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Seehar, Tahir Hussain

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BY
TAHIR HUSSAIN SEEHAR

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DENMARK

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PH.D. DISSERTATION

By

Tahir Hussain Seehar

Department of Energy Technology

Aalborg University, Denmark

AALBORG UNIVERSITY
DENMARK

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PhD supervisor: Associate Professor Saqib Sohail Toor,
Aalborg University Denmark

PhD committee: Associate Professor, Jens Muff (chairman)
Aalborg University

Dr. Klaus Raffelt
Karlsruhe Institute of Technology (KIT)

Associate Professor Souman Rudra
University of Agder

PhD Series: Faculty of Engineering and Science, Aalborg University

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Preface

This PhD thesis mainly contains the outcomes of research work I have performed during the PhD project within the Advanced Biofuel research group at the Faculty of Engineering, Science, and Department of Energy Technology, Aalborg University Denmark.

The journey and the path of PhD study is full of challenges and obstacles with several ups and downs which I experienced and faced but in the end…. It is successfully completed. In this regard, I would like to thank my supervisor, Associate Professor, Saqib Sohail Toor who always encouraged me and was supportive throughout the project.

I would like to express my sincere gratitude to my former supervisor, former research group leader and active head of department (Department of Energy Technology, AAU) Prof. Lasse A. Rosendahl for his suggestions and expert guidance to accomplish the milestones. Furthermore, I should must appreciate the efforts of present research group leader Associate Professor, Thomas Helmer Pedersen and all my colleagues, group members for their continuous guidance and collaboration. In connection with this work, I would like to thank Dr. Ursel Hornung who hosted me for the study abroad studies at KIT University Germany.

I might not neglect to thank Higher Education Commission (HEC) Pakistan and Dawood University of Engineering, Science and Technology, Pakistan for financial support.

Finally, I am really graceful and grateful to my wife for her unconditional support, and care throughout the PhD time period. Additionally, I would like to extend my gratitude to my parents, family members especially my sweet daughter Surhan Fatima for their support and best wishes.

Contents

Nomenclature

Abbreviations, acronyms, and units:

AP	Aqueous phase
Al	Aluminum
As	Arsenic
Btu	British thermal unit
CCA	Chromate copper arsenate
Cr	Chromium
Cu	Copper
Ca	Calcium
CAT	Catalytic
CO	Carbon monoxide
CO_2	Carbon dioxide
CH_4	Methane
CHN	Carbon Hydrogen Nitrogen
℃	Degree Celsius
CW	Construction wood
Cd	Cadmium
CR	Carbon recovery

d.a.f.	Dry ash free
d.b.	Dry basis
DEE	Diethyl ether
EIA	Energy Information Administration
EU	European Union
ER	Energy recovery
Fe	Iron
GCMS	Gas Chromatography- Mass Spectrometry
GHG	Greenhouse gases
H_2	Hydrogen
H/C	Hydrogen/Carbon
HMs	Heavy metals
HHV	Higher heating value
HZW	Hazardous wood
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
kJ	Kilo joule
K/min	Kelvin per minute
K	Potassium
LBNL	Lawrence Berkeley National Laboratory
MPa	Mega Pascal
Mt	Metric tons
Mg	Magnesium

Mm	Millimeter
MXW	Mixed wood
Mn	Manganese
NR	Nitrogen recovery
N_2O	Nitrogen oxide
Ni	Nickel
Na	Sodium
NHZW	Non-hazardous wood
NC	Non-catalytic
NO_x	Nitrogen oxides
O/C	Oxygen/Carbon
P	Phosphorus
Pc	Critical pressure
Pb	Lead
PNNL	Pacific Northwest National Laboratory
REDII	Revised directive on renewable energy
S	Sulfur
Si	Silicon
TOC	Total organic carbon
TGA	Thermo-gravimetric analysis
TN	Total nitrogen
TP	Total phosphorus
UN	United Nations

UNW	Untreated wood
WS	Wheat straw
Zn	Zinc

Thesis details

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Ph.D. Student: Tahir Hussain Seehar

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

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

Main Publications

[A] **T.H. Seehar**, S.S. Toor, A.A. Shah, T.H. Pedersen, L.A. Rosendahl, "Biocrude Production from Wheat Straw at Sub and Supercritical Hydrothermal Liquefaction", Energies 13 (2020) 3114, (doi:10.3390/en13123114)

[B] **T.H. Seehar**, S.S. Toor, A.A. Shah, A.H. Nielsen, T.H. Pedersen, L.A. Rosendahl, "Catalytic hydrothermal liquefaction of contaminated construction wood waste for biocrude production and investigation of fate of heavy metals", Fuel Processing Technology 212 (2021) 106621 (https://doi.org/10.1016/j.fuproc.2020.106621)

[C] **T.H. Seehar**, S.S. Toor, K. Sharma, A.H. Nielsen, T.H. Pedersen, L.A. Rosendahl, "Influence of process conditions on hydrothermal liquefaction of eucalyptus biomass for biocrude production and investigation of the inorganics distribution", Sustainable Energy & Fuels 2021, (DOI: 10.1039/d0se01634a)

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

Publications

[D] F. Conti, S. S. Toor, T. H. Pedersen, **T. H. Seehar**, A. H. Nielsen, L. A. Rosendahl, "Valorization of animal and human wastes through hydrothermal liquefaction for biocrude production and simultaneous recovery of nutrients", Energy Conversion and Management 216 (2020) 112925 (https://doi.org/10.1016/j.enconman.2020.112925)

[E] A.A. Shah, S.S. Toor, **T.H. Seehar**, R.S. Nielsen, A.H. Nielsen, T.H. Pedersen, L.A. Rosendahl, " Bio-Crude Production through Aqueous Phase Recycling of

Hydrothermal Liquefaction of Sewage Sludge", Energies 13 (2020) 493 (doi:10.3390/en13020493)

[F] A.A. Shah, S.S. Toor, **T.H. Seehar**, K.K. Sadetmahaleh, T.H. Pedersen, A.H. Nielsen, L.A. Rosendahl, "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)

[G] S. S. Toor, F. Conti, A. A. Shah, **T. H. Seehar**, L. A. Rosendahl, "Hydrothermal Liquefaction-A Sustainable Solution to the Sewage Sludge Disposal Problem", Advances in Waste-to-Energy Technologies (2019), Chapter 9, 143-163 ISBN 978-1-138-39042-316

Conference contributions

[1] **T.H. Seehar**, F. Conti, A.A. Shah, S.S. Toor, T.H. Pedersen, L.A. Rosendahl, "Techno-Economic feasibility of producing renewable fuels from sewage sludge through Hydrothermal Liquefaction", Poster presentation at 27th EUBCE 2019, Lisbon (Portugal), 27th-30th May 2019.

[2] **T.H. Seehar**, S.S. Toor, A.A. Shah, L.A. Rosendahl, "Production of bio-crude through Hydrothermal Liquefaction of Wheat Straw in Subcritical and Supercritical Water", Oral presentation at tcbiomass 2019, Chicago (USA), October 7-9, 2019.

[3] **T.H. Seehar**, K. Sharma, S.S. Toor, T.H. Pedersen, L.A. Rosendahl, "Catalytic Hydrothermal Liquefaction of Eucalyptus: Effect of Reaction Conditions on Bio-oils Properties", Oral presentation (virtual) at Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products (TCS2020). Organized by: TCS-Washington State University, USA. October 5-7, 2020.

[4] **T.H. Seehar**, S.S. Toor, A.A. Shah, T.H. Pedersen, L.A. Rosendahl, "Supercritical Hydrothermal Liquefaction of Construction Wood Waste for the Production of Biocrude", Oral presentation at 2nd Bioenergy Sustainability Conference (virtual), Organized by: Institute for sustainability- An AIChE Technological Community, USA. October 13-15, 2020.

This thesis has been submitted for assessment in partial fulfillment of the PhD degree. The thesis is based on the 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 rapid growth of energy demand, depletion of fossil fuel reservoirs, global warming and the climate change concerns are the major issues nowadays. To meet the energy demands accompanied with GHG reduction in the transportation sector, renewable energy resources are highly required as an alternate of fossil fuels. In this context, hydrothermal liquefaction (HTL) process is increasingly gaining attention as a promising and efficient technology to produce biofuels. The feedstock flexibility, free from pre-drying requirement and the delivery of high yields- high quality biocrudes from variety of waste streams makes the HTL more sustainable and attractive route. The aim of the present work is to valorize the lignocellulosic feedstocks from three different waste streams to produce biocrude and valuable energy dense products through the HTL process and the investigation of effects of the process conditions on process performance.

In the first study, highly potential feedstock from agriculture waste stream i.e., wheat straw (WS) was processed through HTL process to produce biocrude and additive products. The effects of process temperature (sub-supercritical) and alkali catalyst (K_2CO_3) were investigated in detail. The experimental results revealed that, at 350℃-catalyst condition, HTL has high performance from biocrude yield and energy recovery perspectives. The highest biocrude yield (32.34 wt. %) with lowest solid yield (4.34 wt. %) was achieved by the addition of alkali catalyst at subcritical condition. There was no significant variation was observed for the higher heating value (HHV) of biocrudes at all four conditions that was around 35 MJ/kg. Based on the outcomes of inorganic contents, it was noticed that the majority of micronutrients (Fe, Zn) and macronutrients (P, Ca, Mg) were recovered in the solid phase product that can be proposed to utilize as a soil conditioner etc. Furthermore, to keep consider the advancement of HTL process as a continuous process at commercial scale, the effect of aqueous phase recirculation was also explored. In results, the fruitful consequences were achieved by means of increasing biocrude yield.

In the second study, the construction wood waste (untreated wood, non-hazardous wood, hazardous wood, and mixed wood) from urban waste stream were processed through supercritical hydrothermal liquefaction process. The overall aim was to investigate the effect of impregnation on the performance of the HTL process. Additionally, the objective was to elucidate the fate of heavy metals (Cr, Cu, Ni, and Zn) involved in the liquefaction process and their migration to the different HTL product phases. By the HTL of different waste wood at 400℃, maximum biocrude yield was achieved by processing of untreated wood followed by non-hazardous, hazardous and mixed wood samples. The overall biocrude yield was obtained in range between 24.86 and 36.35 wt.%. By the investigation of fate of heavy metals, it was concluded that the majority (80-95%) of detected heavy metals were migrated to the solid phase product in case of impregnated wood. However, very few amount of

targeted heavy metals were also shifted to the biocrude and aqueous phase that needs proper attention before HTL upgrading process. Through this way, HTL is suggested as a sustainable and promising pathway for the disposal of contaminated wood waste materials by converting into renewable biofuel.

In the third study, eucalyptus biomass from forest waste stream was converted into biocrude through HTL process. The influence of different process parameters (temperature, catalyst) was initially investigated. The effect of process retention time (5, 10, 15, 20, and 25 min) on the biocrude yield and the energy recovery was examined. The major portion (about 65-71%) of obtained biocrude were identified as the fractions containing the nature of gasoline, diesel, jet fuel and maritime fuel range. In case of the chemical composition of biocrudes, the oxygen aromatics and ketones were common compounds in biocrude at all retention times. Additionally, around 21-97% of inorganics were shifted to the solid phase. In overall, it was concluded that the catalytic-subcritical liquefaction at 15 min process retention time is an optimum condition for biofuel production and nutrients recovery.

From the outcomes of above-mentioned studies of the PhD work, it was concluded that the HTL is an efficient and sustainable process to handle the different feedstocks from different waste streams. The energy dense biocrude, the nutrient rich solids, and the organic rich aqueous phase can be utilized as renewable resources for different purposes in different sectors. However, the biocrude from HTL process required upgrading to meet the drop-in fuel quality. The integration of HTL technology with agriculture, urban, and forest waste streams can play the fruitful role to reduce the energy and environmental concerns as well as improve the circular economy.

Resumé

Den hurtige stigning i efterspørgslen på energi på grund af befolkningstilvækst og udtømning af reservoirer med fossile brændsler, global opvarmning og bekymringer om klimaforandringer er store problemstillinger. For at imødekomme efterspørgslen på energi samtidig med en reduktion i udledningen af drivhusgasser i transportsektoren, er der et stort behov for vedvarende energikilder som alternativ til fossile brændstoffer. I den sammenhæng får hydrothermal liquefaction (HTL) processen øget opmærksomhed som en lovende og effektiv teknologi til at producerer biobrændstoffer. Processen er fleksibel med hensyn til input af råmaterialer fra forskellige affaldsstrømme, kræver ikke tørring af råmaterialerne og leverer et stort udbytte af bioråolie af høj kvalitet, hvilket gør HTL til en bæredygtig og attraktiv proces. Målet med dette arbejde er at valorisere råmateriale rigt på lignocellulose fra forskellige typer affaldsstrømme for at producere bioråolie og andre værdifulde produkter med høj energidensitet gennem HTL-processen og undersøge betydningen af procesbetingelserne på resultatet af processen.

I det første studie blev brugen af råmateriale med stort potentiale fra landbruget, dvs. hvedehalm, testet i HTL processen for at producere bioråolie og andre værdifulde produkter. Betydningen af procestemperaturen (sub-superkritisk) og tilsætningen af en alkalisk katalysator (K_2CO_3) blev undersøgt i detaljer. De eksperimentelle resultater viste at ved 350°C og med tilsætning af katalysator har HTL et højt udbytte af bioråolie og høj energigenvinding. Det højeste udbytte af bioråolie (32.34 wt.%) med det laveste udbytte af den faste fraktion (4.34 wt. %) blev opnået ved at tilsætte den alkaliske katalysator ved subkritiske betingelser. Der var ingen betydelig variation i øvre brændværdi af bioråolierne ved de fire testede betingelser. Den øvre brændværdi var omkring 35 MJ/kg. Med hensyn til uorganisk materiale, blev det bemærket at hoveddelen af mikronæringsstoffer (Fe, Zn) og makronæringsstoffer (P, Ca, Mg) blev genvundet i den faste fraktion, som dermed muligvis kan at anvendes som gødning til jord osv. Til sidst blev effekten af at recirkulere vandfasen undersøgt for at bidrage til overvejelser om udvikling af HTL-processen til en kontinuert proces på kommerciel skala. Resultaterne var positive og førte til et øget udbytte af bioråolie.

I det andet studie blev affald fra bygningstræ (ubehandlet træ, ikke-sundhedsskadeligt træ, sundhedsskadeligt træ og blandet træ) behandlet i en superkritisk HTL-proces. Det overordnede mål var at undersøge betydningen af imprægnering på effektiviteten af HTL-processen. Desuden var det et mål at belyse hvor tungmetaller (Cr, Cu, Ni, and Zn) involveret i HTL-processen ender og deres vej gennem de forskellige faser i HTL-processen. Ved HTL af de forskellige typer træaffald ved 400°C blev det maksimale udbytte af råolie opnået ved at brug af ubehandlet træ, efterfulgt af ikke-sundhedsskadeligt, sundhedsskadeligt og blandet træ. Det overordnede udbytte af bioråolie var mellem 24.85 og 36.35 wt. %. Ved undersøgelsen af tungmetallernes vej i processen blev det konkluderet at hoveddelen (80-95%) af de påviste tungmetaller

endte i den faste fraktion ved imprægneret træ. Dog blev en lille del af tungmetallerne også fundet i bioråolien og i vandfasen, hvilket kræver opmærksomhed før opgraderingsprocessen efter HTL. Altså er HTL en bæredygtig og lovende vej til afskaffelse af kontamineret træaffald ved at konvertere det til vedvarende biobrændstof.

I det tredje studie blev eukalyptus-biomasse fra skovaffald konverteret til bioråolie gennem HTL-processen. Betydningen af forskellige procesbetingelser (temperatur, katalysator) blev først undersøgt. Betydningen af opholdstiden i reaktoren (5, 10, 15, 20 og 25 min) på udbyttet af bioråolie blev også undersøgt. En stor del (omkring 65-71%) af bioråolien blev identificeret som fraktioner som indeholdt benzin, diesel og flybrændstof og tung brændselsolie. Med hensyn til den kemiske sammensætning af bioråolien, var oxygenaromater og ketoner almindelige kemiske forbindelser i bioråolien ved alle testede opholdstider i reaktoren. Desuden endte 21-97% af de uorganiske stoffer i den faste fraktion. Det blev konkluderet at de optimale betingelser for produktion af biobrændstof og genindvinding af næringsstoffer var den katalytiske subkritiske HTL-proces med en opholdstid på 15 min i reaktoren.

Fra resultaterne af de ovennævnte studier i denne PhD blev det konkluderet at HTL er en effektiv og bæredygtig proces til at håndtere forskellige råmaterialer fra forskellige affaldsstrømme. Den energitætte bioråolie, den faste fraktion rig på næringsstoffer og vandfasen rig på organiske stoffer, kan udnyttes som vedvarende ressourcer til forskellige formål i forskellige sektorer. Bioråolien fra HTL-processen kræver dog opgradering for at møde kvalitetskravene til drop-in brændstof. Integrationen af HTL-teknologien med affaldsstrømme fra landbrug, by og skov kan bidrage til løsningen på energi- og miljøproblemer og cirkulær økonomi.

Part I: Extended summary

Chapter 1
Introduction

1.1 Global warming and climate change

Climate is considered as the most valuable and natural resource for the survival of living organisms. For years, the global warming and climate change have been addressed as global concerns. Climate change is an existential threat and the most important issue for all the living organisms on the planet earth. Accumulation of greenhouse gasses (GHG) such as carbon dioxide (CO_2), methane (CH_4), nitrogen oxide (N_2O) into the environment from the anthropogenic activities like power plants, industries, transportation, burning of fossil fuels etc is highlighted as the main route cause of global warming [1]. It was reported that the concentration of CO_2 was increased from 320 ppm to 400 ppm in the earths atmosphere from 1958 to 2013 [2]. According to predictions, the overall concentration of CO_2 will be doubled compared to preindustrial revolution through which the average global temperature will increase from 1.5 to 4.5℃ by end of the century [3]. The consequences of increasing global warming are occurring in the form of rising sea levels, heat strokes, unusual heavy rains, and different environmental episodes that significantly affect the natural ecosystem. The imbalance between natural environment and manmade activities would posses the high level of risk to meet the water and food demand for posterity.

Young climate activist Greta Thunberg explained the importance of global warming and climate change during her speech at UN Climate Action Summit 2019 in New York city and pointed that the people are suffering and dying because the entire ecosystems are collapsing [4]. The use of fossil fuels to produce energy in industrial as well as transport sector released significant amount of GHG that cause the premature death of many thousands people in europe [5]. Among them, coal based combustion processes generate the highest amount of CO_2. Based on the recent energy reports, the emissions from the burnings of fossil fuels in the EU countries enlarged from 2600 Mt CO_2 in 1960 to 3500 Mt CO_2 in 2018 [6]. In response to increasingly restrictive emissions requirements, several European countries have changed inefficient coal based power plants. According to the Climate Analytics, The Europe union aims to have a zero- GHG emissions economy by the year 2050, which is the main objective of the European Green Deal. The objective lies in association with the Europeans commitment under the Paris Agreement that targets to keep global warming below 1.5 °C [7]. Figure 1, shows the trend of CO_2 emissions from 1960-2018 in Denmark and the share based on the sectors. It can be observed that, comparatively 1996, the emissions are reduced from 75 Mt to 35 Mt CO_2 in 2018.

However, the data also reflects that transport sector has major contribution in releasing of CO_2 in Denmark. To meet the EU targets of 2050 related to the zero- GHG emissions, the concentration of emission needs to be declined in Denmark.

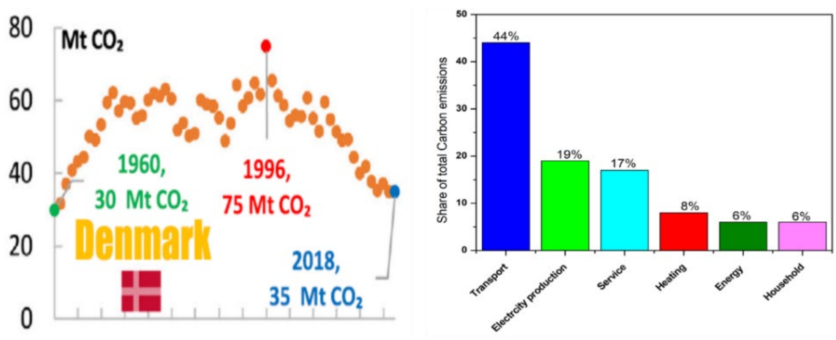

Figure 1: On the left side, Carbon dioxide emissions trend in Denmark 1960-2018 (based on data [6]). On the right side, share of CO_2 emissions in Denmark in 2017, by sector (based on data [13]).

As stated by McGlade et al., if the world is being continuously rely and dependent on fossil fuels in different energy sectors, the global temperature will exceed the critical level of 2℃ [8]. At the other end, the age of fossil fuels are getting decreased by increasing world's population and industrial growth. According to the current statistics, the world´s population is projected to 8 billion in near future with the increasing rate of 1% every year [9]. The population growth creates the demand for food and fuel to meet the daily life requirements. Thus, the dependency upon fossil fuels especially in transportation sector is switching towards renewable resource. The production of transportation fuel from the renewable resources may play a sustainable role for the development of environmental friendly society by reducing the GHG emissions.

Parallel to the environmental issues, the energy crises could not be forgotten. As per Energy Information Administration (EIA), total annual energy consumption surpassed 500 quadrillion Btu in the 2010, which was 282.817 quadrillion Btu in 1980 that is predicted to meet 815 quadrillion Btu in 2040 [10, 11]. On the other hand, it was reported that by combining the gasoline, heavy oil, diesel and jet fuel, the energy supply demand for the transport sectors is approximately 11 billion liters per day throughout the world [12]. To meet the demand of this large mass of energy is a kind of challenging for the concerned industry and seems to be difficult to recover from the conventional resources only like fossil fuels. In results, this challenge attracts researchers, entrepreneurs, etc towards the production of transportation fuel from renewable resources. No doubt, it seems that today the fossil fuels have burdened to meet the energy demands, which are decreasing, and containing negative environmental impacts. To reduce the energy and environmental croncerns, renewable energy resources may play an important role to maintain sustainable development and address energy and environmental challenges.

1.2 Biomass and advanced biofuels

Biomass is well known as organic matter, energy resource that derived from the number of sources and used since centuries for different purposes. Due to abundant natural resources, it was estimated that approximately 100 billion tons of biomass quantity produced annually [14]. It is reported that the global production of lignocellulosic feedstock is approximately 120×10^9 ton per annum that is around 300 times more (in the form of energy) than the requirement of current global energy [15]. The conversion of biomass to bioenergy is considered as renewable energy that has critical importance nowadays to reduce the GHG emissions [16]. According to recent statistics, the energy production from biomass resource has contribution of 5×10^{19} kJ annually that corresponds to 10% of energy consumption globally [1]. This value of energy production is expected to extent 150×10^{19} kJ by 2050 by utilizing the energy production from number of biomass resources [17]. In European perspective, EU Council directed a minimum of 27% of its total energy consumption must be derived from renewable resources like biomass, for that minimum 0.5% of the fuel supply in transportation sector is mandatory produced from 2nd generation biofuels by the year 2030 [18]. The process of shifting from fossil fuel to renewable resource certainly reduce the environmental and energy concerns as well as dependence on non-renewables.

Among the biomass categories, lignocellulosic biomass is famous for their abundant supply, cheap economic values, carbon neutral and environmental friendly nature. The total quantity of CO_2 involved in the production, consumption and releasing by conversion process is net zero that means that utilization of lignocellulosic biomass do not put any environmental burden in the form of carbon emissions [19]. For lignocellulosic biomass especially agricultural and forest feedstocks, a study famous as “Billion Ton Study” reported in USA. According to that study, approximately 241 and 103 million dry tons could be used for biofuel production from agricultural and forest biomass respectively [20]. In the past decades, traditionally, the residual biomass from agricultural and forest sectors has been used for different purposes like heating in general, gasification process for power generation, ethanol via fermentation and for the production of briquette fuels etc. The alternate and environment friendly application for the efficient utilization has introduced for the conversion of forest and agricultural biomass into an advanced biofuels through thermochemical process.

Biofuels produced from the biomass and waste materials are capable of reducing the dependency on fossil fuels, mitigate the environmental concerns and may play an important role to enhance the circular economy. Depending upon the sustainability and ease of use, biofuel feedstock are divided into main three classes i.e., first, second, and third generation. Initially, 1st generation biofuels (bioethanol by the fermentation of sugar and biodiesel through the transesterification of vegetable oil) were introduced that derived from agricultural sources like maize, vegetable oil, sugar and starch etc., that then raised concerns about the food security and results a debate highlighted as "food vs fuel". After that, 2nd generation biofuels were highlighted produced from agricultural, forest residue and non-food crops waste materials that reduce the land-use and food security issues. Presently, more than 90% of total biofuels like the biodiesel and bioethanol are extracted from the edible feedstocks i.e., vegetable oil, grain etc. In this context, it is expected that this pattern might not be the right path for achieving the demand for transport biofuels in the future [21]. Advanced biofuels from number of feedstocks especially waste materials are the alternate and sustainable option to meet the certain demands. In this perspective, lignocellulosic biomass are considered as favorable candidate to produce advanced biofuels due to abundant potential and easily accessible. Through the production of advanced biofuels from different biomass materials, the EU directive on renewable energy (REDII) can meet the renewable energy targets especially an input of 14% of the renewable energy in transportation sector by 2030 [22].

Thermochemical techniques are famous as an energetic and effective conversion methods for the de-polymerization of different biomasses to energy dense products. Fast rate of reactions, variety of feedstocks, and choice of desired products like biocrude, biochar, gasses, and value added chemicals are the favorable points of thermochemical methods [23, 24]. The selection of any thermochemical method (pyrolysis, hydrothermal liquefaction, gasification, carbonization etc.) is mainly depend upon the choice of desired product. Among biomass processing technologies for the production of advanced biofuels, Hydrothermal Liquefaction (HTL) process is getting more attention due to its feedstock flexibility, process conditions, reaction environment, cost-competitiveness and environmental friendly nature [25, 26, 27, 28].

1.3 Hydrothermal Liquefaction

Hydrothermal Liquefaction is one of the thermochemical process that deals with number of feedstocks like dry as well as wet biomasses to produce biocrude and value added products. After the global oil crisis, Appell et al. at the Pittsburgh Energy Research Centre performed HTL process first time in 1970. The pioneer of this process used wood as a feedstock and process at 330–370°C for a retention time of 10–30 min and obtained biocrude yield in range between 45–55% by using sodium bicarbonate ($NaHCO_3$) as a catalyst. Afterwards, the conversion of biomass to biocrude was continued by the Lawrence Berkeley National Laboratory (LBNL) and Shell research laboratory (Netherlands) by dealing different feedstocks [29].

From centuries to minutes, HTL is famous for the production of the biocrude within few minutes (10-30 min) which we used to obtain from nature in the form of fossil fuels that result from the decomposition of plants and animals in centuries. During the HTL process, in the presence of water or another solvent, biomass is directly converted to biocrude that is the main and targeted product of the HTL process. Biocrude is a viscous dark brown liquid contains aromatic and hydrocarbon compounds along with high number of oxygenated compounds [30]. The behavior of water within the process during high temperature and pressure is simultaneously considered as a reactant and catalyst for the biomass decomposition and de-polymerization to produce energy dense biocrude. Additionally, the employment of the catalyst also play an important role and enhance the conversion efficiency of the process. Generally, HTL operates at high temperature range (300-450℃) with elevated pressure (15-35 MPa) in subcritical or supercritical water conditions (T_c = 374°C and P_c = 22.1 MPa) [31, 32]. In the response of high pressure and temperature of water in the HTL reactor, the dielectric constant and the viscosity of water starts decrease that results more solubility for the organic compounds during the reactions. Closer to the water critical point, water becomes in the state with lower viscosity and capability of higher solubility of organic compounds. At this point, due to this behavior, the process efficiency, quality and biocrude increases [33].

During HTL, biomass undergoes to the series of complicated reactions including hydrolysis, decomposition, cracking, dehydration, and condensation mentioned by Nazari et al., and as shown in Figure 2 [29]. The result of the chain reactions, at the downstream of the HTL process, biocrude, biochar, aqueous phase and gasses are obtained in which biocrude is considered as a targeted product of the process. The biocrude from the HTL process possess low carbon footprint as well as low sulfur content that is consider a highlighted advantage to the petroleum-based fuels [34]. Generally, the biocrude yield produced from the HTL varies from 22 to 64% with and the heating value ranges from 27 to 38 MJ kg^{-1} mainly depend upon the type of biomass used and the process operating conditions [32, 35].

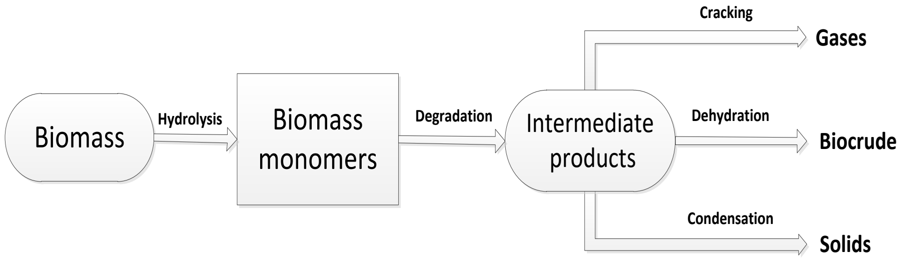

Figure 2: Biomass to Products- HTL process reaction pathway.

1.4 Lignocellulosic fraction in HTL

Lignocellulosic biomass is composed of the complex structure that mainly contains three major components named as cellulose, hemicellulose, and lignin. The rest of the additives that are available in the minor and inconsiderable portion are pectin, protein, and ash etc. Generally, the concentration of carbohydrates in the lignocellulosic biomass are as cellulose 25-44%, hemicellulose 10-44% and lignin 21-44% with ash content around 1-5% [36, 37]. However, the variation in the biomass composition is also related to different parameters like cultivation crop season, storage time, treatment and origin of the feedstock etc. In general, the concentration of cellulose is higher than the hemicellulose and lignin that is considered favorable. As stated by Elliott et al. the biomasses with greater carbohydrates can produce higher biocrude due to the repolymerization whereas the cyclization of lignin fractions in the biocrude can reduce the biocrude yield [38].

The carbohydrates especially cellulose is linear polysaccharide that is made up of D-glucose containing crystalline structure that makes it insoluble in water. Cellulose forms liner homo-polymer chains of 100 to 140,000 units and the each unit is made up of a glucose disaccharide (double sugar), which are linked by a glycosidic bond [39]. The cellulose acts as reinforcing agent that provides additional structural strength. The cellulose and hemicellulose undergo hydrolyzed and convert into simple sugar components, whereas, lignin as a supporting element to the cell structure [40]. In HTL, the subcritical water having greater ionic product break the crystallinity and enhance the decomposition of the cellulose by increasing the process temperature. The hemicellulose is branched shaped polymer, heteropolysaccharide that contains number of monosaccharides mainly xylose, glucose, pentoses, hexoses, and mannose as well as sugar acids with xylan etc. It acts as a hydrated cement that attach cellulose and lignin together. The random and non-crystalline structure of hemicellulose make it easy to hydrolyze. During liquefaction process, hemicellulose easily dissolve in the water that results in the formation of polysaccharides, sugars, acids (acetic, formic acid), and aldehydes. Additionally, lignin is highly complicated and non-carbohydrate polymer (hetero-polymer) with irregular structure and contains monomeric units of alcohols [39]. Normally, within biomass structure, it occupies the space between cellulose and hemicellulose and maintains the strength of primary structure and associate with hemicellulose by covalent bonds. It behaves as a resistant to chemical degradation; however, during HTL processing, many phenolic compounds formed in the result of hydrolysis of ether bonds [29, 37]. In general, it was reported that the lignocellulosic feedstocks with high lignin content have less biocrude yield and lower conversion rate [41]. In the chain of all three main components, hemicellulose and lignin are separately connected to the cellulose with the help of covalent hydrogen bonds.

Besides the process efficiency, the cost of the processing feedstock is an important factor for biofuel production through HTL process. Although the techno-economic studies have reported that HTL is cost competitive than other thermochemical process [25, 26]. However, to reduce the overall cost, waste fractions (like waste from different waste streams) are more suitable for economic point of view. Additionally, the proper utilization and the disposal of waste materials are also mandatory to avoid the environmental pollution. In this way, by processing the waste fractions in HTL results mitigation of environmental pollution by waste management strategy, improve the circular economy by the biocrude production, and value added products.

1.5 Overview of the PhD Project and Thesis Outline

This PhD project explores the different lignocellulosic waste fractions individually from agriculture, urban, and forest waste streams for processing in the HTL to obtain the biocrude and investigate the different aspects associated with the process. Although HTL is not developed at commercial scale yet, the investigation of variety of lignocellulosic biomass may bring the knowledge that helps to make a decision by considering the different opportunities and challenges discussed in this project. The barriers in upscaling the HTL process are also highlighted.

The thesis is constituted by three main studies [A, B, C] focused on different lignocellulosic feedstocks from different sources. The theme, process conditions of processing the feedstocks were designed according to the targeted aims and objects. The schematic present in the Figure 3 demonstrates a summarized outline of all three studies.

The first sub-project is about the investigation of abundantly available waste residue in agriculture sector well known as wheat straw. The study demonstrate the influence of temperature and alkali catalyst on the conversion of wheat straw for biocrude production. The distribution of organic and inorganic contents during sub- and supercritical process environment in HTL products was discussed in detail.

Additionally, the effects of aqueous phase recirculation on product yield and energy recovery were also explored.

The second study was designed to analyze the effects of the impregnation on the performance of HTL process. In that study, two categories of wood (hazardous and non-hazardous) from urban stream were used along with untreated and mixed wood. Additionally, the objective was to examine the fate of heavy metals among HTL products and ultimately evaluate if the impregnation chemicals can be isolated and recovered in the supercritical condition.

The third study was related to the processing of fast growing forest tree named as eucalyptus. In this study, the intention was to assess the effect of different process conditions on HTL process. Furthermore, the role of retention time on biocrude production, energy recovery and migration of nutrients (Ca, P, Mg etc.) and heavy metals (Cr, Cu, Ni etc.) was discussed in detail.

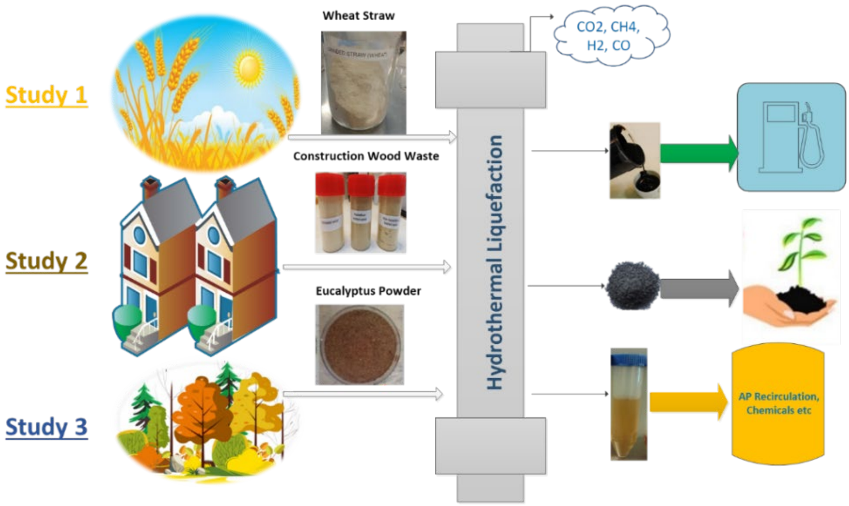

Figure 3: Outline of the PhD project (HTL of lignocellulosic feedstock from three different waste streams for biofuel production).

The present thesis mainly contains two parts: Part I and Part II.

Part I is the comprehensive summery of the PhD project including the research background, experimental methodology, and the core results from the studies in connection to the main publications. This part is divided into following chapters.

Chapter 1: Introduction and background of research work

Chapter 2: Experimental methodology

Chapter 3: Results from HTL of wheat straw (paper A)

Chapter 4: Results from HTL of construction wood (paper B)

Chapter 5: Results from HTL of eucalyptus biomass (paper C)

Chapter 6: Conclusions from all three main studies

Chapter 7: Future perspective and research gapes for future studies

Part II of the thesis contains all the published work during the PhD study. The publications A, B, and C are based on the main work on lignocellulosic biomasses and the outcomes of those three studies are reported and discussed in this thesis as a core contribution of the PhD study. However, the three other publications (D, E, and F) are additional work as a co-author. The one book chapter (publication G) is also mentioned which discussed the different aspects related to HTL process.

Chapter 2
Experimental Methodology

In this chapter, the methodology of the HTL experiments and procedures adopted for products characterizations during the PhD project will be discussed in details. The process conditions and evaluation of HTL products depend upon the scope and objectives of the sub-projects. By dealing with different feedstocks, the issues and challenges during the experimental campaign are also highlighted in this chapter.

2.1 Biomass characterization

Wheat straw, contaminated construction wood waste and eucalyptus biomass were used as a feedstocks for the PhD project individually.

Wheat straw was collected from the wheat crop field located in the Aalborg, Denmark. Initially, the wheat grains were separated from the mixture and sieves (0.5 and 1.0 mm size) were used for segregation. After that, a grinder machine was used to crush the straw into a fine powder suitable for loading into the micro-batch reactors. Additionally, for the second sub-project, the three types of construction wood waste from the urban waste stream i.e., untreated wood (UNW), non-hazardous wood (NHZW), and hazardous wood (HZW) were collected from Reno Nord, Dansk Affaldsforening that is Danish Waste Association Aalborg, Denmark. However, the mixed wood (MXW) was the self-made combination of all three wood categories. In the third study, eucalyptus biomass (free from leaves and bark) was used in powder form originally provided by Repsol S.A, Spain. The origin of the feedstocks is worth to know as their compositions are also depend upon their route and location. For example, the fiber mass composition of wheat straw used in this study having the lignin content only 4.69%, which is much lower than the value as reported by most researchers, .e.g., wheat straw contains 35–45% cellulose, 20–30% hemicelluloses, and around 15% lignin. In that respect, the possible reason for low lignin content may be due to different nature of wheat straw samples (used in the experiments) related to the cultivation crop season, storage time, treatment etc. As described by Patil et al., the fiber mass composition in lignocellulosic biomass is depending on the origin as well [42]. Fahmi et al. also reported low lignin content in wheat straw as 7.5% [43]. After receiving from the primary source, the biomass samples were kept in the lab under health and safety measures to maintain their original state without any contamination or external impacts.

Before processing the biomasses into the HTL process, feedstocks were characterized to investigate the basic parameters like dry matter, moisture content, ash content, higher heating values, elemental analysis as well as heavy metals and inorganics. The moisture analyzer (Kern, MLS) was used to measure the moisture content in the as-received biomasses at 120 °C that reported in the weight percentage. The ash content in the used biomasses was measured by putting the sample in the furnace (775 °C) for up to 6 hours corresponding the heating and cooling time. After cooling down the sample at room temperature, weighed the sample and that remaining mass was considered as ash content. The bomb calorimeter was used to measure the higher heating value of the biomass. However, the HHV of biocrude and solids was calculated by using Channiwala and Parikh correlation [44]. By operating on the CHN mode, the elemental composition of the feedstock was directly measured with the help of elemental analyzer (Perkin Elmer, 2400 Series II) for which very small quantity of sample was required. Additionally, the mass fraction of oxygen content was calculated by the difference. From the elemental analysis, the H/C and O/C ratios were obtained that shows the dehydration and decarboxylation level during the conversion process. The carbohydrates i.e., cellulose, hemicellulose, and lignin contents (in the first study) were detected through FOSS Cyclotec 1093 by following the five days detailed procedure. The inorganic fractions and heavy metal contents in the biomasses and HTL products were investigated though Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) with the help of microwave-assisted acid digestion system.

2.2 Hydrothermal liquefaction experimental setup

The results in this project were obtained from the HTL experiments conducted at lab scale by using micro-batch reactors (Figure 4). For the first study on the HTL of wheat straw, comparatively big stainless steel reactor having the total capacity of 41 mL slurry was used. From which 21 g of total slurry i.e., mixture of feedstock, water, and catalyst was injected in the reactor. The main reason behind the utilization of big reactor was to get more quantity of products especially aqueous phase that was then employed for recirculation experiments. Furthermore, the experiments were conducted in 10 mL reactors for the second and third study on construction wood waste and eucalyptus biomass respectively. For handling and dealing with micro-batch reactors in the safe and technical way, the technical course was completed offered by Hy-lock and Flowteknik Scandinavia on tubing and fitting. Micro-batch reactors are considered as favorable due to the small scale and continuous HTL processing mainly associated with the rapid heating and cooling as compare to the autoclave [45]. Whereas, for autoclave, it takes long time to reach at desired process conditions as well as cooling which may results the increasing in the char formation. Before using for the HTL experiments, the subjected biomasses were pretreated only to reduce their particle size. After the loading of slurry into the reactors corresponding with 20% dry matter of feedstocks, the reactors were sealed and purged with nitrogen gas at 10 MPa to remove the air and proper settlement of slurry in the reactor. The preheated fluidized sand bath (Techne, SBL-2D) was used as a heating source for the reactors. The thermocouples were mounted to assess the temperature continuously. The mechanical agitator was also connected with the sandbath to provide the proper mixing during the reactions. The sandbath was operated at the desired temperature (350 and 400℃) and retention time. By using sandbath as a heating source, it was noted that the reaction temperature has been reached up to mark level in rapid time due to high heating rate i.e 250-450 K/min [46]. The literature supports that low heating rate is also responsible for the char formation [47].

Figure 4: A coupled micro-batch reactor [On the left side], and the fluidized sand bath (Techne, SBL-2D) facility used for the HTL experiments [on the right side].

The monitoring of process conditions in terms of pressure, temperature and time was performed with the help of LabVIEW software. After the completion of process in accordance to the retention time, the reactors were placed in the water bucket for cooling purpose. It is also a fact that by using micro-batch reactors, the output products were obtained in small quantity that may become a kind of barrier to explore more characterizations. However, these small reactors offers a practical approach in the form of screening test with different process conditions. The idea behind the processing of different lignocellulosic feedstock at lab scale is to collect the knowledge and highlight the challenges that may help for stakeholders to scale up the HTL process at commercial level.

2.3 HTL process conditions

2.3.1 Process temperature

Process temperature is one of the key factors that affects the performance of HTL process. The temperature regions i.e., subcritical and supercritical have been widely explored in the literature for different kinds of feedstocks. In both regions, the biomass fractions like carbohydrates and lignin contents effectively convert into intermediates due to the thermal decomposition and hydrolysis reactions [48]. The choice of the temperature in these studies was selected based on targeted objectives. In overall, the lignocellulosic feedstocks were processed at 350 and 400℃. For the production of biocrude, the suitable and optimum process temperature is also depends on the types of biomass used for the HTL process. Literature supports that the intermediate temperature is generally suitable for achieving the higher biocrude yield [49]. However, it is also believed that at supercritical conditions, an enhanced degree of depolymerization occurred in response of reaction rates. The higher degree of depolymerization results in the form of higher biocrude quality in terms of HHV, low oxygen content and lower viscosity [50, 51]. Researchers also stated that at supercritical conditions, generally re-polymerization becomes active that increase the char formation as well enhance the gas yield [49]. However, Castello et al., stated in the review article about continuous HTL process that supercritical condition is not so much costly and energy intensive because of lower compressibility of liquids etc [52]. In this perspective, it is also one of the main objective of the first and third study to investigate the effect of temperature on HTL of lignocellulosic feedstocks i.e wheat straw and eucalyptus. The influence of temperature on the HTL products was discussed in detail in those studies. Additionally, the study on the HTL of different types of contaminated construction wood wastes was investigated at 400℃ in which the key objective was to find out the effect of impregnation on the process efficiency and to explore the fate of heavy metals among HTL products.

2.3.2 Catalyst

Generally, the purpose of utilization of the catalyst in the thermochemical processes is to enhance the rate of reaction and reaction efficiency. It is widely accepted that in HTL process, by the addition of catalyst, biocrude yield become increases which is main product of HTL process. Catalyst can increase the biocrude flow properties and able to reduce the biocrude heteroatoms [35]. Furthermore, it can also enhance the calorific value of the biocrude. At the other end, catalyst also play its role to reduce the char/tar formation during the HTL process. Mostly, two categories of catalyst has been widely investigated for the HTL process i.e., homogeneous and heterogeneous catalyst. Among which, homogeneous catalyst that comprises of alkali salts like potassium carbonate, sodium carbonate and potassium bicarbonate significantly increase the biocrude yield by accelerating the water–gas shift reaction [48]. Additionally, in comparison, these are considered as economic friendly as well. By dealing with alkali salts, Karagöz et al., stated the order of catalyst in terms of activeness in the HTL process as K_2CO_3 > KOH > Na_2CO_3 > NaOH [53]. Literature showed that water and K_2CO_3 react together during HTL and form bicarbonate and hydroxide and the bicarbonate helps to enhance the biocrude yield [54]. Furthermore, potassium salt improves the re-polymerization of biocrude, thus increasing the nonpolarity of biocrude. The increase in the nonpolarity helps in the separation process of biocrude and water. Additionally, K_2CO_3 did not cause corrosion and may use for the HTL plant at commercial scale. It was also reported that some other catalyst like acid catalysts (sulphuric acid) are also responsible for reducing the biocrude yield via HTL process [35].

In this PhD project, the effect of alkali catalyst by processing the lignocellulosic biomasses through HTL was explored in detailed form especially in study A and C by addition of 2% of the total slurry. In both studies, feedstock slurries were used with and without alkali catalyst potassium carbonate (K_2CO_3) at sub- and supercritical conditions. However, in second study catalyst was used for processing the different types of contaminated wood wastes. During the experimental studies, it was observed that catalyst promotes the biocrude yield, reduce solid formation, increase pH value of aqueous phase, and enhance carbon recovery in biocrude. By the addition of the catalyst, the higher total organic carbon (TOC) content was also observed that was recovered by the aqueous phase recirculation strategy. It was observed that during HTL process, the alkali catalyst can not be recovered in the original form in the HTL products. The possible reason is due to their reactions with biomass fragments and form other compounds.

2.3.3 Retention time and reaction environment

Among various parameters, retention time is also the main factor involving in the HTL conversion process associated with biocrude production. In the previous studies, researchers reported different retention time for different feedstock for processing through HTL process [55, 56]. In this PhD study, WS and CW were investigated at 15 min retention time. Whereas, effects of retention time (5, 10, 15, 20, 25 min) by processing the eucalyptus biomass on the HTL products and the conversion process were discussed in detail in the third study. Additionally, the influence of retention time on the fate of heavy metals and inorganic contents was also explored. Here the retention time means the time when the designed temperature is reached and that is obtained very early (below one minute) because of high heating rate. However, the reactor cooling time was excluded.

Before submerging the reactors in the preheated sandbath for HTL process, the reactors were tested with nitrogen gas. The idea was to make sure regarding any leakage in the reactors. After that, reactors were purged with nitrogen gas to avoid the residual air and proper settlement of slurry inside the reactors.

2.4 Recovery of HTL products

At the downstream of HTL process, mainly four products used to obtain as biocrude, solid phase, aqueous phase and the gas phase. The gas phase in these studies was not investigated, as in general it is well known that the main and major gases obtained from the HTL process are carbon dioxide (CO_2), methane (CH_4), hydrogen (H_2), and carbon monoxide (CO) [57]. After completion of the HTL process, the product phases needs to separate carefully. The methodology of the phase separation has its own importance respective to quantity and quality of HTL products.

For the recovery of HTL products, the process diagram is shown in Figure 5 that highlights the main steps involving in the recovery procedure. Additionally, the detailed procedure about the product separation can be found in the attached publications as well. In general, the experimental procedure was followed as highlighted in the previous studies of processing the lignocellulosic feedstocks at micro-batch scale [46, 57]. Initially, after the cool down of HTL reactors at the room temperature, the gasses were vented off from the top of reactor valve. The first product that was collected directly from the reactors without using any solvent was aqueous phase. At this stage, the aim was to maintain the original chemical composition and quality of the aqueous phase that will use for further investigation specifically that was used for the recirculation experiments in the first study. Later on, the reactors were rinsed by introducing the acetone as a solvent and mixture of the products was obtained that contains the biocrude, solids and the residual water accompanied with acetone. The filtration was the next step to get the solids from the mixture for which the filter papers having the particle retention size in range between 5-13 µm. The filter papers then dried for 24 hours with the help of oven at 105℃ and measured on the next day to note the weight difference of filter papers for the calculation of solid yield. After that, the acetone was removed from the mixture by using the rotary evaporator. The remaining fraction in the flask was the biocrude with residual water that was then separated by the addition of Diethyl ether (DEE). The selection of DEE as a solvent was due to its good performance especially immiscibility with water and its low boiling point. Due to the low boiling point, the solvent also evaporated at normal conditions without loss of light fractions of biocrude. The mixture was centrifuged to evaporate the DEE and separate the layers of residual water and biocrude. The samples were kept for centrifugation for four hours and the layer of residual water become visible clearly that was extracted by using syringe. The remaining fraction in the vial is calculated as biocrude yield. It should also be noted that the products separation process may also contains the challenges and chances of the product losses especially during the rinsing of biocrude in round bottle flask after acetone evaporation step. To make sure the validation of results, the experiments were conducted in duplicate or even triplicate. Irrespective to the losses and separation methodology, it is clear that the experimental activities at small scale would be beneficial for the planners and stakeholders to scale up the HTL technology by processing the waste feedstocks from different sectors like agriculture, urban, and forest streams.

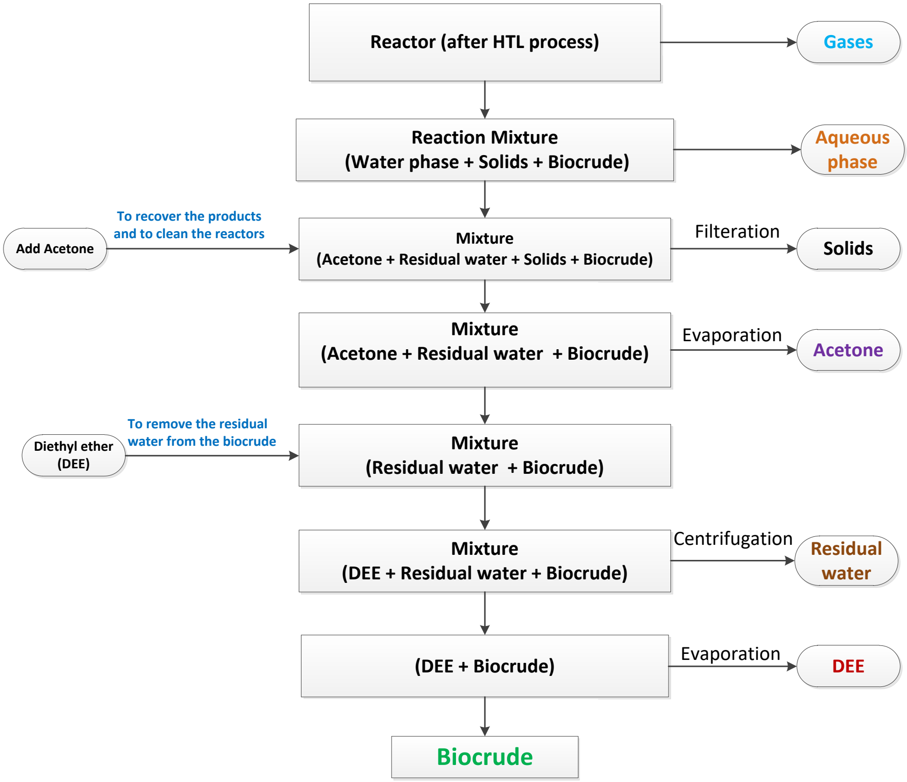

Figure 5: Main steps involved in the collection and recovery procedure of HTL products.

2.5 Products Characterization

After the separation of HTL products, the recovered products were characterized by the different techniques. Before the characterizations, the products like biocrude and solids were also quantified by using following formulas and mentioned as yield. Additionally, the energy recovery, higher heating values and atomic ratios of the biocrude and solids were also determined by using formulas mentioned below.

Biocrude yield (%) = (Weight of the biocrude / Weight of the biomass used) × 100

Solid yield (%) = (Weight of the solid residue / Weight of the biomass used) × 100

Energy Recovery, ER (%) = (HHV of product / HHV of biomass used) × product yield

HHV (MJ/kg) = (0.3491)C + (1.1783)H - (0.1034)O − (0.0151)N

H/C = (weight percent Hydrogen/atomic weight Hydrogen)/ (weight percent Carbon/atomic weight Carbon)

O/C = (weight percent Oxygen/atomic weight Oxygen)/ (weight percent Carbon/atomic weight Carbon)

The biocrudes and solids in all three studies were mainly characterized for the elemental composition (CHN) by the elemental analyzer. However, due to the small quantity of biocrude samples, the HHVs of biocrudes and solids (in all studies) were calculated by using the Channiwala and Parikh correlation [44]. Additionally to investigate the weight loss during the thermal decomposition and the volatility of the biocrudes, the thermogravimetric analysis (TGA) was used. With the help of TGA, the segments of diesel, gasoline, and jet fuel in the obtained were also identified. The different classes and composition of organic compounds present in the biocrudes were explored by the Gas Chromatography- Mass Spectrometry (GCMS) technique. The carbon and nitrogen recoveries (CR, NR) in all product phases were calculated as the ratio of the weight of C and N in the product to the weight of C or N in the feedstock multiplied by the yield of that product phase. Furthermore, the CR and NR in the aqueous phase were determined by measuring the total organic carbon (TOC) and total nitrogen (TN) contents. The nature of aqueous phase like acid, alkaline was identified by pH values.

In all three studies during this PhD project, the composition of the inorganic contents like heavy metals, micro and macronutrients in the HTL product phases was explored and discussed in detail. The samples were measured through the Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) technique with the help of acid digestion of product samples in microwave. The detailed procedure for measuring the inorganic composition was adopted as explained by Conti et al. [57]. Among inorganic and heavy metals contents, aluminum (Al), calcium (Ca), potassium (K), magnesium (Mg), phosphorus (P), iron (Fe), sulfur (S), silicon (Si), sodium (Na), copper (Cu), chromium (Cr), nickel (Ni), zinc (Zn), arsenic (As), cadmium (Cd), lead (Pb), sodium (Na), and manganese (Mn) were measured in total. The fate of heavy metals (Cr, Cu, Ni, and Zn) among HTL products was investigated in study B. However, the rest of the inorganic contents were discussed in studies A and C. To calculate the distribution of the inorganic elements in each product phase, the concentration of element was multiplied by the weight of that product phase. The more explanation about the methodology and analytical techniques used for the products characterizations are also reported in the publications [A, B, C].

Chapter 3

Hydrothermal liquefaction of wheat straw at sub- and supercritical conditions

3.1 Wheat Straw from Agricultural Waste Stream

Wheat straw (WS) is an abundantly available lignocellulosic biomass from agriculture sector specifically wheat crop. With the estimated annual production of 887 million tons, it was considered as 2nd largest potential lignocellulosic feedstock globally [58]. As a rich agricultural residue, WS has a huge potential to produce bioenergy around 47×10^{18} J [59]. However, different problems are associated with the proper utilization of WS residue. Generally, significant amount of WS remains on the field crop due to improper machinery system. Additionally, it is discarded/used in the form of direct burning at the field, soil chopping, or sold for animal feeding etc. In Denmark, straw has also used for fired power plants for heat energy [60]. The emission of trace elements especially chlorine components reduce the life of boilers, chambers running on the straw. The direct burning of straw contains several environmental concerns due to the releasing of particulate matter and other pollutants, which degrade the air quality that results the health diseases as well.

The hydrothermal liquefaction of the WS is an alternate, advanced and an efficient option to reduce the environmental pollution and to produce the energy dense biocrude and additive products. The integration of the agriculture sector with HTL technology may enhance the circular economy because at one end, wheat crops produce grain for food and simultaneously unused residue that can be efficiently used for biocrude production via HTL process. By comparing these different scenarios for the utilization of the straw, Palmieri et al. concluded that the bunches of straw selling for biofuel production is an economic and environmental friendly option as compare to soil chopping or field burning [59].

In study A of this PhD project, the aim was to investigate the utilization of wheat straw for the biocrude production at sub- and supercritical conditions. The effects of process temperature and alkali catalyst (K_2CO_3) were discussed in detail. Additionally, the role of aqueous phase recirculation was also examined for the energy recovery. Furthermore, study A also highlights the recovery of inorganic elements among HTL products.

3.2 Feedstock Characterization

As received from the field crop located locally in Aalborg, Denmark, the wheat straw was crushed and grinded to make a fine powder after the separation of wheat grains. The particle size was adjusted with the help of different sieved in range between 0.5 and 1.0 mm size. From raw form to fine powder, the pictorial views of wheat straw shown in Figure 6. The feedstock in fine powder form is suitable due to working with micro-batch reactors.

Figure 6: From raw form to fine powder- wheat straw for HTL experiments.

The different characterizations of the feedstock are present in the Table 1. It was observed that the WS contains low nitrogen and low ash contents that are favorable for the HTL process from the biocrude quality perspective. The carbohydrates (cellulose and hemicellulose) were in range between 30-37%, however, the lignin composition of WS is quite low in the study that may due to different nature, cultivation crop season, storage time, and treatment etc. The moisture content after grinding was measured as 5.39% that was adjusted to the level of 20 wt. % dry matter by making the slurry with demineralized water for HTL experiments. The higher heating value (16.53 MJ/kg) was directly measured through bomb calorimeter by weighing the biomass samples in range between 0.2 and 0.5 grams.

Table 1. Characterization of wheat straw used for the HTL experiments.

Elemental composition (%, daf) and Fiber elements (%, db)	
Carbon	42.15
Hydrogen	6.21
Nitrogen	0.82
Oxygen (by difference)	50.82
Cellulose	37.92
Hemicellulose	30.24
Lignin	4.69
Ash	6.92
Moisture Content (%, as received)	5.39
Higher heating value (MJ/kg)	16.53
H/C	1.76
O/C	0.91

3.3 Effect of Temperature and Catalyst on HTL products

The wheat straw was processed for the HTL process at four different conditions to examine the effect of temperature (350/400℃) and catalyst (NC/CAT). The effect of both parameters on the biocrude and solid yields is illustrated in Figure 7. From the obtained results, it was observed that temperature and catalyst plays an important role to enhance the biocrude yield. The maximum biocrude yield (32.34 wt. %) was achieved at subcritical condition with the addition of catalyst. Parallel to that, the minimum solid yield (4.34 wt. %) was also obtained at 350℃ condition. The thermal cracking of biocrude compounds into gaseous phase may be the main reason for lower biocrude yield at 400℃. Beside that, the transformation of organic carbon into water soluble in the form of higher TOC in aqueous phase (33.52 g/l) was also detected at supercritical conditions. Another reason for less biocrude yield and high solid yield at supercritical conditions might be due to the water critical point (373.74℃) at which polymerization of macromolecules of biocrude is active to form the gases or condensation reaction to increase solid residue [61].

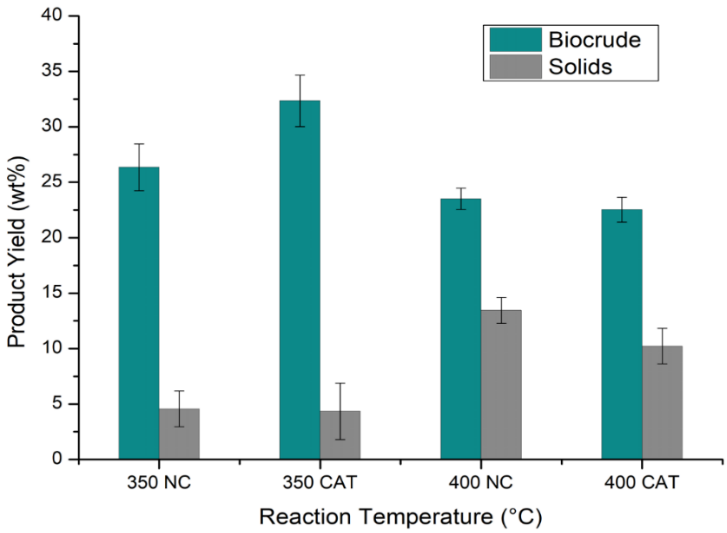

Figure 7: Biocrude and solid yield by the HTL of wheat straw under different process conditions.

By the employment of catalyst, biocrude yield increased by 5.99% while solids remains almost same at subcritical condition. The formation of bicarbonate and hydroxide due to the reactions of catalyst with process water may also enhance the conversion efficiency which results in increasing biocrude yield [62]. In conclusion to the investigation of temperature and catalyst on the HTL products, the conversion process and biocrude production were higher at the subcritical-catalyst condition, whereas no significant effect on biocrude yield was observed at 400℃. However, catalyst reduces the solid residue at supercritical and remains same at subcritical conditions. Parallel to the biocrude yield, the highest energy recovery (69.53%) was achieved at 350℃ and lowest (48.38%) at 400℃.

From the elemental analysis (Table 2), it was noticed that, with increasing temperature, the carbon content in the biocrude was increases from 70.77 to 74.21% and oxygen was reduced from 19.65 to 16.27%. Additionally, the higher heating value of biocrude slightly changed from lower to higher temperature in range between 35.25 and 35.97 MJ/kg that concludes that there is no any significant effect of catalyst on biocrude quality in terms of HHV. The atomic ratios O/C and H/C were in range between 0.16–0.21 and 1.31-1.39 respectively. To improve the quality of biocrude and the significant H/C ratio to meet the petroleum fuel quality, the HTL-upgrading process is required.

Table 2: Elemental composition (%, daf), atomic ratios, higher heating values (MJ/kg) and energy recovery (%) of HTL biocrude at different process conditions.

Samples	C	H	N	O	H/C	O/C	HHV	ER
350NC	70.77	8.25	1.33	19.65	1.39	0.21	35.25	56.18
350CAT	72.61	8.06	1.14	18.19	1.33	0.18	35.54	69.53
400NC	74.21	8.15	1.37	16.27	1.31	0.16	35.97	51.14
400CAT	73.07	8.01	1.64	17.28	1.32	0.17	35.50	48.38

The thermo-gravimetric (TG) curves of biocrudes (Figure 8) also confirms that process temperature has significant impact on the thermal behavior of biocrudes. The TG analysis indicates that about 55 to 60% of biocrudes occupied by the volatile fractions that represents the segments of diesel, gasoline and jet fuel. Whereas, 30 and 20% of heavy residue were left for biocrudes obtained at sub- and supercritical respectively. The detailed representation about the fraction cuts of biocrudes at both conditions are also reported in study A section 3.2.1.

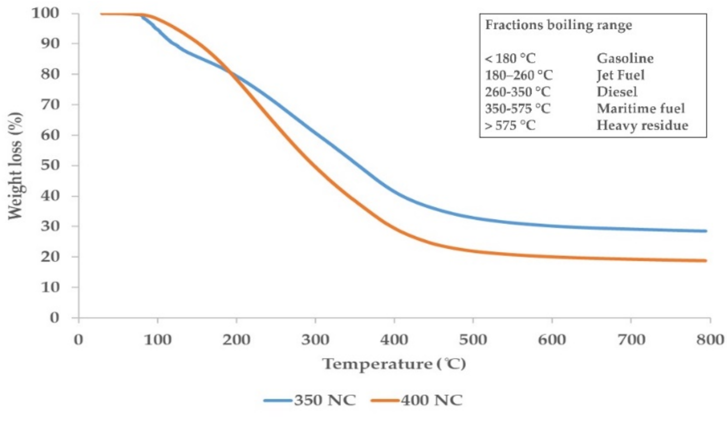

Figure 8: Thermo-gravimetric curves of the HTL- biocrudes at 350 and 400 °C.

The concentrations of the organic compounds (see Table 3 paper [A]) in biocrudes were investigated through GC-MS and the compounds were mainly categorized into six classes as acids, ketones, hydrocarbons, oxygen aromatics, nitrogen compounds and alcohols. The decomposition of hemicellulose available in the WS produced organic acids especially acetic acid [63]. Among acids, n-Hexadecanoic acid and acetic acid has higher concentrations. Phenolic compounds that obtained by the decomposition of lignin fractions were also detected at all four conditions. The higher peak of phenol compounds was observed from 1.75-5.06% at 350℃ catalytic condition. As a lignocellulosic biomass, WS contains very less percentage of nitrogen which results lower nitrogenous compounds in biocrudes only appeared at subcritical condition. From the biocrude quality aspects, it is desire to have very low N containing compounds because those become responsible for NO_x emissions during combustion process and also enhance the viscosity and instability of biocrudes. In that case, hydrotreating is proposed to reduce the heteroatoms and upgrade the HTL-biocrude to achieve the drop-in fuel.

By processing the wheat straw at all four conditions, the nature of aqueous phase was acidic having pH from 3.87-4.19 which then increase up to 6.82 by the addition of catalyst. The possible reason for the acidic nature of aqueous phase might be due to the formation of monomeric sugars due to the hydrolysis of sugar compounds, which then converted into acids. However, variation in pH is also depend upon the operating conditions and biomass composition [64, 65].

The temperature and alkali catalyst also influenced on the concentration of organic carbons (TOC) in the aqueous phase. At subcritical conditions, the TOC was in range between 12.82 – 30.67 g/l which then increased and become maximum (33.52 g/l) at 400℃-catalyst condition. Whereas, the total nitrogen (TN) was lower (0.26-0.58 g/l) due to the lower nitrogen content in the feedstock. To recover the organic carbon from water phase, HTL-aqueous phase was recirculated to the process to investigate the effect of AP-recirculation on biocrude production that will be discussed in section 3.5.

In order to conclude that which process condition is efficient for processing the biomass through HTL process, it is not enough to look at the obtained biocrude and solids yields, but the quality of biocrude and other products also necessary. Other factors contributing to determination of the optimum condition are the carbon recovery (CR) and nitrogen recovery (NR) into the different product phases i.e., biocrude, solids, gasses and aqueous phase [66]. The carbon and nitrogen recovery in the HTL products (Figure 9 and 10 respectively) were calculated as the ratio of the weight of carbon and/or nitrogen in the HTL product phase to the weight of carbon and/or nitrogen in the feedstock used (i.e., wheat straw) multiplied by the product yield. Whereas CR and NR in the aqueous phase were determined by the measurements of TOC and TN. For gases, the mass balance was estimated by the difference. It was noted that the addition of catalyst inclined the CR in biocrudes at subcritical condition and reduced in the gas phase. However, no significant effect of temperature was observed on CR and NR in biocrude in the absence of catalyst. For all different conditions, higher CR was achieved in biocrude at 350 °C that was concluded as an optimum condition for processing the wheat straw through HTL process.

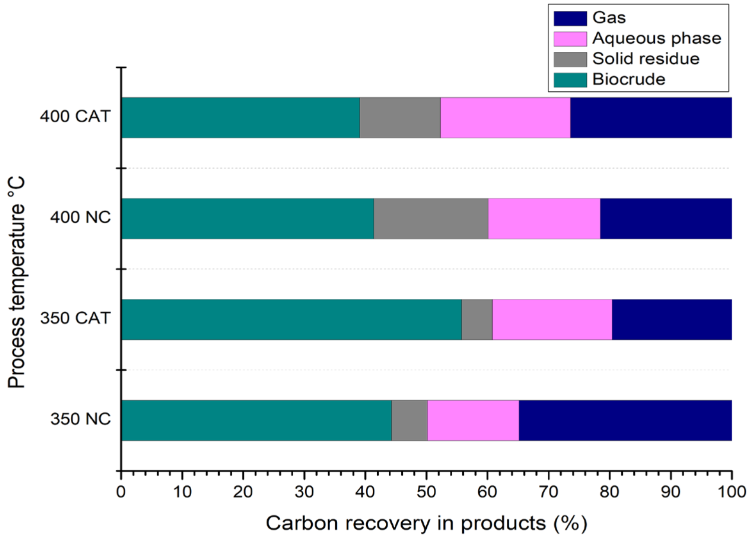

Figure 9: Carbon recovery (CR) in different phases of HTL products at Sub-supercritical, CAT/NC conditions.

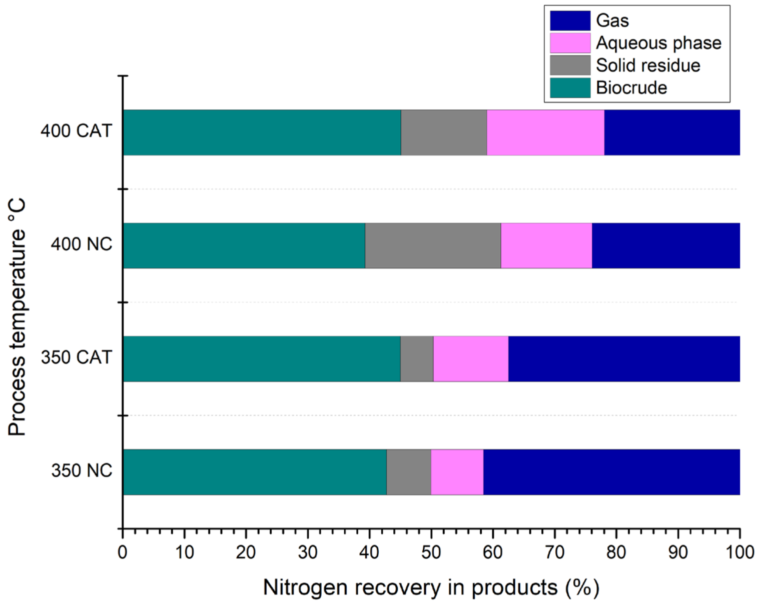

Figure 10: Nitrogen recovery (NR) in different phases of HTL products at Sub-supercritical, CAT/NC conditions.

3.4 Inorganics distribution in HTL Products

During the HTL process, the inorganics shifted from biomass to product phases. The importance to examine the fate of inorganics like heavy metals, macro and micronutrients are essential for the quality perspective as well as from the recovery point of view. In the first study (HTL of WS), the distribution of ten inorganic elements (Al, Ca, K, Mg, P, Fe, S, Zn, Si, and Na) was investigated at both sub- and supercritical conditions highlighted in Figure 11 and 12 respectively. At both conditions, the trend was quite dissimilar regarding the accumulation of inorganics. By comparing both conditions, aluminum (Al), calcium (Ca), Magnesium (Mg), potassium (K) and phosphorus (P) were highly concentrated in the biocrude at subcritical as compared to the supercritical condition. However, sulfur (S), Zinc (Zn) and sodium (Na) shifted more in biocrude at 400℃. For solids, at 350℃, most of the inorganics around 70% migrated to solids except only Al and Mg, which contributes about 50%. Phosphorus at both conditions was found mainly in solids with greater concentration in range between 86-90% that may be in the form of phosphates in relation with alkali elements like calcium and sodium. At supercritical condition, Al, Ca, Mg, Si transferred mostly to the solid phase product and K, Na, S shifted to the aqueous phase. The possible reason behind transfer to the aqueous phase may be the high degree of solubilization of K, Na, and S at higher temperature that enhance ionic product and in response of that, these inorganic compounds concentrated into the aqueous phase [67]. Biocrude at 400℃ was highly contaminated with sulfur content around 60%. Additionally, the heavy metals i.e., Fe and Zn were found in the biocrude with some variations at both conditions. Based upon the ICP results, it was noticed that most of inorganics especially nutrients like macronutrients (P, Ca, Mg), and micronutrients (Fe, Zn) are mostly detected in the solid residue. In that case, HTL-solid phase can be employed as a soil conditioner for the agriculture sector to recover those treasured nutrients.

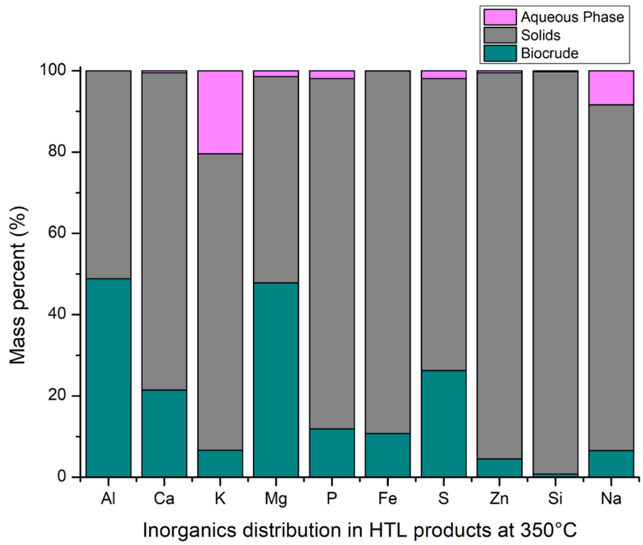

Figure 11: Normalized mass distribution of inorganics elements in the biocrude, solids, and aqueous phase at subcritical condition.

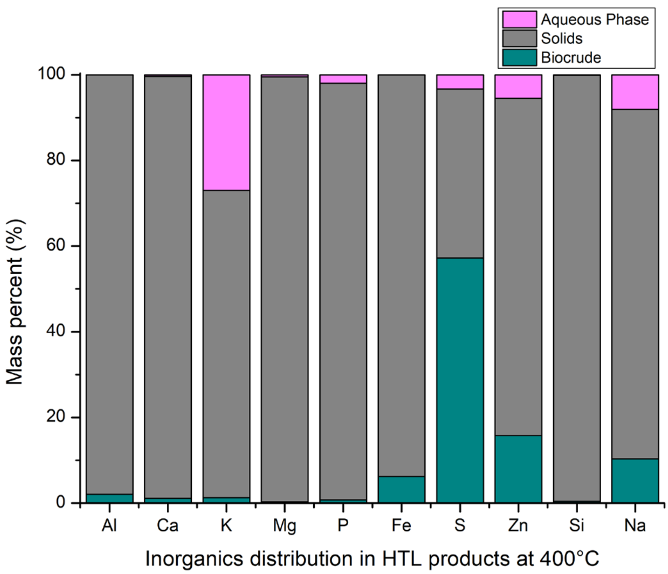

Figure 12: Normalized mass distribution of inorganics elements in the biocrude, solids, and aqueous phase at supercritical condition.

3.5 Aqueous phase recirculation

To recover the organic carbon from obtained HTL- aqueous phase, recirculation strategy was applied. The effect of aqueous phase recirculation on biocrude and solid yield is illustrated in Figure 13. For the recirculation experiments, the 350℃- catalytic condition was chosen due to optimum condition from the experiments of this study. The biocrude yield was inclined from 32.34-38.12% after two cycles. The organic compounds mainly acids available in the aqueous phase play their role to enhance the biocrude yield at each cycle due to the speedy degradation of the organic matter. Accompanied with the biocrude, the solid yield was also increased from 4.34 to 11.33% that is quite double than fresh run. The possible reason for higher solid yield may be the elements available in the aqueous phase that polymerize to form more solids.

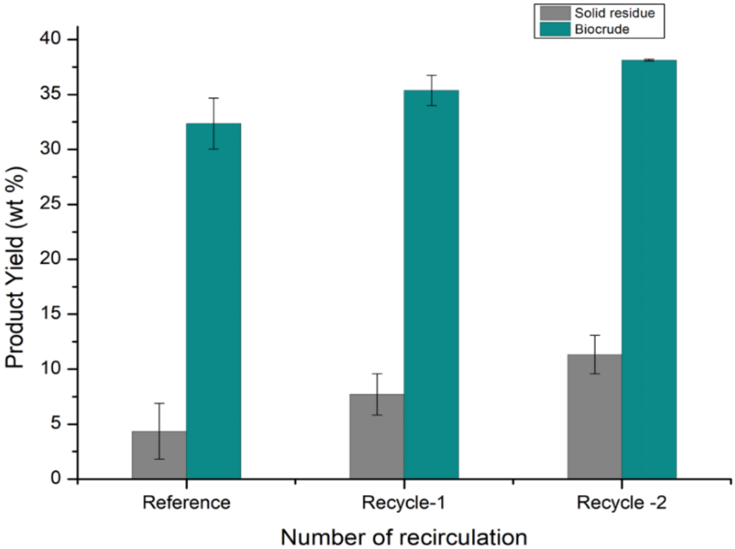

Figure 13: Effect of aqueous phase recirculation on biocrude and solid yield.

Shah et al., conducted the detailed study on aqueous phase recirculation and reported the higher biocrude yield with greater energy recovery [68]. By processing the aqueous phase for recirculation experiments, the energy recovery was also inclined in biocrude from 69.53% to 81.31% that indicate the efficiency sign if it continues for further number of cycles. However, the HHV of obtained biocrudes was almost remain same around 35 MJ/kg due to the approximately same elemental composition of the biocrudes. The utilization of aqueous phase at one end reduces the consumption of fresh water and increase the biocrude yield.

Chapter 4

Hydrothermal liquefaction of contaminated construction wood waste and investigation of fate of heavy metals

4.1 Construction Wood Waste from Urban Waste Stream

Wood wastes from urban waste streams are potentially available especially from construction sector. Construction wood (CW) generally used for the building infrastructures, furniture applications, outdoor wooden pillars etc. In order to prolong the service life of woody material in the variable outdoor environment, wood is used to treat with different substances, toxins, and impregnated agents. The usage of those different chemicals and wood preservatives like chromate copper arsenate (CCA) often contains environmental and health concerns that can possess certain effects on the public health and surrounding atmosphere. Due to the presence of heavy metals (HMs) and other toxic materials, the management and disposal of CW waste become challenging and requires proper attention. Since 1960s approximately 2.7 million tons of HMs impregnated wood waste was generated in Denmark. Furthermore, it enlarged from 17000 tons in 1992 to 100000 in 2010 and stated 80,000 tons in 2018 [69, 70]. At the end, the thousands tons of contaminated wood waste ultimately needs to be disposed of in order to manage the urban waste streams. An efficient and environmental friendly approach to turn dispose of contaminated CW waste into valuable products is the hydrothermal liquefaction (HTL) process.

As mentioned earlier, CW waste decorated with different layers of coating materials that mainly contains HMs especially copper, chromium, nickel etc., and it is one of the challenges for the continuous HTL plant to deal with material contain high concentration of HMs and inorganic contents. Conventionally the biocrude from HTL process needs to be upgraded to obtain the final product as a drop-in fuel [71, 72]. For that, the blending of HTL-biocrude with petroleum fuel is a suggested option by utilizing the existing refinery setup. However, the HMs concentration in the biocrude may have negative impacts on a refinery system. Castello at el., described the importance of the removal of HMs from HTL biocrude because the concentration of HMs may impact on the efficiency and life of catalyst used during the upgrading process [52]. Several studies are reported in the literature focused on the transformation of HMs during HTL of wet biomasses, i.e., manures, sewage sludge, and algal biomass [73, 74, 75]. However, the fate of HMs by processing the lignocellulosic biomass especially CW waste during the HTL process was not available in the scientific literature.

The objective of the study B of this PhD project was to utilize the different types of waste woods (Figure 14) to explore the effect of impregnation on the performance of HTL process. Additionally, the objective was to elucidate the fate of HMs among HTL products in the supercritical catalytic environment. This study may bring an added knowledge to the potential impact on continuous HTL processing at commercial scale. Furthermore, such knowledge will assist in dropping the environmental burden and put a role to improve the circular economy by waste management and biocrude production.

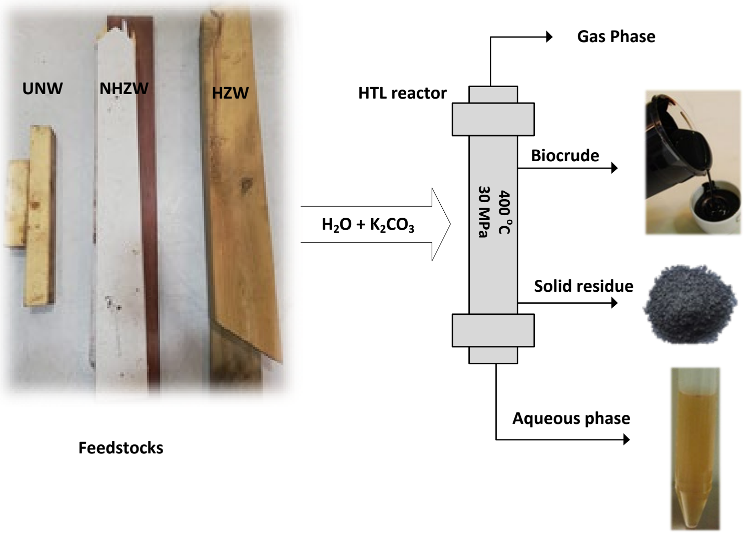

Figure 14: Catalytic- supercritical HTL of different types of construction wood waste for HTL experiments.

The collected wood samples were segregated among four categories. Untreated wood (UNW) which was free from any anthropogenic substances i.e., chemicals. The non-hazardous wood (NHZW) was found with different coating layers of paints, resins, because that is usually used for furniture and decoration purposes. To increase the service life, various chemicals contain Cu and Cr used as wood preservative, concentrated in the hazardous wood (HZW). The mixed wood (MXW) in the experimental campaign was the homogeneous mixture (1:1:1 ratio) of rest three types of wood. The idea behind processing of the MXW was to avoid segregation of different categories of waste wood from urban streams for the continuous HTL plant at commercial scale where the slurry in abundant quantity is prepared by mixing different types of wastes.

4.2 Construction wood waste characterization

Before the HTL experiments, the different types of collected wood samples were characterized in order to investigate the quality and composition. The evaluated parameters have been reported in Table 3. The HZW contain higher amount of ash and HHV than other samples while the moisture content of all wood samples was around 6 %. The carbon in all samples was in range between 46.65-49.90% and the nitrogen content was below 1 %.

Table 3. Feedstock (construction wood waste) characterization.

	Untreated wood	**Non-hazardous wood**	**Hazardous wood**	**Mixed wood**
Moisture (%)	5.27	6.15	6.29	5.57
Ash (%)	0.35	0.81	2.18	0.59
Carbon (%)	46.65	47.99	49.73	47.90
Hydrogen (%)	6.38	6.55	6.72	6.52
Nitrogen (%)	0.68	0.59	0.75	0.71
Oxygen (%)	46.28	44.84	42.78	44.85
HHV (MJ/kg)	19.64	20.59	22.25	19.68
Heavy metals concentration (mg/kg)				
Chromium	1.79	6.87	1.83	3.19
Copper	7.95	1623.28	1987.24	1198.03
Nickel	9.42	116.01	74.37	17.78
Zinc	20.28	24.18	15.42	21.46

For the concentration of HMs in the wood samples, total seven HMs were targeted i.e., Chromium (Cr), Copper (Cu), Nickel (Ni), Zinc (Zn), Arsenic (As), Cadmium (Cd) and lead (Pb) reported in Table 2. Among them As, Cd, and Pb were found below the limit of detection. Cu and Zn were detected with higher concentration in wood samples compared to other heavy metals due to the reason of copper coating materials used as a wood preservative [76]. The NHZW was rich in Cr due to the layers of paint coating because the Cr is widely used in the dyeing and paint industries. The root cause of Ni and Zn may also from the natural as well as anthropogenic activities during the life of wood materials. In overall, it was observed that among all four categories, the concentration of heavy metals in UNW is comparatively less because of being natural and free from artificial impregnation process.

4.3 HTL of construction wood waste

The HTL experiments were conducted by processing the CW samples at supercritical (400 ℃) condition with the addition of catalyst (K_2CO_3) for 15 min retention time. The biocrude and solid yields are highlighted in Figure 15. The UNW produce more biocrude and less solid yield as 36.35% and 10.64% respectively. However, by comparing the NHZW and HZW, the conversion of NHZW result 32.93% biocrude yield which was higher than HZW i.e., 28.22%. Additionally, the MXW shows least efficiency with the biocrude yield 24.86% and solid yield 20.65%.

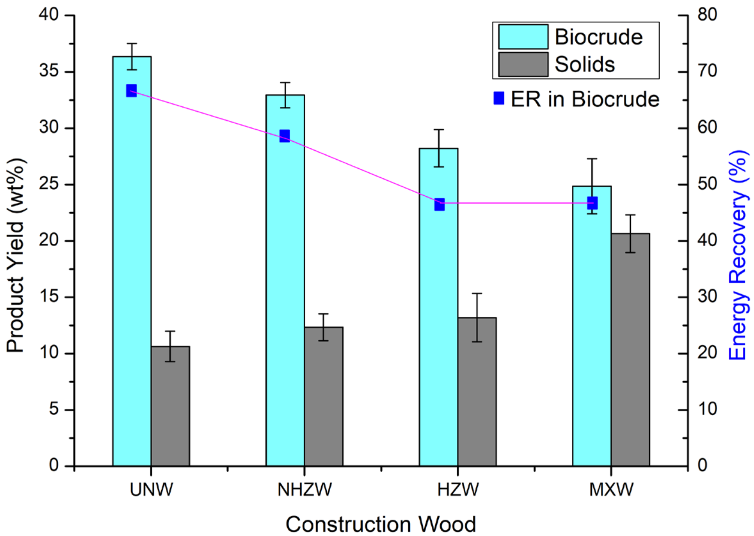

Figure 15: Biocrude along with energy recovery (ER) and solid yield at the catalytic- supercritical HTL condition for construction wood samples.

The overall conversion efficiency and trend associated with the biocrude production was UNW > NHZW > HZW > MXW with the ER in range between 46-66%. The possible reason for variable conversion related to the biocrude and solid yield is mainly the mixing of different nature of materials. All the wood samples except UNW were recognized with the additional layers of different materials that may be the main reason/barrier during the conversion process. However, at the same process conditions, the NHZW produce more biocrude than HZW. In that case, white paint coating may play the key role because it contains different solvents and pigments; resins composed of organic compounds that can increase the biocrude yield. The MXW that was homogenous mixture of rest three wood samples shows very less conversion to biocrude. The mixing of different nature of materials and the antagonistic effect may be the main reasons for lower biocrude yield. The antagonistic is the opposite of synergistic effect due to which less experimental results obtained as compare to theoretical values. During the HTL of different woody biomasses, Jasiunas et al., were also reported the low biocrude yield because of the antagonistic effect at supercritical condition [77]. Additionally, Yang et al., also indicated that during the liquefaction of mixed feedstocks, biocrude yield can be affected by both synergistic as well as antagonistic effects [78]. From the obtained HTL results of CW waste, it was concluded that at supercritical condition, wood impregnation affects the biomass conversion to biocrude. However, a detailed future study is proposed to explore the antagonistic/synergistic effect of different lignocellulosic feedstocks through HTL process.

The elemental analysis of biocrude (Table 4) shows the higher carbon content i.e., 75.62–78.01% which results the HHV in range between 35-37 MJ/kg. Additionally, the oxygen in biocrude (13.41–16.29%) was much lower than the input biomass (42.78–46.28%) that increases the heating values of biocrude.

Table 4: Elemental analysis (%, daf), atomic ratios, and HHV (MJ/kg) of biocrudes produced by the HTL of different waste woods.

Sample	C	H	N	O	H/C	O/C	HHV
UNW	75.62	7.51	0.58	16.29	1.19	0.16	35.82
NHZW	78.01	8.1	0.48	13.41	1.24	0.12	37.02
HZW	76.21	8.32	0.62	14.85	1.31	0.14	36.78
MXW	77.36	8.42	0.71	13.51	1.30	0.13	37.14

The maximum ER (Figure 15) in the biocrude was found by processing the UNW. Even though the MXW has less biocrude yield but it contains higher HHV than other biocrude samples. The H/C and O/C ratios of biocrudes were around 1.19 - 1.31 and 0.12 – 0.16 respectively. However, for which HTL-upgrading process is required to maintain the atomic ratios within the petroleum fuel. At the other end, the solids from the HTL process contains carbon 65.46 and 72.70% that can recovered by utilizing the solids as a heating source or as a biochar for agriculture sector due to the presence of treasured nutrients. It is also essential to mention this here that from the ICP results (which will be discussed in section 4.5), it was noticed that the higher amount of heavy metals transferred into the solid residue. In that respect, it is very important to remove or reduce the concentration of heavy metals from biochar before used them for further applications.

According to biocrude TGA curves (Figure 16) approximately 65–82% of biocrude occupied by the volatile fractions that highlights the nature of gasoline, diesel, jet fuel, and marine fuel range. After heating the biocrude samples at 750℃ it was observed that almost 18-35% remaining in the form of heavy residue. Concerning the heavy residue, it was detected that hazardous wood and mixed wood contains high values that may be due to the occurrence of cyclization and re-polymerization reactions within the biocrude fraction [27].

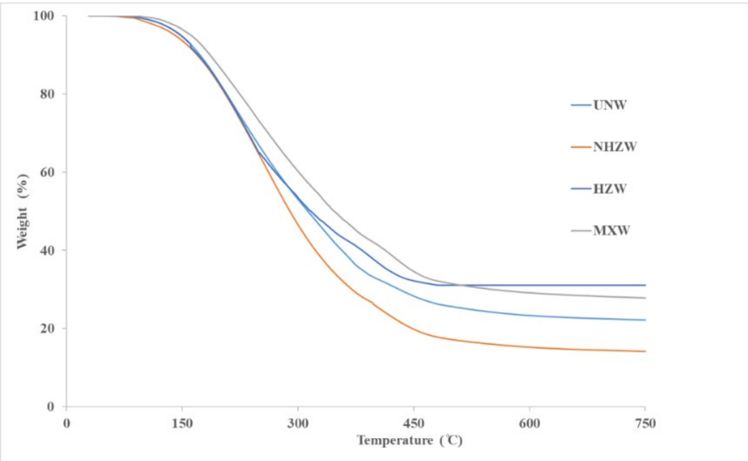

Figure 16: Thermo-gravimetric curve of the biocrudes from the HTL of construction wood waste.

In overall, all the biocrude samples shows the different values of residual fractions. Among them, the biocrude obtained from NHZW has lowest residues left after heating at 750℃.

The nature of aqueous phase from the liquefaction of CW waste was found as an alkaline mainly due to alkali catalyst used in the experiments. The observed values of pH, total organic carbon (TOC) and the total nitrogen content (TN) are reported in Table 5.

Table 5: Characterization of aqueous phase from HTL of construction wood waste.

	pH	**TOC (mg/l)**	**TN (mg/l)**
Untreated wood	7.97	22.81	1.81
Non-hazardous wood	6.80	26.55	1.98
Hazardous wood	6.63	18.51	1.80
Mixed wood	6.42	20.82	1.67

The pH was slightly variable, for impregnated wood it was acidic while for UNW it was observed as 7.97. For the HTL of lignocellulosic biomass at 400℃, Conti et al. reported the pH value of aqueous phase around 6.83 [57]. The nature and the composition of the HTL aqueous phase may have different values mainly depend upon the nature of feedstock as well as process conditions [79]. The presence of organic carbon in the aqueous phase was confirmed by the TOC which was resulted in the range 18.51-26.55 g/l with highest in case of NHZW. The carbon from the aqueous phase can be efficiently recover for increase the biocrude production by recirculation activity which was investigated in the study [A] of this PhD project by dealing with the wheat straw biomass. According to the report from Pacific Northwest National Laboratory (PNNL), it was also suggested that aqueous phase recirculation strategy is an efficient and economic viable for increasing the biocrude yield and quality [80]. The total nitrogen content was quite low (1.67-1.98 g/l) as compared to the protein rich biomasses like sewage sludge and microalgae [27, 72]. Therefore, an aqueous phase that contains significant value of organic carbon and lower nitrogen content is proposed to recirculate within the HTL process to enhance the overall process efficiency.

4.4 Organic composition of biocrudes

The presence of organic compounds in the biocrude obtained from all four types of CW waste are reported in detail in the table (see Table 6 [Paper B]) along with their retention time and peak area. The compounds were categorized into different classes mainly ketones, oxygen aromatics, acids, alcohols, hydrocarbons and nitrogen containing compounds. Among them, oxygenated compounds found in higher concentration like ketones and aldehydes. The higher percentage of oxygen base compounds may lead the instability and lower miscibility with petroleum fuel that may be solve by the HTL upgrading process at commercial scale. The appearance of ketone family compounds is most probably due to the oxygen percentage available in the biomass used that was around 42-46%. The phenolic compounds like [Phenol, 2,3-dimethyl-] was in the result of splitting of carbonyl, C-C bonds by the lignin decomposition [81]. The higher amount of esters and carboxylic acids were detected in biocrude obtained from NHZW followed by MXW samples and lower in UNW and HZW. By the HTL of lignocellulosic feedstock, the development of acids are also stated in past studies due to the utilization of alkaline catalyst [82, 83]. Among hydrocarbons, [Butane 2,3-dimethyl-] identified with higher concentration in all four biocrudes. Only a few nitrogen base compounds were detected which may formed by the dehydration, deamination, and decarboxylation reactions. In that case, it is well known that lower nitrogen compounds in the biocrudes are favorable for the quality perspective because those compounds may lead to instability that can effect on further applications like storage and transportation of biocrude. To enhance the biocrude quality, it is necessary to upgrade the HTL biocrude to reduce the concentration of undesired compounds like acidic and oxygen containing compounds to achieve the drop-in fuel.

4.5 Transformation of heavy metals

The inorganics especially heavy metals are considered as unwanted elements in the bio-refinery process engineering. The presence of heavy metals even in lower concentration can harm the life and efficiency of the catalyst used in the process. Additionally, HMs in the form of impregnation material can also be a barrier during the conversion process to obtain the biocrude. Inside the plants like wood, HMs are generally present in diverse forms that may cause the impurities in cellulose structure and also make a bonding connection with available organic matter, plant crystal structure cells etc. [84]. During the liquefaction process, due to oxidative degradation of the wood structure, HMs released from wood polymers and shifted to product phases [85]. The overall data indicates as reflected in Figure 17, that as per mass bases, majority of HMs migrated to the solid phase product. However, biocrudes were also slightly contaminated by the shifting of HMs especially copper. The main reason is the high concentration of Cu in the form of impregnation material that was also confirmed from the biomass characterization. Comparatively very less amount of HMs transferred to the aqueous phase that is also a good indication for aqueous phase recirculation technique. The relative distribution of HMs in HTL products were calculated and discussed in detail in paper B (section 3.5). Interestingly, it was revealed through relative distribution calculations that in overall scenario, biocrude was more polluted with HMs in case of UNW than rest of three types of wood samples. Copper and Zinc accumulated more to biocrude that was also reported by Conti et al., during the HTL of wastewater-irrigated willow [57]. However a quite low concentration was observed in solids and aqueous phase. For NHZW, about 90–98% HMs migrated in solids, while 1.74 and 8.63% of Ni and Zn shifted into aqueous phase respectively. Additionally by processing the HZW and MXW, majority of HMs moved to the solids but only Cu has around 20% in the biocrude. The higher accumulation of HMs into the solid phase might be due to the inorganic nature of metals and chemical precipitation.

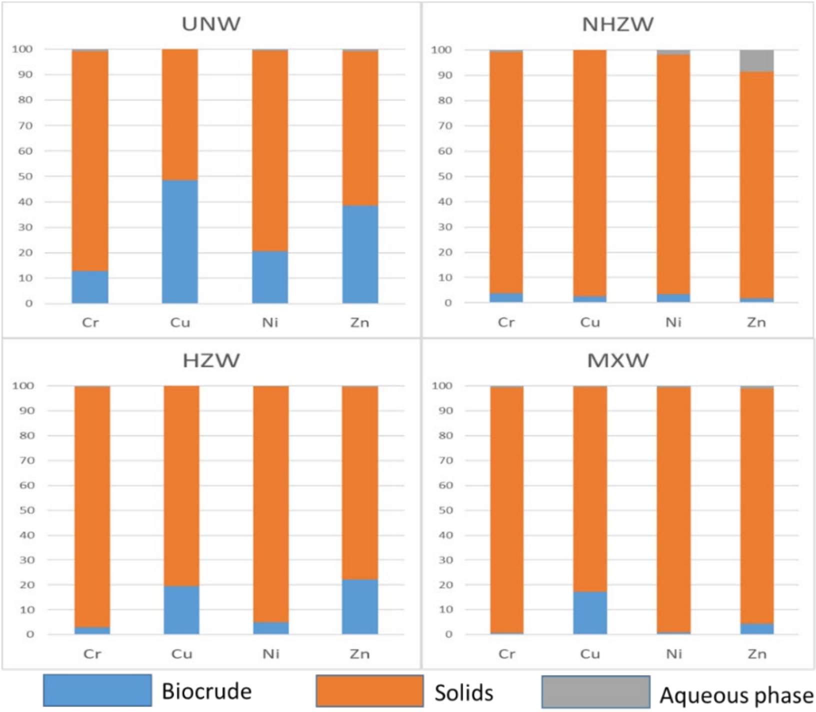

Figure 17: Distribution (weight %) of the HMs among the HTL products by processing the different construction wood wastes.

From the investigation of the fate of HMs, it was concluded that by the liquefaction of construction wood wastes, majority of heavy metals transferred from biomass to solid phase product. However, only small share of metals migrated to the biocrude and the aqueous phase.

Chapter 5

Hydrothermal liquefaction of eucalyptus and study of influence of process parameters

5.1 Eucalyptus biomass

Lignocellulosic biomasses from forest waste stream are well known for their abundant availability, accessibility, less price and carbon neutral. The utilization of forest feedstocks can contribute effectively in the bioenergy sector to achieve EU renewable energy targets by conversion of the waste streams into renewable products.

Eucalyptus is a type of hardwood, mainly famous for its rapid growth rate in short time within the year [86]. The EU regions, Brazil, South American countries, and India have great potential for the eucalyptus cultivation [87]. Conventionally, eucalyptus biomass has different applications that are in wide use for the furniture manufacturing, paper industry, and in the construction sector as well. Due to the potential availability and energy rich characteristics, eucalyptus was used for the HTL process to produce the biocrude and additive products.

Up to now, very few works have been reported on the liquefaction of eucalyptus biomass. Like Wu et al., did HTL of eucalyptus at 260-320℃ by keeping the process time of 30 min by using ethanol and water. The biocrude characterization by GCMS and FTIR was mainly focused in that study [88]. Additionally, the same research group also investigated by introducing different catalyst like KOH, NaOH, and Pd/C by maintaining the same temperature and retention time and concluded that HTL-biocrude, by processing the eucalyptus biomass mainly rich in ketones, esters, phenols and other acidic compounds [89]. The detailed study on the HTL of eucalyptus by considering the effect of different parameters on the process efficiency and obtained products is not available in the scientific literature. Furthermore, this study also investigated the relationship of process retention time with the fate of inorganics, heavy metals among HTL products by processing the eucalyptus biomass. In that respect, the aim of study C of this PhD project was to investigate the influence of process conditions on the HTL products and the conversion process. The products characterization and the fate of inorganics, heavy metals were also explored.

5.2 Characterization of eucalyptus biomass

The eucalyptus biomass was characterized by elemental analysis, higher heating values, ash and moisture content etc., reported in Table 6.

Table 6: Characterization of the eucalyptus biomass.

Moisture (%)	Ash (%)	C (%)	H (%)	N (%)	O (%)	HHV (MJ/kg)	H/C	O/C
5.88	1.15	47.85	5.81	0.10	46.23	18.14	1.45	0.72

The weight percent concentration of inorganic and heavy metal contents in the eucalyptus is highlight in Figure 18. From fifteen elements, the concentration of arsenic and cadmium was very low and below the detection limit. Whereas, the fate of remaining elements (Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, S, and Zn) is investigated.

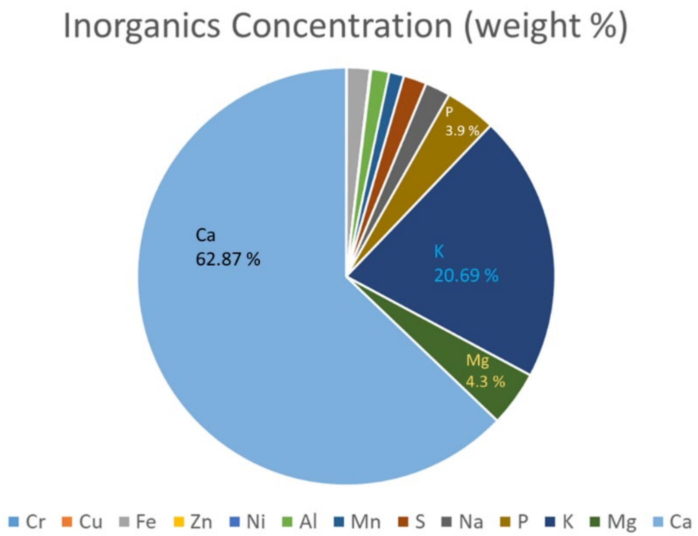

Figure 18: Normalized concentration of inorganic fraction (most abundant elements are highlighted e.g., Ca, K, Mg, and P) in the eucalyptus biomass.

It was observed that eucalyptus biomass has higher concentration of calcium (Ca) and potassium (K) with share of with 62.87 %, 20.69 % respectively. Magnesium (Mg) was found about 460.30 mg/kg contributes around 4.30%. The Ca and Mg rich feedstocks are generally seems as favorable due to the significant recovery of phosphors in the HTL-solid phase product that can be further used in the agricultural sector for the soil conditioning [90]. The Cr, Cu, Ni, and Zn were detected with very less concentration. Lower percentage of HMs in feedstock is promising for HTL process in the conversion of biomass to biocrude; otherwise, it will reduce the process efficiency.

5.3 HTL of Eucalyptus biomass

The effect of reaction conditions on the HTL of eucalyptus biomass was the main theme of this study. Initially, the effect of temperature and alkali catalyst was investigated. Further experiments were performed to explore the optimum condition (related to the biocrude production) in relation with process retention time. The liquefaction experiments were performed under subcritical and supercritical conditions. The biocrude and solid yield results in relation with variable process conditions are reported in the Figure 19.

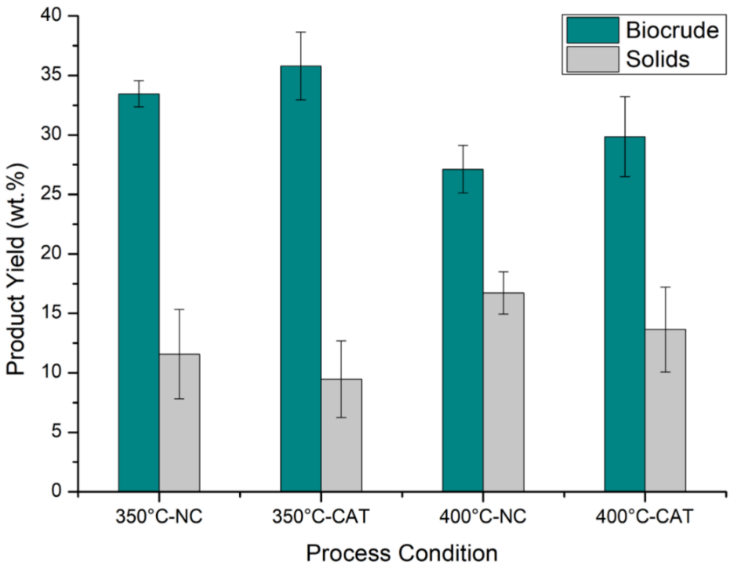

Figure 19: Biocrude and solid yields at 350 and 400℃ conditions with (CAT) and without (NC) catalyst by processing the eucalyptus biomass.

It was observed that temperature and the catalyst play their role on the conversion process in the form of product yields. At subcritical condition, comparatively higher conversion was obtained with biocrude yield 33.45-35.78 wt. % that was enhanced by the addition of catalyst. Furthermore, at supercritical conditions, less biocrude with more solid residue were achieved. The polymerization of biocrude macromolecules, thermal cracking reactions could be the reasons for lower biocrude yield at 400℃. Additionally, higher TOC was measured, which shows the significant transformation of organic carbon into water phase at supercritical conditions. In all four conditions, the addition of the catalyst (K_2CO_3) increased the biocrude and decreased the solid quantity. The possible reason for effective conversion in case of addition of alkali catalyst may be due to the reaction of catalyst with water that leads the formation of hydroxide, bicarbonate that enhance the conversion efficiency [62].

According to the elemental analysis (see section 3.1 [Paper C]), it was noted that the carbon values in obtained biocrude at sub and supercritical HTL was 71.34- 74.85 % and 73.24-74.73 % respectively which results the heating values about 33 MJ/kg. The biocrudes contains low nitrogen (0.39-0.93%) that is in accordance with other HTL-lignocellulosic studies [66]. The maximum energy recovery (65.51%) was calculated along with highest biocrude yield at 350℃ catalytic condition. Whereas, at 400℃ the ER was around 48.37-55.13 %. In overall, it was concluded that the subcritical-catalytic HTL shown as an optimum process condition for the conversion of eucalyptus biomass to the biocrude.

Under the nitrogen environment, the biocrude fractions were also investigated by the thermo-gravimetric analysis. The obtained TGA curves (Figure 20) shows about 70% of the biocrudes were occupied by the volatile fractions demonstrating the nature of gasoline, jet and maritime fuel, and diesel range. Additionally, it was confirmed by TGA results that up to 800 °C, in biocrudes, around 28-35% fractions remains as heavy residues.

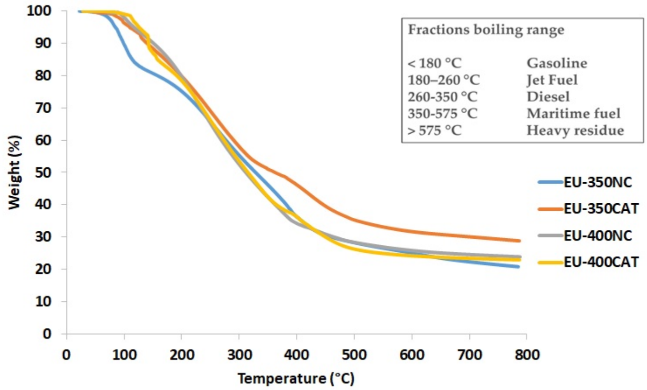

Figure 20: Thermo-gravimetric curves of the HTL- biocrudes by processing the eucalyptus biomass.

The results from GC-MS spectra (see Table 5 [paper C]) of biocrudes obtained at all four conditions shows that the detected compounds are mainly belongs to ketones, carboxylic acids, oxygen-containing aromatics, hydrocarbons, alcohols, and aldehydes functional groups. Those functional group compounds were increased by increasing the temperature from 350 to 400 °C. The ketone group compounds were detected in high concentration. Additionally, the employment of alkali catalyst also promotes the concentration of ketones in biocrude. Furthermore, the different acidic compounds like acetic acid were also appeared at all conditions may be due to the decompositions of biomass fractions like hemicellulose. The oxygen aromatics are detected in a significant amount that shows the declined trend because of higher temperature and employment of alkali catalyst. Moreover, the lower concentration of hydrocarbons (C_6-C_8) were available in biocrudes, which were affected by process conditions. It was concluded from GCMS results that biocrudes produced at 400 °C possess high quality in terms of heteroatoms than that produced at 350 °C.

The aqueous phase obtained by the HTL of eucalyptus biomass was characterized by pH, TOC, TP and TN measurement. According to the obtained pH values, aqueous phase contained acidic nature having range 4.04 - 5.75 may be because of hydrolysis reaction. Additionally, it was also observed that the transformation of organic carbon into the aqueous phase also varied with respect to temperature and catalyst. The employment of catalyst resulted in decrease in TOC values (33.36 to 23.04 g/l and 42.69 to 27.26 g/l) at both sub- and supercritical conditions. However, maximum TOC (42.69 g/l) was found at supercritical condition. At the other end, the total nitrogen (TN) was measured in lower amount (0.15-0.24 g/l) which is in general lower by processing the lignocellulosic feedstock as compared to wet biomasses. Moreover, the aqueous phase has total potassium (TP) in range between 6.68 – 58 g/l that was increased by adding of alkali catalyst. For such case, the recovery of potassium available in the aqueous phase can be done by the aqueous phase recirculation within the process that may result in decreasing the catalyst dosage for the next HTL runs. A detailed study is needed along this path in future to explore that strategy that may also reduce the overall process cost.

5.4 Effect of process retention time

5.4.1. Influence of process retention time on products

The investigation of influence of retention time on the overall process especially biocrude, solid yield, and the fate of inorganics is also a key objective of this study. For that, the optimum condition (biocrude yield perspective) from the base case experiments was chosen i.e., 350-Catalyst. By following the optimum condition, further HTL experiments were conducted by setting the retention time as 5, 10, 15, 20, and 25 min. The results of products yield (biocrude and solids) with ER are shown in Figure 21. From the experimental results, it was revealed that by starting with 5 min retention time, the biocrude yield begin to increase and become maximum at 15 min and after that becomes continuously reduced. The lowest biocrude yield with lowest energy recovery was observed at 25 min process time. The difference in the ER is definitely related to the amount of biocrude obtained. Furthermore, at 5 min retention time, lowest biocrude yield, ER and higher solid yield were measured. It may be due to the less effective de-polymerization and hydrolysis reactions. At the other end, the lower biocrude yield at a higher retention time may be occurred because of secondary thermal cracking reaction of biocrude compounds into aqueous phase or gases. Additionally, the condensation reaction may also responsible for producing more solid residue and reduction of biocrude production at higher retention times.

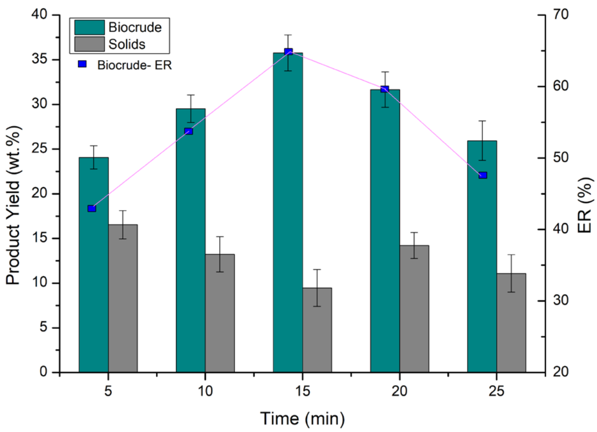

Figure 21: Biocrude yield with energy recovery and solid yield at different process retention time.

The reduction in the biocrude yield by increasing process time is also observed by other researchers. Like Yang et al., and Denial et al., are reported that by investigation of different retention times, the higher retention produces more biocrude yield [91, 92]. Another way, Li et al., reported better biocrude yield (55.03 %) by processing the rice stalk at 325℃ in ethanol for 60 min [93]. In another study, Brand et al., also reported biocrude yield as 65.8% by using ethanol as a solvent for the liquefaction of pinewood at retention time of 120 min [94]. The longer process retention time and consumption of solvent strategy are also debatable from an energy and economic perception for the HTL plant at commercial scale. For these aspects, the detailed techno-economic study is needed to evaluate the influence of retention time on the HTL process economics. In conclusion, the overall trend for biocrude production with respect to retention time was observed as, firstly biocrude yield was increased and then slowly decreased by increasing the process retention time. However, fluctuations in solid yield were also experienced that might be due to the lower degree of re-polymerization.

The elemental analysis (daf basis) of biocrude and solids obtained at different retention times is reported in Table 7. The carbon content in the biocrudes slightly increased (73.13 to 76.38%) for 5 to 20 min and at 25 min it decreased as 72.10%. Whereas, the hydrogen and nitrogen values were quite high at higher holding time. The overall higher heating values of the biocrudes were around 33 MJ/kg; that means did not influenced by the variation of retention times. The HTL-solids also contains the carbon in range between 62-65% and heating values around 23 MJ/kg. Furthermore, the solids are also rich in inorganic contents as well as heavy metals that will be discussed in section 5.4.3.

Table 7: Elemental composition (%, daf) and Higher heating values (MJ/kg) of biocrude, solids at different process retention time.

	Biocrude					**Solids**				
Time (min)	5	10	15	20	25	5	10	15	20	25
Carbon	73.13	74.88	74.85	76.38	72.10	64.28	62.61	64.47	64.98	65.37
Hydrogen	7.57	7.70	7.50	7.83	8.29	3.7	3.55	3.94	3.49	3.92
Nitrogen	1.23	0.17	0.80	0.40	1.96	0.16	0.12	0.37	0.15	1.07
Oxygen	18.07	17.25	16.85	15.39	17.65	31.86	33.72	31.22	31.38	29.64
HHV	32.56	33.42	33.21	34.29	33.08	23.50	22.55	23.91	23.54	24.35

5.4.2. Effect of retention time on organic composition of biocrude

The effect of process retention time on the biocrude organic compounds is shown in Figure 22. The detected compounds were categorized into six main classes. The variation in the concentration of oxygen aromatics, ketones, and acids with respect to retention time was clearly observed. As observed from 5-20 min, the amount of oxygen aromatic compounds initially reduced and then, increased at 25 min. The presence of oxygen aromatics are generally observed in response of breaking of Carbo-Carbon bonds due to the decomposition of lignin fractions [81]. Additionally, compounds from carbonyl groups like ketones and aldehydes were also increased at higher retention time from 5 to 25 min. The carboxylic acids and esters were increased initially and then decreased at higher process time. By the utilization of catalyst, the presence of acidic compounds was also reported by the other researchers by processing the lignocellulosic feedstock [82, 83]. Overall, the hydrocarbons were detected in lower amount but quite increased form 5-15 min and then becomes constant up to 25 min. In case of nitrogen containing compounds, an irregular trend was observed. At 20 min, the higher N compounds were appeared as compared to rest of the conditions. However, at 15 min, the lowest concentration of nitrogen compounds were reported. As it is well known that, the higher amount of N compounds may cause some sort of instability and are not favorable for the biocrude perspective.

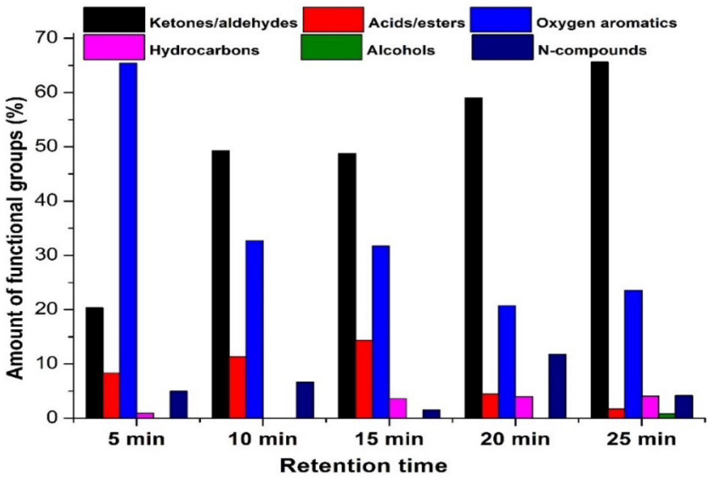

Figure 22: Influence of different retention times on the chemical composition of biocrudes produced at subcritical- catalytic condition

In conclusion, from organic compounds investigation at different retention times, 15 min retention time shows the optimum results for the biocrude production with a lower concentration of heteroatoms.

5.4.3. Influence of temperature and retention time on the inorganics distribution

The influence of the process temperature on the distribution of inorganic contents as well as heavy metals into the HTL products is shown in Figure 23. From the ICP results, it was revealed that, biocrude was somehow (more or less) contaminated by the presence of heavy metals at all conditions. At supercritical, biocrude contain more concentration of Cr, Cu, Zn, Ni, Na, and Ca compared to subcritical condition. It is important to mention that even lower amount of HMs (i.e. 0.5 wt.%) may become destructive for the HTL as well as hydro-treating process [95]. Thus, techniques are needed to decrease the concentration of HMs before biocrude-upgrading practice. Due to the variation of process temperature, the aqueous phase was also affected. The concentrations of Na, Mn, Na, K, Ca, and Mg in the aqueous phase were higher at

350℃. About the K concentration, it can be hypothetically concluded that the concentration of potassium can be recovered or reused by aqueous phase recirculation. The relationship between amount of potassium in the biomass used and the catalyst (K_2CO_3) dosage can be explored in future studies.

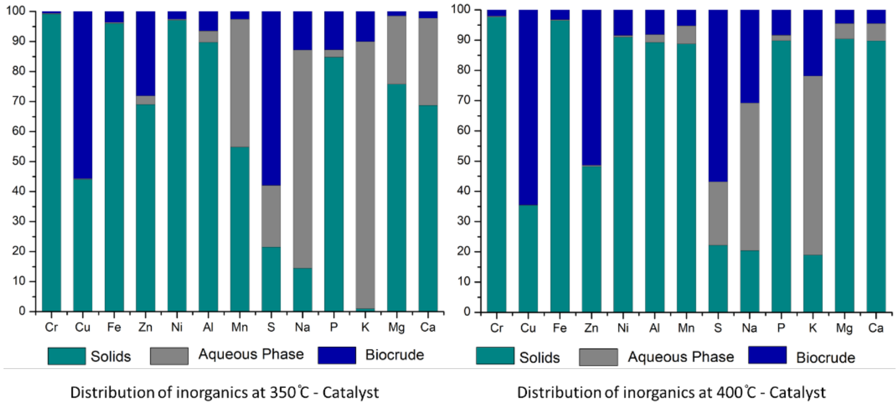

Figure 23: Relative distribution of inorganic contents at sub- and supercritical HTL (with catalyst) conditions.

The majority of inorganics, heavy metals were migrated to the solid phase. Among them sodium and potassium experienced lower in solids. For the other elements, about 21-97% transferred to solids. It was noted that about 84-89% of the phosphorus was recovered in the solid phase. It may be due to the high concentration of calcium and magnesium in eucalyptus, which tend to promote precipitation of the phosphorus in solids [90]. Conventionally, the phosphorus is used to obtain from phosphate rock that is a non-renewable resource, in that case, the recovery of phosphorus from HTL products may set an added value by the integration of HTL with the fertilizer industry to enhance the circular economy [96].

The effect of retention time (5, 15, and 25 min) on the fate of inorganics and heavy metals during the optimum condition (350℃- catalytic) is reflected in Figure 24. The clear trend can be noted for the different concentration of Fe, Ni, Al, Zn, S, and Cu in the biocrude in relation with the retention time. Furthermore, an increase in process time shows higher concentration of HMs (Cr, Cu, Ni, Zn) into the biocrude. The concentration of phosphorus in the aqueous phase is flexible that depends on the process conditions and the compositions of feedstock [97]. The overall results show that the efforts are required to reduce the concentration of HMs in the biocrude if the HTL biocrude is obtained at higher process retention time.

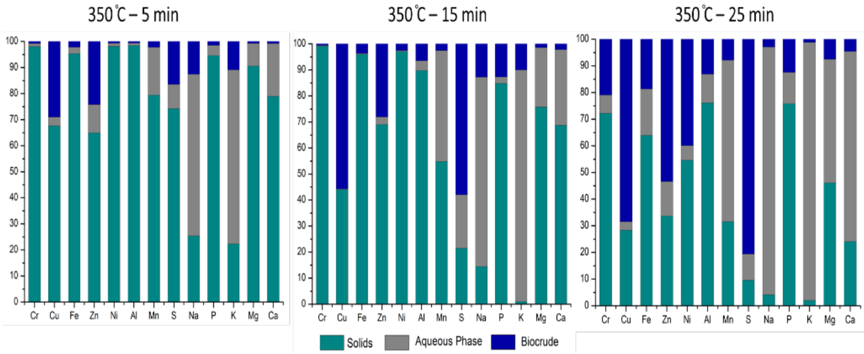

Figure 24: Effect of the retention time on the recovery of inorganic contents in the different phases of HTL products.

By investigation of fate of inorganic contents, it was concluded that a major percentage of targeted inorganics shifted to the HTL solids, while the scenario is quite variable for rest of phase products. Additionally, the transfer of treasured elements like macro and micronutrients into the solids can uplift their value as a soil conditioner but the presence of heavy metals in the solids and biocrude is totally undesirable that can be rectified for further techniques.

Chapter 6

Conclusions

This PhD project focused on the utilization of lignocellulosic waste materials from agriculture, urban, and forest streams for biocrude production through hydrothermal liquefaction process. By applying the designed and targeted themes, different process conditions were applied to explore the effect of subjected feedstocks on the conversion process etc.

In the first study, wheat straw was liquefied at sub and supercritical conditions. The effect of temperature and alkali catalyst was explored in detail. By processing at all four conditions, it was revealed that highest biocrude yield (32.34 wt.%) with higher energy recovery (69.53%) was obtained at 350℃ – catalytic run. The employment of catalyst enhanced the process conversion efficiency. At subcritical conditions, around 44–55% of the carbon recovered in biocrude with HHV of 35 MJ/kg. The HTL- solids were rich in calcium, phosphors, and magnesium concentration that can be efficiently recovered for further applications. Additionally, due to the presence of organic carbons in the HTL-water, the effect of aqueous phase recirculation was also investigated. The aqueous phase recirculation results productive outcomes in the form of enhanced biocrude yield as well as energy recovery. By aqueous phase recirculation, the biocrude yield was inclined from 32.34 to 38.12% after two rounds of recycling. In overall, HTL results suggested that HTL of wheat straw in subcritical could be an effective method to convert agricultural waste to biocrude and valuable energy products.

In the second study, different types of contaminated construction wood waste from urban waste streams were chosen for the supercritical HTL to produce biocrude. The impact of impregnation on conversion process and the fate of heavy metals was investigated. After HTL, from the biocrude yield perspective, the trend was observed as UNW > NHZW > HZW > MXW. The variation in yields was possibly due to the difference in the composition of wood samples. From the experimental results, it was concluded that, the impregnation have an impact on the performance of HTL process, for which the impregnated wood materials comparatively shows less biocrude yield. The TGA curves shown that the obtained biocrudes reflected the fuel range associated with kerosene, diesel and gasoline. By addressing the fate of heavy metals, it was revealed that the majority of the HMs migrated into the solid phase. Some small amounts of HMs, like Cu (2–20%) and Zn (1–21%) in case of impregnated wood were found in the biocrude that may cause a problem for the efficiency and life of catalyst used in the HTL upgrading process. To sum up, from this study, HTL is suggested as a suitable and sustainable route to convert contaminated wood waste into biocrude. Additionally, it helps to manage the waste wood from construction industry and to minimize the socio-economic and environment impacts.

In the third study, to valorize the forest feedstock, the HTL of eucalyptus was performed. The influence of different process conditions (Sub – supercritical, Catalyst/Non catalyst) was initially investigated. After that, the effect of process retention time (5, 10, 15, 20, and 25 min) at optimum condition (350℃- catalytic) was explored. In comparison to supercritical conditions, highest biocrude (35.78%) and energy recovery (65.51%) was achieved at subcritical catalytic condition. However, the average biocrude yield obtained at supercritical was around 27.11- 29.85% with more solids. By investigating the influence of process retention time, biocrude yield was fluctuated with the variation of the process time and obtained in range between 24.08- 35.78%. Whereas, there was no any significant impact on HHV (33 MJ/kg) was observed. The conclusion obtained from the retention time study was summarized that the biocrude and solid yields were varied with respect to process time and become optimum at 15 min. Additionally, for the fate of inorganics and HMs, it was observed that majority of inorganics (about 21-97%) migrated to solids. The fruitful nutrients like Ca, P etc were accumulated in solids accompanied with HMs. It should also be noted that even though the HTL-solids are rich in macro and micronutrients and beneficial for agricultural sector as a soil conditioner but an especial care is needed to removal of HMs before further applications of solids.

Chapter 7

Future Perspectives

During the investigation of lignocellulosic biomasses from agriculture, urban and forest streams through HTL process, following gaps were also highlighted for future studies:

- For the scale up of the HTL process by processing the dry lignocellulosic biomasses like wheat straw, pumpability is seems to be one of the challenges to run the continuous HTL process smoothly. The detailed study on the pumpability aspects of lignocellulosic feedstocks is proposed for future work.

- To address the fate of chlorine during the HTL of wheat straw, which may cause slagging in the reactor and reduce the process efficiency and life of reactor.

- To investigate the removal techniques (with their economic aspects) of heavy metals from HTL-solids when impregnated wood like construction wood waste used for HTL process.

- Co-HTL of contaminated feedstock, i.e., construction wood waste with sewage sludge is suggested to explore the synergistic and/or antagonistic effect that may reduce the HMs concentration in HTL products especially solids.

- Detailed techno-economic analysis is required to investigate the whole value chain by processing the lignocellulosic feedstocks up to the production of drop-in fuel.

- Relationship between potassium concentration in biomass used, aqueous phase from HTL process to the amount of catalyst (K_2CO_3) dosage for the aqueous phase recirculation.

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