrification is not feasible for the heavy transport sector like,

marine, aviation, and long haul road cargo sectors, which are expected to heavily rely on biofuels.

The main alternative to petroleum fuel is biofuel. Because biofuel can be blended with petroleum crude and can be used in the commercially available combustion engines. However, according to the sustainable development strategy (SDS), biofuel shares only 3% of the total fuel demand in 2018. It requires to be three times to achieve the desired target of 10% in 2030. In the current situation, biofuel is associated with light vehicles and road freight, while it is almost negligible in the aviation and marine sector, eg. biofuel contributed less than 0.01% in the aviation sector in 2018 [9].
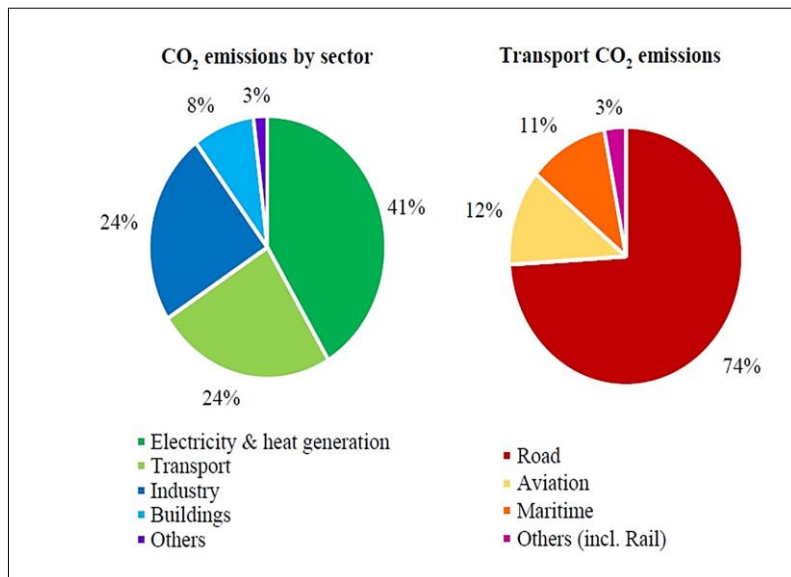
Figure 1. CO_2 emissions from different sectors, adopted from [6,37].

For the reduction in GHG emissions, it is important to ensure the higher productivity of the biofuel, which can turn into drop-in fuels to meet the strict regulations for the aviation sector. The drop-in fuels can be defined as *liquid bio-hydrocarbons that are functionally equivalent to petroleum fuels and are fully compatible with existing petroleum infrastructure"* [10]. The main methods of the production of the drop-in fuels are given below:

- Thermochemical technologies: These technologies work under thermal conversion (280-800°C) of the biomass at higher pressures like Hydrothermal liquefaction, pyrolysis, and gasification. These technologies produce heavy bio-crude, which can be further treated to obtain drop-in fuels.

- Biochemical technologies: These technologies work under biological or enzymatic activities conversion of sugars and cellulose to hydrocarbons, or fatty acids.

- Oleochemical technologies: These technologies work under hydro-processing of high lipid-containing feedstock, which produces hydro-processed esters and fatty acids.

1.3. Hydrothermal Liquefaction (HTL)

Hydrothermal liquefaction is one of the promising techniques for the production of high energy bio-crude. HTL works under moderate temperatures (300-450°C) and high pressures (15-35 MPa) [11]. It produces the bio-crude within 15 minutes, which natural fossils take millions of years to convert into the fossil-crude.

Since HTL is a water-based process, wherein water changes its properties dramatically near and above the critical point (Tc = 374°C and pc = 22 MPa). At this point, the density and dielectric constant of the water decrease from 800 to 150 kg/m^3 and 80 to ~ 2 respectively. These special properties make water to act like a non-polar substance. The ionic product (K_w = [H_3O^+] [OH^-]), which is the indicator of explaining ionic or radical reactions. It first increases and then rapidly declines as the temperature approaches to a critical point. This leads to an increase in the production of the char and gases at supercritical conditions [12]. When HTL is performed at higher pressures 350 bar, the ionic reactions still dominate over the formation of the radicals. This develops further suitability to perform HTL at supercritical states, with higher degree deoxygenation [13,14].

The indispensability of water makes HTL an ideal technology for the processing of wet feedstock (70-85% moisture) and improves the overall process economy by avoiding the expensive drying process. This feature broadens the scope of the HTL process for utilization of the variety of feedstocks containing (carbohydrates, lignin, protein, and lipids) [15].

When wet biomass is heated up under high pressures, it starts the depolymerization of the organic matter via several reactions like hydrolysis, decarboxylation, and dehydration. These reactions form water-soluble intermediates which repolymerize through condensation and form bio-crude. Gas-phase is also produced which contained almost 70-80% of CO_2, followed by other gases like H_2, CH_4, and CO [16]. The basic concept of the HTL is sketched in Figure 2.

The major goal behind the liquefaction of biomass is to reduce the oxygen content, as conventional petroleum contains less than (<1%) of the oxygen content. In HTL processing, the dehydration and decarboxylation reactions take out the oxygen in the form of CO_2 and H_2O. Through the HTL process, 60-70 % of the carbon from the feedstock is usually transferred to the bio-crude with HHVs of 30-38 MJ/kg. The bio-

crude yield and quality vary with several factors such as the composition of the feedstock, process temperature, residence time, type and dosage of catalyst, etc.
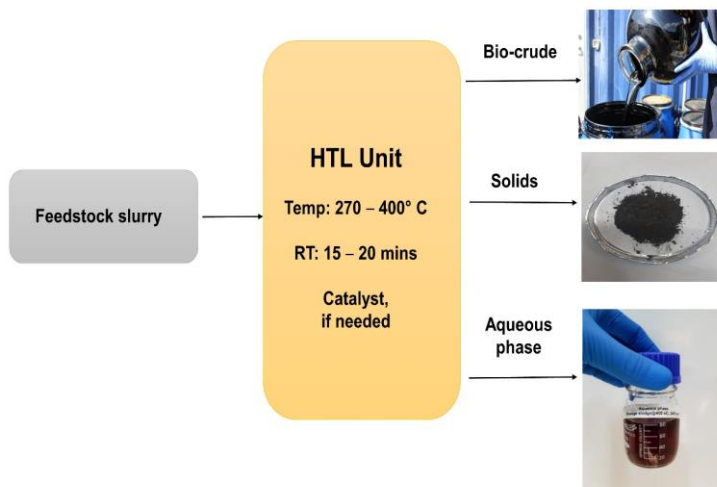
Figure 2. The basic concept of HTL processing.

By the selection of the right parameters, higher bio-crude yields can be obtained. The HTL generated bio-crude still contains heteroatoms as almost 10-20% oxygen, some amount of nitrogen, and sulfur. The concentration of heteroatoms is correlated with feedstock type. These heteroatoms can further be removed by upgrading the bio-crude through the hydro-treatment process.

Depending upon the level of blending, the bio-crude can be directly upgraded in the refinery units. To make this process further economical, nowadays different catalysts NiMo and CoMo are being added with bio-crude to improve the efficiency of the hydro-treatment process. Therefore, HTL with upgrading (hydrotreatment) is considered as a comprehensive process for producing the sustainable quality of the drop-in fuels.

1.4. Utilization of the sewage sludge in HTL

Since HTL is an emerging technology for bio-crude production, the price of the feedstock affects the overall economy and sustainability of HTL processing [17]. It was reported from a techno-economic analysis (TEA) study that the amount of the feedstock is around one-third of the final fuel price [18]. Hence the utilization of the waste feedstocks such as sewage sludge and animal manure could significantly reduce the overall cost of the HTL processibility and promotes the principles of the circular economy [19].

Sewage sludge contains organic-rich material in the form of carbohydrates, proteins, and fats, and a high amount of inorganics with almost 75 to 95% of the moisture [20,21]. It carries contaminants both in the form of inorganics (heavy metals) and organics (polycyclic aromatic hydrocarbons, polychlorinated Biphenyls, pesticides, nanoparticles, etc.). Apart from this, sewage sludge is considered to be hazardous due to the existence of pathogens, like bacteria, protozoa, and other viruses, which lead to threat for living beings [22].

Earlier studies highlighted that in EU-27, around 11 million dried tons of sewage sludge is produced till 2008. From that Germany, United Kingdom, Spain, and France contributed mainly 54%, and it has been increased to over 13 million dried tons in 2020 (Table 1) [23].

Table 1. Sewage sludge production in EU-27, adopted from [23].

S. No.	Country	Sewage sludge - Dried Tons 10^3 / year	Production by Percent
1	Germany	2170	19.80
2	United Kingdom	1771	16.16
3	Spain	1121	10.23
4	France	1059	9.67
5	Italy	1053	9.61
6	Netherlands	348	3.18
7	Austria	254	2.32
8	Sweden	210	1.92
9	Portugal	189	1.72
10	Finland	148	1.35
11	Denmark	140	1.28
12	EU- 27	10957	100.00
	EU- 27 in 2020	Over 13000	------

The disposal of sewage sludge needs special treatment in wastewater systems, which require extra cost and high energy, thus, the safe disposal of sewage sludge has become a bottleneck nowadays [24].

There are two main ways (direct and indirect methods) for the handling and disposal of sewage sludge in the EU. The direct methods are the agricultural sector, and incineration plants (for heat generation). While the indirect methods are thermochemical technologies which include gasification, pyrolysis, and HTL. In the EU, only 38 to 40% of the sewage sludge is being recycled into the agricultural sector due to the declaration of strict regulations against utilizing sludge containing contaminants from EU member states [25]. On the other hand, incineration is based

on combustion principles that burn all the valuable organics of the sewage sludge for heat generation [26]. The cost associated with treated dewatered sewage sludge for the agricultural, with household waste increased up to 210–300 EURO/tonnes-dry-matter [27].

Reutilizing waste sources is a promising option for the formation of valuable products, which supports the concept of a green environment, and biofuel production technologies simultaneously. In the past researchers tried to valorize the sewage sludge through various methods including thermochemical and biological processes, like pyrolysis [28], gasification [29–31], and anaerobic digestion [32,33] for the formation of a variety of products (bio-crude, hydrogen, methane gas, etc.). Gasification and anaerobic digestion processes are particularly recognized for gas production, whereas pyrolysis works on dried feedstocks and leaves a substantial amount of oxygen in the bio-crude.

The HTL technology can easily stand by these challenges due to its high flexibility towards the wet feedstocks, making it suitable for the conversion of the organic matter to bio-crude. Sewage sludge also consists of a high amount of nitrogen and phosphorus which are considered valuable components for the plant's growth. Phosphorus is currently is being extracted from the rocks, which are finite and nonrenewable. In Nitrogen-containing fertilizers, nitrogen was added from the air which consumes an enormous amount of energy and cost. However, in HTL processing, these elements tend to accumulate in the solid and aqueous phases that are the by-products along with bio-crude.

Another advantage of processing waste in HTL is the higher temperatures, which destroy and eliminate biological pathogens and ensure the safe handling of HTL products after the post liquefaction. These all aspects of HTL demonstrate the sustainability of the HTL process.

1.5. Overview of the PhD project and thesis outline

From the aforementioned background, this PhD project aims to utilize the organic potential of the sewage sludge for bio-crude production via HTL processing. In this PhD project, various aspects of the HTL of sewage sludge are addressed like temperature, catalyst, water phase recirculation, pumpability, and co-liquefaction of sewage sludge with other biomass. All these factors are elaborated in detail in the following three studies.

The first study investigates the effect of the temperatures (subcritical and supercritical) and alkali catalyst on the product distribution, especially on the properties of the bio-crude. The main objective of this study is to determine the optimal conditions for the production of the bio-crude by using high ash containing sewage sludge. The fate of inorganics was also explored in this study.

The second study is focused on the detailed investigation of the effects of aqueous phase recycling on the bio-crude properties at subcritical conditions. Previously HTL based aqueous phase was optimized via gasification and anaerobic digestion, by over-passing them, recycling back to the HTL unit could be the best way to establish the sustainability of the HTL processing. Furthermore, acetic acid was also employed as a catalyst to examine its catalytic effect on the bio-crude properties.

The third study is based on the valorization of the sewage sludge as a co-substrate with another waste material swine manure to enhance both pumpability and overall energy recovery of the bio-crude. This study unfolds all the possible challenges of the pumpability of the swine manure. Additionally, the synergistic effects of the co-liquefaction on bio-crude yield and quality were investigated in a detailed manner.

The main outcomes obtained from the PhD project in the light of published publications (Paper A, Paper B, and Paper C), are described in the following chapters.

- Chapter 1: Introduction of the research field.
- Chapter 2: Overall methodology of the experimental work and challenges
- Chapter 3: Results of study 1 (Effect of Process parameters and catalyst on the bio-crude production via Sewage sludge)
- Chapter 4: Results of study 2 (Impact of aqueous phase recycling on the bio-crude properties from sewage sludge).
- Chapter 5: Results of study 3 (Co-liquefaction of the sewage sludge and swine manure, its impact on the pumpability, and investigation of the co-liquefaction synergies on HTL products)
- Chapter 6: The main conclusions drawn from the conducted studies.
- Chapter 7: Recommendations are suggested for future studies.

Chapter 2

Methodology

The second chapter provides the details of all the methodologies that have been adopted in this PhD project. For the comprehensive understanding of the obtained results, this methodological information is very necessary and has high relevance with the overall experimental setup, and recovery of the products. Besides, this chapter also highlights the major challenges faced during the experimental activities.

2.1. Feedstock characterization

For all the studies in this PhD project, the secondary sewage sludge was selected (both wet and dried basis). For the first study, secondary sewage sludge (as-received basis, 27% dry matter) was collected from a wastewater treatment plant from Aalborg East. For the second study, dried secondary sewage sludge pellets were chosen, and thereafter the pellets were grinded by cyclone mill (Foss, Cyclotec 1093) at a particle size of 200 um. For the third study, two feedstocks, secondary sewage sludge and swine manure (as-received basis, both having ~25 % dry matter) were taken for the HTL experiments. The swine manure was collected from the cattle manure farm located in the Aalborg South. The swine manure was mechanically dewatered before being collected by Aalborg university staff.

While carrying out all the experimental activities, the safety precautions were strictly followed to avoid contamination. Samples were handled and placed in the allocated areas for the biohazards, and the authorized person was vaccinated for Polio, hepatitis A, and Tetanus. Before the HTL experiments, the sewage sludge was characterized for its moisture content (MC), inorganic content, and elemental composition. The MC was determined by the moisture analyzer (Kern, MLS) at 120°C. The MC is an important parameter for making the slurry, which describes how much water is required to obtain the desired dry matter content (20-25%) for the experiments.

The ash was measured by heating the dried sewage sludge sample in the electric muffle furnace from room temp to 775°C. The dried sample was used for the ash determination to reduce the risk of error as sewage sludge often contains almost 75 to 90% of moisture. For further confirmation, the thermogravimetric analysis (TGA) was performed at the same temperatures 775°C. However, the limitation of sample weight for TGA could give a bit of uncertainty to the ash values. Thereby furnace values were highly preferred over TGA values for the ash content. The carbohydrates were calculated by using the formula [34]:
Carbohydrates=[(Volatile Matter – Fixed Carbon)–(Crude Proteins + Crude Fats)].
Crude proteins were estimated by multiplying the elemental nitrogen with 6.25 [35].
Whereas the crude fats or lipids were quantified by the Soxhlet method [36].

The elemental composition for the pre-dried sewage sludge sample was analyzed by an elemental analyzer (Perkin Elmer, 2400 Series II by operating at CHN mode). Whereas oxygen was calculated by difference. Sulfur was detected by the ICP-AES analysis. The composition of the sewage sludge used in the first study is given in Table 2.

Table 2. Composition of sewage sludge.

Proximate and ultimate analysis (wt. %)						
MC [a]	VM	FC [c]	Ash	Crude Proteins [b]	Crude Fats [b]	Carbohydrates [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) [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] By Difference.

2.2. Experimental set-up for HTL experiments

The HTL experiments for the first and second studies were carried out in stainless steel (grade 316) micro-batch reactors of 12 ml. While 41 ml reactor was used for the second study (Figure 3). The objective behind the selection of a bigger reactor was to produce a sufficient amount of the aqueous phase which could recirculate back to the reactor for the recycling experiments.

In the first and third studies, the sewage sludge (as-received basis with 75 to 77 % moisture) was injected into the reactor through the syringe. For the second study, the dried sewage sludge powder was injected by the spatula. Subsequently, the solution of the aqueous phase (35-50 % aqueous phase + rest of the freshwater) was added with powdered sewage sludge to adjust the dry matter content (25%) of the slurry.

The reason for choosing the diluted aqueous phase for the recycling experiments is due to the inconsistent production of the aqueous phase, which is associated with a complicated separation procedure. Only 50-60% of total water was recovered as a pure aqueous phase without the addition of any solvent (acetone). The rest of the residual water was collected by applying solvent dichloromethane (DCM). In last, the DCM was allowed to evaporate to obtain the final bio-crude yield.

Once the slurry (catalytic (K_2CO_3) or non-catalytic) was loaded, the reactor was made tightly closed and then purged with nitrogen gas of 10 to 15 bar. In catalytic slurries, K_2CO_3 was used 2 to 2.5 % of the total mass of the prepared slurry, as discussed in section 2.3.2. The pressure transducers and thermocouples were attached to reactors for the continuous monitoring of the pressure and temperature during the HTL experiments. Once the desired temperature was stabilized (350 or 400°C), the reactors were submerged into the pre-heated fluidized sand bath (Techne SBL-2D). To ensure

the proper mixing of the slurry inside the reactor, the mechanical agitator was provided from the top of the sandbath.

Figure 3. The reactor system in HTL experiments

The major aim behind the selection of the batch reactors is to practically screen the conditions, and acquire fundamental data to implement optimum conditions for the continuous scale. Secondly, the batch system is a closed system from which minimum losses of the products can be achieved. In batch systems, the micro-reactors are easy, fast, and reproducible due to their small scale [37]. Moreover, they have an edge over the autoclave, as the autoclave works on slow heating and takes longer times for the heating, which could result in repolymerization reactions and form more char in the product phase.

The micro-batch reactors produce a high heating rate of (250-450 K min-1) [38], which suppresses the char formation. However, the small volume of the micro-reactors gives low amounts of products and increases complexities during product separation, which could incorporate the inconsistency of the results. For these reasons, all the experiments were conducted in duplicates and sometimes triplicates to reduce the risk of errors. A schematic diagram for the overall HTL methodology adopted in the first study is illustrated in Figure 4.
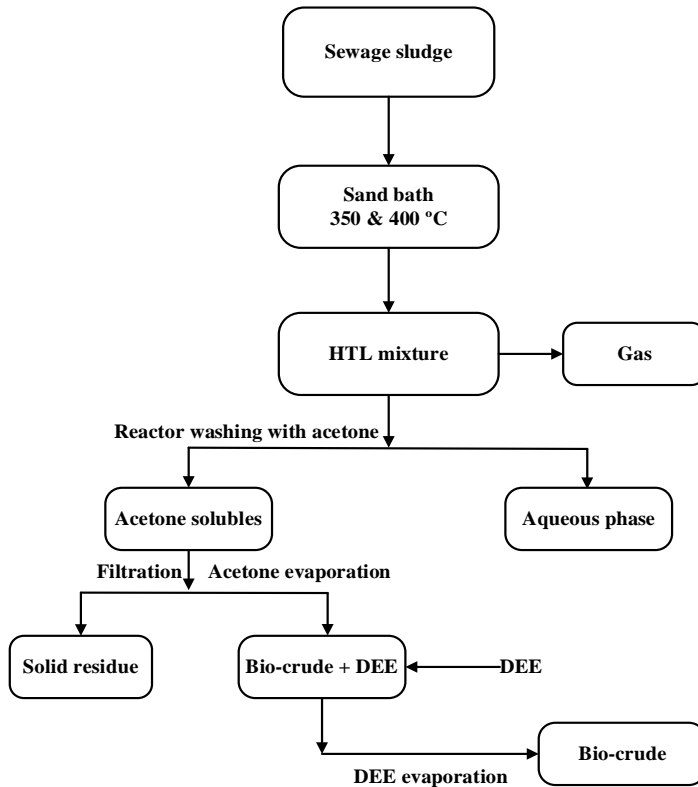
Figure 4. Different steps involved in HTL SS, used in the first study.

2.3. HTL process conditions

2.3.1 Reaction temperature

The temperature is one of the major parameters for the conversion of biomass. Although the majority of the studies were conducted in the subcritical range, maximum up to 300- 370°C [39–41]. There are several reasons for performing HTL experiments in subcritical or near-critical points of water, like the lower dielectric constant, lower density, and a higher degree of hydrophobicity. However, some other publications reported that the supercritical conditions (above 374°C) improve the degree of deoxygenation in the bio-crude [42,43].

Castello et al. reported in the latest review on continuous HTL processing that maintaining supercritical conditions is not very energy extensive due to the lower compressibility and variations in specific heat capacity [11]. Additionally, the continuous plant "CBS1" located at (Aalborg University Denmark), had already concluded an improved bio-crude quality when processing at 400°C [13,44]. In the

first study, both sub and supercritical (350 and 400°C) conditions were used to get the comparative information of the optimum reaction temperatures. For the second and third studies, subcritical conditions (350° C) were selected on account of higher bio-crude yield and energy recovery.

2.3.2. Catalyst

Catalyst also plays a vital role in the reaction medium, mostly two types of catalysts are being used in the field of the HTL, homogenous and heterogeneous [14]. Catalyst promotes the rapid degradation with a higher degree of hydrolysis and reduces char production. Depending upon the composition of the feedstock, both acidic and alkaline conditions are favorable for the conversion of biomass [45].

Acidic conditions give rapid rates of hydrolysis than alkaline conditions, but conversely acidic conditions produce a higher amount of char, which can be beneficial for hydrothermal carbonization. Since the main goal of the HTL is bio-crude production, thus over the years homogenous catalysts (K_2CO_3, Na_2CO_3, NaOH, etc) have been proved as effective materials for the feedstock conversion in HTL.

It has been established that a homogeneous catalyst is mostly suitable for the conversion of the lignocellulosic feedstock like wood etc. However, there was ambiguity regarding the positive effect of the sewage sludge conversion due to its heterogeneous nature and high protein-containing organic matter. For sewage sludge conversion, detailed information on catalytic effect is provided in chapter 3 in section 3.3.

In this PhD project, In the first study, homogeneous catalyst K_2CO_3 was used by 2% of the total mass of the slurry loaded into the reactor. The type and dosage of the catalyst were selected followed by the previous studies [46,47]. In the second study, acetic acid was used (2.5 % of the total slurry). Whereas, in the third study, no catalyst was added to ensure the real impact of co-liquefaction of swine manure with sewage sludge.

2.3.3. Solid loading

Feedstock loading also affects the conversion of the biomass. It refers to the total solid loading in the reactor with respect to water. Many studies reflected that the solid loading between 15 to 25% is favorable for the conversion process [19,48,49]. A lower concentration of solid loading can not standby the cost associated with heat losses, and pumping of the huge amount of water [12]. Oppositely, high loadings could induce pumping issues. Earlier, researchers have tried to pump the lignocellulosic feedstock with different techniques, like under alkaline treatment [50], by mixing with other biomass (microalgae) [51] and adopting thickeners like carboxymethyl cellulose (CMC) [52]. These pumping and mixing issues have been addressed in great depth in the third study of the co-liquefaction of the swine manure with sewage sludge.

For sewage sludge, the dry matter depends upon the recovery point from the wastewater treatment plant, the processibility, geographical area, and mixing of industrial effluent if nearby the treatment plant. Here, in all the studies, almost 25 to 27% of solid loading was loaded into the reactor.

2.3.4. Reaction time (RT)

The reaction time has significant importance after the temperature. It varies from 5 to 60 mins. Shorter RTs produce lower bio-crude yields. While longer RTs (45 or 60 mins) mostly form a higher amount of char due to repolymerization reactions. The selection of RT is taken after the detailed literature survey, which revealed that 15 to 40 mins reaction time is beneficial for the maximum production of the bio-crude fractions in a micro-batch reactor system [48,53]. Here, all three studies were conducted at 15 mins RT excluding the heating time. It was assured that the reactors were heated at a constant temperature for 15 mins.

2.3.5. Reaction atmosphere and pre-pressurizing gas

After sealing the reactors with biomass slurry, the reactors were tested for the leak test by purging N_2 gas at 100 bar. Subsequently, reactors were pre-pressurized with N_2 at 10 bar to remove the residual air from the capillary and to press down the slurry in the reactor. After the completion of the reaction, the pre pressurizing pressure was subtracted from the total pressure produced during the reaction.

2.4. Recovery of HTL products

HTL produces different products along with the desired bio-crude. These different phases need to be separated carefully because the recovery of the products could affect the final bio-crude yield and quality. Thereby, when comparing different studies, it is very necessary to look into the reactor setup, processing conditions, and product recovery procedure.

In all three studies, almost a similar procedure for the recovery of HTL products was adopted. The systematic diagram of the collection and separating all the products are illustrated in Figure 5. In a second study, a slightly different approach was adopted to collect and separate the aqueous phase for the recycling experiments. For detailed information on the separation, is given in the publication Paper B.
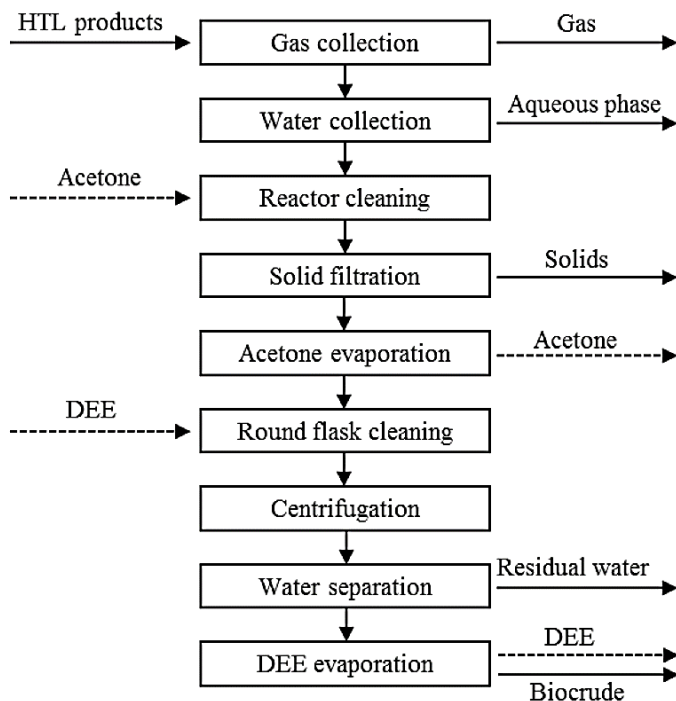
Figure 5. Steps involved in HTL product separation.

The very first step for the product recovery was to collect the gas phase by turning on the gas valves of the reactor. The gas-phase was vented out in all three studies. Then aqueous phase was collected by turning the reactor upside down without the addition of the solvent. Subsequently, the reactor was rinsed with acetone, and a mixture of bio-crude and the solid residue was collected. The solid phase was then separated by vacuum filtration by using filter paper (particle retention: 5–13 μm) and subsequently dried for the overnight period. The remaining mixture containing bio-crude, acetone, and some residual was inserted into the round-bottom flask to evaporate the acetone at 60°C through a rotary evaporation method with suction pressure of 56 kbar. To extract the bio-crude from the flask, the Diethyl ether (DEE) was added. The residual water available in the bio-crude phase formed a distinct layer at the bottom of the vial which could be easily taken out from the syringe. In last, The DEE was evaporated at 40°C and the remaining weight was considered as a bio-crude weight to report the yield.

2.5. Challenges faced during the experimental work

From the above procedure, almost all the products were recovered successfully. Nonetheless, some steps proved to be very complicated, especially the extraction of the aqueous phase. Because the aqueous phase was intermingled with bio-crude and

solid mixture, and it was very difficult to collect the aqueous phase at first without the addition of any solvent. Even though the aqueous phase which was distinctly visualized by the naked eye was collected easily, while 30 to 40% of the aqueous phase remained in the HTL mixture, which was collected by putting DEE or DCM solvents.

Secondly, the collection of the bio-crude from the round-bottom flask was also a complex and time-consuming task. A negligible amount of bio-crude was stuck with the wall of the round bottom flask, which was probably due to the dissolution of the bio-crude components in DEE. Here the DEE was selected by its high immiscibility with water. Apart from the solvent issues, there are always chances of small losses while working with a small amount of the products, as earlier described that microreactors provide the screening results for the conversion of the feedstock into the bio-crude at different HTL process parameters.

2.6. Analysis of HTL products

After the collection of the products, the characterization phase was carried out, the elemental values for the bio-crude and solid samples were detected through the elemental analyzer (Perkin Elmer, 2400 Series II by operating at CHN mode). Whereas, oxygen was calculated by difference. The organic composition of bio-crude was determined by the Gas Chromatography-Mass Spectrometry (GC-MS). Aqueous phase organic composition was also analyzed by using (GC-MS) system in such a way that, at first the water phase was evaporated, and the remaining organics were dissolved in the DCM and then injected into the GCMS system.

The quality of the aqueous phase was determined by total organic carbon (TOC) and total nitrogen (TN) via Hach kits and spectrophotometer. The volatile matter in the bio-crude was analyzed by TGA analysis (TA instrument Discovery), at 750° C under the atmosphere of N_2 gas. The HHV of the bio-crude, could not be detected by bomb calorimeter due to the small bio-crude sample. For HHV calculation, Channiwala, and Parikh´s correlation (equation 6) was used [54]. The ash contents in the bio-crude and solid samples were measured by the TGA as an alternative to a muffle furnace method. Scanning electron microscopy (SEM) was conducted to investigate the morphology of the feedstock (swine manure and sewage sludge).

2.7. Characterization of inorganic elements

The inorganic elements were analyzed through Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). A total of 13 elements were analyzed which include alkaline and some heavy metals namely: Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, and Zn. These elements were mainly distributed in three phases, bio-crude, solids, and the aqueous phase. Before ICP-AES analysis, all the samples were digested in a microwave-assisted acid digestion system, as per the EPA method 3051A

(US. EPA., 2007), by adopting a similar procedure as mentioned by Conti et al. [55]. The elements were quantified by multiplying the concentration of each element in the product phase with the product yield. Whereas the overall distribution in weight (%) of each element among the HTL products was standardized as the concentration of that element in a particular phase, divided by the sum of the total concentration of the desired element obtained in all the phases.

One interesting point was to be noticed here that the reactors were made up of 10-14% Ni and 16-18% Cr [56]. The higher concentrations of these metals were might be due to the partial scratching and intermingling of these metals with HTL products at higher temperatures. This observation requires further research about the degradation of the reactor material with the usage frequency in HTL.

The product yield on a dry ash-free (daf) basis, energy recovery in bio-crude (ER), and carbon recovery (CR) were estimated by using the following equations. Here, Wp and Wf represent the weights of the products and feedstock. Whereas Cp and Cf indicate carbon % in the products and feedstock. Cap denotes the recirculated carbon% from the aqueous phase. For the HHV formula, the CHONA represents the carbon, hydrogen, oxygen, nitrogen, and ash contents respectively.

$$\text{Product yield (\%) in bio} - \text{crude and solid} = \frac{\text{Wp (daf)}}{\text{Wf (daf)}} \times 100 \qquad (1)$$

$$\text{ER (\%) in bio} - \text{crude} = \frac{\text{HHV of bio} - \text{crude}}{\text{HHV of feedstock}} \times \text{bio} - \text{crude yield} \qquad (2)$$

$$\text{CR (\%) in bio} - \text{crude and solids} = \frac{\text{Cp Wp}}{\text{Cf Wf}} \times 100 \qquad (3)$$

$$\text{CR (\%) in aqueous phase} = \frac{\text{TOC (g/l)} \times \text{aqueous phase produced in (l)}}{\text{Cf Wf}} \times 100 \qquad (4)$$

$$\text{CR (\%) in products with recirculation} = \frac{\text{Cp Wp}}{\text{Cf Wf+Cap}} \times \text{bio} - \text{crude yield} \qquad (5)$$

$$HHV = 0.3491\,C + 1.1783\,H - 0.1034\,O - 0.0151\,N - 0.0211\,A \qquad (6)$$

Chapter 3

Hydrothermal liquefaction of sewage sludge at sub and supercritical conditions

3.1. Sewage sludge at Sub and Supercritical conditions

For HTL, sewage sludge is the best candidate to cover up the feedstock prices and improving the efficiency of the HTL processing. Since HTL works under the temperature between (270 to 400°C), however, the majority of the studies were conducted in the subcritical range, mostly under 350°C [34,39,40]. Supercritical range (above 374°C) with higher pressure (300 to 350 bar) attributes to the extremely lower dielectric constant and density of water that assists in the rapid disintegration of the sewage sludge with a higher degree of deoxygenation [57].

Despite the presence of higher inorganic contents in sewage sludge [25], the different catalysts (Na_2CO_3, K_2CO_3, $FeSO_4$, $NiMo/Al_2O_3$, activated carbon, etc) were used to examine their effects in the subcritical range [46–49]. Depending upon the process conditions, and types of catalyst, different conclusions were reported. Some studies stated the positive effects of the catalyst [46,47], while some indicated the negative behavior of catalyst on bio-crude yield [48,49]. Thus, the role of alkali catalyst still needs to be investigated in sub-supercritical water.

Therefore, this study provides comparative data of bio-crude properties, characteristics of the aqueous phase, and carbon and nitrogen balance with and without catalyst (K_2CO_3) at the sub and supercritical water conditions. Additionally, the fate of inorganic elements including K, P, Mg, Na in the HTL products, and pretreatment effects of different agents on ash reduction are also discussed in the last part of the study.

3.2. Sewage sludge properties

The collected sewage sludge was comprised of a significant amount (40%) of ash. Whereas the organic part was composed (48% of carbohydrates, 43% proteins, and almost 8% of fats). The HHV of sewage sludge was 22.15 MJ/kg, the chemical composition and inorganic composition of the sewage sludge is provided in Table 3, and Table 4.

Table 3. Characterization of Sewage sludge.

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) [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] Carbohydrates =[(VM+FC)–(Crude Proteins + Crude Fats)] [58].
[e] By Difference.

Table 4. Inorganic elements in sewage sludge.

Inorganic elements	Concentration (mg/Kg)	Concentration (wt.%)
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
Total sum	96550.0	100

3.3 Effects of temperature and catalyst on bio-crude yield and quality

Four HTL experiments were conducted at sub 350°C and supercritical 400°C conditions with and without catalyst, namely 350-None, 350-Catalytic, 400-None, and 400-Catalytic. In non-catalytic samples at both conditions, the temperature range has affected the bio-crude yield as the almost same magnitude of bio-crude yield ~40% was obtained (Figure 6).

The temperature in the sub and supercritical range decreases the dielectric constant, polarity, and density of the water. This phenomenon increases the solubility of the hydrophobic organic fragments of the biomass (sewage sludge) and accelerates the rate of the hydrolysis reaction. At higher temperature no larger improvement in yield was found, this is particularly due to the critical point of the temperature (critical point: 373.74°C), that disintegrates the bio-crude into the lighter components of the aqueous or gaseous phase [40].
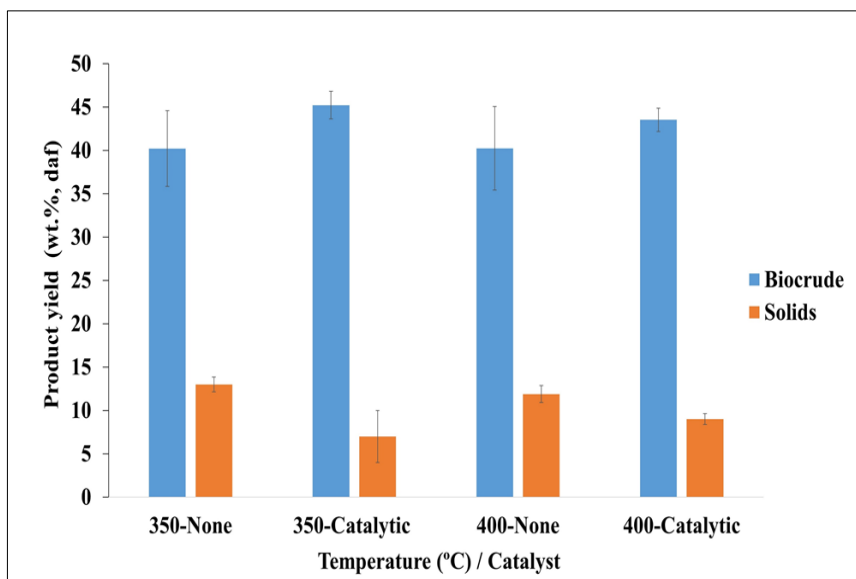
Figure 6. Product yields at the sub and supercritical states.

The addition of the alkali catalyst slightly increased the bio-crudes yields (45 and 43%) at both sub and supercritical conditions respectively. To further elaborate this, the composition of sewage sludge (carbohydrates, proteins, and fats) is taken into consideration. The reaction mechanism of the catalyst with these components is usually different depending upon the chemical composition of the biomass.

Previous studies indicated that alkali catalyst is quite favorable for the conversion of wood with around 80% of carbohydrates [55,59]. Unlike algal studies, which concluded that alkali catalyst is not favorable for the high protein-containing biomass due to the inefficient breakdown of peptide linkages of proteins [45,60,61].

In our case, the increase in bio-crude yield (5%) might be due to the efficient hydrolysis of carbohydrates components (~48%) under alkaline conditions. In the late past, Yokoyama et al. treated sewage sludge in the subcritical range with 2.5% of Na_2CO_3 and experienced a 5% increase in yield with over 50% of carbohydrates

fractions in sewage sludge [46]. The solid yield was 7 to 13%, at both conditions catalyst decreased the solid yield.

Table 5. Elemental composition of bio-crude.

Samples	Elemental analysis (wt. %)				HHV (MJ/kg)	ER (%)
	C	H	N	O[a]		
SS	50.95	7.36	6.91	34.78	22.15	----
350-None	73.68	10.09	5.71	10.52	35.30	63.98
350-Catalytic	75.51	10.56	4.69	9.24	36.60	74.60
400-None	74.60	10.33	5.20	9.88	35.95	65.21
400-Catalytic	75.75	10.22	3.77	10.26	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).

The quality of the bio-crude was assessed in terms of determining its elemental values, energy recovery, and HHVs (Table 5). In non-catalytic samples, the temperature has not influenced the elemental composition, at both temperatures almost comparable values for carbon, hydrogen, and nitrogen were detected as 73–76 %, 10.09–10.56 %, 5.2–5.7 % respectively. Whereas the catalyst shifted more carbon and lower nitrogen towards bio-crude at both sub and supercritical conditions as compared to non-catalytic samples. The absence of catalyst is the main reason behind the higher nitrogen content in the non-catalytic bio-crude. Because the interaction of carbonate ions with ammonium (liberated from amino acids) forms ammonium carbonate that can be dissolved in the aqueous phase. Previously, Chen et al. reported in the algal study that the nitrogen recovery in the bio-crude has the inverse relationship between the concentration of the carbonate ions present in the feedstock [62]. The following equations describe the reaction of the alkali catalyst with ammonium ion [63].

$$K_2CO_3^{-2} + 2NH_4^+ \rightarrow (NH_4)_2CO_3 + 2K^+ \tag{7}$$

$$(NH_4)_2CO_3 \rightarrow NH_3 + CO_2 + H_2O \tag{8}$$
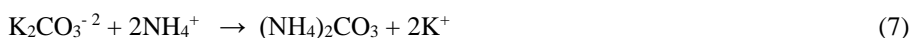
The lowest nitrogen 3.77 % was noticed at 400-Catalytic bio-crude. This may be due to the higher rate of dissolved ammonium carbonate in the aqueous phase at higher temperatures above the critical point. The maximum energy recovery of 74.60 % with the highest HHV (36.60 MJ/Kg) was detected in the 350-Catalytic bio-crude. Nonetheless, the calculated HHVs were relatively lower than the petroleum crude (42-43 MJ/Kg), which means these obtained bio-crudes require upgrading for the removal of the hetero-atoms via hydro-treatment.

The energy ratios of H/C and O/C were also estimated. All H/C ratios were around 1.6, and O/C were in the range of 0.09 to 0.5. The higher ratios of H/C reflected that the majority of the organic matter containing hydrogen was shifted to bio-crude. The

lower O/C ratios were noticed primarily due to the higher degree of deoxygenation reactions like decarboxylation and dehydration. The lower O/C ratio can contribute to the lower viscosity and higher stability of the bio-crude. Both H/C and O/C ratios are plotted in the Van krevelen diagram in Figure 7.
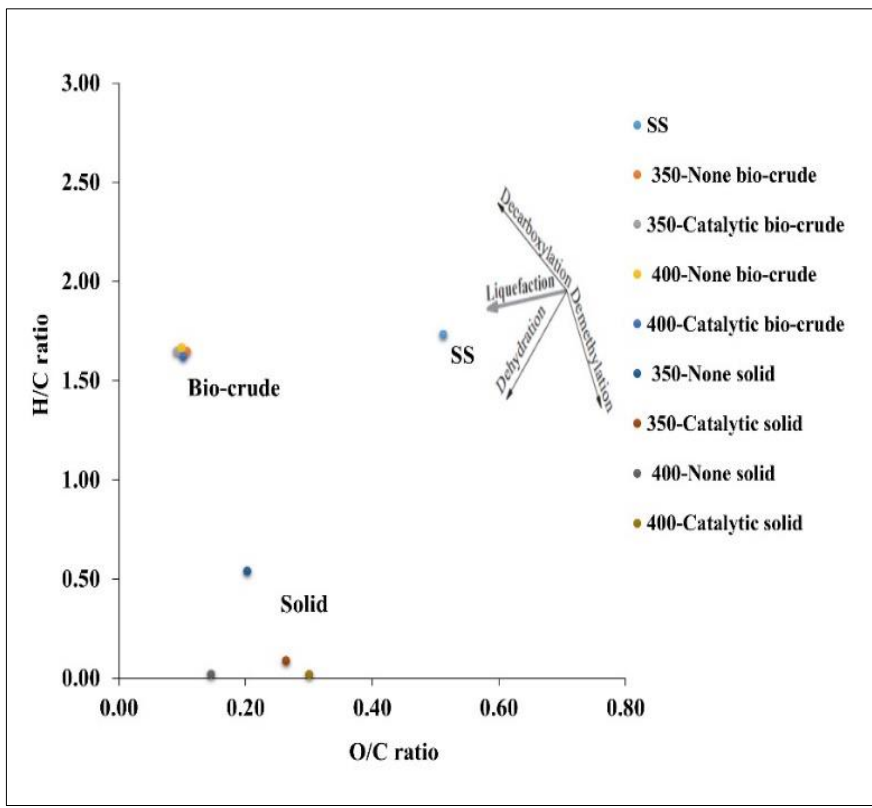

Figure 7. H/C and O/C ratio in Van krevelen diagram.

Figure 8, shows the volatility of all the bio-crudes, as almost all the bio-crudes at the sub and supercritical conditions contained more than 50% of the volatile matter at 350°C. These components denote the fragments of gasoline, diesel, and jet fuel. At higher temperatures (800°C), almost 5 to 20% of the heavy residue was observed.
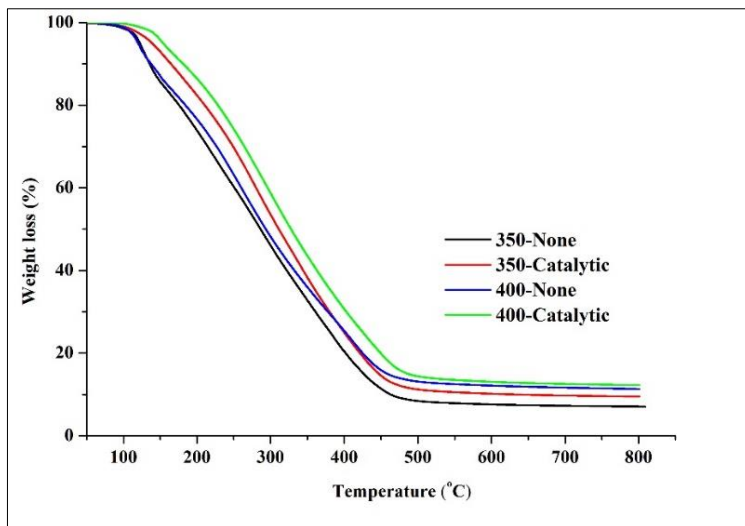
Figure 8. Volatility curves of the bio-crudes.

3.4. Compound composition of the bio-crude

The organic compound of the bio-crude was analyzed by the GCMS system. The organic composition of the bio-crude is categorized into three main groups. N-containing compounds, Oxygenated compounds, and Hydrocarbons. The compounds were detected in the order of Oxygenated compounds>N-containing compounds >Hydrocarbons, as given in Figure 9.

At both temperatures in non-catalytic bio-crudes larger peaks of N&O heterocyclic compounds, like [RT:13.06, 4-Piperidinone-2,2,6,6-tetramethyl] were observed. However, the amides were detected in more or less the same magnitude in all catalytic and non-catalytic conditions. This implies that the presence of N&O heterocyclic compounds were the major reasons for the higher nitrogen content in the non-catalytic bio-crude. In catalytic bio-crude at both conditions, carbonates might accelerate the rate of hydrolysis of the sugars and avoid the interaction of sugars with amino acids (proteins) to form N&O heterocyclic compounds. Previously, Biller et al. noticed a higher amount of amides than N&O heterocyclic compounds in catalytic-derived bio-crude from microalgae [64]. From hydrocarbons, the slightly lower amount of hydrocarbons were seen at supercritical conditions, this might be due to the cracking of long-chain hydrocarbons into short ones, or gases at higher temperatures [28].
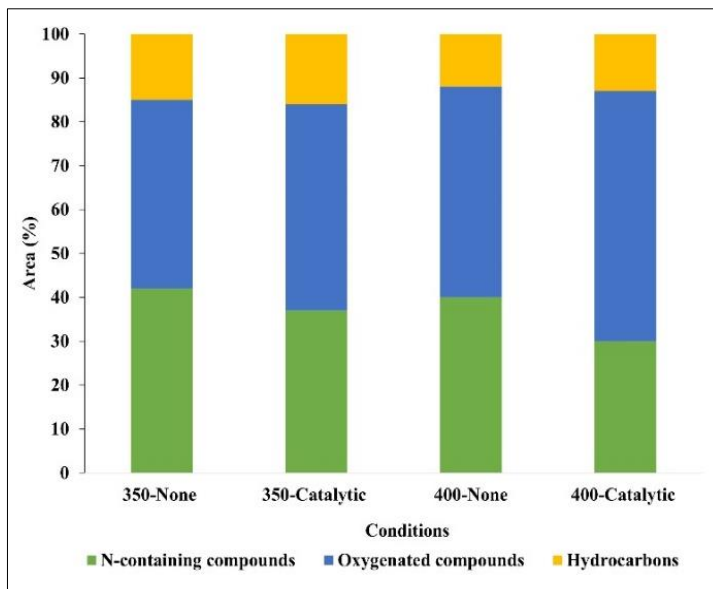
Figure 9. compound composition of the bio-crude

The N-containing compounds like N&O heterocyclic compounds were derived from the Maillard reaction between amino acids and reducing sugars. Some major amides [9-Octadecenamide- (Z), N-Methyldodecanamide, Dodecanamide,], could be originated from deamination, decarboxylation, dehydration reactions of proteins, or acylation reaction between amines and fatty acids [65]. Oxygenated compounds including phenolic compounds, like acids, alcohols and ketones, and phenols, were derived from the hydrolysis, dehydration, decarboxylation, and cyclization of carbohydrates [66]. Fatty acids eg. Hexadecanoic acid was formed from the hydrolysis of lipids.

The long-chain hydrocarbons were probably formed from the decarboxylation of fatty acids. The GCMS results have depicted that 80% of the bio-crude is composed of heteroatoms, which need to be removed before being declared bio-crude as a drop-in fuel. The complete information of all the detected compounds is provided in the supplementary material of Paper A.

3.5. Aqueous phase analysis

The concentration of TOC and TN were determined to evaluate the quality of the aqueous phase. The Catalyst influenced the TOC values, as higher TOC values were obtained in the catalytic samples (Figure 10). This is a fact that catalyst increases the rate of hydrolysis of the carbohydrates which already existed in significant concentration in the sewage sludge. This phenomenon allows the higher solubility of

the hydrophobic components to dissolve in the water phase at the sub and supercritical conditions. Earlier Suzuki et al. also observed the higher TOC values in the aqueous phase with Na_2CO_3 alkali catalyst in the sewage sludge at subcritical range [47]. The supercritical temperature produced higher TOC than subcritical, which might be due to the cracking long chain or cyclic compounds above the critical point. The overall values for the TOCs were in the range of 18 to 27 g/l.
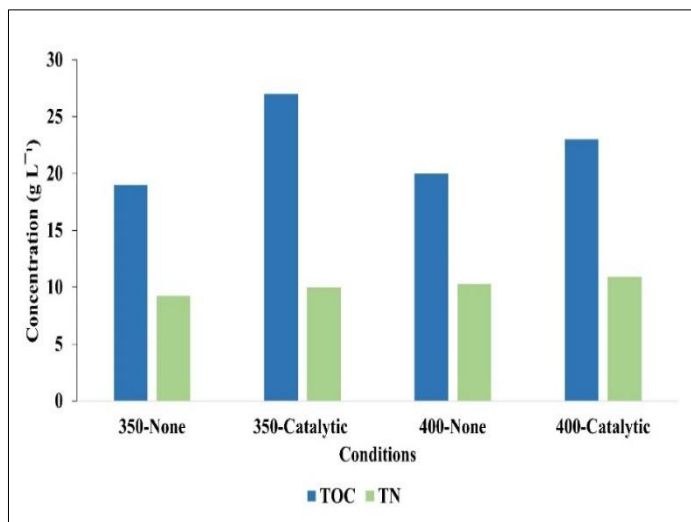

Figure 10. TOC and TN in the aqueous phase.

This organic carbon in the aqueous phase is linked with other compounds like acids, alcohols, etc, that induces the acidity and makes the aqueous phase hazardous for disposal in the ambient environment. In this context, nowadays scientists are strongly suggesting the optimization of the aqueous phase via different routes like recycling back to the HTL unit [67], anaerobic digestion [68], and hydrothermal gasification [69]. TN values were more or less consistent in the range of 8 to 10 g/l. Higher TN values were detected supercritical state.

Sewage sludge is high protein-containing biomass, therefore it is very important to discuss the distribution of the nitrogen in the HTL products. The nitrogen recovery (NR) was determined by the TN values. Figure 11, shows that the majority of the nitrogen over 60% was transferred to the aqueous phase, followed by (20 to 32%) in the bio-crude, (5 to 10%) in the solids, and a very negligible amount in the form of gases. The higher nitrogen in the aqueous phases is due to hydrolysis of the proteins in the water phase, which liberates ammonium by deamination reaction that has high miscibility in water. In both catalytic aqueous phases slightly higher NR was observed as compared to non-catalytic samples, which means the catalyst shifted more nitrogen in the aqueous phase.
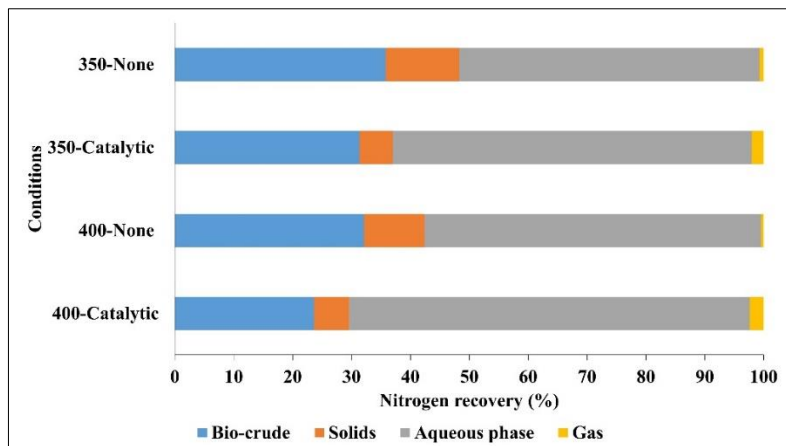
Figure 11. Nitrogen recovery in the HTL products.

3.6. Solid analysis

To close the total mass balance of carbon and nitrogen, the solid phase was also analyzed as a dried ash-free basis (Table 6). It was observed that at both conditions, the major part of solid (excluding ashes 77 to 87%) was covered with carbon 67-77%. Whereas, catalyst reduced the amount of carbon into solids. This is confirmed by a higher amount of carbon in the bio-crude and aqueous phases in catalytic samples.

Table 6. Elemental composition of the 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 was calculated by difference.

3.7. Inorganic elements in HTL products

In the HTL process, the fate of the inorganic elements is very much important in terms of dealing with the high ash containing feedstock. Here, to investigate the effect of temperature conditions, the ICP analysis was conducted of non-catalytic products (bio-crude, solids, and aqueous phase) of 350-None and 400-None.

At both sub and supercritical conditions, it was observed that 80 % mass of all the inorganic elements was recovered in the solid phase except for sodium and potassium, which were exclusively dissolved in the water phase approximately 40 to 50%. Bio-crude contained some heavy metals like Cu, Ni, Fe, and Zn around 1 to 3%.
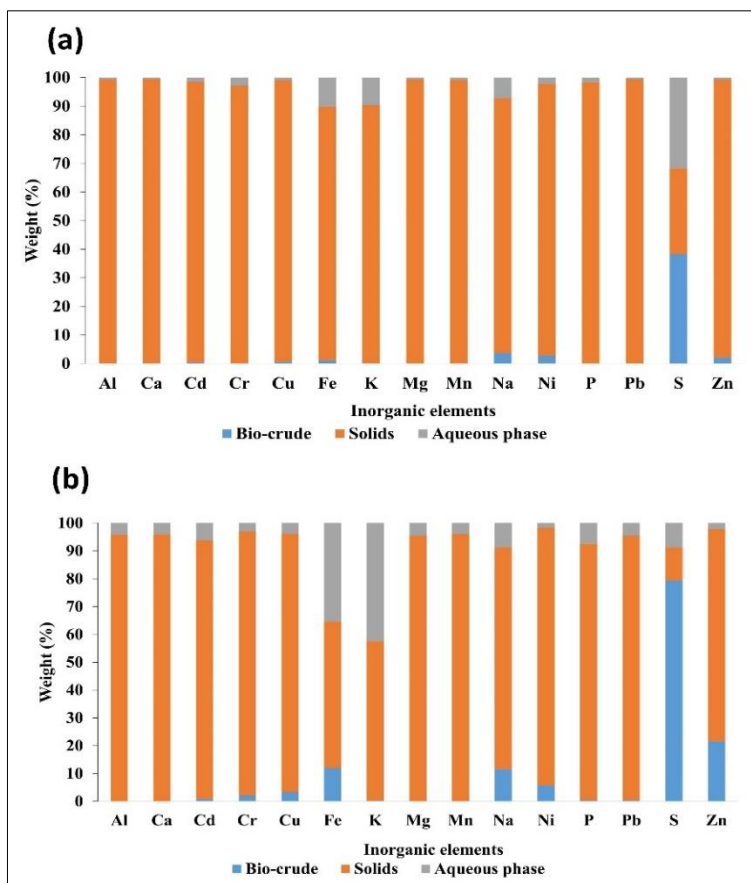
Figure 12. Inorganic elements at (a) 350°C, (b) 400°C.

Sulfur showed a different behavior, as it was almost equally contributed in all the phases, particularly in the bio-crude 40 and 70% for sub and supercritical respectively, as shown in Figure 12. The higher percentage of the sulfur in bio-crude at supercritical may be due to the cleavage of organic compounds containing sulfur in the ring structure at the higher temperature. Similarly, the higher amount of sodium and potassium were collected in the aqueous phase in the supercritical state. This might be due to the breakdown of reactive ash components, which could intermingle with the water phase at 400°C. At both conditions, almost all the phosphorus was shifted towards the solid phase. The distribution of inorganic elements is strongly dependent

upon the degree of solubility. The solubility of the inorganic element changes with the dielectric constant and applied temperature. For instance, at lower temperatures below 200°C, the phosphates are easily dissolved, while they become insoluble at temperatures above the critical point [70]

Although the majority of the inorganic elements like Cu, Ni, Cd, Zn, and P were migrated to the solid phase, they were also transferred to the bio-crude and aqueous phase (K, Na substantially in the aqueous phase). From these observations, we can conclude that the solid phase can be utilized as a hydrochar or fertilizer due to the presence of an immense amount of valuable nutrients like (i.e. P, Ca, Mg, N). Nevertheless, the presence of other heavy metals restricts the direct usage of contaminated hydrochar by environmental protection protocols. Therefore, in future studies, it is recommended to investigate the forms of the inorganics and their potential for the bio-availability.

3.8. Pretreatment of sewage sludge

The handling of high ash-containing feedstocks has always been a challenging task, especially at a larger scale as they produce an enormous amount of solids which can cause blockage in the continuous system [71]. Thus, the pretreatment of the sewage sludge could be a way to decrease the ash content before the liquefaction. Two agents of pretreatment were used, citric acid and the aqueous phase (generated from the sewage sludge in a separate autoclave at 350°C). Here aqueous phase was chosen to minimize the acid cost, and establishing a feasible pretreatment process.
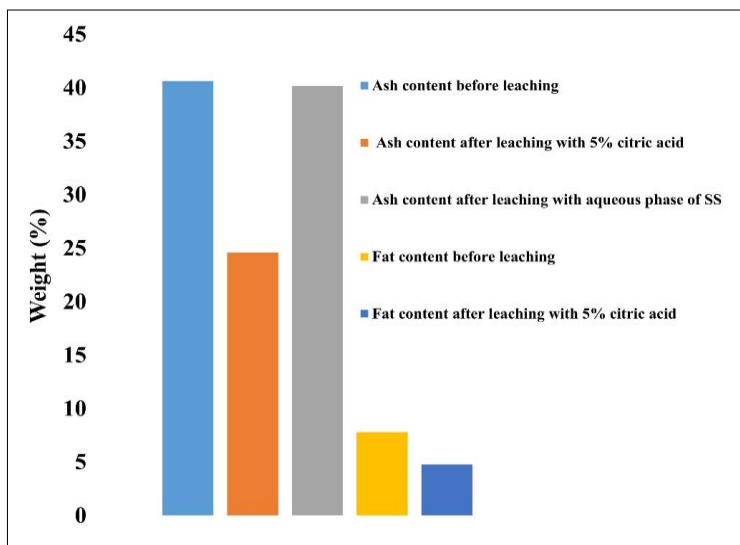

Figure 13. Effect of different agents on the pretreatment of the sewage sludge

The 50 g sewage sludge (73 % moisture) sample was leached with a 500 ml solution of 5% citric acid (Sigma-Aldrich, 99.9%) under the magnetic stirrer of 600 rpm at 30°C for 4 hours. After the experiments, the sewage sludge sample was centrifuged to separate the sewage sludge and aqueous phase. The ash and fat contents were measured from the pretreated sample. For leaching with the aqueous phase, a similar method was adopted, except for the masses. Here, 5 g sewage sludge was mixed with 50 ml of the aqueous phase.

From the citric acid solution, the ash content was decreased from 40 to 24%, which highlighted a 40% decrease in ash content. This observation is similar to the earlier study by Toor et al. who utilized 5% citric acid for the pretreatment of Spent Mushroom Compost (SMC) and experienced a 66% reduction in ash [72]. Apart from the ash reduction, citric acid heavily influenced fat content by reducing from 7.0 to 4.6%, as depicted in Figure 13. This undesired loss of fats would be the adverse aspect of the citric acid because fats or lipids are the most important organic components of the feedstock for the generation of the bio-crude followed by proteins and carbohydrates [64]. Aqueous phase pretreatment did not affect the ash content. The primary cause behind this may be the alkaline nature of the aqueous phase with a lower concentration of acids.

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Chapter 4

Bio-crude production through aqueous phase recycling of hydrothermal liquefaction of sewage sludge

4.1. Aspects of aqueous phase recycling to HTL

Since HTL works on a hydrothermal principle wherein water acts as a reaction medium to facilitate the disintegration of the organic matter. Apart from the bio-crude production, a substantial amount of energy is lost in the form of water-soluble organics [73]. This discharge of water-soluble organics decreases the bio-crude yield and affects the overall economics of the HTL processing.

Over the years, researchers have tried to utilize the HTL produced aqueous phase with other thermochemical or biochemical techniques like gasification [74–76] and anaerobic digestion [77,78], which reflected positive effects on the enhancement of the gas production. People also valorized the aqueous phase for the cultivation of biomass (microalgae) [79,80]. These all systematic approaches require the integration of the HTL processing with others (gasification/anaerobic digestion) which could undermine the sustainability of the HTL processing as stand-alone.

To overcome this problem, the most recent and advanced approach which has been implemented nowadays at the lab and pilot-scale is the recirculation of the aqueous phase back to the HTL unit (as given in Figure 14). This technique can save cost related to the aqueous phase treatment and avoiding the integration of the HTL with other technologies. For dried feedstocks like wood, wheat straw, etc, aqueous phase recirculation is a very viable option as it saves freshwater consumption for HTL slurry formation. For already wet feedstocks like sewage sludge, the addition of the aqueous phase reduces the dry matter content of the feedstock, which ultimately affects the bio-crude yield.

For the wet sewage sludge, there are two possibilities of the optimization of the aqueous phase, either by extracting organics from the aqueous phase by evaporating the water. or by drying the sewage sludge at a certain level to control the dry matter content along with subsequent recycling of the aqueous phase. Several researchers have tried to treat different feedstocks with the aqueous phase recycling like barley straw [67], algae [81], desert shrubs [82], aspen wood [44], DDGS [83]. All these studies revealed the positive effects of the aqueous phase recycling on the bio-crude yield.
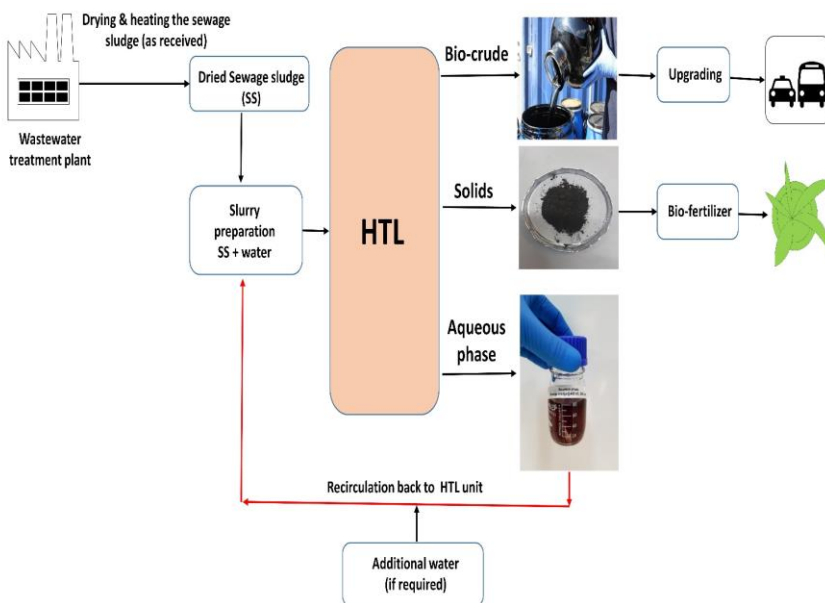
Figure 14. The concept of the aqueous phase recycling with sewage sludge in HTL.

In the available literature, the recirculation of the sewage sludge in HTL has not been reported before. Therefore in this study, the eight experiments of recirculation of the aqueous phase with sewage sludge under the controlled dry matter conditions were performed. This study provides concrete information about the implications of the aqueous phase recycling from high protein-containing waste feedstock (sewage sludge) on the bio-crude properties. The acidic catalyst was also used to investigate the effect of acidic mediums on the HTL products.

4.2. Impact of aqueous phase recycling on bio-crude yield and quality

The baseline experiment or cycle zero (C0) was performed with dried sewage sludge (containing 51% carbohydrates as given in Table 7) and fresh water at 25% dry matter content under subcritical conditions 350°C. Subsequently, eight recycling experiments from C1 to C8 were performed with the diluted aqueous phase, as discussed before in the methodology section 2.2. The diluted aqueous phase (35 to 50% aqueous phase + 50-65 % of freshwater) was recycled because of the inconsistent collection of the aqueous phase during the separation process.

Table 7. Proximate and ultimate analysis (wt.%) of SS.

MC [a]	VM	FC [c]	Ash	Crude Protein [b]	Crude Fat [b]	Carbohydrates [b]
7.54	54.44	11.54	34.02	43.21	4.89	51.89

C [b]	H [b]	N [b]	O [b,d]	H/C	O/C	HHV (MJ/kg) [b]
50.17	7.11	6.90	35.81	1.70	0.54	21.27

[a] As received.
[b] Dry ash-free.
[c] Fixed Carbon: FC = 100-VM-Ash.
[d] By Difference

The bio-crude yield was increased from 25 to 38% after eight aqueous phase recirculation experiments. It was observed that from C1 to C5 the bio-crude increased consistently and then stabilized from C5 to C8, as illustrated in Figure 15. This can also be verified from the consistent TOC values from C5 to C8 (24 to 27 g/l) after five rounds of recycling. The variation in the TOC values was due to the variable dilution ratio of the aqueous phase. The increase in bio-crude yield is due to the saturation of water-soluble organics concentrated in the aqueous phase. During HTL experiments, the light organics tend to intermingle with each other again accumulate together to form heavier components that ultimately form the bio-crude components. The overall solid yield was in the range of 15 to 21%.
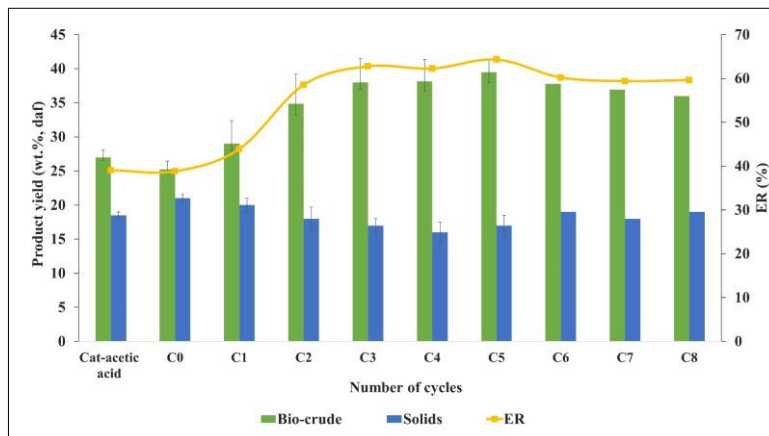

Figure 15. Impact of the aqueous phase recycling on bio-crude yield.

4.3. Influence of the acetic acid on the bio-crude properties

In the recent past, some studies reported that acetic acid is one of the dominant compounds present in the aqueous phase. Zhu et al. liquefied the barley straw at supercritical condition 400°C with three rounds of aqueous phase recycling and found

acetic acid in a substantial amount in the aqueous phase [67]. It can be speculated that acidic acid might have an impact on the bio-crude properties.

To investigate the catalytic impact of the acetic acid, one separate experiment was performed at 350°C and named as (Cat-acetic acid) under 2.5% of the total weight of the slurry or (0.56 Molar concentration). Further High-pressure liquid chromatography (HPLC) was conducted to determine the concentration of the acetic acid in all aqueous phases. The standard samples of the different concertations were prepared and analyzed with the calibration curve with regression constant of (R^2 = 0.999), as provided in the supplementary material of Paper B.
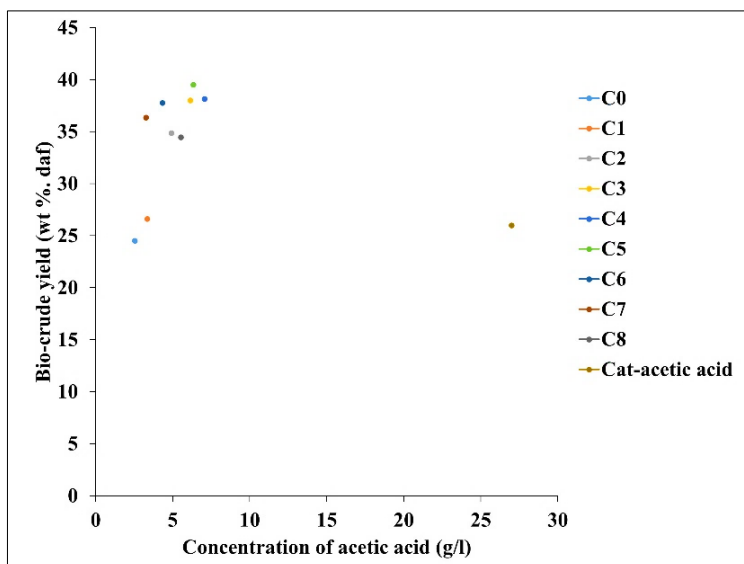
Figure 16. The concentration of acetic acid and bio-crude yield.

With aqueous phase recycling, the concentration of acetic acid in the aqueous phase was increased from 2.4 to 7.1 g/l. However, in the experiments (Cat-acetic acid), where acetic acid was used as a catalyst, the highest amount of acetic acid 27 g/l was found in the aqueous phase. Interestingly, the bio-crude yield at the (Cat-acetic acid) experiment was the same as that of the reference run C0, with only a 1.5% increase in yield as shown in Figure 16. This demonstrates that the higher concentration of acetic acid had a negligible effect on the bio-crude yield. However, it was the recycling effect of the polar organics, which resulted in higher bio-crude. The fluctuation in the concentration of the acetic acid was correlated with the dilution factor.

The elemental composition of the bio-crude is given in Table 8. Carbon values did not show a particular trend but varied from 70 to 74%. However, an increasing trend in the nitrogen content was observed from 5.1 to 7.27%, especially due to the deposition

of the N-containing compounds in the bio-crude from the recycling of the aqueous phase.

Table 8. Elemental composition of bio-crude.

Samples	Elemental analysis (wt. %)				HHV(MJ/kg)	ER (%)
	C	H	N	O^b		
C0	73.85	10.04	4.67	11.44	35.22	38.83
C1	73.89	9.89	5.10	11.12	35.09	43.90
C2	74.56	10.12	5.50	9.82	35.71	58.54
C3	73.65	9.96	5.75	10.64	35.13	62.76
C4	73.28	9.72	6.25	10.75	34.71	62.26
C5	72.65	9.85	6.80	10.70	34.62	64.30
C6	72.84	9.15	7.27	10.74	33.91	60.22
C7	72.09	10.14	6.95	10.82	34.76	59.39
C8	71.27	9.66	7.10	11.97	33.82	59.63
Cat-acetic acid	71.23	9.88	4.90	13.99	33.88	39.09

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

The aqueous phase recycling improved energy recovery (ER) from 38 to 60%. The Cat-acetic acid did not impact the elemental values except slightly higher oxygen was detected, which might be due to a higher conversion rate in the acidic environment, which resulted in higher oxygenates like acids, alcohols, ketones, etc.

The values of H/C versus O/C were plotted in the Van krevelen diagram as illustrated in Figure 17. It was shown that the overall liquefaction was carried out through decarboxylation and dehydration reactions. The higher H/C values (1.5 to 1.69) in the bio-crude indicate the higher transference of carbon and hydrogen in the bio-crude. From all the bio-crudes, the highest degree of deoxygenation 72% was calculated from the second recycle C2 with a maximum HHV of 35.71 MJ/kg.

To investigate the effect of aqueous phase recycling on the thermal behavior of the bio-crude, the TGA analysis was conducted. From Figure 18, it appeared that more than 60% of the mass of all the bio-crudes was composed of volatile fractions under 350°C. This temperature range denotes the components of gasoline, diesel, and jet fuel. Interestingly, the bio-crudes C1 and C8 showed a slightly higher amount of heavier fragments than C0 from 100 to 200°C. This finding can be considered as strong evidence of the aqueous phase recycling. The bio-crude Cat-acetic acid showed almost the same volatile behavior as that of baseline experiments C0. At higher temperatures (800°C), 10 to 15% of the heavy residue was detected. Whereas bio-crude Cat-K_2CO_3 showed a slightly higher 25% heavy residue than all the other bio-crudes. Here, the bio-crude Cat-K_2CO_3 has not been discussed in the detail, because the effect of alkali catalyst has already been discussed in the first study.
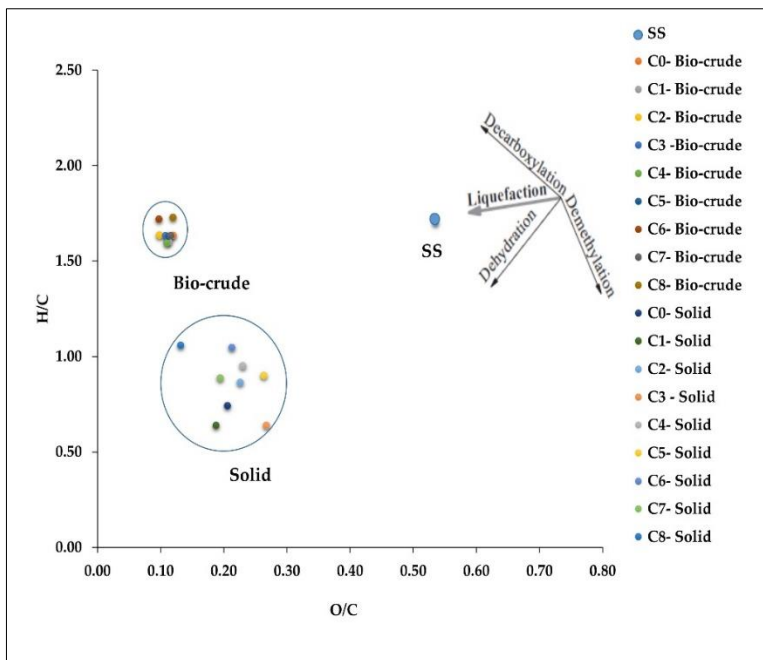
Figure 17. H/C and O/C ratios in the Van kerevelen diagram.
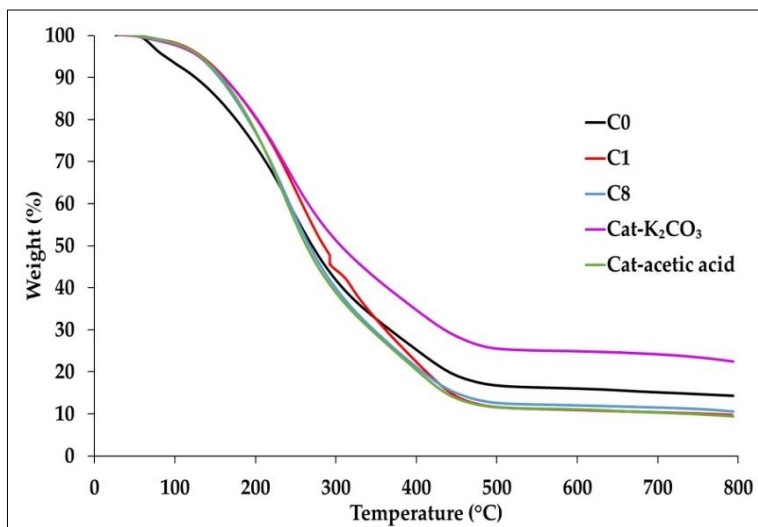
Figure 18. Thermal behavior of the bio-crude.

4.4. Compound composition of bio-crude

Since GCMS operates at 300°C, the temperature limitation could only reveal the fractional (60%) of the total TGA analysis. More than 50% area of the chromatograms was taken for the interpretation of the compounds. The organic composition of the bio-crude was categorized into three main groups. N-containing compounds (N-heterocyclic compounds, amides) Oxygenated compounds (acids, ketones, alcohols, etc), and hydrocarbons.

Figure 19, shows that the N-containing compounds increased from 24 to 53% after five rounds of recycling for C0 and C5 respectively. This increase in N-containing compounds is particularly due to two reasons, 1) the continuous accumulation of the nitrogen-containing compounds via recycling experiments, 2) injection of high protein-containing feed (sewage sludge).
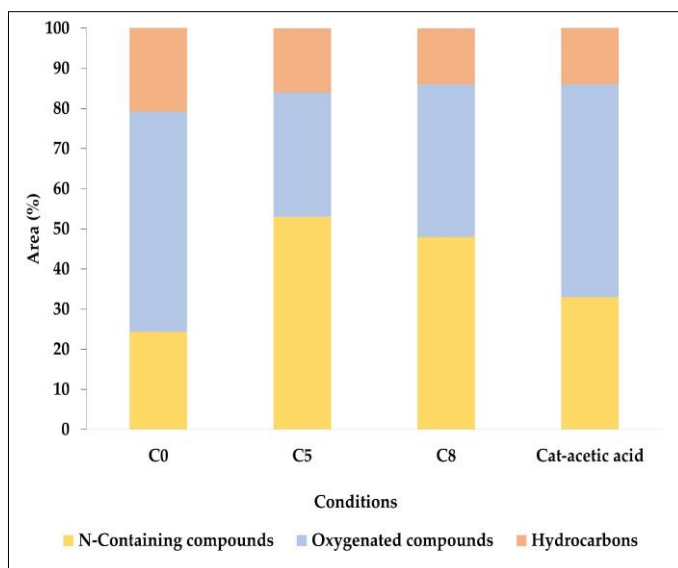
Figure 19. Organic compounds in bio-crude at different cycles.

These N-heterocyclic compounds were derived from the Maillard reaction among sugars and amino acids [39,49]. One interesting point was found that in bio-crudes C5 and C8, some new compounds were observed such as [RT:14.8:   N-Nitro-N-N-pentamethyleneguanidine] and [RT: 16.36: 2-propen-1-amine, N, N-bis-1-methyl-1-ethyl].

Table 9. Organic compounds of sewage sludge detected via GCMS.

| S. No.	RT	Compounds	Peak area (%)			
			C0	C5	C8	Cat-acetic acid
1	2.42	Butane, 2,3-dimethyl-	5.42	4.38	2.63	2.91
2	10.79	Phenol	0.23	0.25	2.12	0.8
3	12.41	p-Cresol	2.54	ND	3.9	2.06
4	13.06	4-Piperidinone, 2,2,6,6-tetramethyl-	4.95	20.42	18.56	ND
5	19.06	Hexadecane	4.48	2.21	4.15	3.31
6	23.44	n-Hexadecanoic acid	5.3	1.63	3.9	7.02
7	25.53	Dodecanamide	5.12	4.19	5.45	6.95
8	25.85	N-Methyldodecanamide	5.27	3.22	3.7	3.35
9	27.11	9-Octadecenamide, (Z)-	9.7	6.39	5.66	17.3
		Total area detected	51.65	55.26	52.84	53.82

ND: Not detected.

Cat-acetic acid bio-crude contained the majority of the oxygenated compounds and only one-third of the N-containing compounds. Abdelmoez et al. stated that acidic conditions favor the decomposition of proteins [84]. This could be the reason for the lower N-heterocyclic compounds in the Cat-acetic acid bio-crude. The efficient catalytic action of acetic acid might divert the direction of amino acids towards amides rather than reacting with sugars to form N-heterocycles. The amides were detected in the same range around 5 to 9%. The reaction pathways of all these compounds have been mentioned before in the first study (section 3.4). The GCMS results clearly shown that aqueous phase recirculation increased the heteroatoms concentration in the bio-crude, which requires upgrading via hydrotreatment to meet the standards of drop-in fuels.

4.5. Aqueous phase characterization

The organic compounds in the aqueous phase were analyzed by the GCMS system. The aqueous phase from the second recycle C2 was chosen for the analysis. Table 10, shows the compounds detected in the organic phase, as these compounds covered 60% of the total 70% of the detected area. The aqueous phase contained mostly N-containing compounds, especially, N-heterocyclic compounds like (2,5.Pyrrolidinedione, 1-methyl-), which produced from the Maillard reaction between sugars and amino acids. Some organic acids like acetic acid, pentanoic acids were also found, which were possibly formed from the hydrolysis and dehydrations of polysaccharides. During the recycling experiments, these short-chain acids act as a precursor for the bio-crude production [83].

Table 10. Compound composition of the aqueous phase of cycle C2.

S.No	RT	Compounds	Formula	Peak Area (%)
1	3.44	Acetic acid	CH_3COOH	5.36
2	7.54	Acetamide	C_2H_5NO	3.09
3	9.14	Acetamide, N-ethyl-	C_4H_9NO	3.03
4	11.44	Pentanoic acid, 4-methyl-	$C_6H_{12}O_2$	3.04
5	12.74	2,5-Pyrrolidinedione, 1-methyl-	$C_5H_7NO_2$	13.54
6	13.18	3-Aminopyridine	$C5H_6N_2$	5.11
7	13.44	2,5-Pyrrolidinedione, 1-ethyl-	$C_6H_9NO_2$	3.51
8	14.36	Cyclooctanone, oxime	$C_9H_{17}NO$	6.18
9	14.51	2-Piperidinone	C_4H_7NO	7.48
10	22.54	4(1H)-Pyridinone,tetrahydro-2,5-dimethyl-1-(1-methylethyl)-	$C_{11}H_{18}N_2O_2$	3.70
11	23.52	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-	$C_{11}H_{18}N_2O_2$	7.19
		Total area detected		70.85%

Madsen et al. characterized the aqueous phase from the different modal compounds and stated a higher concentration of acetic acid from proteins rather than carbohydrates [85]. Thus, it is not very straight forward to predict the actual pathway of the acetic acid formation. Some amides were detected such as acetamide, which was originated from the reaction between acids and amines (liberated from amino acids).

With continuous recycling of the aqueous phase, the TOC and TN values were increased by 2.6 and 2 folds respectively. The TOC values increased from 12 to 27 g/L for C0 to C5 respectively and then stabilized from C6 to C8 with minor variations (Figure 20). This implies that the aqueous phase has already reached its threshold limit of dissolving the water-soluble organics, which prevents the further solubilization of the organics. The same scenario can be seen in the TN values. Many studies related to the aqueous phase recirculation reported the rapid increase in the TOC values with successive recycling. Biller et al. [83] and Pedersen et al. [44], both observed a sharp rise in the TOC values from 25 to 90 g/l and 54 to 136 g/l respectively. In the present study, the gradual rise in TOC is due to the addition of freshwater, which dilutes the concentration of the dissolved organics.

The pH values were also measured from 7.56 to 8.80. a marginal decrease in pH value was noticed, this might be due to the increasing concentration of the acetic acid with recycling. The aqueous phase from the Cat-acetic acid sample has the lowest value 5.86, which depicted the catalytic effect of acidic acid.
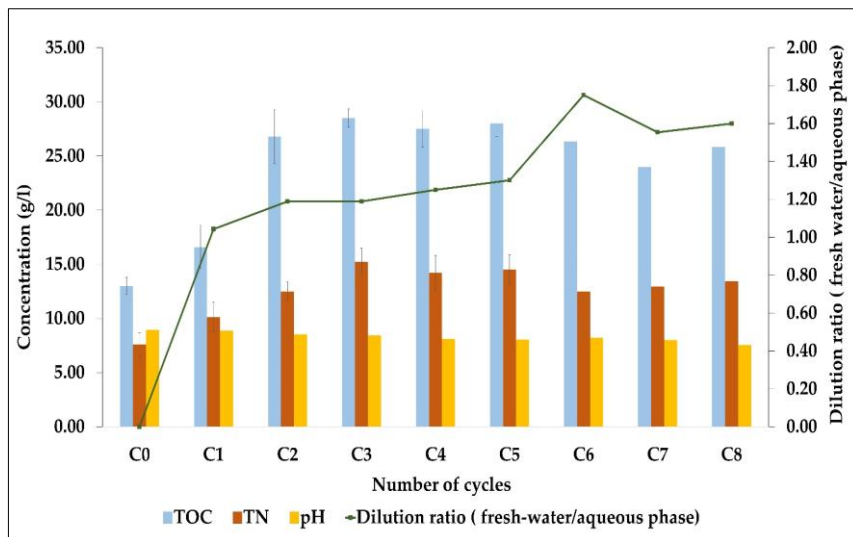
Figure 20. Characterization of the aqueous phase.

4.6. Carbon recovery

The carbon recovery (CR) was also determined in the HTL products. The carbon recovery in the bio-crude and solids was determined by the concentration of carbon in each phase multiplied by the yield of the product. For the aqueous phase, the CR was estimated by TOC from equation (4). For the recirculation experiments, the CR was calculated as the carbon from the feedstock plus the carbon fraction from the aqueous phase via recycling as given in equation (5).

Figure 21, shows that the aqueous phase contained almost 10 to 19% of the carbon, from which 40 to 50% of carbon was recycled back to the HTL system along with the feed. The CR in the aqueous phase via recycling experiments was not increased in higher magnitude, this is because of dilution of the aqueous phase. However, the carbon in the bio-crude was increased from 34 to 46%. This is primarily due to the higher bio-crude yield obtained with successive recycling rounds. However, almost no significant difference in elemental values was observed. The CR in solids varied in the range of 22 to 29%, while gas contained negligible carbon.
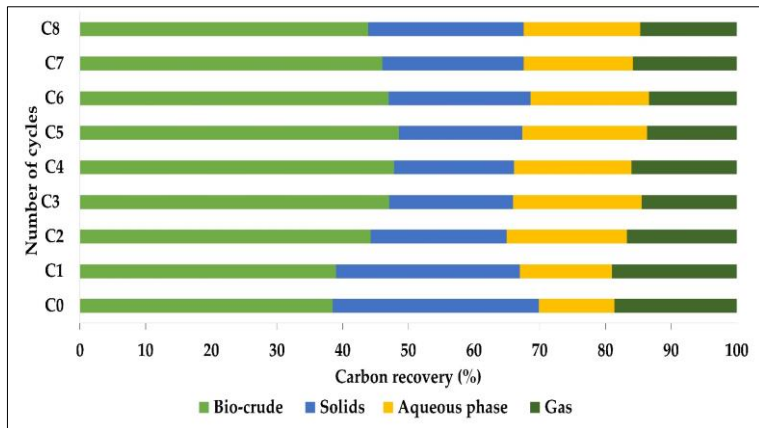
Figure 21. Carbon recovery in the HTL products.

4.7. Effect of aqueous phase recycling on inorganic elements

To examine the effect of aqueous phase recycling and catalytic effect of acetic acid on the distribution of the inorganic elements. The ICP-AES analysis was conducted for some selected inorganic elements, namely: Al, Ca, Fe, K, Mg, Na, P, S, and Si. For the analysis, the products of samples C0, C5, and Cat-acetic acid were selected. It was noticed that at all the conditions. apart from K, Na, and S, all the elements were concentrated in the solids phase. Whereas K and Na were shifted to the aqueous phase (5-20%). It was observed that after the five rounds of recycling the concentration of the K and Na was increased from ~6 to 16-20 % respectively as depicted in Figure 22. This is fairly logical because continuous recycling experiments in the subcritical range disintegrates the alkali metals from the ash compounds, which can be fussed in the aqueous phase.

Sulfur was primarily found in all three phases, especially 60% in bio-crude C5. This sulfur might be transferred from the carbohydrates or proteins. The sample, Cat-acetic acid, showed almost the identical behavior as of the reference run C0. This implies that acidic conditions did not impact the distribution of the inorganic elements. However, phosphorus, an important element for the bio-fertilizers was found in solids. This opens up the opportunity for the utilization of the solids phase for the cultivation of the biomass after the necessary treatment of the toxic heavy elements.
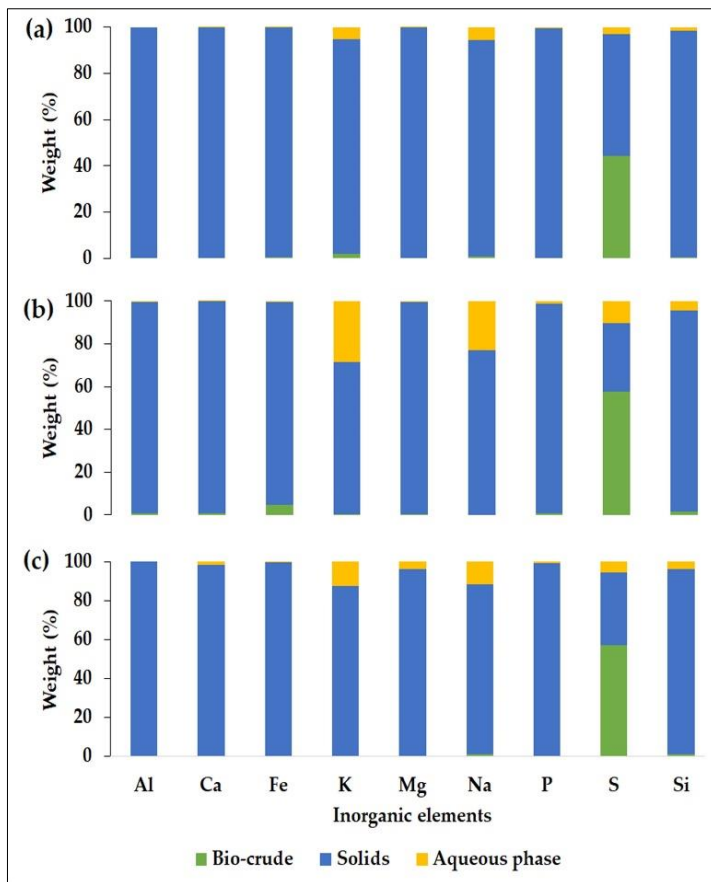
Figure 22. Distribution of the inorganic elements, (a) C0, (b) C5, and (c) Cat-acetic acid.

Chapter 5

Bio-crude production through co-hydrothermal processing of swine manure with sewage sludge to enhance pumpability

5.1. Swine manure and its co-liquefaction

Unlike sewage sludge, swine manure is composed of a lower of ash, and a significant amount of fibrous carbohydrates [86]. Animal manure is the type of waste that has economic worth, especially for the agricultural sector. It is reported that the immense farming culture in the European Union (EU), increased the production of animal manure including swine manure ~295 million dried tons annually [19]. However, some strict regulations from the EU limit the extensive use of swine manure due to the existence of pathogens and other harmful elements [87].

In the recent past, many studies proved that swine manure is also a good option for bio-crude production [19,34,86]. For energy enhancement, the swine manure was also co-liquified with other biomasses like glycerol [88], and mixed algal biomass [62]. For the large continuous HTL plants, pumpability is a crucial problem especially for fibrous feedstocks like swine manure. Biller et al. experienced that the fibrous material can easily be pumped by the addition of some thickeners, and the author successfully pumped miscanthus by using carboxymethyl cellulose (CMC) as a co-substrate [52]. Similarly, Sintamarean et al. also successfully pumped wood with microalgae [51].

Since the elimination of the fibers induces the pretreatment cost which can affect the overall economics of HTL and the fuel price of the bio-crude. Therefore, sewage sludge was selected as a thickening material for enhancing the pumability of the swine manure. Previously sewage sludge was also co-processed with many feedstocks at different ratios, like lignocellulosic [52] and microalgae [89]. All these studies reported the beneficial effects of the co-liquefaction over bio-crude yield and energy recovery.

However, the pumpability aspect of the co-processing of swine manure with sewage sludge, and their subsequent co-liquefaction has not been discussed before in the available literature. Therefore, this study aims to investigate the causes and challenges associated with the pumpability of the swine manure by using sewage sludge as a co-

substrate. Moreover, this study explores the co-liquefaction effects over bio-crude properties with complete information on the distribution of the inorganic elements.

5.2. Characterization of the feedstocks

Two of the original feedstocks SM and SS, and three mixed samples at ratios SM/SS (50:50, 80:20, 20:80) were selected for the analysis. Table 11, highlights the moisture, volatile matter, and ash content in the feedstock. Whereas, Table 12, shows the chemical and elemental composition of the feedstocks. The higher volatile matter was detected in SM than SS because SS contained higher ash (one-third portion of the total mass). Higher proteins were detected in all the SS containing samples. For mixed samples, the values for volatile matter and carbohydrates were not reported. The elemental values in all the mixed samples were detected almost in the proportion of their feedstock ratios.

Table 11. Moisture, volatile matter, and ash content in the feedstock.

Feedstocks	Proximate analysis		
	MC	VM	Ash
SM	76.52	69.15	11.45
SS	75.84	58.54	25.10
SM:SS (50:50)	74.89	---	21.16
SM:SS (80:20)	75.24	---	17.55
SM:SS (20:80)	76.02		23.10

Table 12. Chemical and elemental composition of the feedstock.

Feedstocks	Chemical analysis [a]			Ultimate analysis [a]				
	Carbohydrates	Proteins	Fat	C	H	N	O[b]	HHV (MJ/kg)
SM	80.03	16.08	3.36	46.02	6.10	2.57	45.31	19.54
SS	41.17	53.49	5.33	51.94	7.28	8.33	32.44	23.30
SM:SS (50:50)	---	31.48	---	49.25	6.66	5.04	39.04	21.79
SM:SS (80:20)	---	21.59	---	48.76	6.52	3.45	41.27	20.60
SM:SS (20:80)	---	43.12	---	50.32	6.78	6.98	37.07	22.54

[a] Dried ash-free basis.
[b] Oxygen was calculated by difference = 100- (C+H+N).

5.3. Syringe test and pumpability analysis

To evaluate the pumpability potential of the feedstocks, the syringe test was applied. Previous studies revealed that the syringe is a very fast and efficient method for pumpability analysis [50,51]. Syringe test copies the feed flow through an orifice. The

30 ml syringe was taken with an outlet diameter of 6 mm. If the uniform slurry is passed, then the slurry is called pumpable. If the slurry dewaters and blocks the syringe then it is said to be non-pumpable.

Initially, the mixture of 100 g was prepared under the different feedstock ratios SM/SS (50:50, 70:30, 80:20, and 90:10). The dry matter in prepared mixtures was detected 24-25 %, which shows that both the feedstock were mixed properly as individual feedstock contained almost contained 75% of moisture.
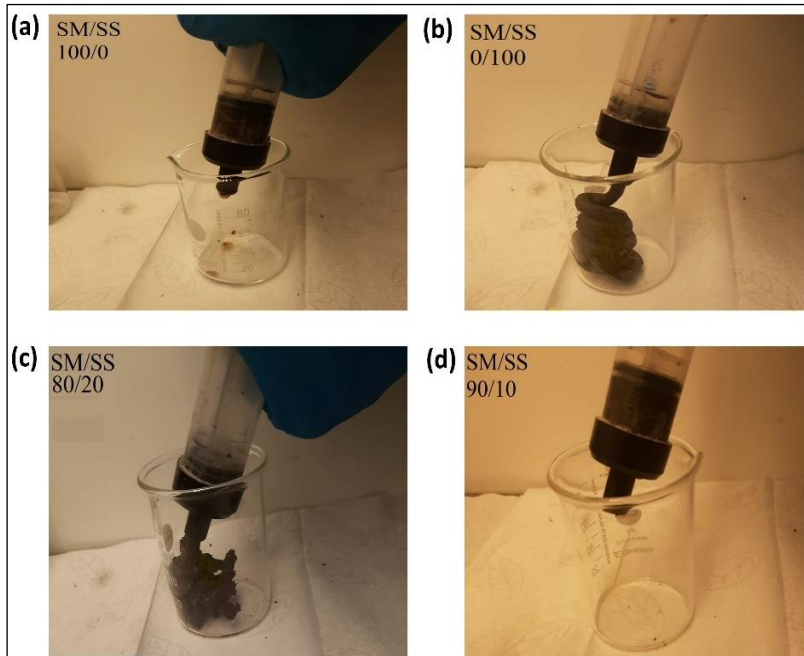

Figure 23. Pumpability analysis, (a) SM, (b) SS, (c) SM/SS (80:20), (d) SM/SS (90:10).

The syringe test revealed that a maximum 80 % of the SM was pumped with 20% of SS under 25% dry matter. When SM was mixed at 90% with SS then blockage of the syringe was observed (Figure 23). Moreover, to get the idea about the effect of the water content, both the feedstocks were made dried, and water was added manually to obtain around 15% dry matter. It was found that water content slightly improved the pumpability of the slurry containing 85 % SM and 15 % SS. Nevertheless, it was the texture and nature of SS that allowed the smooth pumpability of the SM fragments.

The mixed samples gave pumpable slurries due to the presence of extra-polymeric substances (EPS) which are formed by the bacterial activities in the sewage sludge [90]. The second reason could be the presence of substantial amounts of proteins

(40%). During the mixing of SS with SM, the SS particles encapsulated the SM fragments within the pores where water is accumulated. This phenomenon provided a strong binding between the SM and SS fragments and allowed the pumpable slurries. In (SM/SS:90:10), the blockage of the syringe was observed, this is due to the excessive fibrous components of SM, which implies that SS components already acquired their threshold level of absorbing SM fibers.
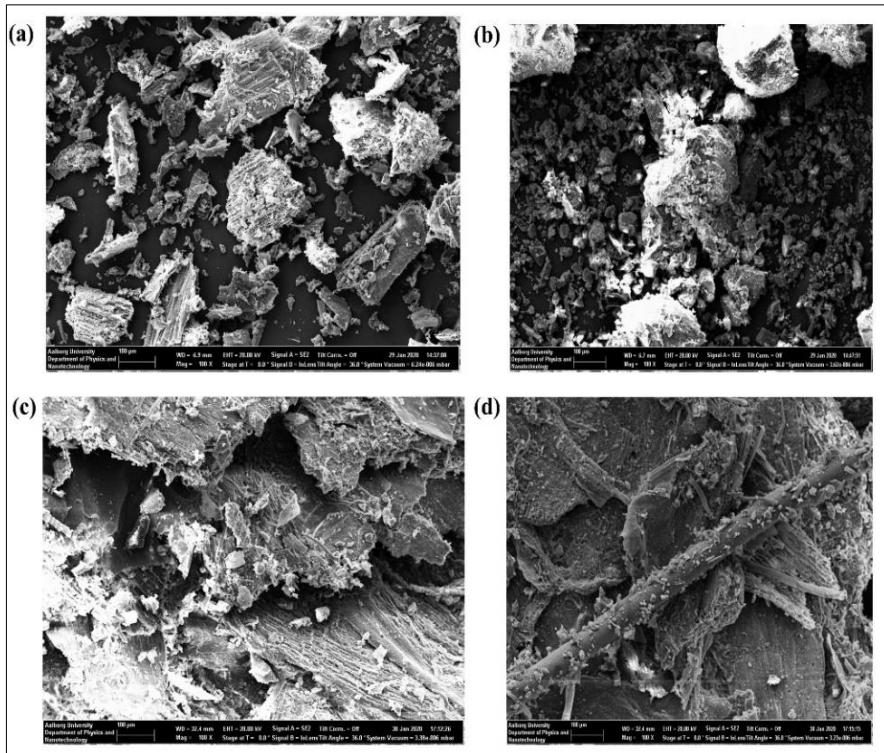

Figure 24. SEM analysis, (a) SM, (b) SS, (c) SM/SS (80:20), (d) SM/SS (90:10).

Previously, Toor et al. found pumpable slurries from Wet distiller's grain with solubles (WDGS) with 35% proteins while processing in the continuous bench-scale plant at Aalborg University [91]. It can be deduced from the above findings that biochemical composition can significantly affect the pumapability of the feedstocks.

The morphological structure of the feedstocks was also analyzed through SEM. Figure 24, highlights four images, where different phases of feedstocks mixtures are observed. Figure 24 (a) shows scattered fibers of SM, (b) the smooth layers of SS components, (c) pumpable slurry of the sample (SM/SS:50:50), and (d) the threshold limit of the SS with SM in (SS/SM:90:10). Earlier, Berglin et al. stated that the moisture content, fiber size, and dry matter content, and degree of dewatering of solid

material can affect the overall pumpability of the feedstock [92]. Despite the easy approach, the syringe test is only indicative and has some limitations like the variation in outlet diameter, shape of the syringe, and the pressure applied by the hand. In the real case scenario, the pressure applied by the piston is around 300 to 350 bar [50], which is quite higher than the pressure applied by the hand.

5.4. Bio-crude from co-liquefaction of swine manure and sewage sludge

From the pumpability analysis, Five samples, namely: SM, SS, SM/SS (50:50), SM/SS (80:20), and SM/SS (20:80) were selected for the HTL experiments. The bio-crude yield in the individual feedstock was lower than the mixed samples. However, SS showed a higher bio-crude yield than SM because of proteins and Fats, as these constituents have a higher conversion rate than carbohydrates in the trend of Fats> proteins> carbohydrates [64].
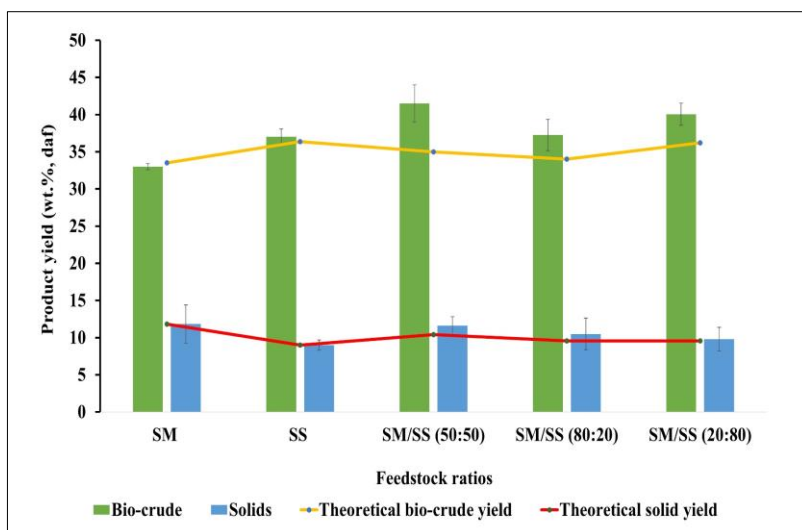
Figure 25. Bio-crude yield at different feedstock ratios.

The higher bio-crude yield in mixed samples could be interpreted by the following postulates. 1) The addition of the proteins and fats fragments from SS with SM. 2) The catalytic action of ash elements especially carbonates of SS over the carbohydrates of SM. 3) The higher ammonium nitrogen (NH_3-N) from the hydrolysis of SS, which could develop an alkaline environment for the efficient hydrolysis of the higher carbohydrates of the SM [52]. The highest bio-crude yield of 42% was found in the sample SM/SS (50:50) with a maximum synergistic ratio of 1.21. The solid yield was noticed in between 9 to 12%, a slightly higher solid yield was observed in the SM sample, which might be due to repolymerization and cyclization reactions and lower conversion rate of carbohydrates in absence of some

catalytic medium. The theoretical yields were also calculated based on the individual feedstock yields and mixing ratios. The experimental yields were fairly higher than the theoretical yields, this replicates the beneficial synergistic effect of co-liquefaction, as illustrated in Figure 25.

Table 13. Quality of the bio-crude.

Samples	Elemental analysis (wt.%)[a]				H/C	O/C	HHV (MJ/kg)	ER	CR
	C	H	N	O[b]					
SM	68.85	9.01	4.10	17.67	1.57	0.19	31.72	53.59	49.37
SS	74.11	9.97	6.13	9.80	1.61	0.10	35.37	56.17	52.79
SM/SS (50:50)	75.35	9.84	4.72	9.10	1.57	0.09	35.74	68.09	63.50
SM/SS (80:20)	70.60	8.83	4.31	15.65	1.50	0.17	32.33	58.45	53.94
SM/SS (20:80)	74.23	9.43	5.54	10.84	1.52	0.10	33.63	59.69	59.34

[a] Dried ash-free basis.
[b] Oxygen was calculated by difference = 100- (C+H+N).

The elemental composition is given in Table 13, which showed higher carbon in the SS bio-crude than SM. Hydrogen was more or less consistent 8-9%. The higher nitrogen was detected in the SS bio-crude due to the presence of proteins. For all the Mixed samples bio-crudes, a higher carbon was noticed than the SM alone, this reflects that SS components (proteins and fats) influenced the composition of the SM, and resulted in more carbon in the bio-crude phase. The maximum energy recovery (68%) with the highest calorific value (35.74 MJ/kg) was calculated from the sample SM/SS (50:50).

Figure 26, shows that ~ 65% of the mass of all the bio-crude was composed of volatiles under 350°C. This range covers the boiling point ranges of gasoline, diesel, and jet fuel. One interesting observation was found that inspite of higher inorganics in the SS, the SS bio-crude contained lower heavy residue as compared to SM at extreme temperatures 750°C. This shows that some repolymerization occurred from carbohydrate fractions of SM during the liquefaction.
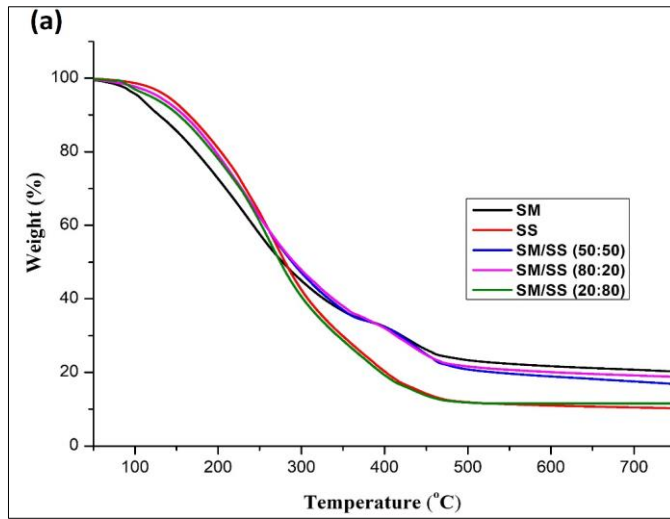
Figure 26. The volatility of the bio-crude at different feedstock ratios.

The solid residues were also analyzed, For SS samples; the higher carbon was transferred to SS solid samples, as given in Table 14.

Table 14. Analysis of solid residue.

Samples	Elemental analysis (wt. %) [a]				H/C	O/C	Ash
	C	H	N	O			
SM	78.54	4.90	2.80	11.86	0.74	0.11	51.00
SS	49.45	5.70	6.10	38.75	1.38	0.58	76.34
SM/SS (50:50)	39.74	2.74	3.63	53.89	0.8	1.01	72.12
SM/SS (80:20)	59.78	3.73	3.00	32.20	0.74	0.40	60.00
SM/SS (20:80)	53.77	3.19	4.10	38.94	0.71	0.54	73.81

[a] Dried-ash free basis.

5.5. Aqueous phase analysis

The SM contained higher TOC values as compared to SS. This indicates the higher degree of solubilization of water-soluble organics into the aqueous phase from SM samples. Whereas lower TOC in the SS could be linked with a higher transference of carbon to the bio-crude and solid phase (as discussed before). The mixed samples demonstrated TOCs in the range of 29 to 37 g/l, as shown in Figure 27.

The higher nitrogen was found in all SS containing samples, but maximum in the SS alone (14 g/l), and lowest in the SM (3 g/l). It is known that the total nitrogen is the sum of organic nitrogen and inorganic nitrogen. Whereas inorganic nitrogen is further

divided into ammonia-N, Nitrate-N, and Nitrate-N. The previous study proved that the concentration of Nitrate-N and Nitrate-N in the inorganic nitrogen only accounted for less than 1%   [93]. In this respect, the ammonia-N was taken as the inorganic nitrogen, and organic nitrogen was calculated by the formula: Organic-N = (Total Nitrogen – Inorganic nitrogen). The results depicted that inorganic nitrogen covered almost 50 to 60% of the magnitude of the total nitrogen, the rest of the nitrogen was termed as organic nitrogen. pH values were measured in the range of 5 to 8. All SS containing samples have higher pH values than SM.

The nitrogen recovery in the HTL products was also estimated. Irrespective of the feedstock ratios, It was found that the major part of the nitrogen 40 to 60% was transferred to the aqueous phase For bio-crudes and solids, the nitrogen contributed 45 to 30 % and 10 to 15% respectively (Figure 28).

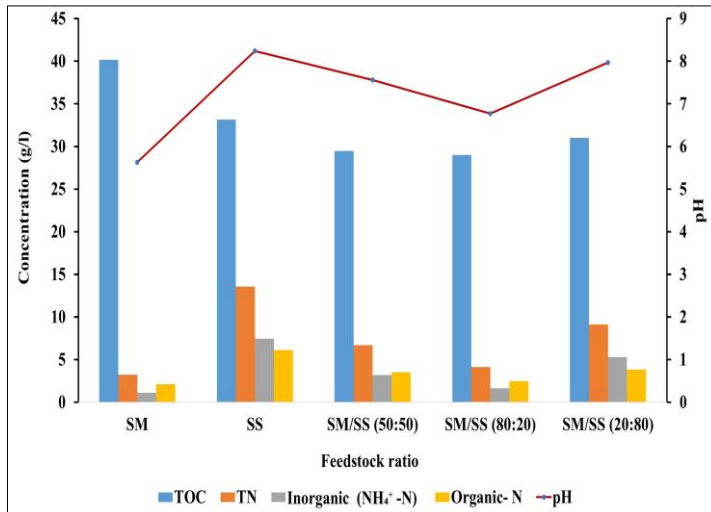Figure 27. Characterization of the aqueous phase.

The dominance of the total nitrogen in the aqueous is due to the hydrolysis of proteins which liberates ammonia and exhibits higher nitrogen in the aqueous phase. This can also be satisfied by other studies, like Chen et al. observed approximately 60% of the nitrogen in the aqueous phase after liquefaction of microalgae in subcritical water [63].
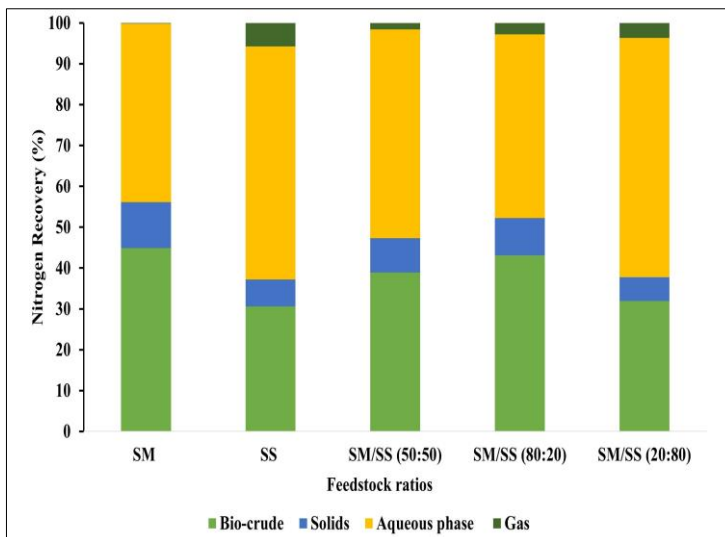
Figure 28. Nitrogen recovery in HTL products.

5.6. Distribution of inorganic elements

The products from three conditions SM, SS, and SM/SS (50:50) were selected for ICP-AES analysis. it was observed that most of the elements like Al, Mg, Ca, Cr, Fe were concentrated in the solid phase. Whereas two alkaline elements sodium and potassium were again dissolved in the aqueous phase in 30 to 60%. In SM alone, a higher amount of Pb was found in the bio-crude, this might be due to the disintegration of some Pb fragments associated with other ions in subcritical water. The Sulfur was the only element that was significantly distributed in all three phases at three conditions. The contribution of the sulfur in the bio-crude accounted for 30 to 55%, as shown in Figure 29.

One interesting finding was observed that feedstock type and feedstock ratio did not affect the overall distribution of the inorganic elements. As all the elements were concentrated to the solid phase. Nevertheless, bio-crude contained some heavy metals like Pb, Cu, Ni, and Fe, which may create adverse problems while upgrading the process of hydrotreatment, like deactivation of the hydrotreatment catalyst, instability, water formation, and coke formation [94].
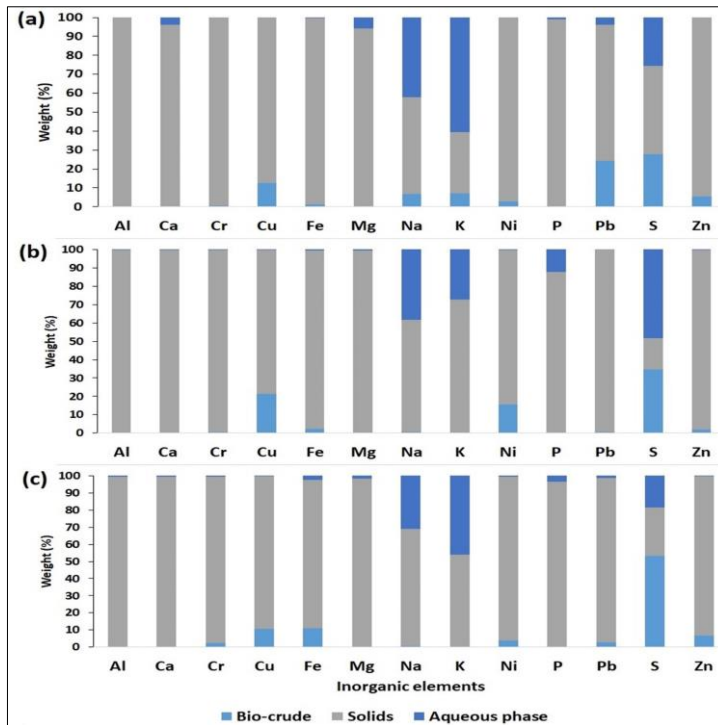
Figure 29. Inorganic elements (a) SM, (b) SS, and (c) SM/SS (50:50).

Till now, the maximum value for the inorganic contents in the suitable biomass for the liquefaction was established around 500 mg/l. However, there is no specific value mentioned for bio-crude [95]. In this regard, the extraction of ash elements before the liquefaction could be a better option before the liquefaction. Therefore, it is suggested to adopt a cost-economic pretreatment method to avoid the transference of heavy metals into the bio-crude.

Chapter 6

Conclusions

HTL is proposed as alternative disposal and simultaneous energy extraction process in the form of bio-crude from sewage sludge in promoting the concepts of waste management and circular economy. This PhD project has investigated the three important aspects of the valorization of the sewage sludge through HTL, its processibility at different temperatures, the impact of aqueous phase recycling, and compatibility of co-liquefaction with other biomass (swine manure). The following conclusions are extracted from the above studies.

From the First study:

- Alkali catalyst increased the bio-crude yield from high carbohydrate-containing sewage sludge with reduction of solid residue at both sub-supercritical conditions.

- The addition of the catalyst resulted in lower nitrogen content in the bio-crude.

- Almost 60% of the mass of all the bio-crudes represented the fractions of gasoline, diesel, and jet fuels.

- A substantial amount of organic carbon (19 to 27 g/l) and total nitrogen was dissolved (~10 g/l) in the aqueous phase, particularly more at supercritical conditions.

- The majority of the ash elements were recovered especially in the solid phase. While potassium and sodium showed a different trend as they were accumulated 30 to 50% in the aqueous phase.

From the Second study:

- The aqueous phase recycling increased the bio-crude yield and energy recovery by 50% after eight rounds of recycling.

- The recycling of the aqueous phase increased the nitrogen content from 4.6 to 7.3 % after eight rounds of recycling.

- The acetic acid was employed as a catalyst, but no significant effect on bio-crude yield and quality was noticed.

- The aqueous phase was comprised of mostly N-heterocyclic, short-chain acids, alcohols, and ketones.

- Phosphorus was mainly recovered in the solid phase; this implies that the solid phase has huge potential to be used extracting material for the phosphorus recovery in the form of struvites.

From the Third study:

- The syringe test demonstrated that SM was easily pumped by the addition of sewage sludge as a co-substrate.

- The maximum bio-crude yield (42%) was achieved at SM/SS (50:50), which showed the synergistic effect of co-liquefaction over bio-crude yield and quality.

- Bio-crude derived from all mixed samples contained higher carbon and HHVs as compared to pure SM-derived bio-crude.

- Aqueous phase analysis showed the TOC range (29 to 40 g/l) and TN range (3 to 14 g/l). However, half of the TN was comprised of inorganic nitrogen.

- The transference of inorganic elements was not highly affected by different mixing ratios of the feedstocks, as the majority of the elements were recovered in the solid phase. Whereas, K, Na dissolved in the aqueous phase, and sulfur was evenly distributed in all three phases.

Chapter 7

Future prospective

The following recommendations can be performed in the continuation of the above studies in the coming future.

- To get a deeper insight into the causes of higher nitrogen in bio-crude in non-alkali catalytic bio-crude, a chemical reaction pathway study of N-containing compounds with the kinetic model is required at the sub and supercritical conditions.

- To establish a mechanism for the phosphorus recovery from the solid phase that can be used as a fertilizer material.

- To develop an extraction method for the recovery of useful elements like sodium and potassium from the aqueous phase, which can later be used as alkali catalysts for HTL of the lignocellulosic and higher carbohydrates containing feedstocks.

- Recycling of the aqueous phase improves bio-crude yield but simultaneously transfers more nitrogen in the bio-crude. Therefore, some TEA studies must be conducted to assess the positive effect of improving bio-crude yield versus the cost associated with upgrading for denitrogenation.

- Since syringe test is only indicative and provides the fundamental knowledge about the pumpablity at laboratory scale. Therefore, a continuous plant scale study needs to be done to compare these batch scale results with the continuous plant. Additionally, in near future, any catalytic study can be a good option to explore its effect on the co-liquefaction of SM and SS.

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