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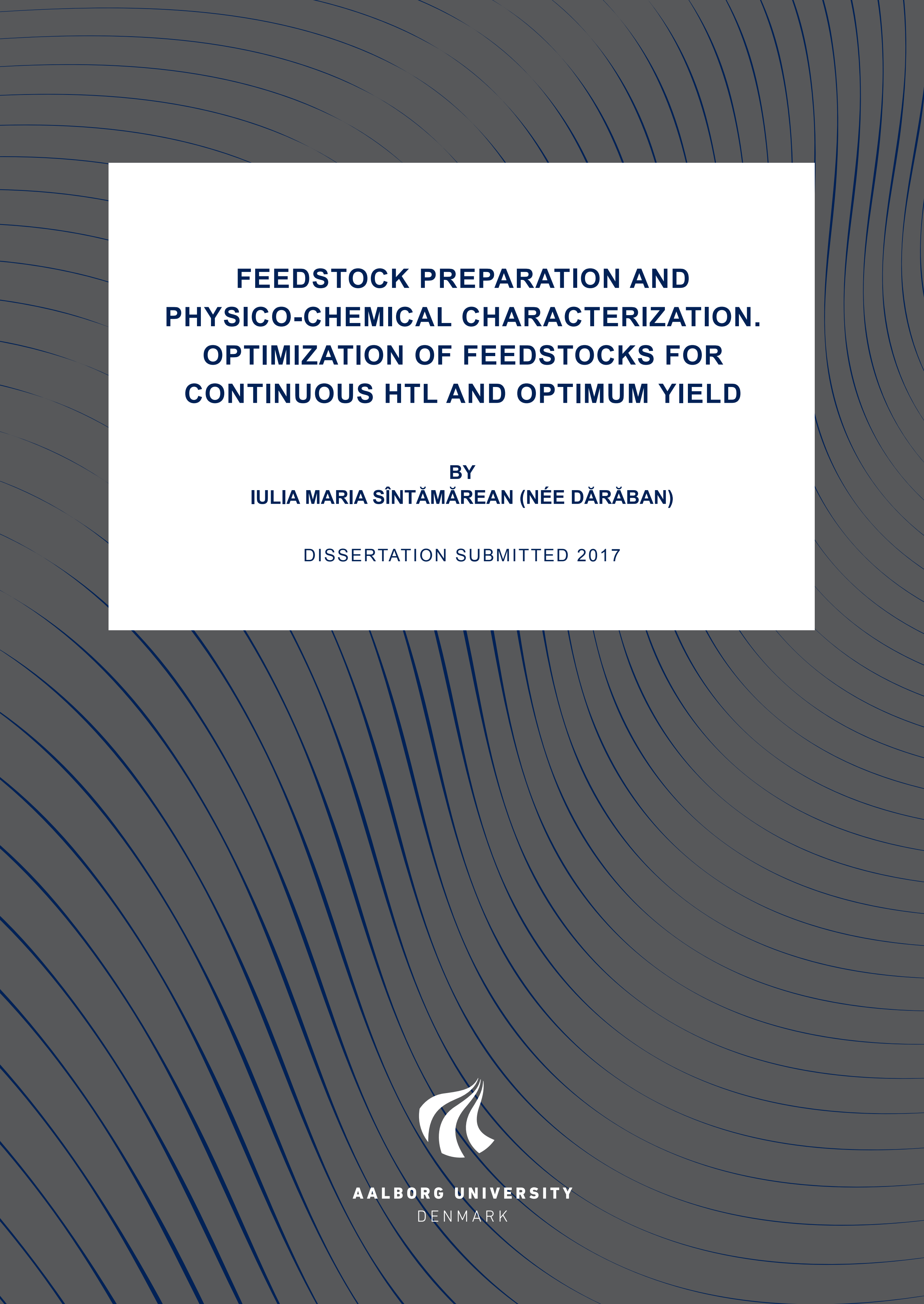

FEEDSTOCK PREPARATION AND PHYSICO-CHEMICAL CHARACTERIZATION. OPTIMIZATION OF FEEDSTOCKS FOR CONTINUOUS HTL AND OPTIMUM YIELD

BY
IULIA MARIA SÎNTĂMĂREAN (NÉE DĂRĂBAN)

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Feedstock preparation and physico-chemical characterization. Optimization of feedstocks for continuous HTL and optimum yield

Ph.D. Dissertation

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Preface

This thesis is made as a completion of the PhD studies carried out at the Faculty of Engineering and Science, Aalborg University, Denmark. The thesis marks the end of my PhD studies, started in August 2014 and completed in February, 2017. This period has been a wonderful experience and a great opportunity to discover the beauty of being a researcher.

I am taking this opportunity to express my deepest gratitude to my supervisor Professor, PhD, Lasse A. Rosendahl, for offering me the chance to conduct this work. I am also grateful for his guidance, professional support, understanding and friendly attitude, that helped me throughout my studies and made the PhD an enjoyable experience.

I am also grateful to my co-supervisor Associate Professor, PhD, Thomas H. Pedersen for valuable guidance and support. Several persons have also contributed academically, practically and with support to this thesis. Therefore, I would like to thanks to my colleagues Associate Professor, PhD, Saqib S. Toor, Federica Conti, Anne V.K. Rasmussen, PhD-fellow, Claus U. Jensen and to the whole crew of Steeper Energy ApS especially to CTO, PhD, Steen B. Iversen and CEO, Perry Toms, for their help throughout the entire process.

Finally, I would like to give special thanks to my spouse who encouraged and inspired me and to my family and friends for being supportive during this period.

Sintamarean

Iulia Maria Sintamarean
Aalborg University, April 2017

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Nomenclature

Abbreviations

BtB	biomass to biofuels
CBS1	Continuous bench scale HTL plant installed at AAU
CO_2	carbon dioxide
DOE	design of experiments
DCM	dichloromethane
DEE	diethyl ether
GHGs	greenhouse gas emissions
hp	horsepower
HTC	Hydrothermal Carbonisation
HTG	Hydrothermal Gasification
HTL	Hydrothermal Liquefaction
HTU	Hydrothermal Upgrading
LHW	liquid hot water
m.c.	moisture content
TGA	Thermogravimetric analysis
TOC	total organic carbon
WHC	water holding capacity
WSO	water soluble organics

Acronyms

db %	dry basis
daf %	dry ash free basis
vol %	volume percentage
wt %	weight percentage

Units

kWh	kilowatt-hour
M	molar concentration
MJ	megajoule (1 joule x 10^6)
Mt	million tonnes (1 tonne x 10^6)
MPa	megapascal
ppm	parts per million (by volume)

Thesis Details

Thesis Title: Pretreatment of biomass for continuous Hydrothermal Liquefaction
Ph.D. Student: Iulia Maria Sintamarean (née Daraban)
Supervisors: Prof. PhD, Lasse Aistrup Rosendahl, Aalborg University
Ass. Prof. PhD, Thomas Helmer Pedersen, Aalborg University

The main body of this thesis consists of the following papers:

[1] **I.M. Daraban**, L.A. Rosendahl, T.H. Pedersen, S.B. Iversen, “Pretreatment methods to obtain pumpable high solid loading wood-water slurries for continuous hydrothermal liquefaction systems” *Biomass and Bioenergy*, vol. 81, no. , pp. 437–443, 2015.

[2] **I.M. Sintamarean**, Ionela F. Grigoras, Claus U. Jensen, Saqib S. Toor, Thomas H. Pedersen, Lasse A. Rosendahl, “Two-stage alkaline hydrothermal liquefaction of wood to biocrude in a continuous bench scale system” *Biomass Conversion and Biorefinery*, pp. 1–11, February 2017.

[3] **I.M. Sintamarean**, T.H. Pedersen, Xueli Zhao, Andrea Kruse, L. A. Rosendahl, “Application of algae as co-substrate to enhance the processability of lignocellulosic feeds for continuous hydrothermal liquefaction” *Industrial and Engineering Chemistry Research*, March 2017.

In addition to the main papers, the following publications have also been made.

[4] I.F. Grigoras, R.E. Stroe, **I.M. Sintamarean**, L. A. Rosendahl, " Effect of biomass pretreatment on the product distribution and composition resulting from the hydrothermal liquefaction of short rotation coppice willow " *Bioresource technology*, vol. 231, pp. 116–123, 2017.

[5] T.H. Pedersen, I.F. Grigoras, J. Hoffmann, S.S. Toor, **I.M. Daraban**, C.U. Jensen, S.B. Iversen, R.B. Madsen, M. Glasius, K.R. Arturi, R.P. Nielsen, E.G. Søgaard, L.A. Rosendahl, “Continuous Hydrothermal Co-liquefaction of Aspen Wood and Glycerol with Water Phase Recirculation” *Applied Energy*, vol. 162, January, pp. 1034–1041, 2016.

Abstract

Hydrothermal liquefaction (HTL) is a thermochemical route to convert a diverse range of biomass substrates into liquid energy carrier. The HTL process includes the preparation of a biomass aqueous slurry and heating the slurry up to sub- or supercritical water conditions to facilitate the biomass dissolution and conversion into biocrude. For continuous HTL processing, the preparation of pumpable biomass slurries is extremely challenging especially when it comes to lignocellulosic biomass. So far, the feedstock pumpability has been a neglected area of research within the hydrothermal processing field because most studies are conducted in batch reactors where pumpability is beyond scope.

In support of the development of continuous hydrothermal liquefaction, this work is focused on elaborating pretreatment strategies to prepare pumpable wood slurries. Methods based on thermochemical treatment as well as strategies based on physical and mechanical pretreatment (consisting of size reduction and mixing of biomass with other substrates) are studied. The impact of the feedstock pretreatment on the biocrude yield and biocrude properties is also investigated. Indicative laboratory tests to predict the pretreated feedstocks pumpability are developed.

One of the pretreatment methods proposed consists in mixing wood powder with recycled biocrude. This strategy was previously used by Pittsburgh Energy Research Center (PERC) to pump wood slurries in a pilot-scale HTL plant but only with limited success. In the PERC process, wood slurry with only 7 % dry matter content could be processed continuously. In this work it is shown that by further reducing the particle size (0.125 mm compared to 0.420 mm) and mixing all three components - wood, biocrude, water - in one step, it is possible to increase the biomass loading of the slurry to 20 % mass fraction. Another improvement of this strategy is the order of mixing the compounds to allow the preparation of homogeneous wood-water-biocrude slurries. It is shown that mixing first the wood with water and adding biocrude afterward, can prevent the phase separation between the biocrude and the water phase. A slurry containing 20 % wood, 40 % water and 40 % recycle biocrude (mass fractions) was successfully processed in a continuous bench scale HTL plant.

Another pretreatment strategy proposed aims direct processing of wood chips, thus reducing the energy input for grinding the wood to fine powder. The pretreatment consists of treating the wood chips in alkaline solution at

180 °C to 200 °C. Wood chips are dissolved and converted into a wood paste of different consistency, depending on the pretreatment conditions applied. A parametric study was carried out and showed that at least 65 % of the wood chips need to be dissolved to obtain pumpable feeds. Such slurries can be obtained with solutions of sodium hydroxide (sodium hydroxide-to-wood ratio of 0.35-0.40) after 2 hours of thermal treatment. HTL studies on the pretreated vs. non-pretreated slurries have shown that the pretreatment of wood has no significant impact on the biocrude yield or elemental composition. Alkaline pretreatment of biomass prior to continuous hydrothermal liquefaction has not been reported in literature yet.

Another strategy that can be used to obtain pumpable wood slurries is the addition of compounds with water binding capacity and thickening properties into the slurry. Seaweeds and microalgae were used as a source of compounds with such properties. Of the algae tested, brown seaweeds, red seaweeds and microalgae could prepare pumpable slurries when mixed with wood in a mass ratio of 1/1. Green seaweeds could not form pumpable mixtures with wood. Besides the higher biomass loading of wood-microalgae slurries (30 % compared to 20 % mass fraction for wood-seaweeds mixtures), microalgae are also advantageous with respect to biocrude yield. Liquefaction experiments showed that microalgae have a major positive impact on the biocrude yield most probably due to the higher lipid and protein content while seaweeds have a slightly negative impact compared to the liquefaction of pure wood. The main drawback of co-processing wood and algae is the transfer of nitrogen and sulfur containing compounds from algae into the biocrude phase. Co-processing of wood and algae is a novel approach in hydrothermal processing field, especially when used as a method to improve the pumpability of lignocellulosic feedstocks.

The main contribution of this work is in developing strategies to prepare pumpable wood slurries for continuous hydrothermal liquefaction. Three pretreatment methods are proposed for processing wood powder (particle size < 0.25 mm) or wood chips (10 mm to 15 mm or larger). Two of the three pretreatment strategies were tested in a continuous bench scale HTL-plant which confirms the technical feasibility of the pretreatment methods proposed but also the good agreement between the laboratory-scale and the large scale pretreatment and pumpability tests.

Resumé

Hydrothermal liquefaction (HTL) er en termokemisk proces til omdannelse af en bred vifte af biomasser til flydende energibærer. HTL processen inkluderer bl.a. forbehandling af en våd fødeblanding (biomasse + vand), som videre tryksættes og opvarmes til under- eller overkritiske betingelser for vand, hvorved processen faciliterer en kemisk omdannelse af biomassen til en bio-råolie. I kontinuerte HTL processer med fødeblandinger baseret pålignocellulosiske biomasser har det vist sig teknisk udfordrende at præparere en sådan fødeblanding, som kan tryksættes og pumpes uden faseseparation (f.eks. væskefase og faststof). Indtil nu har pumpebarheden af fødeblandinger i HTL processer været uden for fokus primært grundet, at HTL forskes hovedsageligt i batchreaktorer, hvor pumpebarhed er en redundant parameter.

For at supportere udviklingen af kontinuerte HTL processer er omdrejningspunktet for denne afhandling at udvikle forbehandlingsstrategier til at præparere pumpebare, lignocellulosiske fødeblandinger. De udviklede strategier baserer sig på termokemisk forbehandling og på fysisk og mekanisk forbehandling (såsom mekanisk neddeling af biomassen og blandinger med andre biomassesubstrater). Indikative testmetoder til at forudsige pumpebarheden af disse forskellige fødeblandinger er ligeledes udviklet. Ud over pumpebarheden evalueres også strategiernes effekt på f.eks. udbyttet af bio-råolie og kvaliteten af denne.

Den første strategi er baseret på at blande træbaseret biomasse med recirkuleret bio-råolie fra HTL processen. Denne strategi har tidligere været anvendt af Pittsburgh Energy Research Center (PERC) til at pumpe træbaserede fødeblandinger i et pilotskala anlæg. PERC var da i stand til at pumpe fødeblandinger med 7 % tørstofindhold. Ved at fin-neddele træet til (0,125 mm i forhold til 0,420 mm) og blande alle tre komponenter - træ, vand, bio-råolie - i et trin, er det lykkedes at opnå et tørstofindhold på 20 %. En anden forbedring af denne strategi er rækkefølgen for blandingen af de forskellige indholdsstoffer (vand, træ, bio-råolie). Det er vist, at blandes træet først med vand og derefter med bio-råolien kan faseseparation forhindres. En fødeblanding indeholdende 20 % træ, 40 % vand og 40 % recirkuleret bio-råolie (massefraktioner) er succesfuldt anvendt i et kontinuerligt pilot-skala HTL-anlæg.

Den anden strategi baserer sig på termokemisk forbehandling af træflis, hvorved energiforbruget til mekanisk fin-neddeling kan undlades. Den

termokemiske forbehandling består i at varmebehandle biomassen ved 180-200 C i en alkalisk opløsning. Ved denne forbehandling opløses og konverteres biomassen til en træpasta af varierende konsistens afhængig af procesbetingelserne. Et parametrisk studie viste, at minimum 65 % af træflisen skal opløses i den alkaliske opløsning førend fødeblandingen er pumpebar. Sådan et resultat kan opnås ved at forbehandle træflisen i en natrium hydroxid opløsning (ved et natrium hydroxid/træflis forhold på 0,3-0,4) i to timer. Efterfølgende, eksperimentelle HTL studier af de forbehandlede og ikke-forbehandlede fødeblandinger efterviste, at forbehandlingen ikke har nogen betydelig effekt på hverken udbytte eller den elementære sammensætning af bio-råolien. Sådan en alkalisk forbehandling, efterfulgt af kontinuert HTL har ikke før været rapporteret.

Den tredje strategi, der kan anvendes til at sikre pumpebare lignocellulosiske fødeblandinger, baseres på samprocessering med andre bio-substrater med høj vandbindingskapacitet og fortykkende egenskaber. Alger er eksempler på substrater med sådanne egenskaber og blev videre undersøgt. Af de forskellige undersøgte alger viste det sig, at både brunalger, rødalger, og mikroalger kan, sammen med lignocellulosisk biomasse, resultere i pumpebare fødeblandinger, når disse blandes i et 1:1 forhold. Det blev yderligere vist, at grønalger ikke er i stand til at forme pumpebare fødeblandinger sammen med træ. Det højeste tørstofindhold (30 %) af fødeblandingen (træ + alge) kan opnås med mikroalger. Hvor brunalger og rødalger viste sig at have en svagt negativ indvirkning på bio-råolie udbyttet, så har mikroalgerne en gavnlig effekt på bio-råolien, antageligvis grundet det høje indhold af lipider og proteiner i mikroalger. Den største ulempe ved samprocessering af træ og alger er overførslen af de nitrogen- og svovlholdige kemiske forbindelser fra algerne til bio-råolien. Samprocessering af træ og alger samt anvendelsen af disse, til at forbedre pumpbarheden af lignocellulosiske råmaterialer, har ikke tidligere været anvendt i HTL.

Det primære bidrag af denne afhandling er udviklingen af strategier til at forberede pumpbarheden af lignocellulosiske fødeblandinger til kontinuerlig HTL. Tre forbehandlingsmetoder til bearbejdning af træpulver (partikelstørrelse <0.25 mm) eller træflis (10 mm til 15 mm eller større) er blevet udviklet. To af de tre forbehandlingsstrategier blev testet i et kontinuerlig pilot-skala HTL-anlæg, hvilket bekræfter den tekniske anvendelighed af de foreslåede forbehandlingsmetoder. Yderligere blev der bevist god sammenhæng mellem laboratorieskala og pilot-skala med hensyn til testmetoderne til at forudsige pumpebarheden af forskellige fødeblandinger.

Abstract

Hydrothermal liquefaction (HTL) este un proces termochimic prin care o gamă variată de biomasă poate fi convertită într-un purtător de energie sub formă lichidă. Procesul de HTL include prepararea unui amestec de biomasă şi apă şi încălzirea acestuia la temperatura sub- sau supercritică a apei, pentru a facilita disoluţia biomasei şi conversia acesteia în bioţiţei. Pentru procesul continuu de HTL, prepararea unui amestec pompabil de biomasă şi apă este foarte dificilă în special în cazul biomasei lignocelulozice (e.g. materiale lemnoase). Până acum, pomparea amestecurilor de biomasă şi apă pentru procesul de HTL a fost o arie de cercetare neglijată deoarece majoritatea studiilor sunt realizate în reactoare de tip şarjă unde pomparea amestecului nu este un obiectiv.

În sprijinul dezvoltării procesului continuu de hydrothermal liquefaction, această lucrare se axează pe elaborarea unor strategii pentru prepararea de amestecuri pompabile de biomasă şi apă. Metode bazate pe tratamente termochimice precum şi tratamente fizice şi mecanice (care constau în reducerea dimensiunii particulelor şi combinarea amestecurilor cu alte substraturi) sunt studiate. Impactul compoziţiei amestecului asupra randamentului şi calităţii bioţiţeiului este de asemenea un aspect important al acestei lucrări. Metode care pot fi folosite în laborator pentru a indica amestecurile pompabile sunt propuse.

Una dintre metodele propuse constă în amestecarea lemnului aflat sub forma de pudră cu bioţiţei reciclat. Această strategie a mai fost aplictă de Pittsburgh Energy Research Center pentru a pompa lemn într-o instalaţie HTL pilot, însă cu un succes limitat. Una dintre îmbunătăţirile aduse acestei metode este creşterea conţinutului de biomasă de la 7 % la 20 %, procente de masă. Această reştere s-a putut realiza prin utilizarea de particule de biomasă de dimensiuni mai mici (0.125 mm comparativ cu 0.420 mm) şi amestecarea celor trei componenţi - lemn, bioţiţei, apă - într-un singur stagiu. O altă îmbunătăţire a acestei strategi este ordinea în care componenţii sunt amestecaţi pentru a permite formarea de amestecuri omogene de lemn, bioţiţei şi apă. S-a arătat că separarea de faze între apă şi bioţiţei poate fi evitată prin amestecarea biomasei cu apă-în prima fază-urmată de adăugarea bioţiţeiului. Un amestec cu un conţinut de 20 % lemn, 40 % apă şi 40 % bioţiţei (procente de masă) a fost procesat cu succes într-un sistem continuu de HTL.

A altă metodă propusă are ca scop procesarea directă a chipsurilor de lemn, reducând astfel energia consumată pentru măcinarea lemnului într-o pudră fină. Procesul constă în tratarea chipsurilor de lemn cu o soluţie alcalină la 180 °C - 200 °C. În urma tratamentului, lemnul este dizolvat iar amestecul de lemn şi apă este convertit într-o pastă de diferite consistenţe, în funcţie de condiţiile de tratament aplicate. Un studiu parametric a fost realizat şi a arătat că cel puţin 65 % din biomasă trebuie dizolvată pentru a obţine amestecuri pompabile. Astfel de amestecuri pot fi obţinute prin utilizarea unei soluţii de hidroxid de sodiu (raport hidroxid de sodiu:biomasă 0.35-0.40) după tratament termic timp de 2 ore la 180 °C. Experimente de HTL cu lemn tratat si lemn netratat prin acest proces termochic, au arătat că tratarea lemnului nu are un impact semnificativ asupra randamentului şi calităţii bioţiţeiului. Tratarea biomasei în mediu alcalin înaintea procesării într-un sistem continuu de hydrothermal liquefaction nu a fost raportată în literatură până acum.

O altă metodă prin care pot fi obţinute amestecuri pompabile de biomasă lemnoasă este prin adăugarea de compuşi cu capacitate de a reţine apa şi cu proprietăţi de îngroşare. Alge marine şi microalge au fost folosite ca sursa de compuşi cu astfel de proprietăţi. Dintre toate algele testate, algele marine brune şi roşii şi microalgele au putut forma amestecuri pompabile cu lemn (sub formă de pudră) când au fost amestecate într-un raport de masă de 1/1. Algele marine verzi nu au putut forma amestecuri pompabile cu lemn. Pe lângă avantajul de a forma amestecuri cu conţinut total de biomasă mai mare (30 % lemn-microalge comparativ cu 20 % lemn-alge marine) microalgele cresc şi randamentul de bioţiţei. Experimentele de HTL au arătat că microalgele au un impact pozitiv major asupra randamentului de bioţiţei în timp ce algele marine au un impact uşor negativ compartiv cu conversia lemnului pur. Principalul dezavantaj în co-procesarea lemnului cu alge este transferul de compuşi care conţin azot şi sulf în bioţiţei. Co-procesarea lemnului cu alge este o abordare nouă în procesul de hydrothermal liquefaction, mai ales când aceasta este folosită cu scopul de a înbunătăţi pompabilitatea amestecurilor lignocelulozice.

Principala contribuţie a acestei lucrări constă în dezvoltarea de strategii pentru a obţine amestecuri pompabile de lemn-apă pentru procesarea continuă în sisteme de hydrothermal liquefaction. Trei metode pentru procesarea lemnului sub formă de pudră (dimensiunea particulelor < 0.25 mm) şi chipsuri de lemn (10 mm - 15 mm sau mai mari) au fost propuse. Două dintre cele trei metode au fost testate într-un sistem HTL continuu, ceea ce confirma fezabilitatea din punct de vedere tehnic a metodelor propuse, dar şi un acord bun între testele de laborator şi cele la scară mai mare.

Part I

Report

Chapter 1

Introduction

Nowadays, there is a large and growing interest in using biomass and other renewable resources for energy production. Increased energy demand and fossil fuel emissions lead to record atmospheric CO_2 concentration of more than 400 ppm in 2016 [6]. CO_2 emissions and other greenhouse gases and anthropogenic factors are the main cause of global warming. The last 30 years have been the warmest decades since 1850. The global mean surface temperature increased over the period 1951-2012 with 0.72 °C (relative to 1850-1900 average) and is estimated to further increase by the end of the 21st century with up to 4.8 °C above the 1986-2005 average (in the worst case scenario) [7]. Such increase of global temperature would generate irreversible global warming and will have serious consequences on climate change, food, water, land availability and national security. In order to avoid such consequences, the global surface temperature increase need to be kept below 2 °C (relative to 1850-1900 average). This objective was adopted by 195 countries in the Paris Agreement from 2015.

As shown in Figure 1.1, in the 2 °C scenario the annual CO_2 emissions in 2040 are reduced with 57 % compared to the levels that could be achieved considering the current trends. In this scenario, the total share of fossil fuels in the primary energy mix declines from 79 % (the share in 2040 in the Current Policies Scenario) to 60 % (the share in 2040 in the 2 °C scenario) and the total renewables share increases from 16 % to 29 % [8]. Today, the renewables cover about 14 % of the world total primary energy supply [9] thus, improvements in this sector are vital to meet the CO_2 emissions reduction target.

Biomass is the largest renewable energy source providing 10 % of world primary energy supply, ten times more than wind and solar together [8]. Biomass can be used to produce bio-electricity, bio-heat, bio-fuels and bio-products. The largest part of the biomass is used today as fire wood in developing countries (for domestic heating and cooking), for heat and power production [10]. Biomass-to-biofuels (BtB) sector has a small contribution to the bioenergy production but new conversion technologies are being developed and the share of biofuels in the transportation sector is expected to increase from 2 % today to 27 % in 2050 [11].

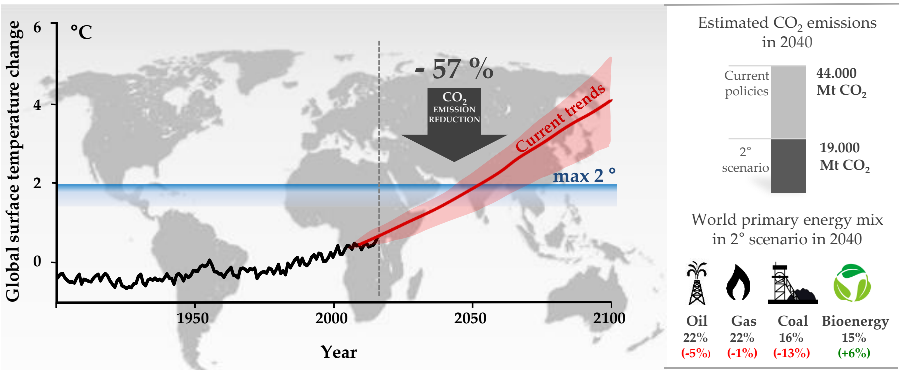


Figure 1.1: The change in global surface temperature, predicted CO_2 emissions and world primary energy mix in 2040 in the Current trends scenario and the 2 °C scenario; measured global surface temperature values relative to 1951-1980 average (data source: [6]) and predicted values relative to 1986-2005 [7]. CO_2 emissions and world primary energy mix data according to [8]

The production of biofuels began in the late 19th century, was resumed in the mid-1970s and flourished between 2000 and 2007 when biofuels accounted for 1.5 % of the world total transport fuels [12], [11]. Nowadays, the production of biofuels is based on bioethanol, biodiesel and a small fraction of biogas, mostly produced in the USA, Brazil and Europe. Bioethanol and biodiesel are obtained from sugar crops and vegetable oils while biogas is obtained from organic wastes (e.g. manure) or dedicated energy crops. These technologies are mature and are already implemented at commercial scale, generally known as conventional or 1^{st} generation biofuel technologies [11]. Because most of the biofuels production is based on bioethanol and biodiesel, the 1^{st} generation biofuels are also known as the edible resource-derived biofuels. Increased production of 1^{st} generation biofuels and other factors, contributed to the global food crisis in 2007-2008, when the price of cereal crops increased dramatically and started a food vs. fuel debate [13]. For this reason, the targets for bioenergy supply in transport sector were reconsidered and in 2015, the European Commission imposed a limit of 7 % share of the final consumption of energy in transport for biofuels obtained from cereal and other crops [14].

In order to achieve a sustainable growth of the biofuels market and to meet the global target of 27 % bioenergy supply in transport sector by 2050, advanced biofuel technologies need to be made commercially available. As shown in Figure 1.2, lignocellulosic and algal biomass need to support the main production of biofuels in future. Alternative routes to obtain biofuels from lignocellulosic biomass (2^{nd} generation biofuels) or from algal biomass (3^{rd} generation biofuels) already exist but only at basic and applied R&D,

demonstration or early-commercial development stage [11].

Second generation biofuels are obtained from lignocellulosic biomass such as wood residues, straw, woody and herbaceous crops, grass etc. Lignocellulosic biomass is advantageous because is not competing with food resources, can be produced at lower cost than food crops [15], can be also available as waste streams and is the most abundant biomass resource on earth [16]. The estimated amount of lignocellulosic biomass used for biofuels production in EU by 2020 is 15 million tones [17]. However, production of biofuels from lignocellulosic biomass is more difficult than the conversion of sugar and oil crops into bioethanol and biodiesel. For biochemical conversion of lignocellulosic biomass (e.g. by fermentation or digestion), first the carbohydrates need to be liberated from the lignocellulosic matrix by applying various destructive chemical or thermo-chemical pretreatment methods. Thermal decomposition of biomass by gasification or pyrolysis also requires biomass pretreatment because the solids need to be dried and milled in order to achieve high heat transfer rates. Processing lignocellulosic biomass through hydrothermal conversion technologies like Hydrothermal Liquefaction or Hydrothermal Gasification, face difficulties related to biomass-water system heterogeneity. In this case, the pretreatment of biomass targets to obtain pumpable slurries. Overall, lignocellulosic biomass conversion into biofuels is difficult due to the rigid structure of biomass. Biomass pretreatment represents a key step in the production of 2^{nd} generation biofuels.

Hydrothermal Liquefaction (HTL) of biomass is an alternative route to

Figure 1.2: The evolution of biofuels share in the transport sector by 2050 and the development of biomass-to-biofuel technologies according to the feedstock used

obtain liquid biofuels from a large range of biomass substrates, including lignocellulosics. Because microorganism are not used in the process, the HTL technology is more flexible in terms of the biomass used. Unlike pyrolysis and gasification where dry solids are used, HTL operates in aqueous medium thus, biomass drying is not required, eliminating the use of energy for drying the biomass. However, the main challenge of this technology for large scale implementation is the preparation of biomass-water mixtures that can be delivered to the reactor under high pressure conditions. Due to this limitation, the HTL technology development has been resumed to small scale implementation in batch or continuous reactors. There were only few attempts to implement the HTL process at pilot-scale but only for short periods of time. A review on the historical development of HTL is given in Chapter 3.

Chapter 2

Thesis objectives and outline

1 Focus area and project objectives

This work is part of the C3BO project founded by the Innovation Fund Denmark Grant No. 1305-00030B. The project aims to demonstrate that HTL is a sustainable and high efficient pathway to produce drop-in fuels from lignocellulosics and other biomass streams. The project is divided in four working packages that covers the whole process chain from biomass to transportation liquid biofuels, including residual streams management and HTL life cycle assessment. The work packages are shown in Figure 2.1.

The current work is part of Work Package 1 and is focused on feedstock pretreatment. The main objective of this study is to develop pretreatment strategies for lignocellulosic biomass, that enables the slurries pumpability at near- or super-critical conditions of water. In the same time, the pretreatment must allow higher biomass loadings than previously achieved in literature for continuous processing of lignocellulosic biomass i.e. at least 20 % mass fraction.

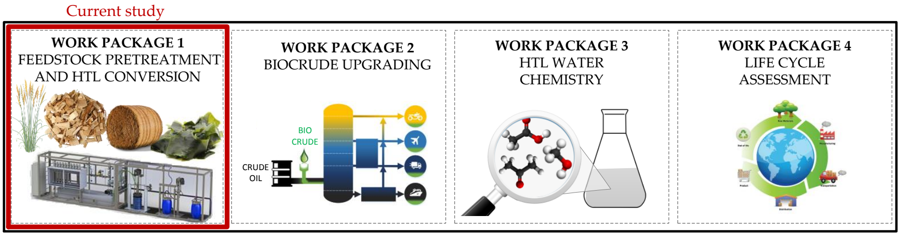


Figure 2.1: C3BO project work packages

2 Research questions

Considering the above mentioned objectives the following research questions are formulated:

1. What experimental methods can be implemented to evaluate the feedstock pumpability?
2. What strategies can be applied to achieve 20 wt % feedstock dry matter content when wood is slurried with recycled biocrude?
3. What thermo-chemical pretreatment can deconstruct the wood chips to an extent that enables the pumpability of concentrated feedstocks?
4. What is the impact of the biomass thermo-chemical pretreatment on the HTL product distribution and biocrude properties?
5. Can the mechanical dewatering of wood slurries be reduced by introducing algae into the mixture? Which algae species perform best as feed stabilizers?
6. What is the impact of co-processing wood and algae on feedstock biomass loading, biocrude yield and biocrude elemental composition?

3 Thesis outline

The thesis is divided in two parts: *Part I Report* contains background knowledge on Hydrothermal Liquefaction and biomass pretreatment. Part I Report also contains a detailed description of the experimental results and is structured in seven chapters as described below. The published articles that describes the topics covered in this thesis are attached in *Part II Publications*.

Chapter 1 presents an overview of the global energy utilization and CO_2 emissions trends. The role of bioenergy and biofuels in Europe and the EU strategies for climate change mitigation are discussed.

The objectives and the outline of this thesis are presented in *Chapter 2*.

Chapter 3 contains a short description of the Hydrothermal Liquefaction process from biomass to final transportation biofuel products. The HTL process development since 1934 until today is discussed and the most representative HTL continuous systems are reviewed. The obstacles in the path to large scale production of HTL biofuels are pointed out.

Chapter 4 is a short review on the existing pretreatment methods for lignocellulosic biomass. The purpose of this chapter is to identify the pretreatment options suitable for the HTL process.

The first pretreatment method proposed in this work is covered in *Chapter 5*. The focus of this chapter is to find strategies to increase the biomass loading in wood-water-biocrude slurries.

Chapter 6 deals with the alkaline pretreatment of wood chips. A parametric study is carried out to identify the optimum pretreatment conditions. Hydrothermal liquefaction experiments at laboratory- and bench scale are performed to study the impact of alkaline pretreatment on biocrude yield and composition.

In *Chapter 7* wood powder is mixed with seaweeds or microalgae to study the ability of algae to prevent feedstock dewatering. Small scale hydrothermal liquefaction experiments with wood-algae mixtures are carried out to determine the impact of algae on biocrude yield and elemental composition.

Finally, the findings of this work are summarize in *Conclusions*. Extra information related to the topics presented in Part I Report can be found as *Appendices*.

Chapter 3

Hydrothermal Liquefaction of biomass

1 HTL process description

Hydrothermal liquefaction (HTL) is a thermochemical route to convert biomass into a high calorific value liquid biofuel. The process consists in preparing a biomass aqueous slurry that is heated to sub- or super-critical water conditions (280 °C - 450 °C). While heated, the biomass is converted into biocrude through various chemical reactions like depolymerization, dehydration, condensation, cyclization etc. Between 30 % and 70 % of the biomass can be converted into biocrude, depending on the chemical composition of the substrate and process conditions (e.g. temperature, catalyst). Besides biocrude, a large fraction of the biomass is converted into water soluble organic compounds, gases and solids. An example of the HTL product distribution resulted from the liquefaction of wood is given in Figure 3.1. For a more detailed description of the HTL process and process chemistry the reader may refer to Peterson et al. [19], Behrendt et al. [20], Toor et al. [21], [22], Akhtar et al.

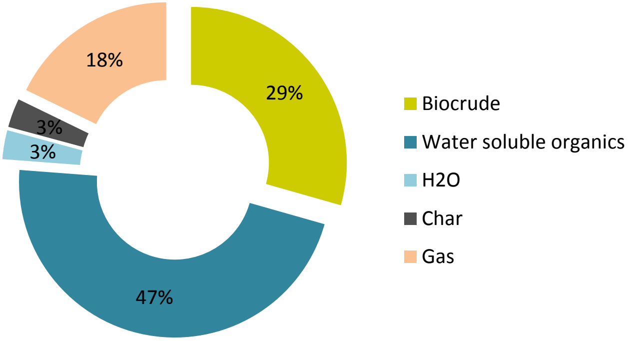


Figure 3.1: The yield of products resulted from hydrothermal liquefaction of wood, according to NREL and PNNL studies [18]

[23], Hoffmann et al. [24].

Figure 3.3 shows the path from biomass to biocrude through HTL and further upgrading steps necessary to convert the biocrude into transportation fuels. The process is divided in three stages: feedstock preparation, feedstock HTL conversion and biocrude upgrading.

Stage 1 - Feedstock preparation consists in one or more of the following steps: biomass selection, proteins or other high value compounds extraction, biomass particle size reduction, biomass leaching for ash removal and finally slurry preparation. Slurry preparation consists in mixing the biomass with the aqueous phase, catalyst and other desired additives. In some cases, slurry preparation involves chemical pretreatment, thermal pretreatment, mechanical pretreatment or a combination of these three. All these steps can be considered biomass and feedstock pretreatment operations.

Stage 2 - Hydrothermal liquefaction consists in converting the biomass into biocrude oil. Before entering the HTL reactor the biomass slurry is heated to desired temperature. Temperature is probably the most investigated factor affecting the HTL process. A large range of process conditions were investigated in literature. Figure 3.2 gives an overview on the temperature-pressure conditions tested for the liquefaction of various types of biomass in lab-scale studies, mostly performed in autoclaves. Many studies concluded that the optimal HTL temperature is between 300 °C and 350 °C, with respect to biocrude yield [26], [27], [28]. There are also studies indicating that liquefaction of biomass in super-critical water conditions is more advanta-

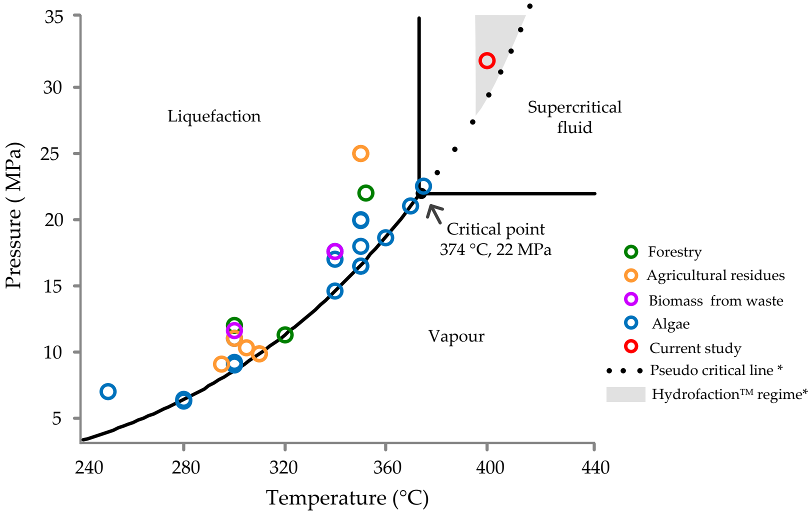


Figure 3.2: Variability of temperature conditions used in different HTL studies. *Pseudo critical line and Hydrofaction^{TM} regime according to [25]

geous with respect to oil quality [29], [30], [31]. The water initially added for slurry preparation is enriched during the HTL process with various water soluble organic compounds resulting from biomass conversion. A study performed on the continuous bench scale HTL unit installed at Aalborg University, shows that the HTL product water phase can be recycled within the process with positive effect on the hydrogen-to-carbon ratio of the biocrude [5]. The study also shows that the total organic carbon (TOC) and the ash content of the water phase increase with every cycle. The linear increase of the ash content in the water phase observed in the study, suggests that large fractions of the alkaline catalyst tends to remain into the water phase. Unfortunately, the increase of organic compounds concentration in the water phase reduced the efficiency of gravimetric separation of biocrude due to the water soluble organic (WSO) compounds acting as biocrude solvent. In batch studies, where oil was separated by solvent extraction, Biller et al. showed that HTL water phase recirculation increases the biocrude yield and the biomass conversion efficiency due to the built-up of organic compounds in the water phase [32].

Stage 3 - Biocrude upgrading is performed at temperatures of about 350 °C - 400 °C with the addition of hydrogen gas and in presence of a heterogeneous catalyst. The biocrude pretreatment aims at removing the oxygen, sulfur and nitrogen from the biocrude oil compounds in order to obtain a refinery compatible product. Experiments indicate that upgraded biocrude can be mixed with crude oil and co-processed in conventional refineries for the production of transportation fuels [33]. A comparison between raw and upgraded HTL biocrude is given in Table 3.1. The table also shows the significant reduction of the biomass oxygen content when converted into biocrude. Between 65 % and 80 % of the oxygen is removed by dehydration and decarboxylation reactions. Dehydration reactions are specific for carbohydrates (due to polyol structure) while decarboxylation reactions are more specific for fatty acids and amino acids [19].

Table 3.1: The elemental composition of biomass, raw- and upgraded biocrude oil and Northen sea crude

	Wood[a]	HTL biocrude [b]	Upgraded HTL biocrude[b]	Northen sea crude[b]
Elemental mass fraction (%)				
C	47.9	83.9	83.8-87.7	86.6
H	6.5	10.4	10.8-12.2	13.1
N	ND	0.4	0.2-0.6	ND
O	45.6	5.3	0.1-5.0	0.3
S	ND	ND	ND	ND
HHV [MJ/kg]	18-19	40.43		44.4

[a] Daraban et al. [1], [b] Jensen et al. [33]

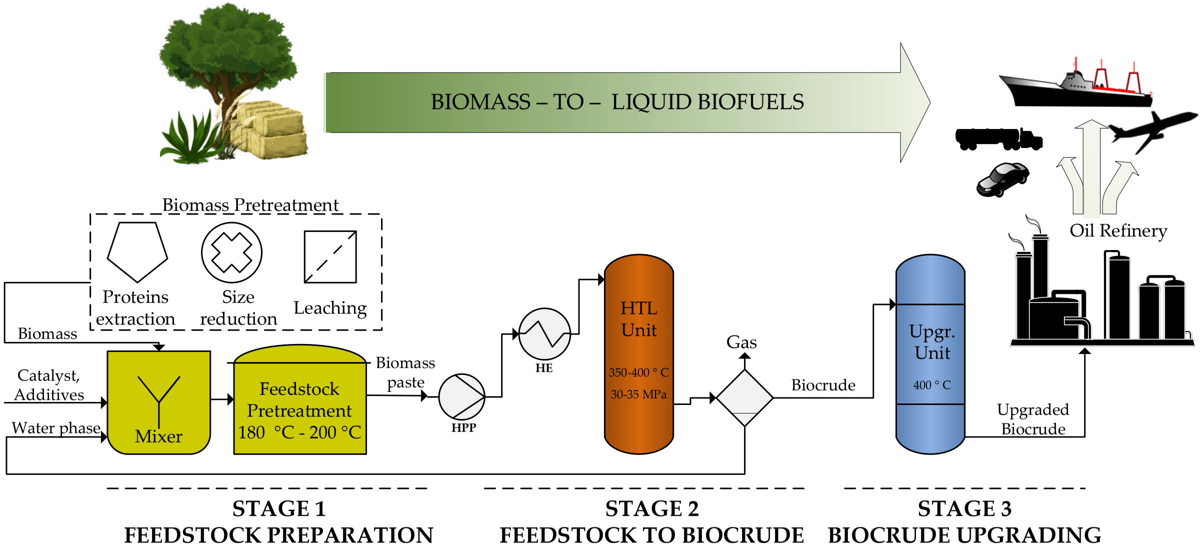


Figure 3.3: The path from biomass to liquid biofuels through Hydrothermal Liquefaction

2 HTL technology roadmap

Hydrothermal liquefaction has been a research topic for more than 80 years. Even so, the research activity is still focused on laboratory scale studies. The development of HTL technology was not continuous, as illustrated in Figure 3.4. There were several attempts to upscale the process around the years with peak crude oil prices (e.g.year 1980 and 2008) but only few projects continued until today. When crude oil prices declined, production of biocrude was considered not economical and in most cases the research activities in bench-, demo-, or pilot-scale were halted. Instead, the small scale studies in universities and research centers worldwide had a constant development, providing continuous knowledge about this process. The experience gained so far from operating continuous HTL systems is important for this study to understand the issues related to feedstock pumpability and how they were approached in the past. For this reason, a review of the most representative HTL continuous systems was carried out.

The proof of concept

First experiments of biomass liquefaction in aqueous medium were reported by E. Berl, between 1934-44. His studies involved wood treatment in the presence of water and various catalyst at temperatures higher than 230 °C. A semi-liquid product "proto product" was obtained. Berl believed that any carbohydrate-containing material can be converted into such product that can be further used as fuel oil or in Diesel engines [34], [35], [36].

Bureau of Mines studies

Berl's studies were resumed by US Bureau of Mines (BOM) around 1970. The Bureau of Mines performed tests on a wide range of lignocellulosic wastes (urban refuse, agricultural wastes, sewage sludge, wood, manure or lignin). Experiments were carried out in autoclaves and a continuous system at temperatures between 250 °C and 380 °C. The novelty introduced by BOM is the liquefaction in presence of CO and water, an idea initially applied to coal liquefaction. The function of CO was not clear but it was noticed that it enhanced the biomass conversion into crude-oil. Researchers at BOM also noticed that the addition of sodium carbonate increased the oil yield. The main findings of the BOM group were: 1) Temperature increase have a significant effect on product quality by reducing the viscosity and the oxygen content; 2) Higher initial CO pressure increase the oil yield; 3) Partial replacement of water with other vehicles or solvents (antracene oil, isoquinoline) reduces the operating pressure and increases the oil yield; 4) The most effective catalysts are the alkali carbonates; 5) Nitrogen bases such as NH_4OH or isoquinoline are also efficient catalysts; however NH_4OH is disadvantageous because the

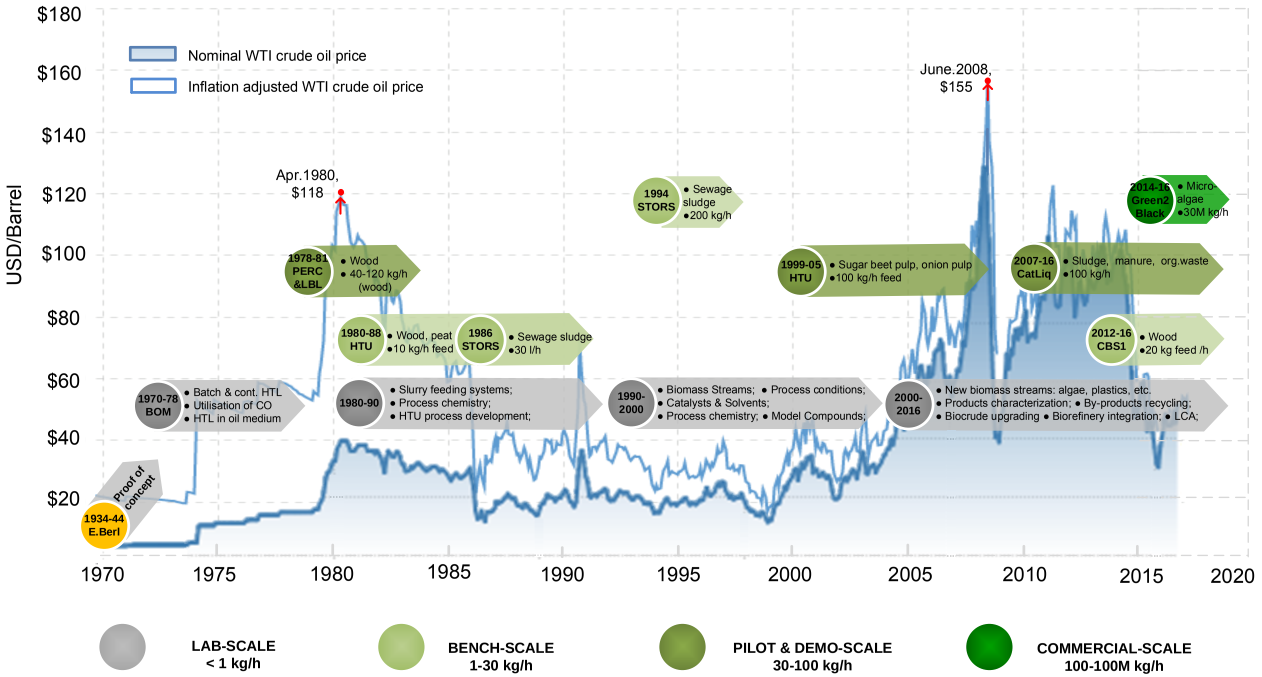


Figure 3.4: The influence of historical crude oil prices on the development of HTL at different scale (source: www.macrotrends.net)

product oil contains higher N concentrations. Oil yields between 30 and 50 wt % were reported [37].

The first HTL pilot plant

Shortly after the batch studies carried out by BOM, the first and largest continuous HTL plant was built (the Albany plant) and operated in the period 1978/81 [38]. The unit was designed to process 1 to 3 tons of wood chips per day but never run at full capacity [39]. Two different versions of the liquefaction process were implemented at the Albany plant. One of the versions was based on the original BOM process, known also as the PERC process, that utilizes antracene oil or recycled product oil to partially replace the water in the feed mixture (see Figure 3.5). The recycled biocrude is used to obtain pumpable wood slurries. Milled wood is mixed with biocrude and pumped into the system. The water phase is injected into the wood-biocrude slurry to form a final feedstock with about 7 wt % dry matter content. Process temperature varies between 300 °C and 370 °C, pressure is around 200 bars and residence time between 20 minutes and 90 minutes [40].

A second version was developed by Lawrence Berkeley Laboratory and is known as the LBL process. The most significant difference between PERC and LBL process is the wood pretreatment method. In the LBL process, wet wood chips were treated with dilute sulfuric acid (< 0.1 %) at 180 °C to dissolve about 30 % of the initial solids and to increase the wood loading. The slurry obtained was further neutralized and processed into a refiner to mechanically break the fibers and to prepare a pumpable slurry [38]. The pretreatment stage is illustrated in Figure 3.6. Even though the initial wood in water concentration was 23 % mass fraction, the pretreated feed was diluted back to less than 15 % mass fraction in order to avoid plugging of the system [39], [38]. Another disadvantage of this pretreatment method was the high amount of alkaline reactant needed to neutralize the feed.

In both versions of the process, potassium carbonate was used as catalyst

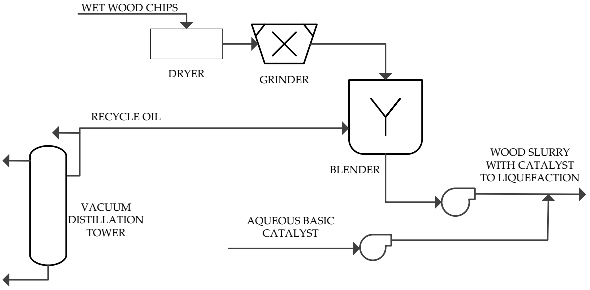


Figure 3.5: Feedstock preparation in the PERC process (adapted from [39])

and a CO-H_2 mixture was co-fed into the reactor. The product oil analyzes indicated similar quality to No. 6 fuel oil. For this reason, the biocrude was considered suitable for steam and power generation [38], [40]. The Albany project demonstrated the technical feasibility of the HTL process [38]. One of the most critical problems was the feed-stream pumpability [39]. Solid loadings of around 10 % mass fraction, high energy consumption to obtain wood flour (particle size below 0.250 mm) or large quantities of alkaline catalyst used to neutralize the acid pretreated feeds increases the biocrude production cost and makes the process "marginally economic at best" [41].

The Sludge To Oil (STORS) process

Pumpability difficulties encountered by the group working at the Albany plant when processing wood, determined researchers at Battelle Pacific Northwest National Laboratories to adopt a "keep it simple strategy" in biomass liquefaction [41]. The simplicity of the process consisted in the lack of a pretreatment step for the feedstock and quitting the use of reducing gases such as the CO-H_2 mixture. To avoid the feedstock pretreatment, sewage sludge was chosen as biomass feed thus, the process was called STORS - Sludge to Oil Reactor System. In 1986, United States Environmental Protection Agency published the results from continuous HTL of municipal sewage sludge in a 30 L/h system. The sludge solid content was 20 % mass fraction [42]. Later, in 1994 research groups in Japan reported results from a larger STORS plant with a capacity of 5 tonne per day sludge [43]. Another difference between STORS and LBL or PERC systems was the lower operating pressure, 10 MPa compared to 20 MPa. However an alkali carbonate catalyst was also used in the STORS system.

Shell's HTU process

Another continuous HTL process was developed by Shell. Experiments at Shell Laboratories in Amsterdam for the HTU process (Hydrothermal Upgrading) were carried out in small autoclaves and a modular bench-scale

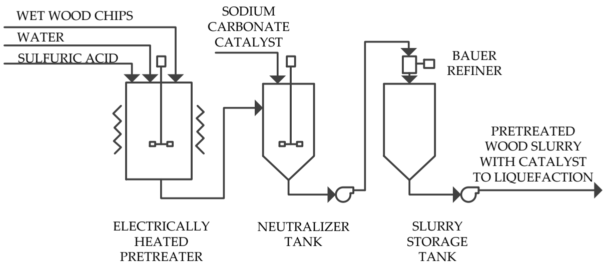


Figure 3.6: Feedstock preparation in the LBL process (adapted from [39])

system with a 1 L reactor (10 kg slurry/h) between 1980 and 1988 [44], [45]. In order to pump the wood slurry through the continuous system, wood powder with particle size of 0.1 mm was used. Peat was also tested. In the purpose of process development, a larger demonstration system was built and officially opened in 1999. The system capacity was about 100 kg/h of feed.

The pumpability issues of these feeds were solved by modifying a commercial available pump [45]. Also, in the HTU process, a Liquid Hot Water (LHW) pretreatment was integrated. The pretreatment process is shown in Figure 3.7. The pretreatment, consists in treating the wood chips in water at 180 °C to 200 °C for 10 minutes to 15 minutes. The authors state that the principle was demonstrated at laboratory scale and that a paste product could be obtained and pumped at 18 MPa [44]. No other additives are mentioned despite the fact that it was stated that the method was adopted from the paper industry [45] where an alkaline reactant is typically used. Yet, the modular bench scale continuous system was operated with wood powder [44] and later, the pilot plant was operated on different feedstock like sugar beet pulp or onion pulp. This may suggest that the pretreatment method described earlier was not suitable for wood chips. In fact, difficulties to pump a feed obtained from wood chips in the modular continuous system were reported by Goudriaan et al. [45].

Based on the successful operation and promising results at the pilot plant, there was interest in up-scaling the HTU plant for treating biomass or organic waste. A technical and economical study showed that the HTU process could be integrated with the protein extraction from grass, reducing the nitrogen content of the HTU feedstock. Unfortunately the project of building the first commercial demonstration plant was abandoned due to disagreements between the the project partners [45].

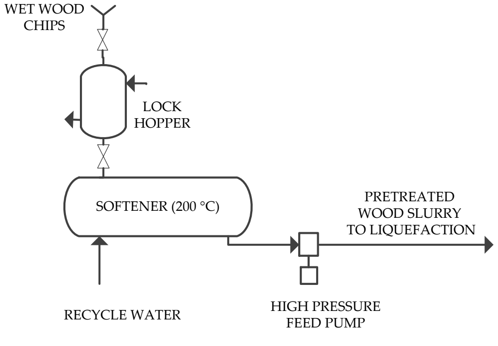


Figure 3.7: Conceptual design of the wood chips pretreatment in the HTU process [44]

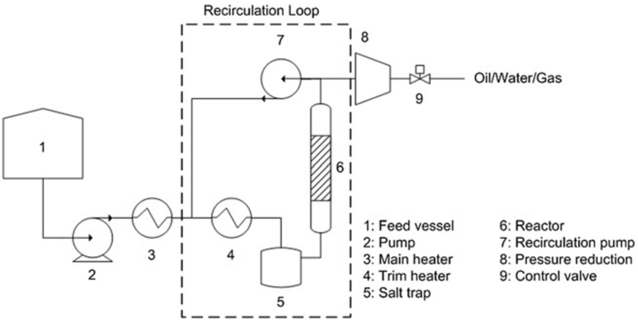


Figure 3.8: Diagram of the CatLiq process [46]

The CatLiq process

The CatLiq process was developed by the Danish company SCF Technologies. The process was designed to convert biomass such as sewage sludge, organic waste, liquid manure or corn silage in a 100 kg/h unit, at about 350 °C [46]. The novelty of this system was the introduction of a product stream recirculation loop meant to maintain a constant temperature of the feed and to collect the salts precipitated. The pilot plant was operated between 2007 and 2010 in Copenhagen and in 2011 was bought and relocated near Istanbul by Altaca Environmental Technologies & Energy. In 2015 the company built a pre-commercial CatLiq plant [47].

The CBS1 plant at Aalborg University

Based on previous studies and efforts to develop and improve the HTL process, a new continuous bench-scale unit was built at Aalborg University in a collaborative effort with Steeper Energy. The CBS1 system capacity is 20 kg/h feed and is operated in semi-continuous mode. A feed barrel of 100 kg is filled with feedstock that is pumped in a single stage into the system. The feed passes first through a section of heaters and afterward through a series of two 5 L tubular reactors. After approximately 15 minutes retention time in the reactors, the product stream is depressurized in the capillary section and cooled. After releasing the gases, the biocrude is separated from the water phase gravimetrically. The solids are trapped in filters that are placed in-line before the capillary section. When emptied, the feed barrel is replaced with a new one containing feedstock and the HTL process is continued [5]. The process flow diagram of the CBS1 plant is shown in Figure 3.9.

In the actual configuration, the CBS1 plant has a feedstock preparation section consisting of a hammer mill and a horizontal screw mixer. The main feedstock tested in the CBS1 plant are based on wood. Usually, to prepare pumpable wood slurries, the biomass flour is mixed with recycled biocrude and a thickening agent. To these, recycled water phase, alkaline catalyst

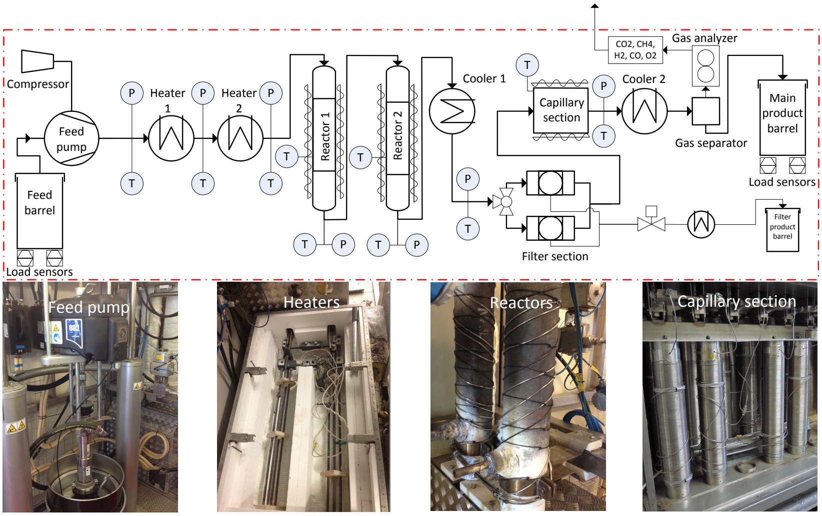


Figure 3.9: The process flow diagram of the CBS1 bench scale continuous HTL plant installed at Aalborg University [5]

(K_2CO_3) and other additives are added. Feedstock biomass loadings between 15 wt % and 20 wt % dry matter are the most common for the wood-based slurries processed in the CBS1 plant. One of the challenges in operating the the continuous bench scale HTL system is the lack of feed preparation alternatives that would offer more flexibility in terms of biomass type, particle size and solid loading.

3 Pumpability of lignocellulosic feedstocks

3.1 Characterization of lignocellulosic feedstocks

Lignocellulosic slurries are highly heterogeneous mixtures, usually characterized by the lack of a continuous, compact aspect and the tendency to separate into a solid- and a liquid phase. The main reasons for this behavior are

- the porous structure,
- the low bulk density and
- the weak interactions with water

of the biomass. These properties are responsible for the low biomass loadings of lignocellulosic slurries (< 15 wt %) and solids dewatering when pressurized.

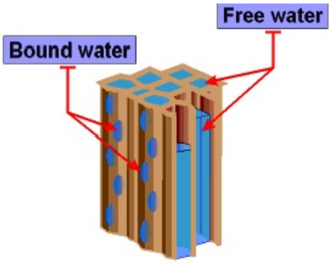


Figure 3.10: Water uptake in wood by physical and chemical means [48]

Lignocellulosics are low density materials with porous structure, as showed in Figure 3.10. When immersed in water, the capillaries are filled with liquid, reducing the volume of liquid in the system that could accommodate new particles. This is why the biomass loading of HTL slurries decreases with the increase of biomass water sorption capacity. Most of the water absorbed is mobile and can be removed when the moistened solids are compressed. Only a small amount is fixed, bound water.

Water sorption capacity of biomass depends on the particle porosity. In general, small particles have higher sorption capacity than coarse particles due to the higher number of accessible pores. Figure 3.11 shows how the biomass loading of the hardwood and softwood slurries decreases when the particle size is reduced from 500 μm to 125 μm. Extensive particle size reduction can significantly diminish the particle porosity which can help to

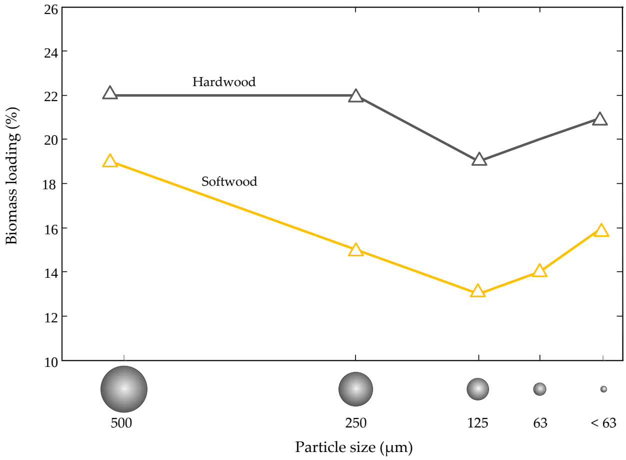


Figure 3.11: The variation of wood-water slurry biomass loading with particle size and wood type (based on data from [49])

increase back the biomass loading of the slurry. This can be noticed in Figure 3.11 for particles smaller than 125 μm. Small particles are advantageous also because they give a more compact aspect to the slurry.

3.2 Pumping systems

Before entering into the heaters and afterward into the HTL reactor, the feedstock is pressurized using a high pressure pump. As shown in Figure 3.12, the pump needs to deliver the feed at 20 MPa - 30MPa according to the temperature at which the HTL conversion will be carried out. A report of PNNL [50] reviews the pumps and pump systems that are able to deliver, at these pressure conditions, highly viscous wood slurries with 15 wt % dry matter content. Based on the response of several pump vendors, the report indicates three types of positive displacement pumps that can meet the HTL needs:

- piston pumps (highest viscosity handling, particle size limitations),
- diaphragm pumps (large particle handling, limited to lower solids content and viscosity),
- lobe pumps (largest particle size and high viscosity handling, pressure built in multiple stages).

Most of the vendors suggested that the pumps need to be connected with other components of the pumping system such as screw feeders - to assist feeding of non-flowing slurries, macerators (upstream) or line injection systems (downstream) [50]. The injection of a liquid into the pressurized feed stream was also mentioned in the Albany HTL plant where the aqueous phase loaded with catalyst was injected into the wood-biocrude slurry after passing through the high pressure piston pump [38] (see Figure 3.5).

The PNNL report shows that delivering the HTL biomass feedstocks at high pressure conditions is a challenging task. Solutions can be found for slurries with 15 wt % dry matter content but feeds with higher biomass loading are at the extreme edge of pumpability [50]. Therefore the necessity to convert the highly viscous biomass slurries into feedstocks that are easier to handle is unquestionable.

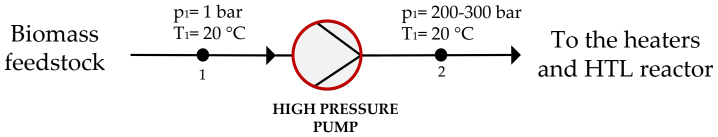


Figure 3.12: The high pressure pump delivering the biomass feedstock to the HTL reactor

3.3 Pumpability criteria

The possibility to evaluate the feed pumpability is important in the feedstock pretreatment design. The pumpability of lignocellulosic feedstock is difficult to predict without an equipment that simulates the conditions in a real high pressure pump. However, few attempts to develop predictive pumpability tests are described in literature.

The slump test

One feedstock testing procedure is the slump tests, proposed by Berglin and co-workers [50]. The method is illustrated in Figure 3.13. A container with conical shape is filled with material. The container is turned upside down and the content discharged on a flat surface. If the feed slumps, like the case of Feed A, the mixture is considered flowable and pumpable. If the material does not change its shape, like Feed B, it is less likely to be pumpable. According to this test, a feedstock containing 13 wt % to 15 wt % wood flour with particle size of 30 μm is pumpable. Increasing the wood particle size to 1.59 mm and the solids content to 18 wt % leads to a feedstock with more dry aspect, less likely to be pumpable. Some pump vendors ensured that slurries like feed A can be pumped with one of the systems described previously.

The sedimentation test

Another test, which targets more the evaluation of the slurry stability rather than the feedstock pumpability, is the sedimentation test. The test

Feed A - pumpable
0.03 mm wood particle size,
13 % to 15 % solids
Flowable feed

Feed B – likely pumpable
1.59 mm wood particle size,
18 % solids
Dewatering is evident

Figure 3.13: The slump test proposed by [50] to evaluate the feed pumpability

was used by Lappa et al. [51] to evaluate the effect of various pretreatment methods on the stability of grass suspensions in water (particle size <80 μm). The slurries are left to stand non-stirred for a certain time and the settling of particles is monitored. This test is useful to identify slurries that can have a uniform distribution of biomass in non-stirred containers, like for example in the pump feed barrel or in the storage tank. A non-stable feed - according to this test - will be unsuitable for pumping under high pressure conditions due to the high risk of solids dewatering.

In this work, the feedstock pumpability is evaluated according to the syringe test, described in Chapter 5 and the centrifugation test, described in Chapter 7. One of the advantages of these tests over the slump test is the small sample volume. More, comparative studies showed a good agreement between these tests and the feedstock pumpability in the CBS1 continuous HTL plant.

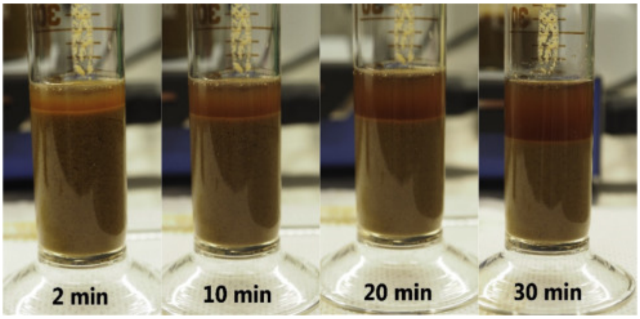


Figure 3.14: The sedimentation test used to evaluate the stability with standing of feed containing 10 wt % Miscanthus Giganteus in water [51]

Chapter 4

A short review of lignocellulosic biomass pretreatment methods

Pretreatment of biomass is applied in any Biomass-to-Biofuels (BtB) technology. The pretreatment prepares the biomass for the downstream processing. Some pretreatments consist only in biomass drying and size reduction e.g. in gasification or pyrolysis. Other pretreatments are more elaborated and aim a selective removal of biomass compounds like in fermentation, digestion or paper pulp production.

Hydrothermal Liquefaction lacks a well established pretreatment method to prepares pumpable biomass-water slurries. The problem is unique amongst BtB technologies due to the high pressure conditions combined with high biomass loadings required. The available pretreatment methods for lignocellulosic biomass are further discussed briefly. The effects of the pretreatment on the lignocellulosic biomass structure are highlighted.

1 Aqueous pretreatment

Aqueous pretreatment methods are mainly used prior to fermentation and digestion processes to increase the biomass digestibility. Liquid hot water pretreatment, steam explosion and steam pretreatment are most common aqueous pretreatment methods. The main effect of aqueous pretreatment on lignocellulosic biomass is the hemicellulose removal by hydrolysis. These reaction are promoted by temperature and acidic conditions. The main purpose of hemicellulose removal is to generate larger pores in the biomass structure and to increase the exposure of cellulose to enzymatic hydrolysis. Aqueous pretreatment can be implemented with low operational and capital costs compared to other pretreatment methods [52].

Liquid hot water (LHW) pretreatment consists in treating the biomass at 200 °C to 230 °C for short retention times (15 min). At these conditions, the water pH decreases promoting acid catalyzed reactions. These are mainly hemicellulose hydrolysis reactions that release sugars and organic acids. Due to the continuous increase of water acidity as the reactions advance, hot water pretreatment is also called autohydrolysis. The sugars generated from hemicellulose hydrolysis can be further degraded to furfural. Lignin removal during liquid hot water pretreatment is not significant but lignin-cellulose linkages are affected by acidic conditions. The effect is a lignin rearrangement in the lignocellulosic matrix rather than removal by dissolution. The effect of liquid hot water pretreatment on cellulose is only the reduction of the degree of polymerization and probably a reduction of crystallinity without dissolving the cellulose [52].

Steam explosion is performed at 160 °C to 260 °C with high pressure saturated steam. The steam enters in direct contact with the biomass for a certain retention time (seconds to few minutes) followed by a sudden pressure reduction that creates an "explosion" inside the solid particle. Both particle size reduction and hemicellulose removal are achieved [53]. Compared to liquid hot water pretreatment, steam explosion generates higher yields of hemicellulose monomers [54]. Steam explosion is considered one of the most cost effective pretreatment method for lignocellulosics [55], [53]. Size reduction by steam explosion is less energy intensive than conventional milling methods [56].

Steam pretreatment differs from the steam explosion by the fact that the quick depressurization is not implemented. During steam pretreatment, the biomass is contacted with steam at temperature up to 240 °C in a closed vessel. The pretreatment effect on biomass is hemicellulose removal by hydrolysis, catalyzed by the acidic character of water at these conditions and the formation of organic acids formed in situ [57].

2 Acid pretreatment

Acid pretreatment targets the biomass hydrolysis to produce sugars from hemicellulose, the increase of cellulose enzymatic hydrolysis or the production of chemicals e.g. levulinic acid, furfural. Lignin removal remains low in acid pretreatment [58]. The acid pretreatment is usually performed with dilute acids at low, moderate (< 160 °C) or high (> 160 °C) temperature conditions. Less drastic conditions (low temperature) targets the removal and hydrolysis of hemicellulose into sugars but further degradation to furfural or other compounds may occur at moderate temperature. The most common acids used are sulfuric acid, nitric acid, hydrochloric acid or phosphoric acid. More aggressive conditions promote cellulose hydrolysis and degradation to chemicals [57], [55], [53]. For example, the Biofine Process treats the lignocellulosic biomass with 1.5 % to 3 % H_2SO_4 at 190 °C - 220 °C to hydrolyze hemicellulose and cellulose and further convert them to furfural and levulinic acid [59]. The disadvantages of acid pretreatment are the high capital cost of the equipment and the need to neutralize the product streams [58].

3 Alkaline pretreatment

While aqueous and acid pretreatments target hemicellulose and cellulose hydrolysis, the most important feature of alkaline pretreatment is lignin removal. Notably, is the utilization of alkaline pretreatment in the paper pulp production. If biomass delignification is the only purpose of the pretreatment, the process needs to be carefully controlled because alkaline conditions can alter the structure of all lignocellulosic biomass components: hemicellulose, lignin and cellulose. The extent to which the biomass is decomposed depends on the process conditions employed. The pretreatment temperature may vary from room temperature with long retention times of hours or even days, to 180 °C - 200 °C for shorter retention times. Common alkaline reactants are sodium- and potassium hydroxides, sodium- and potassium carbonates and lime. Biomass degradation can be enhanced by introducing oxidative agents (oxygen, hydrogen peroxide) to the reaction medium [60].

4 Other pretreatment methods

Organosolv pretreatment

Organosolv process consists in treating the biomass with mixtures of organic solvents and water at temperatures up to 200 °C. The main objective is lignin separation but hemicellulose conversion to sugars and furfural also occurs. Organosolv pretreatment is known as a biomass fractionation method because the lignocellulosic biomass components are concentrated in separate streams. The organosolv product is divided into a lignin fraction (soluble in the organic phase), an aqueous stream containing the hemicellulose products (mainly monomers and oligomers) and a cellulose-rich solid fraction [61]. The main advantage of this method is the possibility to recover the organic solvent by distillation. For this reason, the most efficient and economical solvents are the low boiling point alcohols such as methanol and ethanol. High boiling point alcohols like glycerol are also used to remove lignin due to their advantage to allow pretreatment at atmospheric pressure [62]. Acids can be added to catalyze the process [63]. The organosolv process is also used in paper pulp production.

Oxidative pretreatment

Oxidative pretreatment is performed at room temperature (except the wet oxidation) and targets hemicellulose and lignin removal by the addition of oxidizing agents to the biomass-water mixtures. Oxidizing agents can be peracetic acid (lignin selective), hydrogen peroxide (H_2O_2:biomass ratio higher than 0.25 for significant delignification) or even mixtures with alkaline agents like NaOH and peracetic acid [57]. Other oxidative agents are ozone, oxygen or air. One of the interesting features of the oxidative pretreatment is that converts the lignin into carboxylic acids [63].

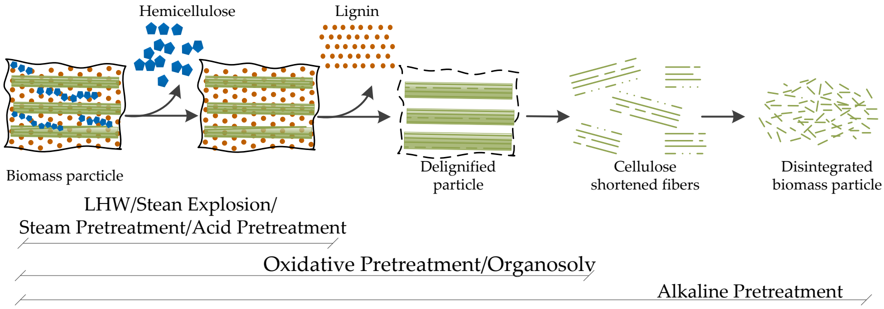


Figure 4.1: The effect of various pretreatment methods on biomass deconstruction

5 Biomass particle size reduction

Mechanical pretreatment methods of lignocellulosic biomass are common in biomass-to-biofuels technologies. They are used for biomass particle size reduction or for biomass decomposition into the main botanical parts [64]. Particle size reduction is essential in thermochemical processes like pyrolysis and gasification where high heat transfer rates through the solid particle are required. As an alternative to chemical pretreatment, mechanical pretreatment of biomass is used in bioconversion technologies (fermentation and digestion) to increase the accessibility of cellulose for enzymatic action.

Biomass size reduction can be performed with various equipment, depending on the output particle size required and the biomass processed. The first stage of size reduction is performed by chipping (for wood) or shredding (for herbaceous plants) to bring the material to a size suitable for further milling. The subsequent mechanical pretreatment can be performed with various equipment, depending on the biomass processed and desired particle size.

The main effect of particle size reduction is the increase of surface area. When particle size is reduced to the range of millimeters or below, specific surface area increases significantly for all lignocellulosic materials. Further comminution using ball-, disk- or compression milling performed in several passes/cycles can reduce the particle size to the range of micrometers or nanometers. At this level, the cellulose crystallinity is reduced [64] i.e. that more amorphous regions in the cellulose polymer are created and the biomass recalcitrance is reduced [57]. Biomass size reduction impacts also the material bulk density. Small particles have a better packing ability and reduced porosity, resulting with increased bulk density.

The energy input for biomass size reduction dependent on the final particle size and the type of mill used [65], as shown in Figure 4.2. The energy consumption for producing wood chips is assumed to be about 50 kWh/ton [65]. The energy consumption needed for grinding straw, grass or corn stover is with more than 50 % lower compared to hardwood [66]. The most suitable mills for fibrous materials like wood and herbaceous plants are the knife and hammer mills [67]. These mills allow a biomass moisture content up to 10-15 wt % [64], that can be achieved by air-drying of the material. In the context of large scale HTL processing, particle size of 2 to 6 mm is desired [50] from economic considerations but this size range would require chemical pretreatment to prepare pumpable feeds.

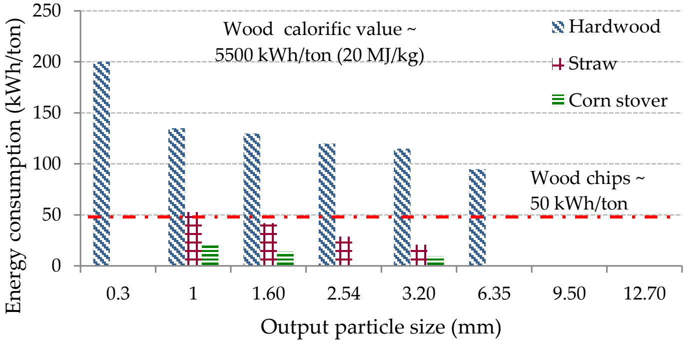


Figure 4.2: Energy consumed by a 15 hp hammer mill for grinding biomass with m.c. 4-8 wt % (based on data from [67], [68] and [66])

6 Conclusions

Figure 4.1 summarizes the chemical pretreatment methods discussed above. It can be noticed that hemicellulose is the biomass constituent that is removed from the biomass structure by all pretreatment methods. Lignin can be dissolved by alkaline solutions, organic solvents or oxidizing agents. Cellulose is the most resistant to chemical degradation. However, alkaline conditions and strong acids can convert the cellulose into sugars or further into other chemical compounds. The utilization of alkaline pretreatment for HTL feedstocks is more advantageous than acid pretreatment because it can increase the biocrude yield and reduce the solids formation [21]. For this reason, alkaline pretreatment is considered the most appropriate pretreatment method for HTL feeds and is investigated in more detail in Chapter 6. Biomass milling to fine powder was also considered as alternative option for HTL feedstock pretreatment. Based on data in Figure 4.2, about 4 % of the wood energy (considering heating value of 19 MJ/kg) is consumed for milling the biomass with a hammer mill, to particle size of 0.3 mm. This suggests that particle size reduction might also be a feasible pretreatment method for lignocellulosic materials.

Chapter 5

Recycling of HTL biocrude for slurry make-up

1 Introduction

Transportation of milled wood in heavy oil medium was probably the first attempt to pump wood slurries in a continuous HTL reactor. The concept was developed by the US Bureau of Mines in 1971. The idea was demonstrated at the Albany pilot plant where recycled biocrude was used as vehicle after a start-up run with anthracene oil. After drying, the wood chips were ground to about 0.42 mm. Milled wood was slurried with the oil carrier and pumped to the liquefaction unit. An aqueous stream loaded with the alkaline catalyst was injected into the wood-oil slurry, as showed in Figure 3.5. The final biomass fraction in the feed was around 7 wt %. The main disadvantages of this pretreatment method were the high energy requirements from drying and grinding the wood and the low biomass loading of the feedstock [38], [39], [40].

In this work, co-processing wood and recycled biocrude method is investigated in more detail and optimized to increase the mass fraction of solids to 20 %. The parameters studied are the biomass particle size and the water-to-biocrude ratio. Another objective of this study is to develop a feedstock preparation strategy to obtain pumpable, non-separable slurries from wood, recycled water phase and biocrude and to evaluate the slurries flow behavior and viscosity.

2 Materials and methods

Raw materials

Wood slurries were prepared with aspen sawdust of different size distribution: sawdust sample SD1 has 85 % of the particles smaller than 125 μm, sawdust sample SD2 has 51.5 % of particles smaller than 125 μm and sawdust sample SD3 contains particles between 250 μm and 125 μm. The size distribution of the sawdust samples is given in Table 5.1. The size distribution of the sawdust samples was determined with a Retsch vibratory sieve shaker.

Slurry preparation and pumpability test

The slurries were prepared by mixing wood with HTL product water phase and biocrude oil obtained from the CBS1 plant. All slurries contain 20 % mass fraction dried wood. The slurries pumpability was evaluated using the syringe test. This test aims to simulate the behavior of the slurry when passed through an orifice. The testing procedure consists in loading the syringe tube with feedstock and slowly discharging it by pressing the plunger. A successful test is considered when the mixture can be discharged as a homogeneous material. Unsuccessful test leads to the formation of a solid cake in the syringe tube and clogging of the orifice. The syringe test is advantageous because a) is simple and fast, b) no expensive equipment is necessary, c) is in good agreement with the performance of the high pressure piston pump used in the CBS1 plant. However, the pressure applied in the syringe test is not representative for the real case therefore, it should be considered that the syringe test is only indicative.

Rheological characterization

The viscosity of the slurries was measured with a Brookfield RV-DV II-Pro rotational viscometer. Due to the high consistency of the samples, special T-bar spindles were used together with a helipath stand. The spindles are rotating in a helical path and move upwards and downwards through the sample to avoid channeling and phase separation. For these spindles, the share rate calculation is not possible therefore rotational speed was plotted against viscosity.

3 Results and discussion

Mixtures of wood, HTL recycled water phase and HTL biocrude with different sawdust size distribution and water-to-biocrude mass ratios were visually examined and tested for pumpability. As shown in Table 5.2, the mixtures

Table 5.1: Characterization of aspen sawdust samples used for wood-water-biocrude slurries preparation [1]

Sawdust	Bulk density (kg m^{-3})	d_{50} (mm)	Sawdust composition (% mass fraction)		
			0.250 mm - 0.125 mm	0.125 mm - 0.063 mm	0.063 mm
SD1	429	0.063	15.00	35.00	50.00
SD2	369	0.121	32.98	22.68	28.86
S125	330	-	100.00	0.00	0.00

SD: size distribution, S125: single particles of 0.125 mm are divided in three categories according to the sawdust size distribution (SD1, SD2 and S125). For each group, five mixtures with different water-to-biocrude ratios are prepared (10/70, 20/60, 30/50, 40/40 and 50/30). In total, 15 mixtures are analyzed. All slurries contain 20 % mass fraction of wood.

From Table 5.2 it can be noticed that all slurries have paste- or solid-like consistency determined primarily by the wood particle size: fine particles form pastes while coarser particles tend to give the slurry a solid-like aspect. The increase of slurry consistency with the particle size can be explained by the fact that the liquid phase is absorbed by the porous solid material. The observations in Table 5.2 suggest that coarser particles (0.125 mm - 0.250 mm) have higher sorption capacity compared to fine particles (< 0.125 mm). This might be due to the increased number of large pores in coarse particles. Similar observations were done by Trinh et al. [69] who showed that oil sorption capacity is higher for wood compared to pyrolysis char due to higher amounts and larger pores in wood particles. However, the sorption of biocrude in wood particles is limited which means that above a critical point (in mixtures # 9, # 10, # 14 and # 15 the critical point is 40 wt % biocrude), the biocrude added will no longer be absorbed into the wood particle pores. The excess fluid will accommodate the solids and will make the slurry thinner and more compact.

The syringe test was applied to all slurries to evaluate their pumpability. From Table 5.2 it can be concluded that all slurries with paste consistency,

Table 5.2: Experimental design and pumpability test results for wood-water-biocrude slurries [1]

Exp.No	Wood (wt %)	Water (wt %)	Biocrude (wt %)	Pumpability	Visual aspect
			SD1, d_{85}=0.125 mm, ρ=429 kg m^{-3}		
#1	20	70	10	x	paste*
#2	20	60	20	✓	paste
#3	20	50	30	✓	paste
#4	20	40	40	✓	paste
#5	20	30	50	✓	paste
			SD2, $d_{51.5}$=0.125 mm, ρ=369 kg m^{-3}		
#6	20	70	10	x	solid
#7	20	60	20	x	solid
#8	20	50	30	x	solid
#9	20	40	40	✓	paste
#10	20	30	50	✓	paste
			S125, d_0=0.125 mm, ρ=330 kg m^{-3}		
#11	20	70	10	x	solid
#12	20	60	20	x	solid
#13	20	50	30	x	solid
#14	20	40	40	x	paste
#15	20	30	50	x	paste

* Phase separation occurs.

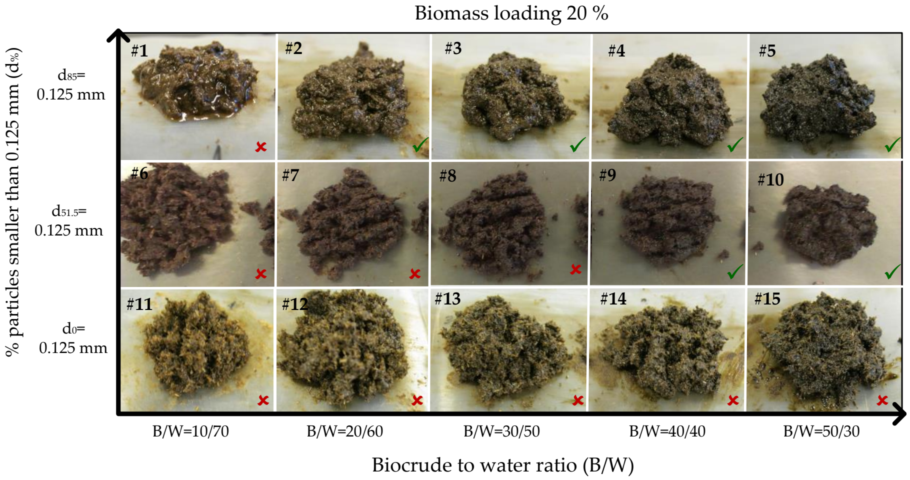


Figure 5.1: The effect of wood particle size and biocrude-to-water ratio on slurry pumpability according to the syringe test [1]

except those that undergo phase separation with standing, are pumpable. As discussed above, fine particles are preferred to prepare paste-like mixtures in a wide range of biocrude-to-water ratios. This offers more flexibility to adjust the feedstock composition according to the process requirements. An exception to the rule "paste slurries are pumpable" are the experiments # 14 and # 15. Here, the mixtures failed the syringe test because dewatering occurred when mixtures were passed through the syringe. Most probably, this was due to the large particle that bridged and blocked the syringe orifice. This underlines an observation made by PNNL in one of their report where the authors point out that feedstock pumpability it is also a matter of pump design and scale [50]. Probably with a syringe that has higher outlet diameter,

Figure 5.2: The effect of compounds mixing order on slurry homogeneity. The slurries have identical composition: 20 wt % wood (SD2), 40 wt % recycled water phase and 40 wt % recycled biocrude [49]

the feeds would have passed the test.

To confirm the pumpability of the wood-water-biocrude feedstock, a mixture was prepared according to the composition in experiment # 9. The feedstock was successfully pumped into the CBS1 continuous HTL system (described in Chapter 2) for several hours, at 30 MPa using a high pressure piston pump.

The aspect of the samples can be visualized in Figure 5.1. It can be noticed that as the biocrude-to-water ratio increases, the color of the mixtures is darker suggesting the presence of biocrude in the interparticle voids. Higher the amount of free biocrude is, more compact and easy-to-flow slurries are obtained. The negative impact of coarse particles on slurry homogeneity can be noticed in experiments # 11 to # 15. Here, the volume of the solid matter is higher compared to fine particles (see bulk density in Table 5.2) making more difficult to incorporate the wood particles into the biocrude phase. This ease the particles agglomeration when forced through an orifice and explains the failure to pumpability test.

In Figure 5.1, experiment # 1 the phase separation of the slurry with standing can be noticed. This occurred due to the large fraction of water in the slurry that could not be absorbed by the wood particles. Therefore, the free water separated from the biocrude phase when mixed together. In this case, the phase separation can be avoided by reducing the amount of water in the mixture. More specifically, the over-saturation of the biomass need to be avoided.

The phase separation between the slurry components can be also prevented by following a certain mixing strategy. Figure 5.2 shows two slurries prepared in two different sequences: case A - wood is mixed with biocrude first and case B - wood is mixed with water first. The figure indicates that

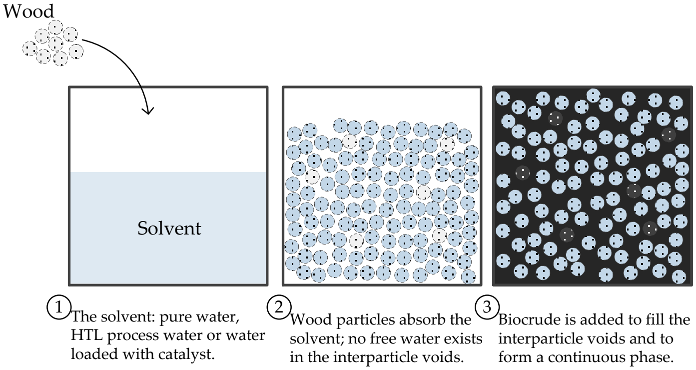


Figure 5.3: Schematic representation of the mixing strategy applied for the wood-water-biocrude slurries

in case A, the phase separation occurs immediately because the water cannot penetrate the oil film formed at the wood particle surface. In case B, where the water is added first and absorbed into the wood particles, a homogeneous slurry is obtained after the addition of biocrude.

Figure 5.3 illustrates the concept of the mixing strategy used in case B, from Figure 5.2. The wood particles are immersed in the water phase where they absorb the liquid and swell. At this stage, the ratio between the wood and the liquid need to be adjusted such that all the liquid is absorbed by the solid phase. While the water acts as pore filling material, the biocrude oil covers the surface of the wood particle, blocking the pores and preventing dewatering under pressure conditions. At the same time, the biocrude acts as carrier fluid for the solid particles. Following this mixing strategy, non-separable slurries can be obtained.

Figure 5.4 shows the impact of wood particle size on the slurries viscosity. For this study, mixtures were prepared from sawdust with size distribution SD1, SD2 and S125. All mixtures contain 30 % mass fraction water phase and 50 % mass fraction biocrude. The slurries viscosity vary from about 6000 Pa s at low speed to less than 100 Pa s at higher speed which suggests a shear thinning (pseudoplastic) behavior. The particle size has a small impact on the slurry viscosity. However it can be noticed that the viscosity increases with the particle size.

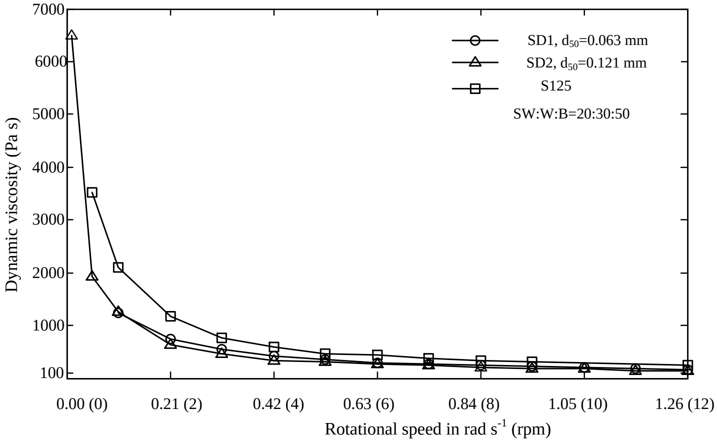


Figure 5.4: Wood-water-biocrude slurries flow behavior [1]

4 Conclusions

The original PERC method to pump wood in an oil vehicle can be optimized to increase the biomass loading and to improve the flexibility of slurry preparation. As shown in Table 5.3 the main differences between the PERC and the proposed feedstock preparation methods are the wood particle size and the mixing order of the components. Reducing the wood particle size from 0.42 mm to < 0.125 mm allows an increase of the biomass loading from 7 % to 20 % mass fraction. The pumpability of a wood slurry containing 20 wt % wood, 40 wt % biocrude and 40 wt % water was demonstrated in a continuous HTL plant. The main disadvantage of this method remains the energy input for downsizing the wood to fine powder but small particles are required to achieve high solid loadings. Therefore, there is a trade-off between costs related to downsizing the biomass and the benefits of having higher biomass loading.

Table 5.3: Comparison between the feedstock composition prepare according to the original PERC version and the proposed optimized method

	PERC [39],[38]	Optimized PERC
Wood particle size (μm)	420	<125
Biomass loading (wt %)	7-10	20
Biocrude in slurry (wt %)	20-30	> 20
Mixing order	wood-biocrude-water	wood-water-biocrude

Chapter 6

Deconstruction of biomass by alkaline pretreatment for continuous HTL

1 Introduction

One approach to prepare pumpable HTL feeds is mechanical downsizing of the biomass that can be combined with various techniques to keep the particles suspended in the slurry e.g. by co-processing with recycled biocrude or by co-processing with thickening agents. The main disadvantage of this approach is the energy input required for drying and milling the biomass to particle size smaller than 0.1 mm. An alternative pretreatment method to mechanical downsizing of biomass is the thermo-chemical pretreatment. In the past, several thermo-chemical pretreatment methods were implemented in continuous hydrothermal liquefaction systems, as discussed in Section 3.2. Notable are the acid hydrolysis of wood in the LBL process and the hot water pretreatment in the Shell's HTU process.

Previous attempts to solve the pumpability problem by disintegrating the biomass had limited success because extensive degradation of biomass could not be achieved through hydrothermal pretreatment in acidic or water medium. While acid and aqueous pretreatments are suitable for hemicellulose and cellulose degradation, the alkaline conditions can alter simultaneously the whole structure of biomass, including lignin [70]. This can lead to a complete dissolution of biomass which would significantly ease the pumpability of wood slurries. Alkaline pretreatment of biomass was not reported yet as part of a continuous HTL systems. The concept of lignocellulosic biomass pretreatment with NaOH is illustrated in Figure 6.1.

Wood decomposition under alkaline conditions is a well known process from pulp and paper industry. Soda pulping, the process based on the utilization of sodium hydroxide as reactant, was the first chemical pulping processes introduced in the 1850s. Later, soda pulping was replaced by more lignin selective methods such as sulfite or sulfate (Kraft) pulping [71]. Though soda pulping is scarcely used today for chemical pulp production, it might be a suitable method to prepare pumpable feeds for hydrothermal systems. The process can be tailored to dissolve the biomass to an extent that enables the pumpability of lignocellulosic feeds. The advantage of soda pulping over the sulfite or sulfate pulping, as a pretreatment method for HTL feeds, is the absence of sulfur containing reactants that could contaminate the biocrude product.

The pulping process consists in treating lignocellulosic biomass, primarily wood, with NaOH (soda pulping), a mixture of NaOH and Na_2S (the Kraft process) or a mixture of SO_2 and alkaline hydroxides or carbonates (sulfite pulping). The temperatures usually do not exceed 180 °C and the reaction time may vary from 15-20 minutes to 5 hours. The solution pH ranges between 13 and 14 and the the alkali consumption is approximately 150 kg NaOH per ton of wood. The objective of the pulping process is to fractionate the biomass into a solid phase of cellulose fibers and a liquid phase consisting of dissolved lignin and hemicellulose [71], [70]. This is difficult to achieve in hot solutions of strong bases (e.g. NaOH) because they promote also cellulose dissolution. Instead, extensive degradation of biomass, including the cellulose fibers, is desired for HTL slurries. This could reduce the wood feedstock heterogeneity and enable the pumpability of concentrated slurries.

The focus of this work is to design an alkaline pretreatment process that dissolves the wood chips to an extent that allows processing of concentrated feeds with solid mass fraction of at least 20 %, in continuous HTL systems. The method proposed is solid biomass dissolution in lean sodium hydroxide solution at 160 °C to 200 °C. The impact of temperature, reactant con-

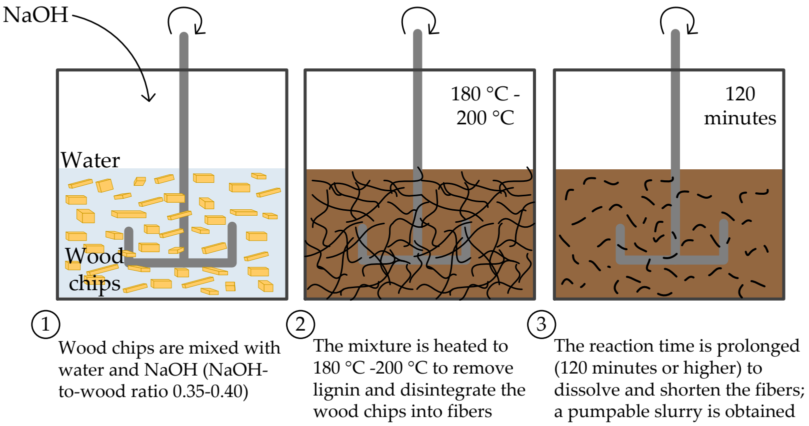


Figure 6.1: Schematic representation of alkaline pretreatment of wood chips

centration, reaction time and biomass particle size on biomass dissolution is evaluated and the optimum alkaline pretreatment conditions to prepare pumpable slurries are identified. Another objective of this investigation is to evaluate the effect of the alkaline pretreatment on the HTL product distribution and biocrude quality. For this, HTL experiments using pre-treated and non-pretreated wood are carried out. The whole process with the pretreatment stage included is tested in a continuous bench scale HTL system.

2 Materials and methods

Biomass

Hybrid poplar and willow chips were used to investigate the effect of alkaline pretreatment on biomass dissolution. Poplar chips were used for the small scale pretreatment tests and willow chips for bench scale pretreatment and HTL experiments. Different raw materials were used for the bench scale test due to the fact that poplar chips were not available in larger quantities. As shown in Table 6.1, the main difference between the two wood species is the lignin content, higher for willow. The wood chips were provided by Ny Vraa Bioenergi I/S, Tylstrup Denmark. Poplar chips were obtained from trees of five years old, cut into chips up to 20 mm width, on site. Willow chips were obtained from two years old coppice, harvested in the same period and cut into chunks of 20 to 70 mm long. The chemical and elemental composition of poplar and willow is given in Table 6.1.

For laboratory scale experiments, the bark and the chips from branches were removed to select only wood stem parts for pretreatment experiments and biomass characterization. Also the wood chips were separated into three particle size classes: small particles 3 mm to 5 mm, medium particles 5 mm to 10 mm and large particles 10 mm to 14 mm. The particle size classification

Figure 6.2: Raw biomass as received from supplier: hybrid poplar chips (left) and willow coppice (right)

Table 6.1: Elemental and chemical composition of the biomass used for alkaline pretreatment and HTL experiments. Values are given as mass fraction per dry-basis [2]

	Element mass fraction (%)				**Polymer mass fraction (%)**			**Ash (%)**
	C	H	N	O*	Cellulose	Hemicellulose	Lignin	
Poplar	47	6	n.d.	46	60	18	13	1
Willow	48	6	n.d.	44	53	15	20	2

*by difference n.d.= not detected

was performed according to the EN15149 100 standard procedure.

Design of Experiments

The variation of wood dissolved mass fraction with the process conditions was analyzed using a full factorial experimental design. The main objective of the designed experiments is to screen the most significant factors that affect the process. Four variables were selected: temperature, reaction time, solution alkalinity and wood particle size. To each variable was attributed a maximum and a minimum value. The choice of the factors and their levels is discussed in more detail in Appendix A. Experiments were performed in triplicates at the center point. Finally, the experimental matrix consists of 19 experiments. The levels of the variables investigated in this study are given in Table 6.2. The measured output was the percent of wood dissolved. The Reliasoft DOE and the Umetrics MODDE software were used to generate the experimental design and to interpret the data.

Screening tests aim to reduce the number of process variables by identifying and excluding from further consideration those factors that do not have a significant impact on the output. Screening tests require the utilization of the Design Of Experiments (DOE) and statistical interpretation of the results. The DOE technique consists in choosing a set of variables that may influence the system or the process investigated. To each variable is attributed at least a minimum and a maximum value. The variables are called 'factors' and their values are named 'factor levels'. A medium point between the minimum and

Table 6.2: Summary of the experimental design used for screening of alkaline pretreatment process variables

Factors (process variables)	**Levels (min and max values)**	**Central point**
Temperature	160 and 200 °C	180 °C
Reaction time	30 min and 240 min	135 min
NaOH-to-wood ratio	0.32 and 0.40	0.36
Wood particle size	3-5 mm and 10-14 mm	5-10 mm
Number of factors	4	
Number of levels/factor	2	
Repetitions at central point	3	
Total number of experiments	= 24 + 3 = 19	

the maximum value of a variable can be defined and is known as 'the center point' of the factor. At the center point values, an experiment is performed usually in triplicates in order to evaluate the experimental error. Quantification of the experimental error will improve the accuracy when calculating factors effect on the system response. Finally, the experimental design consists in a number of experiments that represents all combinations between factors and their levels. When the number of variables in DOE is higher than two, a software is usually used to facilitate the calculations.

Pretreatment experiments

For the small scale pretreatment experiments a 400 cm^3 electrically heated batch reactor equipped with stirrer and cooling coil was used. In a typical run, 10 g of wood chips and 40 g of NaOH solution were loaded into the reactor. The concentration of the NaOH solution was varied according to the experimental design: between 8 % and 10 % of the liquor mass fraction i.e. 0.32 to 0.40 NaOH-to-wood mass ratio. The wood mass fraction in slurry was fixed to 20 % on dry basis. The wood and the NaOH solution were mixed directly into the autoclave. The reactor was closed and heating started. After approximately 30 to 40 minutes, the reactor reached the the set point and the slurry was held at this temperature for 30 minutes to 240 minutes, according to the experimental design (time at T_{max}). The temperature profiles of the pretreatment experiments are shown in Figure 6.3. After cooling down the reactor, the product was collected and the vessel, the cooling coil and the stirrer were thoroughly washed with distilled water. The pretreated slurry was filtered on Whatman filter paper (particle retention 5-13 μm) to determine the fraction of undissolved wood. Filtered solids were dried at 105 °C to constant

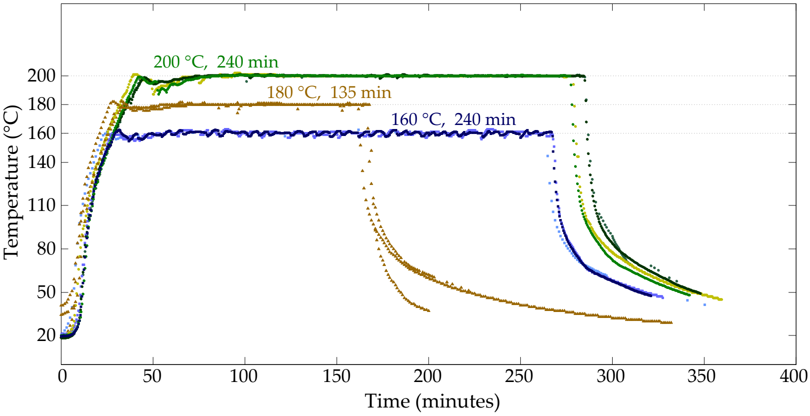


Figure 6.3: Temperature profiles of the pretreatment experiments performed in the 400 cm^3 autoclave

weight and the percent of biomass dissolved was determined gravimetrically.

Bench scale pretreatment runs were performed in an 80 L paddle digester provided by Thünen Institute of Wood Research, Hamburg. The objective of bench scale pretreatment was two-fold: to validate the results obtained in the small scale reactor and to prepare 100 kg of wood paste for HTL processing in the continuous HTL system. Therefore, the optimum conditions identified in small scale pretreatment tests were applied for the conversion of willow chips in pumpable feedstock. The pretreatment conditions were 180 °C, NaOH to wood ratio 0.40, reaction time 120 minutes. The heating time of the 80 L reactor was similar to the one in the 0.4 L autoclave: approximately 30 minutes. The 100 kg wood paste was prepared in four batches to limit the reactor loading to about half of its capacity. 5 kg of wood and 20 kg of NaOH solution were loaded in each batch. A good mixing of the slurry was provided by a central paddle. The reactor and the feedstock before and after pretreatment are shown in Figure 6.8.

Pumpability test

The pumpability test was performed using a syringe, as previously described in Chapter 5. The syringe test was applied to the pretreated feedstock to determine the critical amount of biomass that need to be dissolved to obtain pumpable feeds.

Hydrothermal liquefaction experiments

HTL experiments were carried out in 10 mL stainless steel tubular batch reactors at 400 °C and 32–33 MPa for 10 minutes. After closing the reactors, they were purged with nitrogen for air removal and pre-pressurized with approximately 2 MPa N_2. All experiments were performed in duplicates. Two reactors were inserted simultaneously into a pre-heated fluidized sand bath (Techne SBL-2D) and reached the final temperature in about 2 minutes. After 15 minutes, the reactors was removed from the sand bath and cooled in

Figure 6.4: The syringe test applied to an alkaline pretreated feed showing the homogeneity of the feed after the test [2]

a water bath. After cooling, the gases were released and the content of the reactors was poured into a vessel. The reactors were thoroughly rinsed with acetone. The liquid poured out from the reactor was mixed with the acetone used to wash the reactor and filtered for solids separation. The solids were further washed with distilled water and dried over night at 105 °C. The acetone filtrate was evaporated under reduced pressure in a rotary evaporator to remove the acetone. By the end of the evaporation process, a mixture of water phase and biocrude was obtained. Diethyl ether (DEE) was added into the mixture to transfer the biocrude into a preweighed collection tube and to extract the water phase. Because the water phase did not separated from the biocrude-DEE mixture, few drops of hydrochloric acid (HCl 1M) was added followed by tubes centrifugation. The decanted water phase was carefully extracted with a syringe and the DEE solvent was evaporated at atmospheric pressure in a 60 °C water bath until the sample reached a constant weight. The biocrude yield was determined gravimetrically and further analyzed for moisture content and elemental composition. The gas yield was calculated using the ideal gas law in Equation 6.1 where m is the mass of gas product (g), P is the pressure measured in the reactor at the end of reaction after cooling (bar), for simplification V is considered the volume of the reactor (L), R is the ideal gas constant 0.083 (L bar $K^{-1}mol^{-1}$) and T is the temperature at which the pressure of gases was measured (K).

$$m_{gas}(g) = \frac{P \cdot V \cdot M}{R \cdot T} \tag{6.1}$$

Bench scale HTL test was performed on the CBS1 continuous HTL system. The system is described in more detail in Chapter 3 (see Figure 3.9). The operating conditions were similar to those applied in the small scale batch experiments: 400 °C, 30 MPa and 15 minutes retention time. The biocrude oil was separated gravimetrically from the water phase and further analyzed for elemental composition and heating value.

Analytical procedure

For the chemical composition of the biomass, a Foss FibertecTM 1020 Fiber Analyzer equipment was used. The cellulose, hemicellulose and lignin content were determined according to the Foss procedure (modified to eliminate the use of amylase). The ash content was measured at 575 °C for 6 hours. The viscosity of the pretreated slurry was measured with a Brookfield RV-DV II-Pro rotational viscometer and cylindrical spindle SC4-21.

The heating value of the biocrude was measured with an IKA C2000 Basic calorimeter. The carbon, hydrogen and nitrogen content of biomass and biocrude was measured using a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer. The oxygen content was determined by difference assuming that the amount of sulfur in biomass is negligible and therefore in biocrude as well. The inorganic elements (Na and K) in biocrude were measured with an inductively coupled plasma-optical emission spectroscopy (ICP-OES) instrument at the department of Chemistry and Environment Engineering, Aalborg University. The composition of the gas phase was analyzed using a Shimadzu, Tracera GC-2010 Plus Gas Chromatograph equipped with a Restek micropacked column (length 2.0 m, I.D. 0.53 mm) and a BID detector.

Measurements were repeated in duplicates or triplicates and the mean values are reported.

3 Results and discussion

3.1 Alkaline hydrothermal pretreatment - screening and optimization tests

The effect of pretreatment variables on wood dissolution and feedstock pumpability

In Table 6.3 the impact of pretreatment temperature, reactant concentration, reaction time and wood particle size on the mass fraction of wood dissolved is given. The values of wood dissolved mass fraction were used to quantify the impact of each variable on the wood dissolution. The effects of each variable are plotted in Figure 6.5. The values represent the average of the biomass dissolved mass fraction when one factor level is constant and the other factor levels are varied i.e. the average of 8 experiments.

The results show that wood dissolution is significantly affected by the increase of pretreatment temperature. On average, 35 % more wood is dissolved at 200 °C compared to 160 °C. Reaction time and solution alkalinity have a lower impact but still significant. When reaction time is prolonged from 30 minutes to 240 minutes or when the NaOH-to-wood ratio is increased from 0.32 to 0.40, the amount of wood dissolved increases with about 15 % percent points. The impact of wood particle size on wood dissolution is relative low. Larger wood chips dissolve slower than smaller chips.

Table 6.3: The variation of the solids dissolved mass fraction (%) with the pretreatment conditions and wood chips size. At the central point (180 °C, 0.36 NaOH-to-wood ratio, 135 minutes, 5-10 mm particle size) the mass fraction of wood dissolved on average was 61 ± 6 [2]

NaOH-T-t*	**Particle size (mm)**		**NaOH-T-t***	**Particle size (mm)**	
	3-5	10-15		3-5	10-15
0.32-160-30	23	17	0.40-160-30	27	27
0.32-160-240	34	33	0.40-160-240	53	48
0.32-200-30	62	57	0.40-200-30	71	71
0.32-200-240	71	60	0.40-200-240	87	84

*NaOH-to-wood mass fraction-Temperature (°C) - Reaction time (minutes)

An interaction between reaction time (factor D) and solution alkalinity (factor B) is indicated in Figure 6.5 (B*D) suggesting that the effect produced by one of these factor is dependent on the value of the second factor. For example, when solution alkalinity is increased the mass fraction of wood dissolved increases with 9 % percent points at 30 minutes reaction time and with 19 % percent points at 240 minutes reaction time. The impact of pretreatment process variables on feedstock aspect can be visualized in Figure 6.6.

The positive and significant effect of temperature on the fraction of wood dissolved was expected. It is well known that once temperature increases, the wood compounds are more susceptible to degradation. For example, carbohydrates degrade during the heating period, at temperatures lower than 150 °C. At 150 - 160 °C, most of the hemicellulose is already dissolved and lignin degradation becomes significant [72], [70], [73]. Cellulose starts to decompose only at around 170 °C [70]. These suggest that at 200 °C, the maximum pretreatment temperature tested in this work, all wood constituents should be dissolved. As noticed from Table 6.3 even at the most drastic conditions, a small fraction of fibers (13 % -16 % of initial wood mass fraction) could be separated. This might be explained by the fact that at high temperatures, the reducing groups of cellulose are stabilized and therefore depolymerization is stopped or slowed down [71], [72], [73]. The presence of undissolved fibers in the final product my also be explained by the association between polymer chains, reaction favored by the high content of biomass in the slurry (20 % mass fraction) [73].

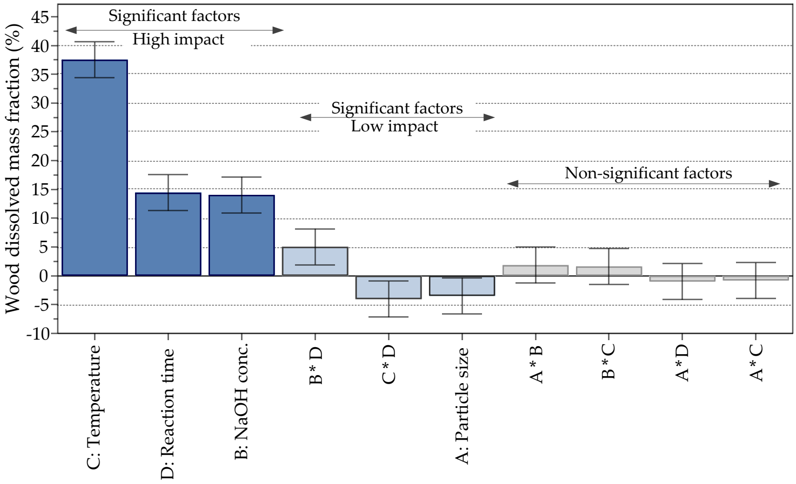


Figure 6.5: The change of wood dissolved mass fraction (%) when a process variable is increased from its low level to high level [2]

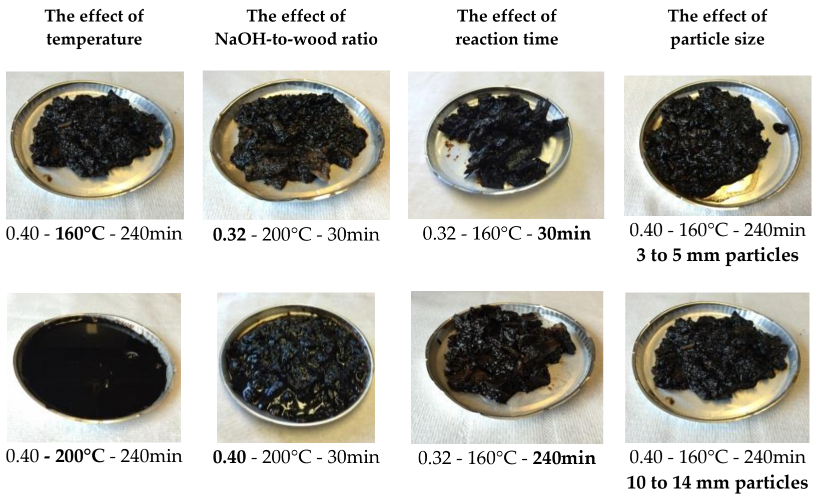


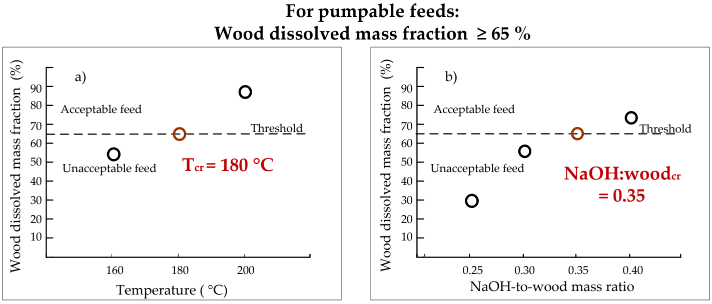
Figure 6.6: The impact of process conditions on biomass dissolution and product aspect. Samples visualise the resulting pulps [2]

Table 6.4: Alkaline hydrothermal pretreatment conditions optimization using the one-factor-at-a-time (OFAT) strategy. Designed experiments previously performed showed that factors interactions have a low impact on the output and the factor particle size can be eliminated. For the optimization tests medium size (5 mm to 10 mm) wood chips were used [2]

Temperature (°C)	**NaOH-to-wood ratio**	**Time at Tmax (min)**	**Wood dissolved mass fraction (%)**	**Feed pumpability (Syringe test)**
Fixed factors: temperature 180 °C, reaction time 120 min Variable factor: NaOH-to-wood ratio				
180	0.25	120	28	x
180	0.30	120	55	x*
180	0.35	120	65	yes
180	0.40	120	72	yes
Fixed factors: temperature 180 °C, NaOH-to-wood ratio 0.35 Variable factor: reaction time				
180	0.35	30	56	x*
180	0.35	60	62	yes*
180	0.35	120	65	yes
180	0.35	180	68	yes
180	0.35	240	71	yes
Fixed factors: NaOH-to-wood ratio 0.35, reaction time 120 min Variable factor: temperature				
160	0.35	120	54	x
180	0.35	120	65	yes
200	0.35	120	88	yes

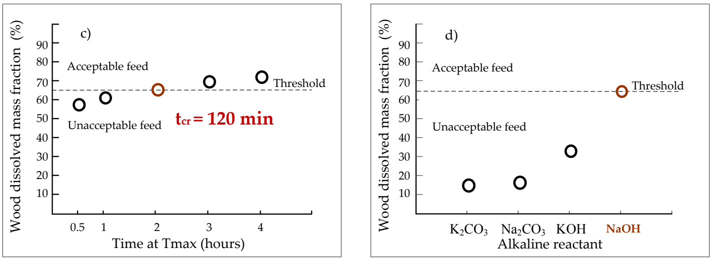
* The product consisted of softened wood chips that required maceration

Once the most important factors are identified, additional experiments


For pumpable feeds:
Wood dissolved mass fraction ≥ 65 %

a) The effect of temperature on wood dissolution at 0.35 NaOH-to-wood ratio and 2h reaction time

b) The effect of alkali loading on wood dissolution at 180 °C and 2h reaction time



c) The effect of reaction time on wood dissolution at 180 °C and 0.35 NaOH-to-wood ratio

d) The effect of alkaline reactant type on wood dissolution at 180 °C, 0.35 alkali-to-wood ratio and 4h reaction time

Figure 6.7: Identification of critical alkaline pretreatment conditions. The effect of NaOH loading, reaction time, temperature and reactant type on wood dissolved mass fraction (%); 5 mm to 10 mm poplar wood chips were used in all experiments [2]

can be performed for process optimization. Three out of four variables investigated showed a significant impact on biomass dissolution: reaction temperature, reaction time and solution alkalinity. Also, it was established that the interactions between the factors are not significant. Therefore, the One Factor At Time (OFAT) strategy was further used to optimize the pretreatment process. 10 more experiments were introduced to explore in more detail the impact of temperature, reaction time and solution alkalinity on wood dissolution. The optimization criterion was the pretreated feed pumpability, evaluated according to the syringe test.

As shown in Figure 6.7 a), 180 °C is the critical temperature to obtain paste-like feeds that pass the syringe test. The increase of temperature to 200 °C leads to extensive wood degradation and liquid-like mixtures but such high temperatures might be too costly for large scale implementation. The variation of wood dissolved mass fraction with the NaOH concentration, at 180 °C and 2 hours reaction time, is shown in Figure 6.7 b). At these conditions, the critical value of NaOH-to-wood mass ratio is 0.35. With the values for temperature and NaOH-to-wood mass ratio fixed at 180 °C and

Figure 6.8: Willow slurry before (left) and after pretreatment (right) in an 80 L digester

0.35, the effect of the reaction time was studied. As shown in Figure 6.7 c) the reduction of the reaction time below 2 hours generates feeds that do not comply with the pumpability criteria. On the other hand an increase of the reaction time above 2 hours do not increase significantly the wood dissolved mass fraction. Therefore, 120 minutes is considered an reasonable reaction time for wood pretreatment at 180 °C and 0.35 NaOH-to-wood mass ratio.

Bench scale pretreatment of willow chips

A batch of 100 kg of wood paste was prepared from willow coppice. Because the particle size of willow chips was considerable bigger than the size of poplar chips used in laboratory scale pretreatment tests (10-14 mm vs. 20-70 mm), a higher alkali loading was used to ensure that a pumpable paste is obtained. The pretreatment conditions were: 180 °C, NaOH to wood ratio 0.40, reaction time 120 minutes. After pretreatment, approximately 70 % of the initial willow chips were dissolved which is in accordance to the laboratory scale experiments. The product had a paste-like consistency and passed the syringe test. The slurry pH was around 12, indicating an excess of alkaline reactant.

The effect of alkaline reactant type on wood dissolution

The aggressive attack of NaOH compared to other alkalis is clear from Figure 6.7 d) and Table 6.5. The amount of wood dissolved with sodium and potassium carbonates is significantly lower than the amount of wood dissolved with sodium hydroxide. This is because sodium hydroxide has strong

Table 6.5: The effect of the alkaline reactant type on the wood dissolved mass fraction after hydrothermal pretreatment at 180 °C, for 240 minutes and 0.35 NaOH-to-wood ratio; wood particle size 5 to 10 mm

	NaOH	**KOH**	**Na_2CO_3**	**K_2CO_3**
Wood dissolved mass fraction (%)	63.6	32.1	13.8	13.7

nucleophilicity compared to carbonates, enhancing the wood delignification. Carbonates may react with water to form hydroxyl ions according to Equations 6.3 and 6.4 but the concentration of hydroxyl ions in these solutions is lower compared to NaOH solutions. Although both NaOH and KOH are strong bases that completely dissociates in water, less wood was dissolved with KOH solution than with NaOH solution. This can be explained by the higher molecular weight of KOH and consequently lower molar concentration of the KOH solution.

$$NaOH_{(aq)} - > Na^{+} + OH^{-}_{(aq)} \tag{6.2}$$

$$Na_2CO3_{(aq)} - > 2Na^{+}_{(aq)} + CO_3^{2-}{}_{(aq)} \tag{6.3}$$

$$CO_3^{2-}{}_{(aq)} + H_2O_{(l)} - > HCO_3^{-}{}_{(aq)} + OH^{-}_{(aq)} \tag{6.4}$$

Lignin depolymerization is based on the cleavage of carbon-to-oxygen linkages, mainly ether linkages [75], [71]. The most abundant bond in the lignin structure is the β-O-4 aryl ether bond, which represents 50 % to 60 % of all lignin linkages [71] (see also the lignin structure in Appendix C). Studies on model compounds showed that these reactions occur by nucleophilic attack (of hydroxyl or sulfide ions) at the β-carbon in the phenylpropane unit, according to the mechanism in Figure 6.9. The β-O-4 aryl ether linkages are present in etherified or free phenolic structures. Only in the former

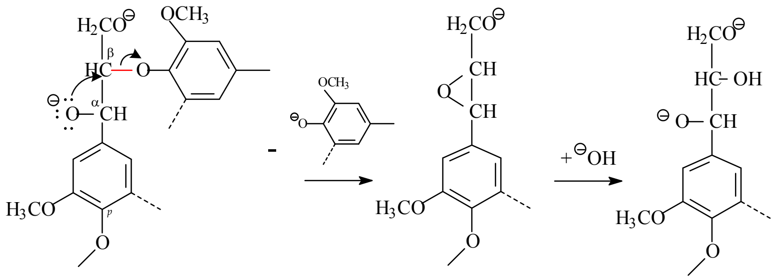


Figure 6.9: Lignin depolymerization by cleavage of β-O-4 aryl ether bond in nonphenolic phenylpropane units according to the mechanism proposed by Gierer [74]; this is one of the most important reaction in alkaline delignification [75]

case, the β-O-4 aryl ether bond is cleaved in presence of hydroxyl ions [71]. The reaction generates phenolic hydroxyl groups that further combines with sodium to give soluble sodium phenolates. This is the key process involved in alkaline solvolysis of lignin [71], [75]. Other bonds that are cleaved in alkaline conditions are the α-ether bonds and to a small extent the carbon-carbon bonds [74], [75], [71].

Depolymerization of carbohydrates in alkaline conditions occurs by hydrolysis. These reactions are slower than acid hydrolysis. Alkaline conditions promote rearrangements of aldoses and ketoses to structures that allows the cleavage of the glycosidic bond. The end group of the polysaccharides chain is thus removed and is further converted into various carboxylic and hydroxy acids, as shown in Figure 6.10. This endwise mechanism is known as the *peeling* reaction. The remaining polysaccharides chain will continue to loose monosaccharides units until the end group is stabilized. Xylan is one of the most resistant hemicellulose to alkali degradation and cellulose looses only 50 glucose units per molecule in Kraft pulping [71]. Due to its crystalline structure and high degree of polymerization, cellulose is more resistant to degradation than hemicellulose. However, at more drastic conditions (higher temperature and/or alkalinity), extensive dissolution of cellulose can be achieved. A study showed that in 3M NaOH solution, at 170-190 °C cellulose was completely dissolved after 2-4 hours, while in 1M NaOH solution a solid residue was obtained. 70 % to 80 % of cellulose was converted into various carboxylic acids [76]. These results underlines to need to apply drastic alkaline pretreatment conditions to achieve extensive biomass dissolution which is crucial in preparing pumpable HTL slurries.

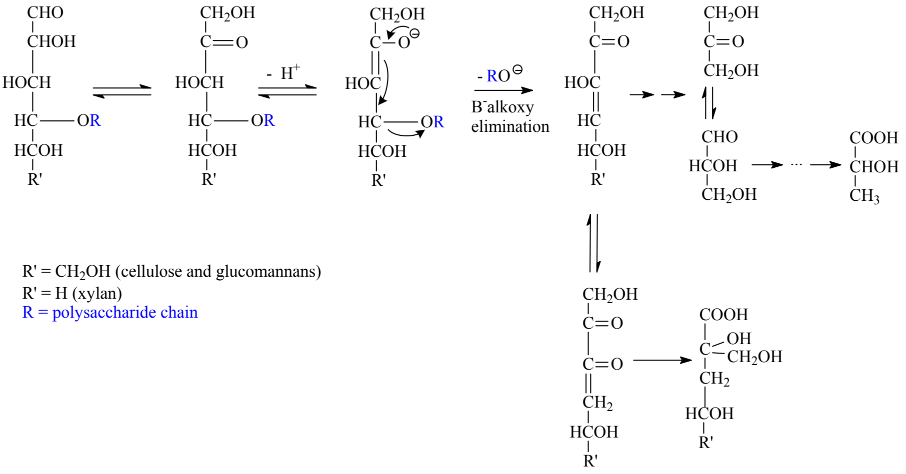


Figure 6.10: The simplified mechanism of polysaccharides peeling reactions [71]

The effect of lignocellulosic substrate on biomass dissolution

Poplar and willow chips of 5 mm to 10 mm width, barley straw and meadow grass stems of 10 mm to 30 mm long, were subjected to alkaline pretreatment at 180 °C, for 240 minutes in sodium hydroxide solution (0.35 NaOH-to-biomass ratio). The results given in Table 6.6 show that the mass fraction of solids dissolved for straw and grass is lower compared to poplar wood chips. One factor that could affect the biomass dissolution is the bulk density. Straw and grass have a higher volume-to-weight ratio compared to wood. This determines a poor contact between the alkaline solution and the solid phase which is detrimental for the reaction rates.

Another factor that could influence the biomass dissolution is the chemical composition of biomass. Higher hemicellulose and lignin content may decrease more rapidly the solution alkalinity due to the fact that the alkaline reactant is consumed in neutralization reactions. It is estimated that about 25 % of the alkali loading in Kraft pulping is used for the neutralization of the lignin degradation product and about 60 % to 70 % is involved in the neutralization of the acids derived from polysaccharides [75], [71]. As shown in Table 6.6, grass and straw have higher hemicellulose content than the wood species and willow has higher lignin content than poplar which may explain the variations in the biomass dissolved mass fraction.

Pretreatment product characterization

Despite the large fraction of organic acids formed during alkaline pretreatment, the pH of the feedstock has a basic character. This suggests the excess of alkaline reactant in the feedstock that could serve as catalyst in the subsequent HTL conversion step. Figure 6.11 shows that the pretreated feedstock pH decreases with the increase of dissolved biomass fraction i.e. that the concentration of hydroxide ions drops as the degradation reactions advance, as previously discussed. At dissolved biomass fraction above 70 %, the pH of the slurry is close to 9, the minimum value to keep the lignin dissolved in the solution [71].

Figure 6.12 shows a non-Newtonian shear thinning flow behavior of the pretreated slurry. The viscosity decreases from about 3500 mPa s at low shear rate to 270 mPa s at high shear rate values.

Table 6.6: The effect of the biomass type on dissolved mass fraction of solids after alkaline hydrothermal pretreatment at 180 °C, for 240 minutes and 0.35 NaOH-to-biomass ratio

	Hybrid poplar	**Willow**	**Meadow grass**	**Barley straw**
Biomass dissolved (wt %)	64	43	44	33
Biomass composition (wt %, db)				
Lignin	13	20	7	6
Hemicellulose	18	15	30	25
Cellulose	60	53	42	49

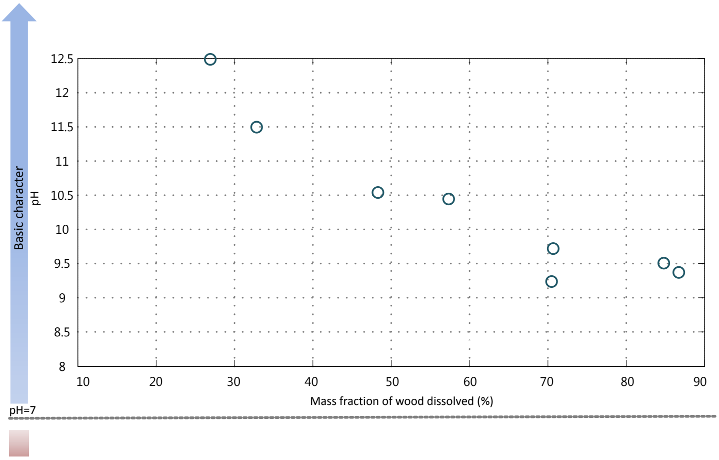


Figure 6.11: Variation of the alkaline pretreated feedstock pH with the wood dissolved mass fraction

A literature survey on chemical composition of pulping spent liquors was carried out to identify possible degradation compounds in the pretreated feedstock. A detailed list is given in Appendix B. Phenolic compounds with various molecular weights as well as sugars, hydroxy carboxylic acids, alcohols, cellulose fibers and others were found in black liquors. The phenolic compounds are derived from lignin while the organic acids mostly originates from cellulose and hemicellulose. It is estimated that every polysaccharides monomer removed by peeling, generates 1.6 equivalents of hydroxy acids [71]. Extractives may generate long chain compounds such as fatty alcohols or fatty acids.

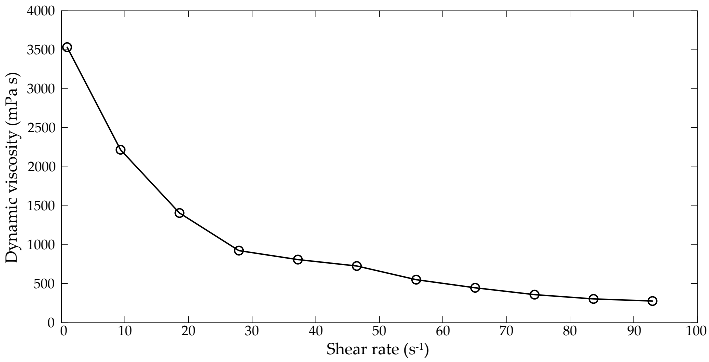


Figure 6.12: The variation of viscosity with the shear rate for an alkaline pretreated wood paste at 180 °C for 120 minutes with NaOH-to-wood ratio of 0.40

3.2 Hydrothermal liquefaction of alkaline pretreated feedstock

HTL in continuous bench-scale system

To prove the technological feasibility of continuous processing alkaline pretreated feedstock, the 100 kg wood paste prepared from willow chips was further converted into the continuous HTL system. The second objective of the continuous liquefaction test was to compare the biocrude yield and elemental composition with a previous baseline run where raw wood was liquefied. Comparative tests will show the impact of wood pretreatment on product distribution and biocrude quality.

The composition of the alkaline pretreated wood paste was adjusted to obtain a feedstock with similar composition as the baseline feedstock. Therefore, to the willow paste was added an oil vehicle and small amounts of other additives as described in Table 6.7. Upon oil addition, the feedstock viscosity was considerably reduced which allowed to further increase the biomass loading from 20 % to 25 % mass fraction by adding fresh wood powder. The feedstock was pumped into the system with a high pressure piston pump for about 4 hours, at 30-32 MPa.

The yield, the heating value and the elemental composition of the biocrude oils obtained from the pretreated and non-pretreated wood is given in Table 6.7. Surprisingly, despite the extensive degradation of wood prior to liquefaction, the pretreatment stage did not affected the biocrude yield. The biocrude oil from pretreated wood has higher carbon and lower oxygen content. A possible source of the small differences between the biocrude oils could be the fact that the pretreated willow was mixed with raw wood. To confirm this hypothesis, the experiments were repeated in small scale batch reactors where freshly pretreated willow and milled willow were liquefied. This topic is covered in the next section.

Because the alkali loading in the feedstock is high (35 % to 40 % of the biomass weight), it was important to determine the concentration of the inorganics in the biocrude. As shown in Table 6.7 the total amount of Na and K in the biocrude is less than 2 wt % i.e. about 5 wt % of the elemental Na and K in the feedstock is found in the biocrude. The main fraction of these elements is found in the water phase and the solids formed. In this context, water phase recirculation could be an option for alkalies recovery.

The advantage of alkaline pretreatment is that allows processing wood chips instead of wood powder, reducing the need for milling the wood. An additional advantage is the increase of dry matter in the feedstock. In this study, the wood content in the feedstock was increased from 18 wt % to 25 wt % by alkaline pretreatment. However, the amount of NaOH used is not negligible and its recovery is difficult. Therefore, methods to reduce the

the alkali loading in the pretreatment stage need to be further investigated. For example, the chemical pretreatment can be combined with mechanical operations or the HTL product water phase can be recycled.

HTL in micro reactors

Pretreated and non-pretreated willow slurries were subjected to HTL at 400 °C for 15 minutes, in small scale batch reactors. The slurries contain only wood, water and NaOH without other additives. For the non-pretreated feedstock, the willow was milled to fine powder (< 0.25 mm). The pre-treated slurry was prepared at the same conditions used in the 80 L digester (180 °C, 0.40 NaOH-to-wood ratio, 120 minutes reaction time). Table 6.8 shows the feedstocks composition, the HTL product distribution, the biocrude elemental analysis and the gas phase composition.

Similar to the results from the continuous system operation, the biocrude yield was not affected by the feedstock pretreatment stage. Notable are the lower biocrude yield values in batch experiments (25 wt %) compared to the continuous system (44 wt %). The biocrude yields are reported on dry ba-

Table 6.7: Feedstock composition, biocrude yield and biocrude elemental composition from continuous HTL of non-pretreated and pretreated wood at 400 °C in 20 kg/h feed capacity system [2]

	Continuous bench-scale system	
	Raw wood HTL	**Pretreated wood HTL**
FEED		
Biomass	Wood powder	Pretreated wood chips and wood powder
Total biomass in feed (wt %, db)	18	25
Water-to-biomass ratio	2.9	1.8
Alkaline-to-biomass ratio	0.27	0.30
Oil medium (wt %)	18	18
Other additives (ethanol, thickeners) (wt %)	5	5
BIOCRUDE		
Yield (wt %)	44	44
HHV (MJ/kg)	36	36
C (wt %, db)	72	77
H (wt %, db)	9.6	8.9
N (wt %, db)	0.85	1.1
O*	18	13
H/C	1.6	1.4
O/C	0.19	0.13
Na (wt %)	-	1.2
K (wt %)	-	0.58
Ash (wt %)	3.9	5.3
WATER PHASE		
Na (g/L)	-	13.5
K (g/L)	-	10.3

*by difference

sis in both cases thus, the moisture content of the oils cannot explain the difference. The main reason for the large difference between the values is attributed to the separation procedure. As previously mentioned, the biocrude was separated gravimetrically in the continuous system and by solvent extraction in laboratory scale tests. When separating the oil by solvent evaporation, volatile compounds from the oil phase are also removed, decreasing the amount of oil recovered. Another source of error is the type of solvent used. Depending on the biocrude chemical compounds, the solubility of oil is different in various solvents. For example acetone might be a better solvent for a biocrude sample than diethylether i.e. more organic compounds are recovered into the biocrude-solvent mixture which finally leads to higher biocrude yields. For these reasons, the biocrude yield values from small scale HTL experiments can be used only for the comparison purpose, to confirm that the pretreatment of biomass has no impact on biocrude yield. The biocrude yield obtained from the continuous system is the one that reflects best the real values.

The elemental composition of the biocrude oils is also slightly affected by the pretreatment stage. Like the results in the continuous system, the biocrude from the pretreated wood has higher carbon and lower oxygen con-

Table 6.8: Feedstock composition, biocrude yield and biocrude elemental composition from HTL of non-pretreated and pretreated wood at 400 °C in 10 mL micro reactors

	Batch micro reactors	
	Raw wood HTL	**Pretreated wood HTL**
FEED		
Biomass	Raw willow powder	Pretreated willow chips
Total biomass in feed (wt %, db)	20.0	20.0
Water-to-biomass ratio	3.6	3.6
Alkaline-to-biomass ratio	0.40	0.40
Other additives	none	none
BIOCRUDE		
Yield (wt %)	25.4	24.9
C (wt %, db)	81.4	85.8
H (wt %, db)	9.2	9.0
N (wt %, db)	0.49	0.57
O[a]	8.9	4.7
H/C	1.35	1.25
O/C	0.08	0.04
SOLIDS		
Yield (wt %)	6.3	7.4
GAS PHASE		
Yield[b] (wt %)	23.3	29.2
CO_2 (vol. %)	48.1	48.0
CO (vol. %)	1.0	1.0
H_2 (vol. %)	47.9	46.9

[a]by difference [b]calculated with Equation 6.1

tent.

The gas phase is composed of approximately equal volume fractions of CO_2 and H_2. This composition is different compared to the gas phase produced by non-catalytic HTL where around 90 % vol. of the gas phase is CO_2 [77], [18]. The presence of higher fractions of hydrogen and lower fractions of carbon dioxide in the gas phase may be explained by the catalytic effect of sodium hydroxide on the water gas shift reaction [78]. This result also suggests that larger fractions of CO (compared to non-catalytic HTL) are generated in presence of the alkaline reactant, possibly as a result of oxygen removal through decarbonylation reactions.

4 Conclusions

Alkaline pretreatment prior to continuous HTL processing is a technologically feasible method to prepare pumpable feeds from woody biomass. Wood chips can be converted into a paste slurry by thermochemical pretreatment in NaOH solution at 180 °C for 120 minutes with a NaOH-to-wood mass fraction of 0.35-0.40. The pretreatment has no impact on biocrude yield or elemental composition, demonstrated in both continuous bench scale HTL system and small scale batch reactors. Continuous processing of an alkaline pretreated feedstock with 25 wt % biomass loading at 30 MPa was proven. This is the highest biomass loading of a wood-based feedstock that was continuously processed in an HTL system. However, the large amounts of alkaline reactant used (35 % to 40 % of the biomass weight) clearly indicates that recovery options for NaOH or methods to reduce the alkaline reactant concentration need to be developed to make the pretreatment process economical.

Chapter 7

Co-processing of wood and algae to improve the processability of HTL feeds

1 Introduction

Non-terrestrial biomass, microalgae and seaweeds, represents a promising alternative biomass resources for bioenergy production. Compared to terrestrial biomass, algae have higher grow rate, higher photosynthetic activity i.e. higher CO_2 absorption capacity and do not need arable land for growing [79], [80]. Other advantages of algae biomass are that they can be cultivated in waste waters and do not compete with food crops [81]. Figure 7.1 shows that also with respect to the elemental composition, algae are more advantageous than lignocellulosics. Because algae have lower oxygen and higher carbon content, the resulting biocrude oils will have the elemental composition closer to the ideal case of conventional fuels. However, compared to lignocellulosics, algae contain larger fractions of nitrogen and sulfur that is distributed into the biocrude phase. Also, the production costs for algae are high and they are difficult to store due to fast degradation. These represent major disadvantages for marine biomass.

Lignocellulosic biomass is the most abundant biomass resource on earth [16], [82]. While the biological treatment technologies have difficulties in converting lignocellulosic biomass into biofuels due to biomass recalcitrance [83], [84], the process conditions in hydrothermal liquefaction (HTL) can disrupt more easily the structure of biomass. But, continuous processing of lignocellulosic biomass faces other difficulties related to the pumpability of the aqueous slurries. Because lignocellulosics are low density materials that slightly interact with water, most often the slurries separate in a solid and a liquid phase under pressure conditions or even with standing. Unlike lignocellulosic materials, algae form more homogeneous mixtures, easier to pump, as demonstrated in several studies [85], [86], [87]. Large scale HTL plants like the ones operated by Sapphire energy Inc., Algenol biotech LLC, Genifuel Corporation or Muradel Pty. Ltd. confirms the possibility to process algae slurries in continuous HTL systems [88].

For these reasons, co-processing of wood and algae is proposed in this work as a method to improve the processability of lignocellulosic aqueous slurries. The polysaccharides contained in algae could be utilized as water holding agents and viscosifiers, properties that can prevent slurries from dewatering and phase separation. As an added benefit, previous study showed that co-processing of microalgae with other biomass streams like manure [89], rice husk [90], coal [91] or seaweeds [92] can be an effective method to increase the biocrude yield due to the fact that microalgae compounds have lower thermal resistance and higher conversion into biocrude.

Previous study on hydrothermal liquefaction of algae shows that microalgae generate higher biocrude yields compared to seaweeds. The values reported in literature for biocrude yield from microalgae vary between 18 wt % [93] and 83 wt % [94] (on dry ash free basis) and the biocrude yield obtained from seaweeds vary between 4 wt % [28] and 36 wt % [95]. These differences are explained by the higher content of lipids and proteins in microalgae. The large variation between the biocrude yields are also affected by the hydrothermal liquefaction conditions (temperature, reaction time, catalyst). The most advantageous conditions (with respect to biocrude yield) for hydrothermal liquefaction of algae are temperatures near the critical point of water [96], [97], [98] and reaction times up to 15 minutes [99], [100]. For

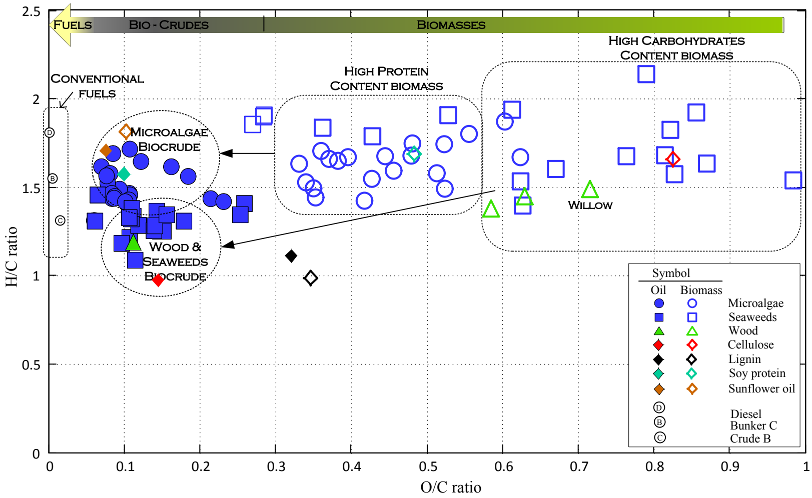


Figure 7.1: Van Krevelen diagram of wood, algae, their model compounds and the biocrude oils obtained by Hydrothermal Liquefaction; A list of sources from where the data were collected is given in Appendix D

algae with high content of carbohydrates alkaline catalysts are recommended because they reduce the char formation and increase the biocrude yield [93], [24].

This work studies the technical feasibility of using seaweeds and microalgae as wood slurries stabilizers. Green-, brown- and red- seaweeds are used to prepare wood-algae slurries with 15 wt % to 20 wt % dry matter content and microalgae are used to prepare mixtures with wood with 30 wt % dry matter content. The mixtures are tested for resistance to mechanical dewatering using the syringe and the centrifugation test. The mixtures are further liquefied at supercritical water conditions, in presence of an alkaline catalyst, to compare the effect of algae addition on the HTL product distribution, biocrude elemental composition and boiling point distribution. To the best knowledge of the author, co-liquefaction of algae and wood has not been reported in literature yet, especially as a method to improve the lignocellulosic feeds processability in continuous HTL systems.

2 Materials and methods

Raw materials

Wood-algae mixtures were prepared from willow powder and various species of seaweeds and microalgae. Willow wood chips (see Chapter 6 for details) and seaweeds were milled with a FOSS Cyclotec mill. The powders mostly consist of particles smaller than 0.250 mm, with the size distribution given in Table 7.1. Fresh seaweeds: *Laminaria Digitata* (cultivated) and *Palmaria Palmata* (wild harvested) were provided by Ocean Rainforest

Figure 7.2: Defrosted macroalgae *Palmaria Palmata* (left) and *Laminaria Digitata* (right) as received from the supplier

Table 7.1: Size distribution of milled willow and algae powders [3]

	d_{50}	Particles mass fraction (%)		
	(mm)	0.250 mm - 0.125 mm	0.125 mm - 0.050 mm	< 0.050 mm
Willow	0.130	38.0	23.0	25.2
Seaweeds	0.115	38.7	34.7	20.3

and were collected in March 2016 from the Faroe Islands. After collection, the algae were immediately frozen for transport. When received, the seaweeds were defrosted, dried at room temperature for 3 days and afterward in the oven at 60 °C. Green seaweed *Ulva spp.* and microalgae *Chlorella Vulgaris* were provided from commercial sources (Porto-Muiños S.L. and Algomed®). The biomass was analyzed for elemental composition, chemical composition, heating value and ash content. Chemical and elemental composition of algae are given in Table 7.2.

Analytical methods

Lipids were measured by Soxhlet extraction with a chloroform-methanol mixture, according to the method described by [101] and [102]: 2 g of algae were extracted with 350 mL of solvent (chloroform-methanol 2:1 v/v) for 5 h to 6 h, into a single thickness cellulose thimble. After extraction, the solvent was removed at 35 °C and the samples were dried for 1 h at 105 °C. The mass fraction of lipids was determined gravimetrically. Proteins were calculated using the nitrogen-protein conversion factor (N-factor) of 4.58 determined by [103]. The N-factor correlation is based on 10 microalgae species and has a standard deviation of 0.11. The fraction of carbohydrates was determined by difference.

Elemental analysis was performed with a vario MACRO cube Elementar

Table 7.2: Characterization of willow and algae biomass (on dry basis) [3]

	Green seaweed *Ulva spp.*	**Brown seaweed** *L. Digitata*	**Red seaweed** *P. Palmata*	**Microalgae** *C. Vulgaris*
Polymer mass fractions (%)				
Lipids	6.8±0.0	10.1±1.2	9.1±0.8	16.3±0.2
Proteins	7.8	10.5	20.4	40.3
Carbohydrates	54.8	44.4	47.6	35.4
Elemental composition (wt %)				
C	41.7±0.8	36.5±1.6	37.1±0.7	50.1±0.2
H	6.3±0.2	5.0±0.0	5.5±0.3	7.1±0.4
N	1.7±0.0	2.3±0.0	4.5±0.0	8.8±0.0
S	1.2±1.7	2.2±0.5	2.0±0.0	1.1±1.1
O*	18.6	19.0	28.0	24.9
Ash (wt %)	30.5±0.5	35.0±0.4	22.9±0.1	8.0±0.5
HHV (MJ/kg)	11.8±0.3	12.2±0.1	15.2±0.1	22.1±0.0

*by difference (100-C-H-N-S-Ash)

analyzer. The heating value (HHV) of the biomass was measured with an IKA C2000 Basic calorimeter and the ash content was measured at 575 °C for 6 hours according to the ASTM E1755-01 standard procedure.

The thermogravimetric (TGA) analysis of biocrude oils was performed with a PerkinElmer STA6000 TG/DSC instrument. The samples were heated in nitrogen atmosphere (gas flow rate 20 mL/min) from 50 °C to 1000 °C with a heating rate of 10 °C/min.

The water holding capacity (WHC) of algae and wood was measured using the method described by Sosulski [104] and Yaich et al. [105]. Slurries containing 12 % solids were prepared from water and biomass sample. After 60 minutes rest time at room temperature, the mixtures were centrifuged at 3000 g for 25 min at 25 °C. A fraction of the liquid was absorbed into the biomass and the rest separated in a top layer. After removing the supernatant liquid, the tubes containing the samples were dried in oven for 25 minutes at 50 °C to remove all free water left. The mass fraction of water absorbed by the biomass was determined gravimetrically.

Viscosity of the algal slurries was measured with a Brookfield RV-DV II-Pro rotational viscometer.

Slurry preparation and pumpability tests

The wood-algae slurries were prepared by first pouring the algae powder into a well agitated solution (water or NaOH 1M solution). The wood powder was added last, the mixtures were stirred well, covered with parafilm and left 60 minutes to rest. The total biomass loading of the mixtures varies between

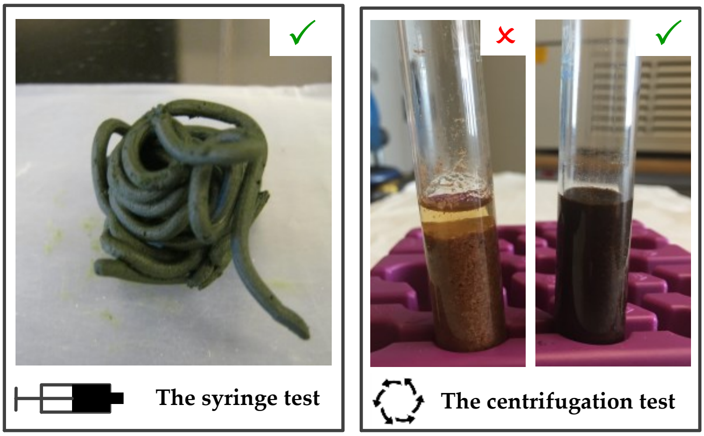


Figure 7.3: An algae-water feed with 35 wt % microalgae content that passed the syringe test (left) and wood-water slurries centrifuged at 3000 g for 10 minutes (right): the feed that undergo phase separation contains 15 wt % wood, 85 wt % water and the stable feed contain 10 wt % wood, 10 wt % brown seaweed, 80 wt % solution NaOH 1M

15 wt % and 30 wt % and the ratio between algae and wood between 0.00 and 3.00. After 60 minutes, the samples were subjected to pumpability tests as shown in Figure 7.3.

The syringe test was used throughout this work and is described in more detailed in Chapter 5. An additional test was introduced to evaluate feed stability (solids dewatering) under more harsh conditions compared to the syringe test. In this test, similar to the the water holding capacity test, the slurries are subjected to centrifugal forces of 3000 g for 10 min at 25 °C. Slurry dewatering is monitored. Stable feeds are those that do not separate, as shown in Figure 7.3.

The feeds that successfully pass both tests (pass through the syringe homogeneously and do not separate after centrifugation) are considered to have a higher likelihood to be pumpable under HTL conditions (30 MPa) than the feeds that pass only the syringe test.

Hydrothermal liquefaction experiments

The setup and the product separation procedure for hydrothermal liquefaction experiments are described in more detail in Chapter 6. The separation procedure is summarized in Figure 7.4. The HTL experimental conditions were: 400 °C, 15 minutes, feedstock biomass loading 20 wt %. After separation, the moisture content, the elemental composition and the boiling point distribution of the biocrude oils were determined. The biocrude yield was expressed on oil dry basis and biomass dry ash free basis.

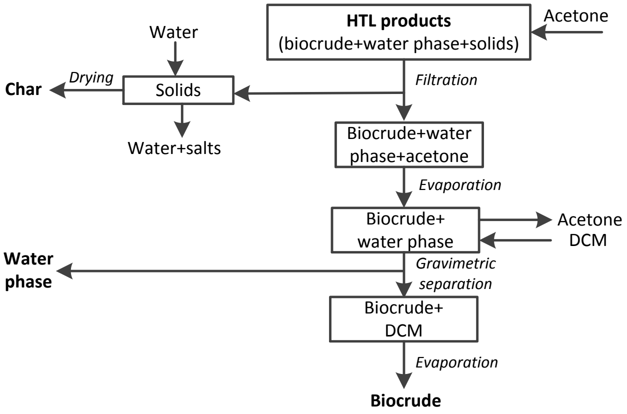


Figure 7.4: Schematic representation of the HTL product separation procedure [3]

3 Results and discussion

3.1 Seaweeds and microalgae as wood-slurries stabilizers

Wood is a porous, low density biomass that forms heterogeneous slurries with water. As shown in Figure 7.5 (left), the phase separation between wood and water occurs either by floating or by settling of wood particles. Floating is caused by the internal, inaccessible voids of the coarse particles or wood chips. Settling occurs for small wood particles (<100-200 μm) when the internal pores are filled with liquid, which cause the increase of wood particle density above the density of water. This is possible because the density of the wood cell wall is about 1.5 g cm^{-3} [106].

Phase separation between the water and wood or other porous materials can be prevented by increasing the viscosity of the liquid phase. Solids dewatering under high pressure conditions can be prevented by adding materials with high water holding capacity into the feedstock composition. Experiments with carboxymethyl cellulose (CMC), a cellulose-derived viscosifier with high water holding capacity ($\approx$42 g/g [107]), showed that when added into a wood slurry, it can successfully avoid mechanical dewatering of the feedstock (see Figure 7.6). More, the phase separation between wood and water (settling or floating) was preveneted and the wood slurries gained a continuous, paste-like aspect in presence of CMC. Recycled HTL water phase (the water phase has a slightly basic character) could also be used without affecting the water holding capacity of CMC.

The water uptake by CMC or other polysaccharides is assumed to take place by adsorption at various polar groups in the polymer structure. According to the strength of the interactions, the water adsorbed can be nonfreezing water (strongest interactions), freezing water and free water. The

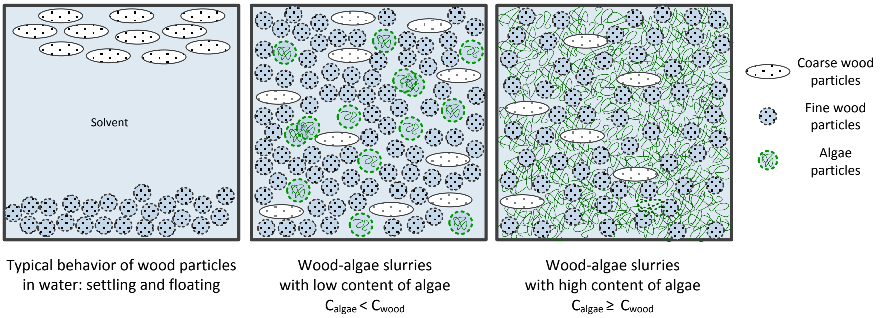


Figure 7.5: Schematic representation of phase separation in wood aqueous slurries and stabilization with algae hydrocolloids; high concentration of algae in the slurry is needed to ensure the contact and the entanglement of hydrocolloids [3]

presence of counter ions may influence the water adsorption capacity [108]. In Appendix E, a lists of possible water adsorption sites and the number of water molecules bound by each group is given. The table shows that up to 24 water molecules can be adsorbed at one site. The groups that can bound the highest number of water molecules are the SO_3^- and COO^- when assisted by H^+ or Na^+ ions (the protonated- or the ionic form of the group).

Algae contain various polysaccharides with groups that can act as water sorption sites. Ulvans in green seaweeds, alginates and fucoidans in brown seaweeds or carrageenan and agar in red seaweeds are long chain polysaccharides, with thickening and water sorption properties, known also as hydrocolloids [109] and widely used in food industry. As shown in Appendix E, these polysaccharides contain various SO_3^- and COO^- groups. This suggests that algae can be used directly in the wood slurries as water absorbent materials.

Figure 7.7 shows the measured water holding capacity of the four algae species investigated in this work: *Ulva spp.*, *L. Digitata*, *P. Palmata*, *Chlorella Vulgaris* and willow. Because alkaline catalysts are often used in hydrothermal liquefaction of biomass [21], the effect of NaOH on biomass water holding capacity was evaluated. The results indicate that wood and green seaweed have the highest WHC values 5.5 g H_2O/g biomass, followed by brown- and red seaweed 3.7 - 4.0 g H_2O/g biomass and microalgae 2.2 g H_2O/g biomass. Previous work measured similar WHC for *Ulva lactuca* 6.7 g water/g [105] but higher values for *Laminaria digitata* (20 g water/g sample [110]). Higher values were probably obtained due to different experimental

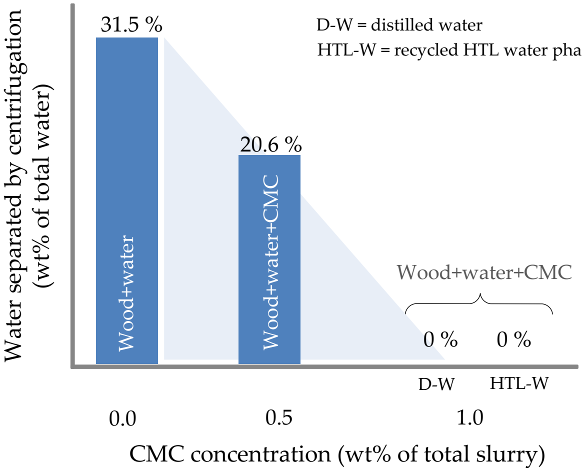


Figure 7.6: The effect of CMC addition into a wood slurry on the free water content reduction; water separation was measured by centrifugation

procedures: in the work cited, the slurry was maintained for 16 hours before centrifugation, while in this work the rest time period was only 1 hour. The WHC decreases in presence of NaOH for wood and green seaweed and increases for the other algae with 28 % for brown seaweed, with 8 % for red seaweed and with 32 % for microalgae. Another observation is that high WHC values correspond to high porosity materials e.g. wood and low WHC values correspond to materials that have no porous structure e.g. microalgae. This suggests that the WHC measured for wood and seaweeds includes the water absorbed physically into the porous structure of the particles. The water absorbed by physical means into the biomass, it can be removed easily under pressure conditions therefore, materials like wood and green seaweeds are not able to form stable slurries under pressure condition. Brown- and red seaweeds are situated between these two extremes, suggesting that the WHC is due to both physical and chemical absorption.

Single-component wood and algae slurries characterization

Mixtures of 15 wt % dry matter content were prepared from algae and willow and were tested for their resistance to dewatering under the syringe- and the centrifugation test. The slurries appearance and texture is also described in Table 7.3. The comparison shows that wood slurries are significantly different from algae slurries. While wood form non-cohesive and non-stable mixture, algae form in general less viscous, cohesive pastes. According to the syringe test, algae slurries are stable but dewatering occurs under centrifugal forces, for all slurries prepared from seaweeds and water. For the brown seaweed, the slurry stability under centrifugal forces is improved in presence of NaOH. Microalgae form liquid-like mixtures at 15 wt % dry matter content and paste-like mixtures at 30 wt % dry matter content. Concentrated microalgae pastes are cohesive and very stable in both water and NaOH solution. The viscosity of all mixtures (except green seaweed) increases in NaOH solution.

Comparing the WHC of the biomass with the slurries stability, opposite trends are noticed: materials with high WHC undergo phase separation easily (e.g. wood, green seaweeds) while materials with low WHC are very stable (e.g. microalgae). As discussed earlier, this can be explained by the fact that high values of water holding capacity are, to a great extent, due to physical absorption of water into the pores and not chemical absorption of water. This makes the water holding capacity of biomass (or at least the WHC measured by the centrifugation method) a misleading parameter to predict the slurries stability and pumpability.

Despite this unclear correlation between WHC and slurries stability, the WHC parameter might be useful to calculate with approximation, the slurries maximum biomass loading, the point where the texture of the slurries changes from paste-like to solid-like consistency. The measured WHC of

Table 7.3: Characterization of wood and algae slurries in water and NaOH 1M solution; the effect biomass type, biomass loading and solution pH on the slurries stability, viscosity and texture [3]

Biomass type	Solids dry matter content (wt%)	Slurry texture		Dewatering *syringe test*		Dewatering *centrifugation test*		Viscosity[a] (Pa s)	
		H_2O	NaOH	H_2O	NaOH	H_2O	NaOH	H_2O	NaOH
Wood	15	Two-phases material, non-cohesive	Non-flowing, thick paste, non-cohesive	x	x	x	x	-	-
Green seaweed	15	Non-flowing, thick paste, cohesive	Flowing, thin paste, cohesive	✓	x	x	x	22	1.7
Brown seaweed	15	Flowing, thin paste, cohesive	Non-flowing, thick paste, cohesive	✓	✓	x	✓	29	~300[b]
Red seaweed	15	Flowing, thin paste, non-cohesive	Flowing, thin paste, cohesive	✓	✓	x	x	5	30
Microalgae	15	Flowing, liquid	Flowing, liquid	-	-	x	x	~0.09[b]	~0.16[b]
Microalgae	30	Non-flowing, thin paste, cohesive	Non-flowing, very thick paste, cohesive	✓	✓	✓	✓	65	-

[a] dynamic viscosity measured at shear rate of 2 s^{-1} at 20 °C [b] values predicted by extrapolation of the viscosity measurements performed at shear rate values below or above 2 s^{-1}.

wood and algae was used to calculate the critical concentration of the slurries (C*) using the proposed Equation 7.1. The equation calculates the theoretical maximum dry matter content of the slurry when 100 g of water are mixed with biomass. The equation was obtained by assuming that the maximum amount of water absorbed by 1 g of biomass is given by the WHC parameter. From here, the maximum concentration of a biomass-water slurry (C*) was derived. When the slurry biomass loading equals the C* value, the slurry consistency changes from paste-like to very thick paste or solid-like consistency. Table 7.4 shows a good correlation between the calculated and the experimental C* values.

$$C^*(wt\%) = \frac{m_{biomass}}{m_{biomass} + m_{H2O}} \cdot 100 = \frac{100/WHC}{100 + (100/WHC)} \cdot 100 \qquad (7.1)$$

The thickening property of algae was evaluated by measuring the slurries viscosity. Figure 7.8 shows the viscosity-shear rate profile of seaweed slurries with 15 wt % dry matter content and microalgae slurry with 30 wt % dry matter content, in both water and NaOH solution. The results show that microalgae develop the highest viscosity followed by brown seaweeds. These are also the algae that form the most stable slurries. The lowest viscosity value corresponds to the red seaweed slurry. Similar with the trends in WHC, the presence of NaOH increases the viscosity of red seaweed slurry

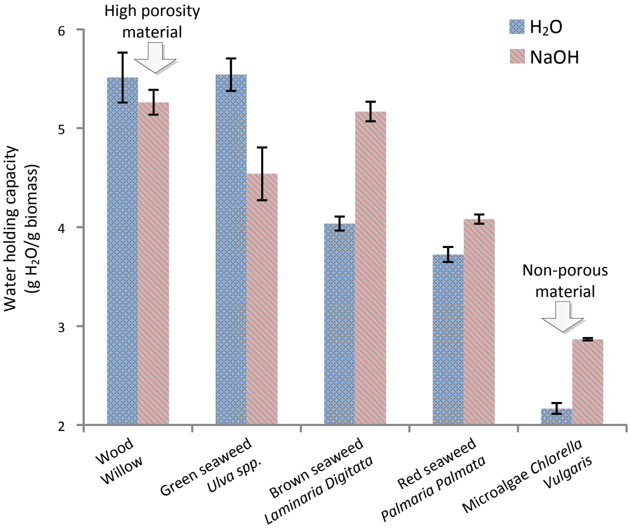


Figure 7.7: The water holding capacity of wood and algae biomass, measured by the centrifugation method. The maximum biomass loading of the wood-algae-water slurries is indicated with star symbols [3]

Table 7.4: A comaprison between theoretical and experimental maximum biomass loading in wood and algae slurries to obtain thick pastes [3]

		C* (wt %)	
	WHC ($g_{H2O}/g_{biomass}$)	Calculated with Equation 7.1	Experimental
Willow	5.5±0.3	15.4	15.0
Green seaweed	5.5±0.2	15.3	15.0
Brown seaweed	4.0±0.1	20.0	20.0
Red seaweed	3.7±0.1	21.3	20.0
Microalgae	2.2±0.1	31.3	35.0

and decreases the viscosity of green seaweed mixture.

Two-component wood-algae slurries characterization

According to Table 7.3, single component brown seaweeds or microalgae slurries, might be suitable for continuous processing in HTL systems. However, the interest of this work was to evaluate the possibility to pump mixtures of wood and algae. In this purpose, wood was gradually added in algae solutions to identify the algae-to-wood mass ratio at which slurries are pumpable (according to the syringe test). Figure 7.9 shows the results based on willow-brown seaweed mixtures.

Figure 7.9 indicates that paste-like, non-separable slurries are obtained when the mass fraction of algae in slurry equals or is higher than the mass fraction of wood. The critical algae-to-wood ratio (R*) identified for brown seaweed *Laminaria Digitata*-willow mixtures is 1/1. At this ratio, willow form paste-like mixtures that pass the syringe test, as shown in Figure 7.10.

In Table 7.5 the stability of willow-algae slurries, containing 15-30 wt % total biomass loading with a mass ratio of 1/1 (wood/algae) is compared. The biomass loading was adjusted to obtain thick paste-like mixtures. The

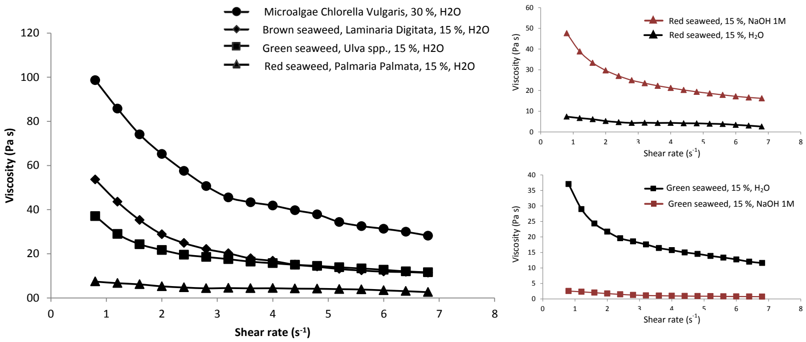


Figure 7.8: The viscosity of the algae pastes in water and sodium hydroxide solution against the shear rate [3]

Table 7.5: The effect of algae type and solution pH on the stability of wood-algae slurries according to the syringe and the centrifugation test [3]

Biomass	R	Solids dry matter content (wt%)	Dewatering *syringe test*		Dewatering *centrifugation test*	
			H_2O	NaOH 1M	H_2O	NaOH 1M
Wood-green seaweed	1/1	15	x	x	x	x
Wood-brown seaweed	1/1	20	✓	✓	x	✓
Wood-red seaweed	1/1	20	✓	✓	x	✓
Wood-microalgae	1/1	30	✓	✓	x	✓

R:wood/algae mass ratio

two-component wood-brown seaweeds slurry is stable under the syringe test but separates under centrifugal forces. Like the single-component brown seaweed slurry, mechanical dewatering is prevented in presence of NaOH. All other algae follow the same behavior, except the green seaweed *Ulva spp.* that cannot form stable mixtures with wood.

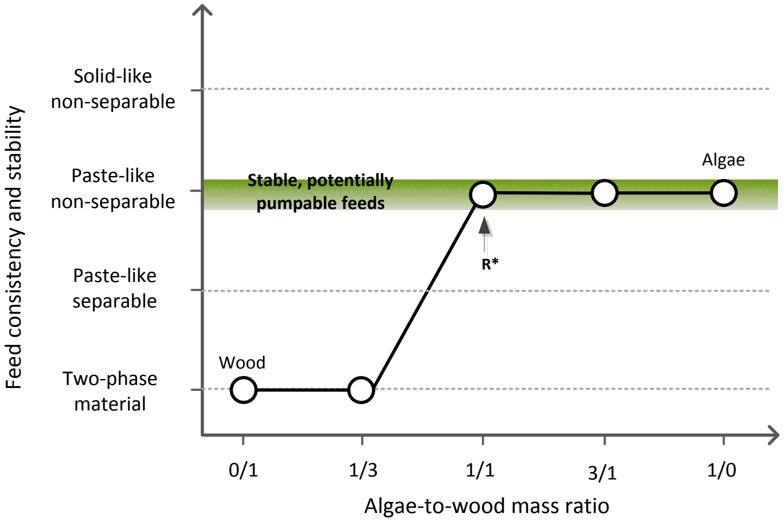


Figure 7.9: The variation of feed stability (acc to the syringe test) with the increase of algae mass fraction; a study case for mixtures of willow and brown seaweed *Laminaria Digitata*; total dry matter of wood-algae slurries is 20 wt %; single-component wood slurry 15 wt %, single-component seaweed slurry 20 wt % [3]

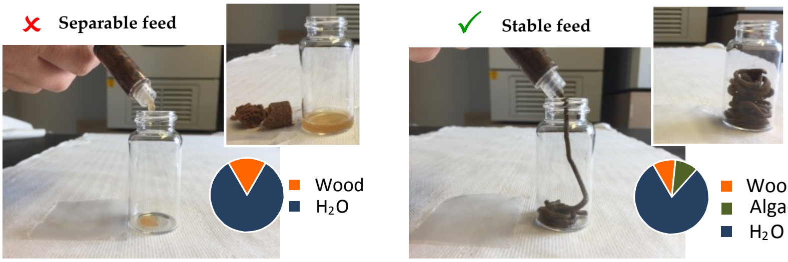


Figure 7.10: The syringe test applied to a mixture containing 15 wt % wood, 85 wt % water (left) and a mixture containing 10 wt % wood, 10 wt % brown seaweed, 80 wt % water (right) [3]

3.2 Hydrothermal liquefaction of wood-algae mixtures

Supercritical hydrothermal liquefaction of willow-algae mixtures was carried out at 400 °C and 15 minutes. All slurries contain 20 wt % biomass loading, wood-to-algae mass fraction of 1/1 and 2.8 wt % to 3.4 wt % NaOH. For comparison, a base-line willow feed was also converted. The composition of the five feedstocks and the HTL product distribution is given in Table 7.6.

Compared to single-component wood feed, the fraction of organic matter in the microalgae-wood slurry is with 13.5 % higher. As discussed earlier, this is due to microalgae unicellular structure that allows higher biomass loadings but also due to the low ash content of microalgae.In wood-seaweed slurries, the fraction of organic matter increases with only 1.3-2.5 %, relative to willow slurry. This is due to higher water sorption capacity of seaweeds and high ash content, 23 % to 35 % (see Table 7.2).

The impact of co-processing wood and algae on biocrude yield is significant for microalgae and low for all seaweeds. The biocrude oil yield increases from 28.5 wt % for willow alone to 41.8 wt % when willow is co-processed with microalgae but decreases to 21.6 - 25.5 wt % when willow is co-processed with seaweeds. Also the carbon recovery has higher values for willow-microalgae biocrude compared to willow or willow-seaweeds derived oils. These differences can be explained by the chemical composition of algae. While microalgae have high content in proteins and fats, seaweeds are rich in carbohydrates (see Table 7.2). Previous study on corn starch (350 °C, no catalyst) showed a conversion of only 15 wt % carbohydrates into biocrude [111]. Another study conducted on algae polysaccharides obtained biocrude yield below 5 wt % (280 °C, no catalyst) [112]. At supercritical conditions, higher biocrude yields were obtained from glucose and xylose, between 28 wt % to 30 wt % (400 °C, with Na_2CO_3) [113]. Proteins have slightly higher conversion into biocrude than carbohydrates 16-30 wt % [111], [93] and up to 80 wt % of lipids can be converted into biocrude according to [93]. Therefore, the high protein and lipid content of microalgae can explain the higher biocrude yields.

The fraction of carbohydrates that are not converted into biocrude are transferred into the water phase, form gaseous compounds or solid products. According to [112], 61 wt % of carbohydrates are degraded into water soluble compounds, 25 wt % form gases and only 9 wt % form solids. Typical water soluble compounds are carboxylic acids, ketones or alcohols. Proteins also generates large fractions of water soluble compounds (35 wt % to 80 wt %) but low amounts of solid and gaseous products [93], [111]. These findings are in agreement with the results in Table 7.6 which shows that between 49 wt % and 66 wt % of the biomass organic matter is converted into water soluble organics and gaseous products.

Table 7.6 shows the elemental composition of biocrude oils. It can be noticed that the biocrudes are similar in terms of carbon and hydrogen content except the biocrue derived from the willow-green seaweed algae that has the lowest content of carbon and hydrogen and the highest content of oxygen. Compared to pure willow biocrude, the algae derived oils have higher concentrations of nitrogen and sulfur. Wood-microalgae derived biocrude has the highest nitrogen content (4.8 wt %) and wood-red seaweed biocrude the highest sulfur content (0.31 wt %). The elemental balance indicates that be-

Table 7.6: Feedstock characterization and HTL product distribution [3]

	Willow	Willow+ green seaweed	Willow + brown seaweed	Willow + red seaweed	Willow + microalgae
Feed composition					
Total biomass (wt%, db)	15.3	20.0	20.0	20.0	30.0
Organic matter (wt%, daf)	15.0	16.8	16.3	17.5	28.5
NaOH (wt% of total feed)	3.4	3.2	3.2	3.2	2.8
Water/biomass ratio	5.7	4.0	4.0	4.0	2.3
Algae /wood ratio	0.0	1.0	1.0	1.0	1.0
Product yields (wt%, db)					
Biocrude	28.5±1.0	24.3±1.0	25.5±0.9	21.6±2.1	41.8±0.1
Char	6.6±1.3	16.2±1.7	10.5±0.7	12.5±0.4	9.2±0.5
WSO + gas (by diff.)	64.9	59.5	64.0	65.9	49.0
Biocrude					
C (wt%, db)	81.0±1.0	71.3±5.3	79.5±1.0	79.8±1.9	74.0±1.5
H (wt%, db)	7.8±1.6	6.7±0.9	7.6±0.6	7.8±0.4	8.0±0.1
N (wt%, db)	1.2±0.0	2.1±0.2	2.0±0.0	3.1±0.3	4.8±0.0
S (wt%, db)	0.06±0.0	0.18±0.0	0.23±0.0	0.31±0.0	0.26±0.0
O*	9.9	19.7	10.7	9.0	12.9
Carbon recovery (%)	48.2	38.7	48.0	40.6	63.1

*by difference (100-C-H-N-S); WSO = water soluble organics

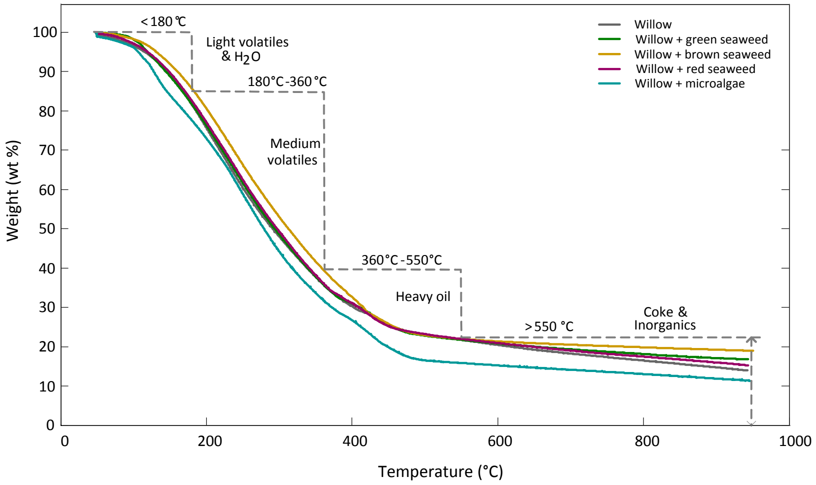


Figure 7.11: TGA curves of biocrude oils obtained from the liquefaction of willow and willow-algae mixtures at 400 °C for 15 minutes [3]

tween 30 wt % and 60 wt % of the nitrogen and between 5 wt % and 20 wt % of the sulfur contained in the biomass is transferred into the biocrude phase. Similar to sulfur, 5 wt % to 15 wt % of the oxygen in biomass is transferred into the biocrude.

Figure 7.11 shows the thermogravimetric curves of the five biocrude oils. It can be noticed that the degradation of the biocrude oils occurs in one step between 100 °C and 360 °C. Until 360 °C, 60 wt % to 68 wt % of the biocrude weight is lost. Approximately 50 wt % of the biocrude weight evaporates between 180 °C and 360 °C, corresponding to the jet and diesel fuel distillate range. Only small variations between the boiling point distribution of the biocrude oils were noticed (see also Table 7.7). This may suggest that despite the differences in the chemical composition of biomass, willow and seaweeds generate oil compounds with similar boiling properties. Lipids might be converted into compounds with higher boiling point like hexade-

Table 7.7: Boiling point distribution of biocrude oils obtained from the liquefaction of willow and willow-algae feedstock combinations (wt %) [3]

Distillate range	**Willow**	**Willow + green seaweed**	**Willow + brown seaweed**	**Willow + red seaweed**	**Willow + microalgae**
Gasoline <180 °C	18.4	18.3	14.3	17.4	22.4
Jet&Diesel 180 °C-360 °C	45.6	45.8	46.0	46.3	45.6
Fuel oil 360 °C-550 °C	14.2	14.2	17.7	14.3	16.2
Coke&Ash >550 °C	21.8	21.7	22.0	22.0	15.8

cane or heptadecane [93]. This may be one of the reasons why the TGA curve of willow-microalgae biocrude distinguishes from the willow and willow-seaweed biocrudes.

4 Conclusions

Brown seaweeds, red seaweeds and microalgae can be used to improve the pumpability of wood slurries while green seaweeds showed poor stabilizing ability. The critical algae-to-wood mass ratio is 1/1. Below this value, wood-algae mixtures are prone to phase separation when pressurized. The most stable slurries are those prepared with microalgae and brown seaweeds. Besides improving the processability of wood slurries, microalgae have two other benefits over seaweeds: a) increased slurry biomass loading and b) increased biocrude yield. By co-processing wood and microalgae, the biomass loading was increased with 100 % and the biocrude yield with about 46 %. The disadvantages of using algae for biocrude production is the transfer of nitrogen and sulfur into the biocrude phase. Seaweeds have also the disadvantage of high ash content.

Conclusions

This work proposes three pretreatment methods to obtain pumpable feeds for continuous hydrothermal liquefaction of lignocellulosic biomass, in particular wood. Two pretreatment methods are focused on processing wood flours (particle size < 0.25 mm) and one on processing wood chips (10 mm to 15 mm or larger). The pretreatment strategies are presented in Figure 7.12.

The first method consists in co-processing milled wood with water and recycled biocrude. Suspending wood particles in an oil medium instead of water, ensures the formation of a more homogeneous slurry. More, because the solid particles are coated with a layer of biocrude, they slip one over another when are in close contact, and reduce the risk of clogging. The challenge of mixing together the oil and the water phase is solved by following a specific mixing order namely, wood->water->biocrude. The water will be absorbed by the wood and therefore will not be in direct contact with the biocrude phase. However, over-saturation of wood with water may cause phase separation and needs to be avoided. It was also found that the utilization of wood particle smaller than 125 μm is compulsory to achieve high biomass loadings. A slurry containing 20 wt % wood powder, 40 wt % recycled water phase and 40 wt % recycled biocrude was successfully pumped at 30 MPa in the continuous bench scale HTL plant installed at Aalborg University.

An alternative pretreatment method is the hydrothermal alkaline pretreatment. In this case, wood chips can be directly processed, saving the energy input for milling. At 180 °C to 200 °C and in presence of sodium hydroxide, 10 mm to 15 mm wood chips are converted into a wood paste. Pumpable slurries are obtained when more than 65 wt % of the wood chips are dissolved. This can be achieved at sodium hydroxide-to-wood ratio of 0.35 to 0.40 and after 2 hours of thermal treatment. The pumpability of alkaline pretreated feedstock was proven in the continuous bench scale HTL plant, where 100 kg of willow paste was mixed with fresh wood powder to obtain a slurry with 25 wt % dry matter content. The slurry was successfully pumped for about four hours. Continuous processing of a wood-based feedstock with such high biomass loading as well as the concept of alkaline pretreatment prior to continuous HTL, are contributions above state-of-the-art.

Co-processing wood with algae or other biomass substrates that have water holding capacity and thickening properties is another interesting method to prepare pumpable feeds. The water holding capacity is used to avoid feedstock dewatering under high pressure conditions, while thickening properties are used to keep the wood particles in suspension. Brown seaweeds, red seaweeds or microalgae can be used in this purpose. Wood-seaweeds mixtures with 20 wt % biomass content and wood-microalgae mixtures with 30 wt % biomass content and with an algae-to-wood ratio of 1/1, showed positive response to laboratory scale pumpability tests. Continuous processing of these mixtures in the hydrothermal liquefaction continuous plant will be validated in the near future. With respect to biocrude yield, seaweeds have a slightly negative impact while microalgae increase the biocrude yield with almost 50 %. The transfer of nitrogen and sulfur compounds from algae into the biocrude phase unfortunately cannot be avoided, which is one of the disadvantages of co-processing wood and algae. Wood and algae co-liquefaction is a novel approach in hydrothermal processing, especially when is used as a method to improve the pumpability of lignocellulosic feedstocks.

Lignocellulosic biomass it is probably the most difficult feedstock to pump in continuous hydrothermal systems. However, its high availability compels to find solutions to overcome the challenges raised by these materials. This work introduces new strategies to tackle the problem of wood slurries pumpability and opens new topics for research, that are listed in the section *Future work*.

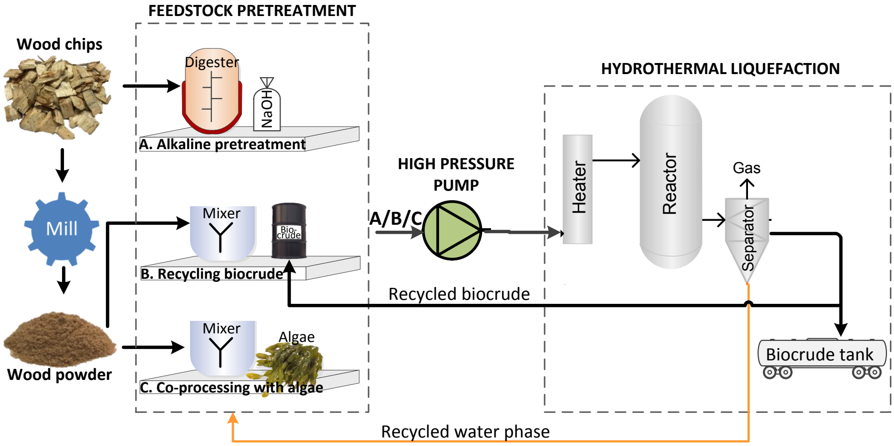


Figure 7.12: Schematic representation of the pretreatment strategies integrated into the continuous HTL process

Future work

The topics that could be of interest for further investigation are as follows:

- To study the impact biocrude recirculation on the biocrude chemical- and elemental composition;
- To develop methods for the reduction of NaOH consumption during alkaline pretreatment and/or NaOH recovery options;
- To determine the distribution of alkalies in biocrude, water phase and solids resulted from hydrothermal liquefaction;
- To identify alternative biomass substrates or industrial waste streams that have water holding capacity and thickening properties and could replace the algae.

Appendices

A Design of the alkaline pretreatment experiments

Choosing the levels of the factors is one of the most important steps in Design of Experiments (DOE). The factor levels should have a large enough range to highlight the output variation and they also should be constrained by the practical considerations. The choice of the levels of the factors in the alkaline pretreatment experiments is further discussed.

NaOH concentration Typically, in Kraft and Soda pulping the NaOH concentration is around 16-20 wt % of wood, [71] which for a wood-water slurry containing 20 wt % wood, corresponds to 3.2 to 4 wt % NaOH in the solution. As mentioned before, the HTL pretreatment targets a more extensive degradation of wood fibers than the pulping process does. Since NaOH reacts with all wood constituents (lignin, cellulose, hemicellulose) it is clear that higher NaOH concentrations will enhance the wood degradation. However it is preferred to keep the NaOH concentration as low as possible due to economical considerations. In order to determine the NaOH concentration range able to disintegrate the wood chips, preliminary experiments at 200 °C were performed (time at Tmax 2h). It was found that 20 wt % NaOH solution is enough to completely dissolve 20 mm wood chips. On the other hand, 5 to 8 wt % NaOH concentration was unable to dissolve 1 mm wood particles. Instead, using NaOH concentration between 8 and 10 wt %, the decomposition of both 1 mm and 20 mm chips was achieved at different degrees. Thus, the low and the high level of NaOH concentration chosen for further investigation was 8 wt % and 10 wt % NaOH solution concentration.

Temperature The temperature range studied is 160-200 °C. The lower limit was established considering the fact that wood delignification starts at about 150-160 °C in alkaline medium and cellulose degradation starts around 170 °C. Similar temperature range 155-175 °C is also used in the Kraft and Soda pulping, thus 160 °C should ensure at least the liberation of cellulose fibers. The upper limit of 200 °C was established based on practical considerations. The pump cost increases when temperature exceeds 200 °C. Same temperature of 200 °C was used in the Shell's continuous liquefaction plant (the HTU plant) to pretreat the wood chips [114]. Their choice might be also influenced by the equipment cost.

Time at Tmax Time at the maximum (final) temperature varies in the pulping process with the chemicals used, chemicals loading and process temperature. In general, the pulping time may vary from 30 minutes to several hours. In this work, the upper limit of time at final temperature was set at 4 h to ensure wood degradation even at low alkali loadings and/or low temperature level. The lower limit is set to 30 min to underline the effect of time on the wood dissolution degree.

Particle size Two particle size ranges were chosen for this study. Small particles have the size in the range of 5-3.15 mm. The upper limit of the particle size is 10-14 mm. In the Kraft process, wood chips of 15-22 mm length and 6-50 mm width are typically used [70].

B Chemical compounds identified in black liquors

Wood constituent	Alkaline degradation products
Cellulose	
Carboxylic acids	Glucoisosaccharinic, Formic, Lactic 3,4-Dideoxypentonic, 3,4-Dideoxyhexaric Glycolic
Polymeric cellulose	
Hemicellulose	
Carboxylic acids	2-Hydroxybutanoic, 3-Deoxypentoic, Xyloisosaccharinic, 2,3 Dideoxypentaric,Lactic, Glycolic, Acetic
Lignin	
Monolignols	4-Hydroxyphenyl compounds
Phenolic acids	4-Hydroxybenzoic, 3,4-Dihydroxybenzoic, Vanilic, Syringic
Phenolic alkanols	Arylethanols, Arylpropanols, Arylglycerols
Other phenolic	Catechol, 3,4-Dihydroxybenzaldehyde
Nonphenolic	Benzoic acid, Aliphatic carboxylic acids
Dimeric aromatic c.	
Lignans	
HMW lignin	>500 Da
Extractives	Tall oil compounds, Fatty alcohols, Diterpene alcohols, Triterpenoids, Steroids, Polyprenols, Fatty and Resin acids

According to [76], [115], [116]

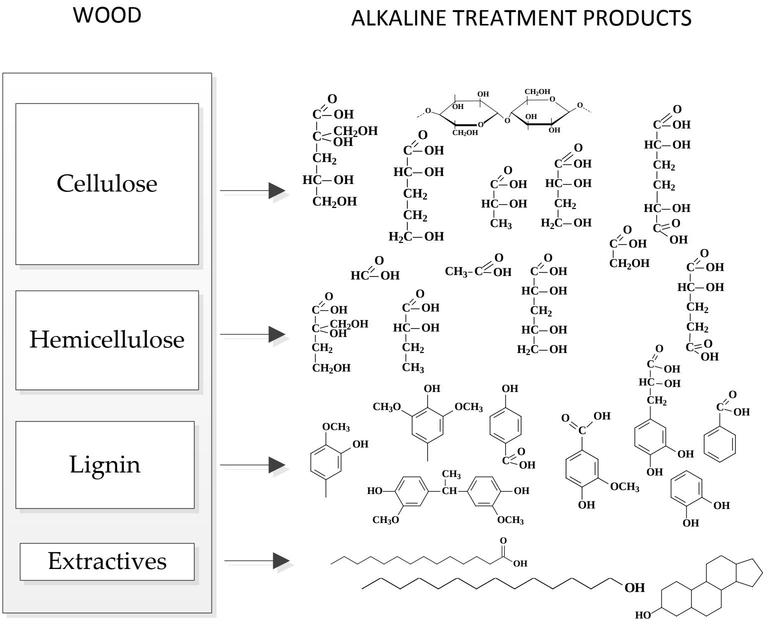
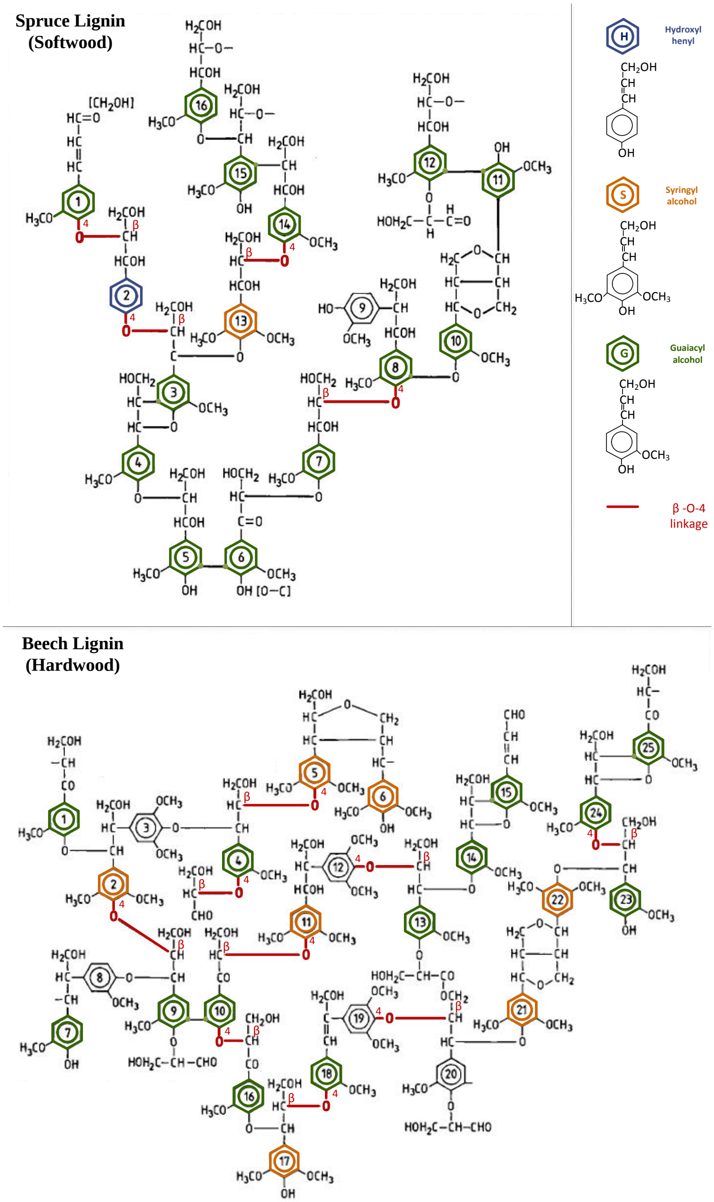


Figure 13: Possible compounds in the alkaline pretreated feedstock

C Structural model of softwood and hardwood lignin



*adapted from [117] and [118]

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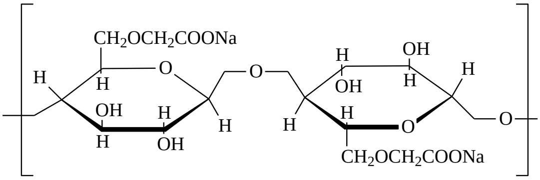
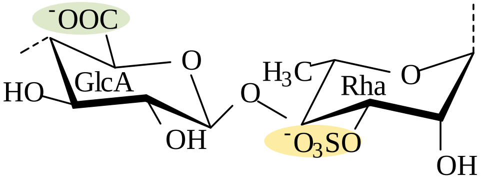
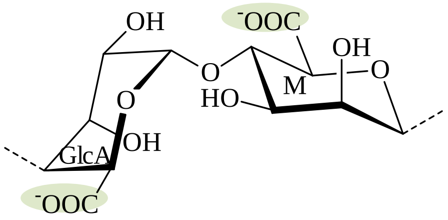
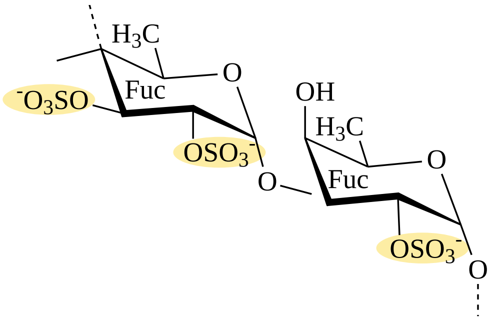
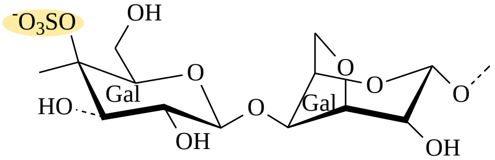
E The chemical structure of algae polysaccharides and carboxymethyl cellulose

Compound	**Properties**
Carboxymethyl cellulose (CMC) 	Soluble in hot and cold water; unstable at low pH; develop viscosity; high water holding capacity [109], [107]
Ulvan (in green seaweeds) 	Soluble in water; develop low viscosity; [119], [120]
Alginate (in brown seaweeds) 	Sodium- and potassium salts are soluble in cold water; form gels in presence of calcium ions; develop high viscosity; water binding properties [121], [119]
Fucoidan (in brown seaweeds) 	Soluble in water and alkaline solutions; develop low viscosity [119]

κ-carrageenan (in red seaweeds) 	Soluble in water; develop high viscosity in hot water; form gels in presence of calcium and potassium ions [122]

GlcA=glucuronic acid; Rha=rhamnose; M=mannuronic acid; Gal=galactose

Table 9: Master table of specific adsorption of water molecules as a function of polar groups and some counterions [108]

Group	Type of water [a]	Cation	n per site [b]
OH	nfb	-	1.35
COO-	nfb	H+	1.8
COO-	nfb	Na+	7.2
COO-	nfb	Ca+	6.3
SO3-	nfb	H+	4.1
SO3-	nfb	Na+	2.0
SO3-	nfb	Ca+	2.3
COO-	fb	H+	2.0
COO-	fb	Na+	14.1
COO-	fb	Ca+	7.4
SO3-	fb	H+	20.2
SO3-	fb	Na+	8.1
SO3-	fb	Ca+	3.8

[a] nf, Non-freezing bound water; f, freezing bound water [b] at relative humidity RH=98

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Part II

Publications

Paper A

Pretreatment methods to obtain pumpable high solid loading wood-water slurries for continuous hydrothermal liquefaction systems

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Research paper

Pretreatment methods to obtain pumpable high solid loading wood–water slurries for continuous hydrothermal liquefaction systems

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ABSTRACT

Feedstock pretreatment is a prerequisite step for continuous processing of lignocellulosic biomass through HTL, in order to facilitate the pumpability of biomass aqueous slurries. Until now, HTL feedstock pumpability could only be achieved at solid mass content below 15%. In this work, two pretreatment methods to obtain wood-based slurries with more than 20% solid mass content, for continuous processing in HTL systems, are proposed. The effect of biomass particle size and pretreatment method on the feedstock pumpability is analyzed. The experimental results show that pumpable wood-based slurries containing 20% solids can be prepared using recycle HTL biocrude as carrier fluid, if particles smaller than 0.125 mm are used. The recycle biocrude concentration used for slurry make-up is strongly affected by the sawdust size distribution. A second pretreatment option is feedstock thermal treatment with alkalis. This method is less sensitive to particle size or wood type. 1 mm particles of either softwood or hardwood could be converted into pumpable liquid feedstock by thermal treatment with NaOH at 180 °C. Wood-water-biocrude slurries viscosity is reduced from 100 to 1000 Pa s to about 1 Pa s, when thermal treatment is applied.

1. Introduction

Despite the fact that Hydrothermal Liquefaction (HTL) offers a promising alternative to liquid fossil fuels and its technical feasibility has already been proven [1,2], the technology is still in the research and development stage. One of the main difficulties in operating continuous HTL systems is related to the pumpability of biomass aqueous slurries due to high pressures required. This is valid especially for lignocellulosic materials (e.g. wood, straws, stover, grass) that are susceptible to phase separation when mixed with water and pressurized.

Several pretreatment methods have been applied to lignocellulosic biomass slurries to enable their processing in continuous HTL systems. However, their solid content could not be increased above 15% dry-matter solid mass content. There is an interest to exceed this limit as higher feed dry matter content can positively impact the process economy. Technological difficulties related to feed preparation restricted the implementation of HTL technology to only few continuous demonstration or pilot plants, operated for short periods and made the batch experiments more convenient for HTL studies.

Hydrothermal Liquefaction is a thermochemical route to convert wet biomass into liquid biofuels. Two of the often touted benefits of HTL are the flexibility in terms of biomass and the ability of using biomass in aqueous medium without spending valuable energy on drying. The process is carried out in aqueous reaction environment at sub- or super-critical water conditions. Most of the studies report reaction conditions in the sub-critical regime with temperature and pressure values varying between 280 and 370 °C and 10–25 MPa [3]. Based on literature, the HTL biocrudes have elemental compositions in the range of 62 %–82 % carbon, 6 %–10 % hydrogen, 1% sulfur, 5 %–25 % oxygen and higher heating values of 28–37 MJ kg^{-1}, depending on the feedstock and process conditions. Promising results have been proven by moving the process conditions into the super-critical regime obtaining higher yields and

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better HTL biocrudes quality (higher carbon and hydrogen mass fraction, higher heating value and lower oxygen mass fraction) [4–6].

The first attempt to process lignocellulosic biomass in a continuous HTL system was the Albany project, the largest continuous liquefaction pilot plant operated from 1978 to 1981. The technology was implemented in two versions, PERC and LBL, distinguished by the feedstock pretreatment method used. The PERC process, developed by Pittsburgh Energy Research Center, used recycle biocrude as vehicle, to facilitate the wood slurries pumpability. In this way, slurries containing around 7% mass content wood particle of 0.42 mm, could be pumped continuously for up to 572 h. To increase the solids concentration and to avoid the recirculation of large amount of biocrude, Lawrence Berkeley Laboratory developed the LBL process, that uses sulfuric acid to prehydrolyze the wood in aqueous environment. In this way, 23% mass fraction of solids could be accommodated but mixtures were diluted back to 12% to obtain pumpable slurries. The low solid loadings, the costs related to wood size reduction and pretreatment, together with other technical difficulties and declining crude oil prices, lead to interruption of the experiments at Albany plant. Other pumping and pretreatment methods of wood biomass for HTL application were tested at small scale in several laboratories around the world like University of Toronto, University of Sherbrooke, Royal Institute of Technology in Stockholm and Technical Research Center in Espoo, Finland, where various pump types, particle sizes and carrier media were tested [1,7]. Despite these efforts, cost effective solutions to produce pumpable high solid loading slurries at high pressures, were not formulated yet.

The difficulties related to lignocellulosic biomass pumpability have drawn the interest to other biomass resources that may be slurried with water without settling or that are already found in a liquid form. This concept was applied in processes like STORS (Sludge to Oil Reactor System), HTU® (Hydro Thermal Upgrading) and CatLiq® (Catalytic Liquidification). The pumpability issues were avoided by using non-wood and easy to handle biomass such as sewage sludge (the STORS process), manure, corn silage, DDGS or liquid wastes (for example the CatLiq process). Recently, algae were also processed in smaller scale continuous plants at University of Sydney and Pacific Northwest National Laboratory (PNNL) [8,9].

Lignocellulosic biomass pretreatment methods are more developed in the field of biochemical conversion technologies. In this case, the pretreatment is designed to separate the biomass components and to facilitate their exposure to bacteria, microorganisms and enzymes. Pretreatment processes using acid hydrolysis, lime, liquid hot water, ammonia and steam explosion are the most studied [10] but their effect on HTL slurries processability is questionable either because of the chemical environment, costs or the ability to form pumpable slurries. For the purpose of producing biocrude through HTL, an alkaline environment is preferable.

Recently, a new HTL technology called Hydrofaction™, was developed by Steeper Energy. A Continuous Bench Scale (CBS1) facility was installed at Aalborg University, in a collaborative effort with the company. The process is carried out at super-critical water conditions, at 390 °C–420 °C and 30 MPa–35 MPa. The plant is processing woody biomass and has a capacity of 20 kg h^{-1} feed. A schematic of the CBS1 process flow is shown in Fig. 1. A pretreatment unit is designed for solid biomass comminution and slurry preparation. A high pressure piston pump delivers the feedstock at 30 MPa–35 MPa. The stream is further heated and fed to the reactors. The product stream is cooled, depressurized and collected for separation of the biocrude from the water and mineral phase [11].

This work investigates two pretreatment methods to obtain 20% solids loading wood-based slurries for HTL applications and for feeding the CBS1 system in particular. The two pretreatment strategies are:

- *Feedstock pretreatment method 1:* Pumping wood biomass using recycle HTL biocrude as vehicle and,
- *Feedstock pretreatment method 2:* Wood dissolution in aqueous medium by thermal treatment with NaOH.

2. Materials and methods

Scandinavian aspen (*Populus tremula*) and pine (*Pinus sylvestris*) sawdust were used to prepare the slurries in this study. The sawdust samples were obtained from wood chips (free of bark), milled and supplied by Euromilling A/S, Denmark. When received in the lab, the sawdust samples were screened and classified in groups of various particle sizes, 105 °C oven dried and stored in plastic bags. The chemical and elemental composition of the wood samples was also determined. The lignin, cellulose and hemicellulose content was determined using a Foss Fibertec™ 1020 Fiber Analyzer and the C, H, N, O content was measured using a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer. Measurements were repeated in duplicate and the mean value is reported in Table 1.

For the preparation of the wood-water-biocrude slurries, aspen sawdust of two different size distributions (SD1 and SD2) and sawdust of 0.125 mm particle size (S125) were used. The sawdust size distribution was determined using a Retsch vibratory sieve shaker. The two size distributions SD1 and SD2 are characterized by the median diameter, d_{50}, of 0.063 mm and 0.121 mm respectively. The sawdust mixtures are distinguished by the concentration of particles smaller than 0.125 mm; 85% in the case of SD1 and 52% in the case of SD2. The third sample constitutes of 0.125 mm particles (between 0.125 mm and 0.250 mm). The bulk density of the sawdust samples was determined by measuring the mass of sawdust in a certain volume. Because large variations between density measurements occurred with this method, tapped apparent bulk density was measured by applying short time vibrations to the sample until the bulk volume reached a stationary level. The composition and characterization of the sawdust samples are given in Table 2. According to data in Table 2, the sawdust bulk density increases with the concentration of fine particles, as noticed by Refs. [12,13]. This may be explained by the ability of fines to structure and compact due to higher degree of freedom.

The biocrude used for the preparation of the wood–water–biocrude slurries was produced from wood at the CBS1 (Continuous Bench Scale 1) facility and is characterized by water mass content of 1% and viscosity of 71 mPa s (at 25 °C). The water used for slurries preparation was HTL effluent water, obtained by phase separation of the product stream at the CBS1. Slurries were prepared by first mixing sawdust with water and biocrude was added after, in mass ratios given in Table 3. Mixing the compounds in two stages, ensures a faster homogenization and avoids sawdust dewatering. Proper stirring was provided to ensure uniform distribution of the solids in the entire volume. Slurries solid mass content was fixed at 20%.

For the alkali thermal treatment experiments, aspen and pine sawdust of 0.125 mm, 0.250 mm and 1 mm particle diameter were used (see Table 5). The cooking liquor was prepared by diluting sodium hydroxide (NaOH) standard solution of 32% from Sigma Aldrich. The experiments were carried out in 1 L batch reactor, electrically heated and equipped with stirrer. In each run, the reactor was loaded with 50 g sawdust and 200 g NaOH solution of 5%, 10% or 20% NaOH concentration. After mixing the components, the reactor was sealed, purged with nitrogen, heater and stirrer

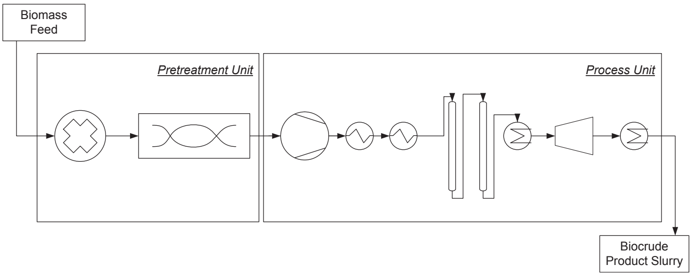

Fig. 1. Schematic of the continuous bench scale (CBS1) unit process flow [11].

Table 1
Chemical and elemental composition of the biomass samples used for slurries preparation.

	Scandinavian aspen (*Populus tremula*)	Scandinavian pine (*Pinus sylvestris*)
Polymer mass fractions - daf (%):		
Cellulose	47.13 ± 0.12	52.36 ± 0.08
Hemicellulose	19.64 ± 0.30	16.30 ± 0.11
Lignin	22.11 ± 0.15	24.79 ± 0.06
Element mass fractions - db (%)		
C	47.91 ± 0.08	47.26 ± 0.07
H	6.47 ± 0.13	6.66 ± 0.05
N	ND	ND
O[a]	45.61	46.08

[a] By difference; ND = not detected; daf = dry ash free; db = dry basis.

Table 2
Characterization of sawdust samples used for wood–water–biocrude slurries preparation.

Sawdust	Bulk density (kg m^{-3})	d_{50} (mm)	Sawdust composition (% mass fraction)		
			0.250 mm–0.125 mm	0.125 mm–0.063 mm	0.063 mm
SD1	429	0.063	15.00	35.00	50.00
SD2	369	0.121	32.98	22.68	28.86
S125	330	–	100.00	0.00	0.00

SD: size distribution, S125: single particles of 0.125 mm.

turned on. When the heater reached the set temperature of 180 °C, the pressure inside the reactor indicated 0.9 MPa and the reactor was kept at these conditions for 120 min. When the reaction ended, the reactor was cooled down to room temperature and the product collected.

The pumpability tests were performed both at laboratory scale and in the bench scale continuous plant CBS1. At laboratory scale, a 12 cm^3 syringe was used for testing the slurries pumpability. The syringe outlet diameter was 3.38 mm and the inlet to outlet diameter ratio 4.7. The slurry pumpability was tested by filling the syringe with feedstock and applying pressure to empty the content. The syringe test was passed if no phase separation or tube blocking occurred. At the CBS1 unit, a high pressure piston pump was used to feed the HTL system at 30 MPa. Comparative tests shown that there is a good agreement between the syringe test and the CBS1 pump performances thus for research purposes the pumpability test was performed at laboratory scale due to its simplicity, reduced amount of materials required and fast results.

Table 3
The effect of particle size and biocrude to water mass ratios on wood–water–biocrude slurry behaviour.

Wood (%)	Water (%)	Biocrude (%)	SD1, $d_{85} = 0.125$ mm		SD2, $d_{51.5} = 0.125$ mm		S125, $d_0 = 0.125$ mm	
			Paste	Solid	Paste	Solid	Paste	Solid
20	70	10	x[a]			x		x
20	60	20	x			x		x
20	50	30	x			x		x
20	40	40	x		x		x	
20	30	50	x		x		x	

[a] Phase separation occurs.

The viscosity of the pretreated feedstock was measured using a Brookfield RV-DV II-Pro rotational viscometer. T-bar spindles were

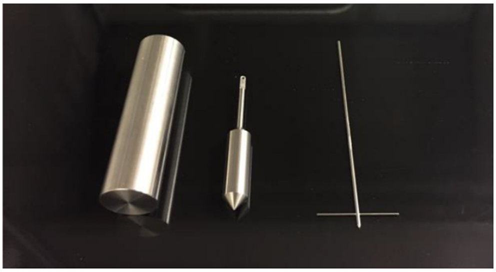

Fig. 2. T-bar, ULA and SC4 spindles used for slurries viscosity measurements with the Brookfield RV-DV II-pro rotational viscometer.

used for the sawdust-water-biocrude slurries and cylindrical spindles SC4-21 and ULA for thermal treated samples (see Fig. 2). Because there is no defined shear rate for the T-bar spindles, the viscosity and rotational speed data were plotted, instead of viscosity against shear rate, to evaluate the slurry flow behavior.

3. Results and discussion

3.1. Feedstock pretreatment method 1: recycling HTL biocrude and water phase for slurry make-up

Fifteen wood–water–biocrude mixtures were prepared in five different mass ratios for each of the three sawdust samples SD1, SD2 and S125. All slurries had solid mass content of 20% and only the biocrude and water concentration varies, as shown in Table 3. As described in Section 2, the mixtures were prepared in two stages in order to avoid separation of the oil and the water phase. Wood was mixed with water first, allowing the water sorption into the wood pores, followed by biocrude addition. Thus, the water phase acts as pores filling material while the biocrude blocks the pores and fills the interparticle spaces and serves as carrier fluid for the moist biomass particles.

The effect of the sawdust particle size and the biocrude to water ratio on the slurry consistency was analyzed using three sawdust mixtures of different size distribution and five biocrude to water ratios. The experimental results in Table 3 show that mixtures prepared had either paste- or solid-like aspect (see also Fig. 3). The main contribution to the phase transition from paste to solid consistency is assigned to the particle size since there are none or only few samples that are sensitive to biocrude to water ratio variation, but their consistency changes readily with the sawdust size distribution.

According to data in Table 3, sawdust samples with higher content of coarse particles (SD125 and SD2) form solid-like slurries at low biocrude and high water concentrations. For these sawdust samples, the phase transition from solid to paste consistency occurs when biocrude to water ratio is equal to or higher than 1. The finely grinded sawdust mixture SD1, is not sensitive to biocrude to water ratio variations and forms paste-like mixtures at any slurry composition. From these observations it may be concluded that coarser particles have higher sorption capacity for both water and biocrude. A possible explanation is that the volume of internal voids but also the number of large pores increase with the particle size. Similar observation was done by other workers when comparing the pyrolysis oil absorption into pyrolysis char and wood [14]. Higher oil absorption capacity occurred for wood compared to char due to higher amounts of large pores in the case of wood. This led to lower solid loading of slurries prepared from wood.

Table 4
Experimental design and pumpability test results for different wood–water–biocrude mass ratio slurries.

Exp. no	Wood (%)	Water (%)	Biocrude (%)	Pumpability
	SD1, $d_{85} = 0.125$ mm, $\rho = 429$ kg m^{-3}			
1	20	70	10	x
2	20	60	20	✓
3	20	50	30	✓
4	20	40	40	✓
5	20	30	50	✓
	SD2, $d_{51.5} = 0.125$ mm, $\rho = 369$ kg m^{-3}			
6	20	70	10	x
7	20	60	20	x
8	20	50	30	x
9	20	40	40	✓
10	20	30	50	✓
	S125, $d_0 = 0.125$ mm, $\rho = 330$ kg m^{-3}			
11	20	70	10	x
12	20	60	20	x
13	20	50	30	x
14	20	40	40	x
15	20	30	50	x

Of all samples prepared, one slurry showed phase separation when mixing was completed. This occurred in the case of the finest grinded sawdust mixture (SD1) when mixed with 70% water and 10% biocrude. The phase separation occurred due to the oversaturation of sawdust with water, the slurry homogeneity being compromised by the excess water. This experiment indicates that the sawdust oversaturation with water should be avoided when wood–water–biocrude mixtures are prepared.

From the discussion above, it can be concluded that coarse particles have better sorption capacity than fines. They easily form solid-like mixtures and paste slurries are obtained only at high biocrude concentration. In contrast to coarse particles, fines form pumpable paste-like slurries at low and high biocrude concentrations providing the possibility to choose the feedstock composition that best fits the process requirements.

The effect of the consistency on the slurry pumpability was tested by subjecting all mixtures prepared to the pumpability test.

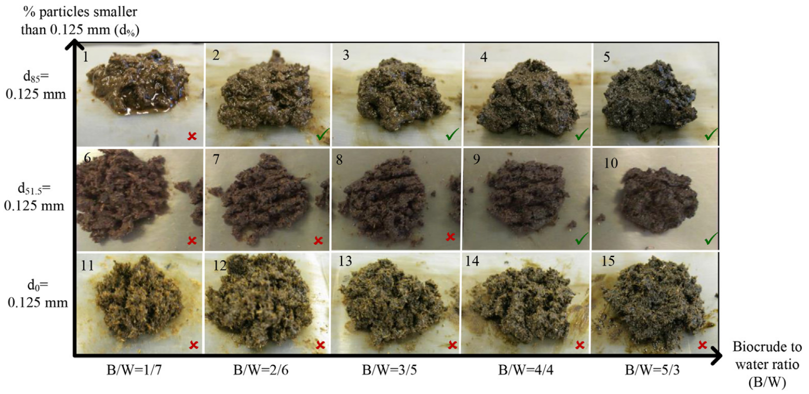

Fig. 3. The effect of particle size and biocrude to water ratio on slurry pumpability.

The results given in Table 4 show that generally, paste-like consistency ensures the slurry pumpability excepting two cases: slurries that undergo phase separation before pumping and slurries obtained from single particles of 0.125 mm. In both cases, the pumpability test failed due to slurry dewatering that occurred when pressure was applied. This underlines the need to avoid the sawdust oversaturation but do not exclude the possibility to pump wood particles of 0.125 mm or coarser. As PNNL suggested in their study on commercial options for feeding slurries for HTL application [15], feedstock pumpability is also a matter of pump design and scale, thus these factors need to be considered when the particle size or the solid loading limitations are set.

From Table 4 it can be noticed that the difficulty to prepare pumpable slurries increases as the particle size increases and the bulk density decreases. More, the flexibility in terms of slurry composition is significantly reduced as bulk density decreases. The correlation between pumping difficulties and low bulk density biomass was also mentioned by other authors [7,15].

The feedstock prepared according to Experiment 9 (20% wood with SD1, 40% water and 40% biocrude) was used as feed at CBS1 unit and was fed continuously for several hours. A high pressure piston pump delivered the feedstock at 30 MPa with a flow rate of 20 kg h^{-1}.

Apart from the fact that size reduction is a highly energy consuming process, fine particles are advantageous in any way, for wood–water–biocrude mixtures pumpability. Due to the small pores size, they provide flexibility in terms of feedstock composition and pump choice, possibly higher solid loadings, lower biocrude and higher water concentrations.

3.2. Feedstock pretreatment method 2: alkaline thermal treatment

The utilisation of low bulk density biomass for slurries preparation involves several limitation such as particle size, solids concentration or liquid phase composition. Thus, wood dissolution may reduce these constraints by breaking the lignocellulosic complex into smaller compounds, soluble in water. Unlike wood–water–biocrude slurries, one phase wood-based feedstock may be obtained with this method. The utilization of recycle biocrude is avoided.

Unlike paper pulp production, carbohydrates dissolution and cellulose fibers fragmentation is desired to facilitate the feedstock pumpability at high pressure. For this reason sodium hydroxide was chosen as reactant, being the most aggressive to polysaccharides dissolution and cellulose fibers degradation but also a good delignification agent. Pretreatment temperature and time were chosen beyond or close to the maximum limits used in soda pulping. Thus, all thermal pretreatment experiments were performed at 180 °C for 120 min. Both aspen and pine sawdust samples and three classes of particle sizes were tested. The experimental design and results are presented in Table 5.

The results show that the consistency of the pretreatment product changes from wood liquid solutions to thick pastes or even solid product by decreasing the concentration of the sodium hydroxide solution from 20 % to 10 % and ultimately to 5%. This trend was expected since it is known that sodium hydroxide promotes the lignin depolymerization and carbohydrates alkaline hydrolysis reactions. In the same time, a significant proportion of sodium hydroxide is consumed to neutralize the hydroxy acids formed by polysaccharides degradation [16]. Thus, it can be concluded that a higher alkali charge will result in a higher rate of wood degradation due to the excess of reactant. However, it was not clear what the boundaries of this process are in terms of sodium hydroxide concentration and what the impact of the particle size is on wood dissolution.

According to the results in Table 5, NaOH concentration is the most important parameter in this pretreatment method. At 20% NaOH concentration the effect of particle size on wood dissolution degree is minor with respect to slurry pumpability. Instead, the phase transition from liquid to paste-like consistency changes when NaOH concentration is reduced to 10%. In this case, the 1 mm wood particles were partially degraded and a two phase but stable slurry was obtained. Further decrease of the NaOH concentration reduces more the degradation effect, leading to the formation of a solid material. The appearance of all five pretreated slurries is shown in Fig. 4.

Pumpability test for the liquid pulps obtained was not required since one phase, liquid wood feedstock was obtained. The other two samples were subjected to the pumpability test. Despite the amount of undissolved wood fibers, the paste slurry could be easily pumped. The solid feedstock obtained, consisting almost entirely of wood fibers, did not pass the pumpability test due to syringe clogging with wood fibers.

These results indicate that the pumpability of thermal treated slurries mostly depends on the wood to sodium hydroxide ratio. For the 1 mm wood particles used, 10% NaOH was the minimum concentration for which liquid pumpable feedstock was obtained. This pretreatment method is advantageous because it offers the possibility of treating a wide range of particle size and most likely various low bulk density biomass streams. However, feed pumpability at 180 °C involves extra costs for pump acquisition. Pretreatment optimization to minimize the processing temperature and the pretreatment costs represents an area for further research. Another aspect that will be investigated is the impact of processing alkaline treated feeds on chemical reaction pathways and consequently on HTL biocrude product quality. There are few considerations based on which a positive impact of lignocellulosic biomass alkaline pretreatment on HTL biocrude production is expected. One of them is that hydrothermal liquefaction under alkaline conditions is considered advantageous because it may increase the biocrude yield and reduce the char formation 3. More, dissolution of the solid matter prior to the HTL conversion might contribute to the reduction of the HTL conversion time considering that the solids dissolution is the rate determining step of biomass liquefaction [17].

Table 5
Experimental design and pumpability test results for thermal pretreatment of wood with sodium hydroxide.

Exp. no	Sawdust		NaOH mass fraction in solution (%)	NaOH:wood mass ratio	Feedstock characterisation		Pumpability
	Type	Size			Viscosity at 24 °C[a] (mPa s)	Phase transition	
1	S. Aspen	0 mm–0.125 mm	20	0.8:1	76.00	Liquid	✓
2	S. Aspen	0.250 mm–1 mm	20	0.8:1	82.40	Liquid	✓
3	S. Pine	1 mm	20	0.8:1	60.96	Liquid	✓
4	S. Pine	1 mm	10	0.4:1	677.00	Paste	✓
5	S. Pine	1 mm	5	0.2:1	–	Solid	x

[a] Shear rate = 49 s^{-1}.

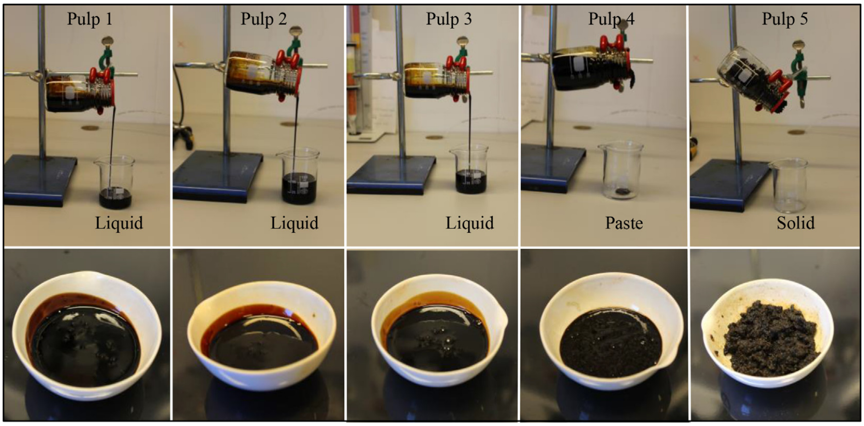

Fig. 4. Thermal treated wood–water slurries; the effect of particle size, wood type and NaOH concentration on the feedstock consistency.

3.3. *Rheological characterization of the slurries*

The slurries viscosity was measured to study their flow behavior and how this is affected by the sawdust particle size and pretreatment method. Similar studies were done for sawdust-aqueous slurries [18,19] or sawdust–biocrude slurries 14 at solid concentration that do not exceed 15%. In this work, viscosity measurements of the sawdust-water-biocrude mixtures and thermal treated slurries, consisting of 20% solid mass loading are reported.

Fig. 5 and Fig. 6 show the effect of a speed ramp on slurries viscosity. Fig. 5 shows the tests performed on wood–water–biocrude slurries prepared from SD1, SD2 and S125 sawdust mixtures containing 20% solids, 30% water and 50% biocrude. Non-Newtonian shear thinning behavior with a steep drop of viscosity is observed at low rotational speed followed by a slow decrease of viscosity beyond 0.21 rad s^{-1} (2 rpm). This trend is specific for very shear thinning fluids and was also noticed in wood-water mixtures 18. The authors attribute this behavior to the solid–liquid phase interactions which makes the material difficult to deform at low rotational speeds. There is a limited effect of the particle size on slurry viscosity. The highest viscosity values correspond to slurries based on 0.125 mm particles. Slurries viscosity values range between 100 Pa s and 1000 Pa s, measured at room temperature.

In Fig. 6, the viscosity of the four pumpable thermal treated slurries (experiment 1–4 in Table 5) is plotted against the shear rate. As in the case of wood-water-biocrude slurries, non-Newtonian shear thinning behavior is noticed. The transition from liquid-to paste-like consistency is marked by the viscosity increase with about ten times. It can be noticed that the increase of viscosity is mostly caused by the NaOH concentration and the effect of wood particle size or wood type is less pronounced. In comparison to wood–water–biocrude mixtures, thermal treatment reduces significantly the slurry viscosity and consequently the pumpability difficulties.

4. Conclusions

Pumpable wood slurries of 20% solid loading could be prepared by mixing the wood–water slurry with recycle HTL biocrude or by

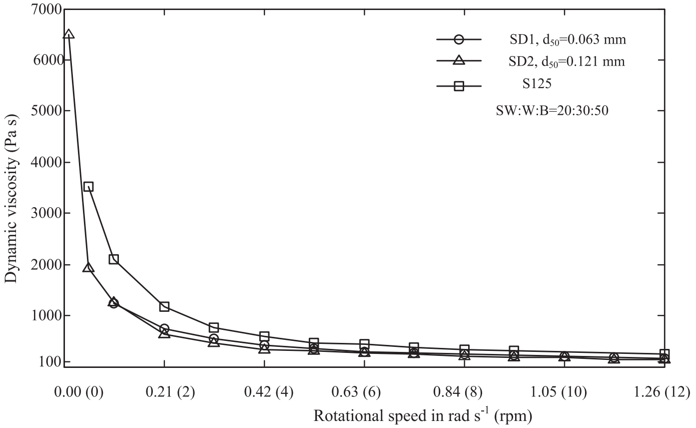

Fig. 5. The effect of particle size on wood–water–biocrude slurries viscosity.

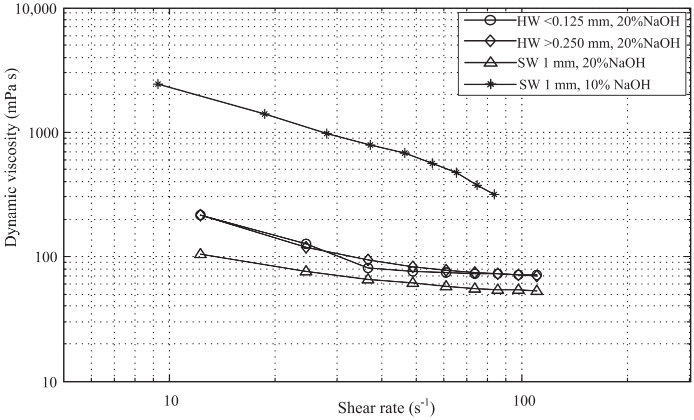

Fig. 6. The effect of particle size, wood type and NaOH concentration on the thermal treated slurries viscosity.

treating the wood–water mixture with NaOH at 180 °C.

Particle size was found to be the most important parameter for the wood–water–biocrude slurries pumpability. Small particles are advantageous for this pretreatment method as they form more easily paste-like slurries. Wood flour with 50% particles smaller than 0.063 mm (the rest smaller than 0.250 mm) ensures the pumpability of 20% solid loading slurries at any biocrude to water ratio between 0.3 and 1.6. The main drawback of this pretreatment method continues to be the costs related to biomass downsizing to these size ranges. However, small particle sizes are needed to prepare high concentrated wood slurries. In the PERC process 0.42 mm wood particles were used to prepare 7% solid loading feeds. The utilization of particles smaller than 0.125 mm, as shown in this study, enables the pumpability of 20% solid mass content mixtures. Thus, there is a trade-off between the benefits of grinding and the benefits of having higher throughput, in the case of wood–water–biocrude feeds.

Wood dissolution by thermal treatment with NaOH is less affected by the wood particle size but is significantly influenced by the NaOH concentration. Pumpable liquid feedstock could be obtained using 10% NaOH concentration for the treatment of 1 mm wood particles. These slurries have lower viscosity compared to the wood–water–biocrude mixtures. This may significantly reduce the pumpability difficulties. Thermal treatment with alkalis might be considered a promising pretreatment strategy for wood and other lignocellulosic biomass, prior to pumping into the HTL system. A more detailed investigation on the effect of particle size and pulping conditions on the feedstock pumpability will be carried out in a future work.

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Paper B

Two-stage alkaline hydrothermal liquefaction of wood to biocrude in a continuous bench scale system

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ORIGINAL ARTICLE

Two-stage alkaline hydrothermal liquefaction of wood to biocrude in a continuous bench-scale system

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Abstract Feedstock pumpability is one of the main obstacles for continuous processing of biomass through hydrothermal liquefaction (HTL), due to their tendency to form heterogeneous slurries. In this work, a novel strategy is proposed to ensure lignocellulosic feed pumpability in HTL processing, even while applying elevated biomass loadings. In the first stage, a pumpable feed is prepared by an alkaline treatment of coarse wood chips at 180 °C, 120-min reaction time, and 0.35 NaOH-to-wood ratio. In a subsequent stage, the treated feedstock is converted into a biocrude in a continuously operated 20 kg/h scale unit. In total, 100 kg of wood paste with 25% dry matter is processed at 400 °C and 30 MPa, demonstrating the usefulness of this two-stage liquefaction strategy. An additional advantage liquefaction of such pretreated wood shows increased biocrude yields with approximately 10% compared to the case where non-pretreated wood is liquefied.

Keywords Lignocellulosic · Feedstock pumpability · Alkaline pretreatment · Biocrude

1 Introduction

In the transition from fossil fuels to renewables, biofuels can potentially replace up to 27% of transportation fuels by 2050, thus contributing to 7%-point reduction in CO_2 emissions, in the 2 °C global temperature increase scenario (IEA, 2012).

Hydrothermal liquefaction (HTL) is a promising route to convert non-food biomass into liquid biofuels. The process operates on an aqueous biomass slurry that is pressurized to maintain water in its liquid state, and then heated to sub- or supercritical water conditions (300–400 °C). At these conditions, biomass decomposes into its major constituents, which subsequently undergo further chemical changes such as depolymerization, dehydration, condensation, and cyclization. The main product of this complex process is the biocrude. The biocrude oil is insoluble in water and is composed of hundreds of oxygenated chemical compounds [1]. Depending on process parameters and the feedstock used, up to 80% of the biomass can be converted into biocrude [2, 3]. The rest of the biomass is converted into water-soluble compounds, gaseous products, and a small fraction of solids.

As continuous processing is a prerequisite for implementing the HTL process at relevant scales, feedstock must be pumpable at high dry matter loading. This has been and still is one of the major obstacles that must be overcome. Because most HTL studies are focused on batch experiments, this problem is often ignored in literature and poorly understood. When a biomass feedstock is processed in a continuous HTL system, slurry dewatering may occur, causing dry processing giving rise to char deposit formation and even clogging. In small scale systems, the problem has been tackled by reducing the particle size below 0.250 mm and/or the solids content below 10% [4–6]. In larger scale continuous systems, where feedstock biomass loading is important for the process economy, efforts have been made to increase the dry matter content of the feed stream. Options tested have been to use an oil vehicle to carry the solid particles (the PERC process), to decompose the wood into fibers by acid hydrolysis (the LBL process) [7], or to use biomass streams that are already in liquid form (e.g., sewage sludge, manure). Even so, the dry matter content of the feedstock could not exceed 15% mass fraction in case of lignocellulosic

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materials [8]. To reduce the energy consumption for particle size reduction and to allow higher biomass loadings, this work proposes a two-stage hydrothermal liquefaction process where extensive biomass dissolution is achieved in the first stage at 180 to 200 °C followed by conversion of the resulting biomass paste into biocrude at sub- or supercritical water conditions (see Fig. 1). The first stage—pretreatment—is performed in alkaline conditions with excess of alkaline reactant; thus, the second stage—HTL—will also be carried out in alkaline environment. Such an alkaline environment is beneficial for both biomass pretreatment and liquefaction, as it may increase the biomass degradation effect, the biomass conversion, and the biocrude yield while reducing the gas and solid products formation [9–16].

Alkaline pretreatment is one of the methods used in the pulp and paper industry to isolate the cellulose fibers from the lignocellulosic matrix or in the second-generation bioethanol production to remove the lignin and to increase the enzymatic hydrolysis of biomass. The most common alkaline reagents used in the alkaline pretreatment of biomass are sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium carbonate (Na_2CO_3), and lime ($Ca(OH)_2$) [17]. According to the pretreatment conditions employed and the alkaline reagent used, the process can be tailored to remove lignin, hemicellulose, and even cellulose from the lignocellulosic matrix. The pretreatment temperature may vary from room temperature with retention times of hours or days, up to 200 °C with shorter retention times. NaOH has the most destructive effect on the lignocellulosic biomass and was used in the first chemical pulping process in the 1850s [18]. Soda pulping process was later replaced with more lignin-selective methods and is scarcely used nowadays for chemical pulp production. However, a pretreatment process similar to soda pulping may be effectively used to prepare pumpable feeds for hydrothermal processing. The aggressive attack of NaOH on all biomass constituents (lignin, hemicellulose, cellulose) will lead to biomass dissolution, reducing considerably the difficulty to handle heterogeneous biomass aqueous slurries under high-pressure conditions. The technical feasibility of using NaOH to solubilize the biomass as pretreatment method for HTL feedstocks has not been reported yet in literature.

In this study, wood alkaline hydrothermal pretreatment followed by hydrothermal liquefaction at supercritical water conditions was performed. First, laboratory-scale experiments were carried out to identify the alkaline pretreatment conditions required to obtain pumpable feedstocks. The optimum pretreatment conditions identified were used to prepare a batch of 100 kg of wood pulp that was converted in a bench-scale continuous HTL system with a capacity of 20 kg/h feed. The effect of the first stage—pretreatment on biocrude oil yield and elemental and chemical composition—was evaluated.

2 Materials and methods

2.1 Raw material

In the pretreatment experiments, hybrid poplar chips were used, while in the bench scale, willow chips were converted. Both poplar and willow, provided by Ny Vraa Bioenergi I/S, Tylstrup, Denmark, were 5-year-old trees cut in the winter of 2014. Bark and chips from branches were removed so only the wood stem parts were used. Poplar chips were 20 mm width and were separated into three particle size classes, small (3 to 5 mm), medium (5 to 10 mm), and large (10 to 14 mm). The willow was cut into chunks of 20 to 70 mm long. The chemical and elemental composition of poplar and willow is given in Table 1. Different raw materials were used for the small- and the bench-scale tests due to the lack of availability of poplar chips in larger quantities. As shown in Table 1, poplar and willow have similar elemental and chemical composition. For this reason, it was assumed that the impact of the raw material type on the pretreatment and HTL experimental results will not be significant.

2.2 Pretreatment experiments

Small scale pretreatment experiments were performed in a 400 cm^3 electrically heated batch reactor. The reactor was equipped with stirrer and cooling coil. For a batch test, 50 g of wood slurry was prepared from 10 g wood chips and 40 g NaOH solution. The concentration of the NaOH solution varied between 8 and 10% mass fraction, corresponding to NaOH-to-wood ratio of 0.32 and 0.40, respectively. Reaction time, particle size, and temperature were varied as well. All mixtures contained 20% wood mass fraction on dry basis (liquid-to-biomass ratio 4:1). After loading and closing the reactor, a heating period of 30 to 40 min was required to reach the set temperature. When reactor temperature reached the set point, the mixture was held at this temperature for desired reaction time (30 to 240 min). At the end of reaction, the reactor was cooled down and the product collected. The reactor, cooling coil, and the stirrer were thoroughly washed with distilled water that afterwards was filtered to recover the

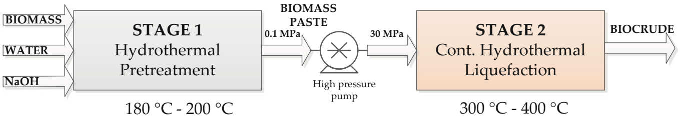


Fig. 1 Conceptual scheme of the two-stage alkaline hydrothermal liquefaction of biomass

Table 1 Elemental and chemical composition of the biomass used for alkaline pretreatment and HTL experiments. Values are given as per dry basis

	Element mass fraction				Polymer mass fraction			Ash (%)
	C	H	N	O[a]	Cellulose	Hemicellulose	Lignin	
Poplar	47	6	n.d.	46	60	18	13	1
Willow	48	6	n.d.	46	53	15	20	2

n.d. not detected

[a] By difference

solids. The amount of solids dissolved during the pretreatment was determined by filtering the pretreatment product on Whatman filter paper (qualitative filter paper grade 413, particle retention 5–13 μm) under vacuum, followed by drying at 105 °C to constant weight. Dried residue was weighed and the percent of biomass dissolved was determined gravimetrically (reported as percent of initial biomass on dry basis).

The objective of the small scale pretreatment experiments was to select the most significant factors that influence wood dissolution in the alkaline pretreatment stage. For these tests, a full factorial design with four variables at two levels and three experiments at the center points was used to study the variation of wood dissolved mass fraction with the process conditions. The process variables and their levels were (1) reaction temperature 160 and 200 °C, (2) reaction time 30 and 240 min, (3) NaOH-to-wood ratio 0.32 and 0.40, and (4) wood particle size 3 to 5 mm and 10 to 15 mm. A total of 19 experiments were carried out for factor screening. For each experiment, the percent of biomass dissolved was measured. Statistical interpretation of the results was performed using the Umetrics MODDE software and the effects of each variable were calculated. For a set of pretreatment conditions (180 °C, 120 min, 0.35 alkali-to-wood ratio), the impact of the alkaline reactant type on wood dissolution was also investigated by replacing the NaOH with Na_2CO_3, KOH, and K_2CO_3.

Bench-scale pretreatment was performed in an 80-L paddle digester, specially designed for pulping of annual plants under industry-like conditions. The equipment was provided by Thünen Institute of Wood Research, Hamburg. The reactor was heated with steam indirectly via a jacket. The digester was filled in the upright position and then was brought in horizontal position for processing. A central paddle, which can operate at different speed, provided a good mixing. One hundred kilograms of feedstock were prepared in four batches. In each batch, 5 kg of willow chips were mixed with 20 kg of NaOH solution of 10% mass fraction (NaOH-to-wood ratio of 0.40) and were processed at 180 °C for 120 min. The heating time was approximately 30 min.

2.3 Pumpability test

The pretreated feedstocks were tested for their pumpability using the syringe test. The syringe test aims at mimicking the flow of the feed forced through an orifice, albeit at lower pressures than HTL. The sample is loaded into the syringe tube and the material is discharged by applying pressure to the plunger. The feedstock is considered pumpable if the feed behaves like a homogeneous material, as shown in Fig. 2 and without slurry dewatering. The advantages of the syringe test are (a) the test is quick and easy, (b) does not require special laboratory equipment, and (c) can be implemented in laboratory or on site. However, although good indicative results come from this test, there are also several drawbacks of the syringe test like (a) the pressure applied is not comparable to the pressure at which the feed will be pumped which means that pumpability is only indicated and (b) the test result depends on the pressure applied, the volume of sample, and the syringe outlet diameter.

2.4 Hydrothermal liquefaction experiments

Small-scale HTL experiments were carried out in 10-mL stainless steel tubular batch reactors at 400 °C and 32–33 MPa for 10 min. In a typical run, approximately 7 g of feedstock was loaded into the reactor. The reactor was purged with nitrogen for removal of residual air and pre-pressurized with approximately 2 MPa nitrogen. All experiments were performed in triplicates. The reactors were heated in a pre-heated fluidized sand bath (Techne SBL-2D) and reached the final temperature in about 2 min. After that, the reactor was removed from the fluidized sand bath and cooled in a water bath. After cooling, the gases were released and the liquid and solid products in the reactor were collected and separated. First, the water phase was poured out of the reactor and filtered using a Whatman filter paper to remove the solids. Afterwards, the reactor was washed with acetone to recover the biocrude oil. The

Fig. 2 The syringe test applied to an alkaline pretreated feed showing the homogeneity of the feed after the test

acetone-biocrude mixture was filtered and evaporated under reduced pressure (0.060 MPa at 40 °C), in a rotary evaporator to remove the acetone. The biocrude obtained after acetone evaporation was mixed with hydrochloric acid (HCl)—5.12 vol.%—and centrifuged to separate the oil phase from the remaining water.

Continuous processing of the alkaline-pretreated feedstock was carried out at 400 °C and 30 MPa. The continuous bench-scale unit has a capacity of 20 kg/h feed and consists of two serial heaters (with heating rate of 200–400 °C/min), two 5-L serial reactors, a cooler, a capillary section for depressurization of the product stream, and a product separation section. The pretreated feedstock was loaded into a 100-kg feed barrel and fed into the system using a high-pressure piston pump. After approximately 4 h of continuous operation, the feed barrel was emptied and the liquid products collected (water phase and biocrude phase). The biocrude was separated gravimetrically from the water phase in a separation funnel and the biocrude yield was measured. The oil was also analyzed for elemental and chemical composition. A schematic diagram of the continuous bench-scale HTL plant is shown in Fig. 3. The system is described in more detail by Pedersen et al. [19].

A summary of the experimental conditions used for biomass pretreatment and HTL at laboratory and bench scale is given in Table 2.

2.5 Analytical procedure

The cellulose, hemicellulose, and lignin content of the biomass samples were determined using a Foss FibertecTM 1020 Fiber Analyzer according to the Foss procedure (modified to eliminate the use of amylase. Elemental analysis was performed with a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer. The water content of the biocrude oils was measured by Karl Fischer titration. Higher heating value of the biomass was measured with an IKA C2000 Basic calorimeter and the ash content was measured at 575 °C for 6 h. The Na and K content in the biocrude ash was quantified using inductively coupled plasma optical emission spectroscopy (ICP-OES).

The chemical composition of the biocrude oils was analyzed by gas chromatography-mass spectrometry (GC-MS). The instrument used was Thermo Scientific Trace 1300 GC equipped with a single quadrupole MS. The analyses were carried out in electron ionization (EI) mode, with an Agilent HP 5-ms column, 30 m long, 0.25-mm ID, and 0.25-µm film thickness. The samples were diluted with dichloromethane (DCM) and analyzed using the following program: 40 °C for 2 min, 5 °C/min to 180 °C, and 10 °C/min to 300 °C.

3 Results and discussion

3.1 Stage 1 hydrothermal pretreatment—screening and optimization tests

Table 3 shows the variation of wood dissolved mass fraction with temperature, solution alkalinity, reaction time, and wood chip size. Based on these values, the impact of each variable

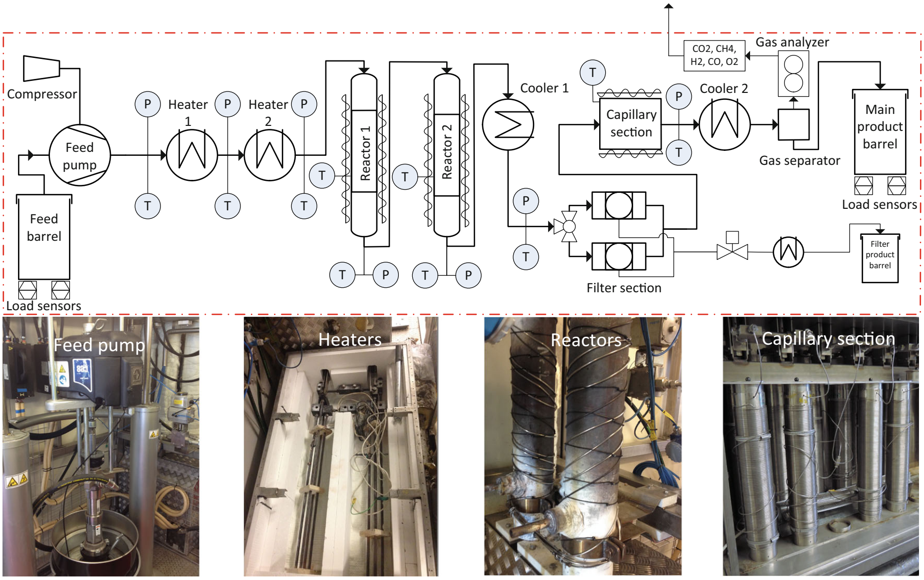


Fig. 3 Process flow diagram of the continuous bench-scale HTL plant [20]

Table 2 Experimental conditions used in the laboratory- and bench-scale experiments

Biomass	Laboratory scale Poplar chips 3–14 mm	Bench scale Willow chips 20–70 mm
Pretreatment conditions		
Reactor volume (L)	0.4	80
Liquor-to- biomass ratio	4:1	4:1
NaOH-to-biomass ratio	0.32–0.40	0.40
Temperature (°C)	160–200	180
Heating time (min)	30–40	30
Reaction time (min)	30–240	120
HTL conditions		
System size	10 mL	20 kg/h
Temperature (°C)	400	400
Reaction time (min)	10	10–15
Other alkalis	none	K_2CO_3

on the amount of wood dissolved was calculated and plotted in Fig. 4.

The results indicate that the pretreatment temperature has the highest impact on wood dissolution followed by reaction time and NaOH-to-wood ratio. The mass fraction of wood chips dissolved increases with about 35% when pretreatment temperature is raised from 160 to 200 °C. The increase of wood dissolved mass fraction with the temperature can be explained by the fact that as temperature increases, more wood constituents suffer degradation. During the heating period (up to 150 °C), carbohydrates start to degrade by peeling reactions of the reducing end groups. As temperature increases to 150–160 °C, advanced degradation of hemicellulose occurs by hydrolysis, increasing the number of reducing end groups and consequently enhancing the polymer chain erosion. Delignification accelerates significantly in the same temperature region [21–23]. However, cellulose degradation starts only around 170 °C [22]. Like hemicellulose, its degradation occurs by peeling reactions and hydrolysis. Higher temperatures enhance cellulose depolymerization until the reducing groups are stabilized [21, 23, 18]. This may explain why wood chips could not be dissolved completely. Even at the most drastic conditions, a solid fraction mainly consisting of short fibers could be separated. The formation of the solids (long chain fibers) may also be related to the high content of biomass in the slurry (20% mass fraction) that may favor the association between polymer chains [21].

Table 3 The variation of the solid dissolved mass fraction (%) with the pretreatment conditions and wood chip size. At the central points (180 °C, 0.36 NaOH-to-wood ratio, 135 min), the mass fraction of wood dissolved on average was 60.7 ± 6.2%

NaOH-T-t[a]	Particle size (mm)		NaOH-T-t[a]	Particle size (mm)	
	3–5	10–15		3–5	10–15
0.32-160-30	23	17	0.40-160-30	27	27
0.32-160-240	34	33	0.40-160-240	53	48
0.32-200-30	62	57	0.40-200-30	71	71
0.32-200-240	71	60	0.40-200-240	87	84

[a] NaOH-to-wood mass fraction-temperature (°C)-reaction time (min)

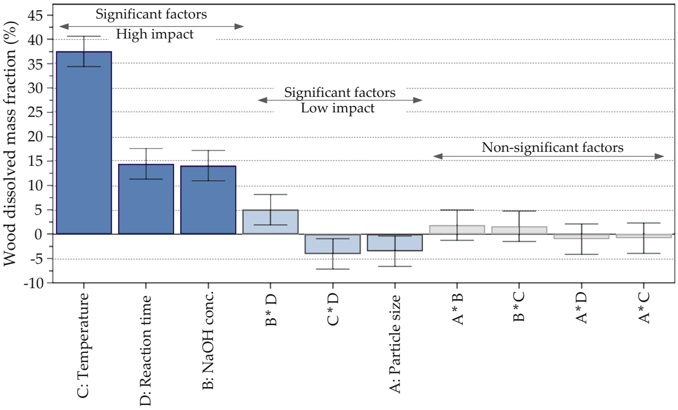
Reaction time and solution alkalinity are the second most important variables. The impact of increasing the reaction time from 30 to 240 min or the NaOH-to-wood ratio from 0.32 to 0.40 is about 15% increase of the biomass dissolved. An interaction between these two factors is indicated in Fig. 4 (B*D). This means that the effect of one of the factors on the output variable (wood dissolved mass fraction) is dependent on the value of the second factor with which it interacts. For example, the average wood dissolved mass fraction increases with the increase of sodium hydroxide concentration by 9% when reaction time is 30 min and by 19% when reaction time is 240 min.

The wood particle size has a negative but relatively low impact on wood dissolution. An increase of wood particle size from approximately 5 up to 14 mm can reduce the amount of biomass dissolved with about 5%. The effect of the alkaline hydrothermal pretreatment conditions on the product aspect can be visualized in Fig. 5.

Designed experiments showed that the impact of wood particle size on biomass dissolved fraction is not significant thus this factor can be eliminated from a further optimization study. More, it was determined that the interactions between factors have a low impact on the output variable which means that the relationship between variables and the output is approximately linear. In this context, the utilization of a single-factor design or a one-factor-at-a-time (OFAT) optimization strategy is appropriate. In this case, the optimization criterion was the pretreated feedstock response to the syringe test (yes/no).

From Table 4 and Fig. 6, it can be noticed that approximately 65% of the initial wood needs to be dissolved to pass the syringe test and that the critical pretreatment conditions are reaction temperature 180 °C, reaction time 120 min, and

Fig. 4 The change of wood dissolved mass fraction (%) when a pretreatment process variable is increased from its low level to high level



NaOH-to-wood ratio 0.35. In Fig. 6d, the effect of NaOH is also compared with other alkaline bases and salts. Sodium and potassium carbonates were less effective in wood dissolution compared to sodium hydroxide. This is because carbonates have poor nucleophilicity, reducing the biomass delignification. Potassium hydroxide was less efficient than sodium hydroxide due to lower molar concentration of KOH solution compared to the NaOH solution at the same reactant-to-wood mass ratio.

The pretreatment experiments and the syringe test applied to the partially dissolved wood-based slurries indicate that pumpable feeds with 20% dry matter content can be obtained by treating the wood chips at 180–200 °C in NaOH solution with NaOH-to-wood ratio of 0.35–0.40. To validate these results, a batch of 100 kg of willow feedstock was prepared at 180 °C with a NaOH-to-wood ratio of 0.40 and 120 min at maximum temperature. A higher NaOH-to-wood ratio than the critical value of 0.35 was chosen because for the bench-scale pretreatment, willow chips with particle size significantly higher than the particles used in the optimization test (up to five times longer and two times thicker) were used. The wood paste obtained passed the syringe test and was used as feedstock for the second stage—HTL in the continuous bench-scale plant.

3.2 Stage 2 hydrothermal liquefaction of pretreated feedstock

3.2.1 HTL in continuous bench-scale system—proving the technological feasibility of continuous processing wood-based feeds with high dry matter content by two-stage hydrothermal liquefaction

Besides liquefaction of alkaline pretreated wood, a baseline test with non-pretreated wood was carried out into the continuous bench-scale system. To pump the non-pretreated wood, biomass grinding to fine powder was necessary as well as the addition of an oil vehicle into the feedstock composition. The same amount of oil vehicle was added to the pretreated wood slurry to obtain a feedstock with similar composition as the

Fig. 5 The impact of process conditions on biomass dissolution and product aspect. Samples visualize the resulting pulps

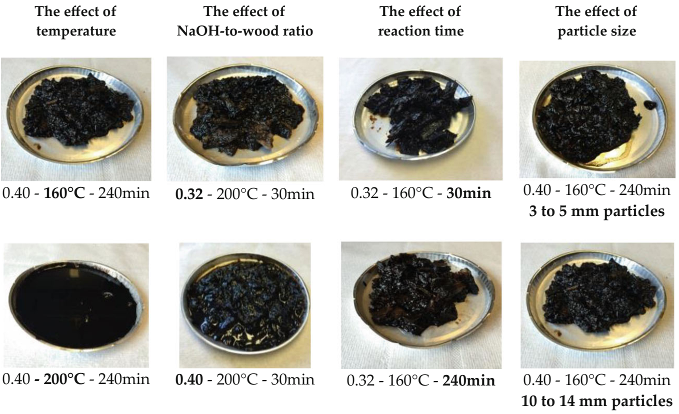


Table 4 Alkaline hydrothermal pretreatment condition optimization using the one-factor-at-a-time (OFAT) strategy. Designed experiments previously performed showed that factor interactions have a low impact on the output and the factor particle size can be eliminated. For the optimization tests, medium size (5 to 10 mm) wood chips were used

Temperature (°C)	NaOH-to-wood ratio	Time at Tmax (min)	Wood dissolved mass fraction (%)	Feed pumpability (syringe test)
Fixed factors: temperature 180 °C, reaction time 120 min				
Variable factor: NaOH-to-wood ratio				
180	0.25	120	28	x
180	0.30	120	55	x[a]
180	0.35	120	65	✓
180	0.40	120	72	✓
Fixed factors: temperature 180 °C, NaOH-to-wood ratio 0.35				
Variable factor: reaction time				
180	0.35	30	56	x[a]
180	0.35	60	62	✓[a]
180	0.35	120	65	✓
180	0.35	180	68	✓
180	0.35	240	71	✓
Fixed factors: NaOH-to-wood ratio 0.35, reaction time 120 min				
Variable factor: temperature				
160	0.35	120	54	x
180	0.35	120	65	✓
200	0.35	120	88	✓

[a] The product consisted of softened wood chips that required maceration

baseline. Upon mixing the pretreated wood with oil, the feed viscosity was reduced which allowed the addition of fresh wood powder. Thus, the biomass loading of the feed containing pretreated wood was increased from 20 to 25% mass fraction. The composition of the two feedstocks is given in Table 5. Batches of 100 kg of each feedstock were prepared and pumped at 30–32 MPa using a high-pressure piston pump and were continuously processed for about 4 h into the HTL system.

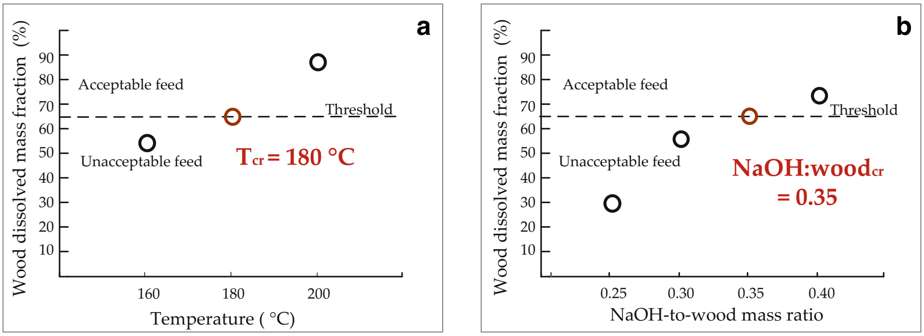
Alkaline hydrothermal liquefaction of wood in a two-stage process is advantageous because it allows processing of feeds with high biomass loading and reduces the need for mechanical downsizing of the biomass. As shown in Table 5, wood chips instead of wood powder were used in the two-stage HTL strategy. More, the biomass loading of the feed in the two-stage process was increased from 18 to 25% mass fraction due to wood dissolution and co-processing with raw biomass. Continuous processing of feedstock based on woody biomass, with such high dry matter content was not reported yet. However, the high amount of NaOH used, between 35 and 40% of the biomass weight, represents the main disadvantage of the alkaline pretreatment process. Methods to reduce the NaOH consumption, e.g., by combining the chemical pretreatment with mechanical operations or alkali reactant recovery by water phase recirculation, need to be further investigated in order to make the pretreatment process economical.

Despite the high fraction of alkalis in the feedstock, the ash content in the biocrude is between 3.9 and 5.3% mass fraction. Na and K represent about 34% of the biocrude ash content, i.e., that less than 5% of the elemental Na and K added into the feedstock was transferred into the biocrude. Therefore, most of the inorganic matter in the feed is transferred into the water phase and is involved in the solid formation. This confirms that water phase recirculation could be an option to recover the alkaline reactant used in the pretreatment stage.

The results given in Table 5 indicate that the yield, the elemental composition, and the heating value of the biocrude oils were not significantly affected by the pretreatment stage. It is worth to mention that the biocrudes analyzed were not obtained under steady-state conditions which are usually achieved after processing 400 kg of feedstock or more. The main focus of the bench-scale test was to demonstrate that by pretreating the wood prior to HTL, pumpable feeds with improved biomass loading can be obtained. To further investigate the effect of wood pretreatment on the biocrude yield and composition, comparative HTL experiments in micro reactors were carried out.

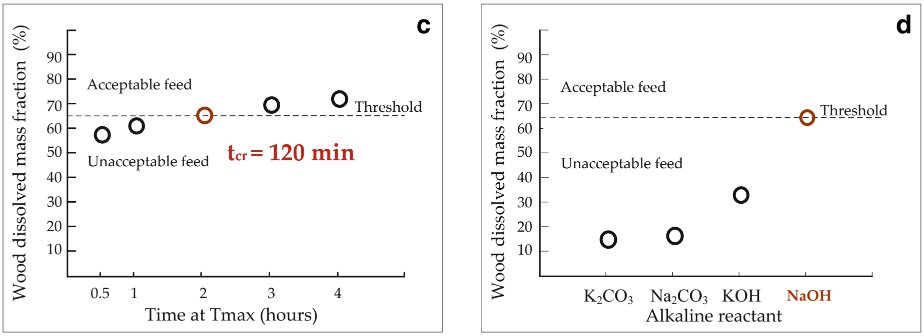
3.2.2 HTL in micro reactors—the effect of biomass pretreatment stage on biocrude yield and composition

The alkaline pretreated wood paste was liquefied at 400 °C and 30 MPa in 10-mL batch reactors without the addition of other additives. A baseline test with non-pretreated wood and identical alkaline reactant concentration was carried out. The feed composition, the yield, and the elemental composition of the biocrudes obtained after the HTL conversion of the two slurries are given in Table 6.



The effect of temperature on wood dissolution at 0.35 NaOH-to-wood ratio and 2h reaction time

The effect of alkali loading on wood dissolution at 180 °C and 2h reaction time



The effect of reaction time on wood dissolution at 180 °C and 0.35 NaOH-to-wood ratio

The effect of alkaline reactant type on wood dissolution at 180 °C, 0.35 alkali-to-wood ratio and 2h reaction time

Fig. 6 Identification of critical alkaline pretreatment conditions. The effect of NaOH loading, reaction time, temperature, and reactant type on wood dissolved mass fraction (%); 5–10 mm poplar wood chips were used in all experiments

Unlike the results obtained in the continuous HTL system, the alkaline pretreatment of wood determined an increase of the biocrude yield with about 10%. This may confirm the hypothesis that due to the addition of raw wood in the pretreated feedstock, the effect of the first stage pretreatment on biocrude yield was reduced. The increase of biocrude yield may be due to several reasons: (a) initial biomass dissolution created a more homogeneous medium for the HTL reactions ensuring a better distribution of reactants and higher mass transfer rates and (b) due to biomass dissolution, which is considered the rate determining step in biomass liquefaction [24], the rates of the reactions generating oil compounds were increased.

Like the biocrude oils obtained in the continuous system, the elemental composition was not affected by the pretreatment stage. Lower oxygen fractions were measured for the oils obtained in micro reactors. This might be related to the oil separation procedures applied in the two cases. Unlike the oils obtained in the bench-scale system that are separated gravimetrically, small scale liquefaction requires oil separation with solvents. During the solvent evaporation process, some of the oil compounds may be lost affecting the elemental composition of the sample. The oil separation procedure may explain also the lower biocrude yield obtained in batch experiments in the case of non-pretreated wood.

From Table 7, it can be noticed that only small variations between the peak areas of the compounds identified by GC-MS exist suggesting a very similar chemical composition of the two biocrudes. The volatile compounds identified were mainly oxygenated aromatic and cyclic structures, typical for HTL biocrudes based on lignocellulosic biomass. Most common compounds were ketones and phenols but alcohols and other compounds were also identified. The small variations in elemental and chemical composition of the biocrudes obtained by one-stage and two-stage HTL suggest that the biocrude quality is not affected by the pretreatment stage, considering that the oils were obtained from the same substrate—wood. However, it is important to mention that the characterization of the biocrudes chemical composition is based only on the volatile fraction of the oil which represents

Table 5 Feedstock composition, biocrude yield, and biocrude elemental composition from continuous HTL of pretreated and non-pretreated wood at 400 °C in 20 kg/h feed capacity system

	Continuous bench-scale system	
	One-stage HTL	Two-stage HTL
Feed		
Biomass	Non-pretreated wood powder	Alkaline pretreated wood chips and raw wood powder
Total biomass in feed (% db)	18	25
Water-to-biomass ratio	2.9	1.8
Alkaline-to-biomass ratio (NaOH and K_2CO_3)	0.27	0.30
Oil medium (%)	18	18
Other additives (ethanol, thickeners) (%)	5.0	5.0
Biocrude		
Yield (% db)	44	44
HHV (MJ/kg)	36	36
C (% db)	72	77
H (% db)	9.6	8.9
N (% db)	0.85	1.1
O[a]	18	13
H/C	1.6	1.4
O/C	0.19	0.13
Na (%)	–	1.2
K (%)	–	0.58
Ash (%)	3.9	5.3

[a] By difference (100-C-H-N)

about half of the sample weight. Characterization of the non-volatile fraction of the biocrude would provide a complete understanding of the effect of biomass alkaline pretreatment on the biocrude chemical composition and will be covered in a future work.

4 Conclusions

This work proves the technological feasibility of preparing pumpable wood feedstocks with high dry matter content by applying a two-stage hydrothermal liquefaction strategy. In the first stage,

Table 6 Feedstock composition, biocrude yield, and biocrude elemental composition from HTL of pretreated and non-pretreated wood at 400 °C in 10-mL micro reactors [25]

	Batch micro reactors	
	One-stage HTL	Two-stage HTL
Feed		
Biomass	Non-pretreated wood powder	Alkaline pretreated wood chips
Total biomass in feed (% db)	20	20
Water-to-biomass ratio	3.6	3.6
Alkaline-to-biomass ratio	0.40	0.40
Other additives	none	none
Biocrude		
Yield (% db)	31	42
C (% db)	84	82
H (% db)	9.4	9.0
N (% db)	1.6	1.6
O[a]	5.3	7.2
H/C	1.3	1.3
O/C	0.05	0.07

[a] By difference (100-C-H-N)

Table 7 Classification of chemical compounds detected by GC-MS in biocrude oils obtained from HTL of non-pretreated (one-stage HTL) and pretreated wood (two-stage HTL) in batch micro reactors (HTL conditions 400 °C, 32–33 MPa, 10 min) [25]

	Chemical compound	Formula	MW	Peak area (%)	
				One-stage HTL	Two-stage HTL
Alcohols	3-penten-2-ol	$C_5H_{10}O$	86	5.0	3.4
	4-methyl-2-pentanol	$C_6H_{14}O$	102	2.3	1.8
	5-octen-1-ol	$C_8H_{16}O$	128	1.5	1.5
	2-methyl-1-hexadecanol	$C_{17}H_{36}O$	256	1.6	1.5
Ketones	Cyclopentanone	C_5H_8O	84	0.43	0.46
	2-methyl-cyclopentanone	$C_6H_{10}O$	98	1.8	1.5
	4-hydroxy-4-methyl-2-pentanone	$C_6H_{12}O_2$	116	2.8	2.7
	3-methyl-cyclohexanone	$C_7H_{12}O$	112	1.9	1.3
	2-methyl-2-cyclopenten-1-one	C_6H_8O	96	0.42	0.5
	2,3-dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	110	0.36	0.5
	3-methyl-2-cyclopenten-1-one	C_6H_8O	96	0.00	0.00
	3,4-dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	110	1.0	0.47
	2,3-dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	110	0.43	0.70
	3,4-dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	110	0.00	0.47
	2,3-dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	110	1.0	1.2
	2,3,4-trimethyl-2-cyclopenten-1-one	$C_8H_{12}O$	124	1.1	1.2
	3-isopropyl-2-cyclopenten-1-one	$C_8H_{12}O$	124	0.0	0.82
	2,3,4,5-tetramethyl-2-cyclopenten-1-one	$C_9H_{14}O$	138	0.6	0.75
	3-isopropyl-2-cyclopenten-1-one	$C_8H_{12}O$	124	0.0	0.00
	2,2-dimethylcyclohexyl methyl ketone	$C_{10}H_{18}O$	154	3.4	3.4
Phenols	Phenol	C_6H_6O	94	0.66	0.83
	m-cresol	C_7H_8O	108	0.55	0.79
	p-cresol	C_7H_8O	108	0.52	0.63
	2-methoxy-phenol	$C_7H_8O_2$	124	1.3	1.8
	2,3-xylenol	$C_8H_{10}O$	122	0.60	0.72
	2-methoxy-4-methyl-phenol (creosol)	$C_8H_{12}O_2$	138	3.0	2.7
	2,3,6-trimethyl-phenol	$C_9H_{12}O$	136	0.93	0.84
	4-ethyl-2-methoxy-phenol(p-ethylguaiacol)	$C_9H_{12}O_2$	152	0.59	0.47
	2,6-dimethoxy-phenol	$C_8H_{10}O_3$	154	0.47	0.51
	2-methoxy-4-propyl-phenol	$C_{10}H_{14}O_2$	166	0.00	0.00
	4-methoxy-3-(methoxymethyl)-phenol	$C_9H_{12}O_3$	168	0.00	0.46
	Butylated hydroxytoluene	$C_{15}H_{24}O$	220	11	11
Esters	2-propenoic acid, 3-(1-acetyl-2,2-dimethylcyclopentyl)-,methyl ester	$C_{13}H_{20}O_3$	224	0.82	1.0
	Terephthalic acid, bis(2-ethylhexyl)ester	$C_{24}H_{38}O_4$	390	0.00	0.00
Others	2-chloro-2-methyl-butane	$C_5H_{11}Cl$	106	18	13
	2,5,8-trimethyl-1,2,3,4-tetrahydro-1-naphthol	$C_{13}H_{18}O$	190	0.00	0.00
	9-hexadecenoic acid	$C_{16}H_{30}O_2$	254	0.63	0.65
Total				64	60

pumpable feedstocks are prepared by alkaline hydrothermal pretreatment of biomass at 180 to 200 °C and NaOH-to-biomass ratio of 0.35 to 0.40. The pretreatment dissolves more than 65% of the biomass, improving significantly the feed pumpability. Comparative studies show that alkaline pretreatment stage has no significant impact on biocrude elemental and chemical composition or heating value. Small-scale batch studies indicate that wood pretreatment prior to HTL increase the biocrude yield with approximately 10% but the continuous bench-scale tests are less conclusive and more data from continuous processing are needed. The wood-based slurry containing 25% dry matter content was successfully pumped at 30 MPa using a high-pressure piston pump. For lignocellulosic biomass, continuous processing of feedstocks with such high solid loading is a first breakthrough.

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Paper C

Application of algae as co-substrate to enhance the processability of lignocellulosic feeds for continuous hydrothermal liquefaction

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Application of Algae as Cosubstrate To Enhance the Processability of Willow Wood for Continuous Hydrothermal Liquefaction

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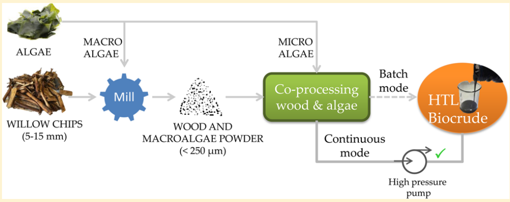
ABSTRACT: This work proposes a novel strategy to improve the continuous processing of wood slurries in hydrothermal liquefaction systems by coprocessing with algae. Of all algae tested, brown seaweeds and microalgae perform best in preventing slurries dewatering, the main reason for pumpability issues with wood slurries. Rheological tests (viscosity–shear rate profile) indicate that the addition of these two algae to the wood slurry causes the highest increase in viscosity, which coincides with improved wood slurries stability and pumpability. Hydrothermal liquefaction of wood-algae slurries at 400 °C and 15 min in 10 mL tubular batch reactors shows that macroalgae slightly decrease the biocrude yield from 28.5 to 21.6–25.5 wt %, while microalgae increase the biocrude yield by more than 40% relative to pure wood liquefaction due to the lower biocrude yields from macroalgae carbohydrates and higher fractions of lipids and proteins in microalgae. Another benefit of microalgae addition is that the total biomass loading and the organic mass fraction of the slurry can be increased by 100% and 90%, respectively. Therefore, when coprocessed with wood, microalgae can improve the wood feedstock pumpability, biomass loading, organic matter, and biocrude yield.



1. INTRODUCTION

Macroalgae have been used for centuries for the extraction of polysaccharides with thickening and gelling properties. Today, brown and red seaweed extracts together represent about 18% of the total market value for food hydrocolloids.[1] Algae are also considered as an important resource for bioenergy production. The high growth rate, high CO_2 absorption capacity, cultivation on nonarable land, and versatility in terms of chemical composition represent important advantages of marine biomass over terrestrial biomass.[2,3] For these reasons, algal biomass was intensively investigated for the suitability to produce a new generation of biofuels, known as third generation biofuels.[4]

Second generation biofuels are those obtained from lignocellulosic biomass such as wood, straw, and other plant biomass. These materials are challenging for conventional biomass-to-biofuel conversion technologies (fermentation, digestion) due to their recalcitrance to biological treatments.[5,6] The chemical structure of lignocellulosic materials can be more easily disrupted under thermochemical treatments such as hydrothermal liquefaction (HTL).[7] In this case, a combination of high pressure (20–30 MPa), high temperature (300–400 °C), and water catalytic properties leads to fast conversion of biomass into biocrude oil compounds. However, in case of HTL processing, another challenge arises from the low density of lignocellulosic matter that limits the dry matter content of the feedstock and promotes phase separation between the solid biomass and the liquid water during pressurization. The phase separation represents a major obstacle to pump aqueous slurries at pressures of 20–30 MPa. Previous work shows that fine milling, chemical pretreatment, or slurry makeup with various additives are compulsory for continuous processing of wood in HTL systems where slurries with a maximum wood concentration of 17 wt % were processed.[8−10] While wood and other lignocellulosic materials require special treatment to obtain pumpable aqueous slurries, continuous liquefaction of algae pastes can be implemented quite easily.[11−13] As described by Elliott et al., algae form “puree-like” feedstocks either simply after mixing of dried algae with water or after dewatering and wet milling of the raw algae.[11,12]

To improve the processability of lignocellulosic aqueous slurries, this work proposes coprocessing wood with materials that have thickening and water binding properties, in this case algae. Microalgae were previously used as costream in HTL of rice husk,[14] manure,[15] coal,[16] macroalgae,[17] or synthetic polymers.[18] These studies, except the case of algae-manure coprocessing, showed that the addition of microalgae into the feedstock has a positive effect on the biocrude yield due to lower thermal resistance and higher conversion into biocrude of microalgae compounds. Coprocessing of wood with macro- and microalgae has not yet been reported. Moreover, the coprocessing of algae and lignocellulosics with the purpose to

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Table 1. Chemical Composition, Elemental Composition, and Ash Content of Algae Samples (wt %, Dry Basis)

	willow (genus *Salix*)	green seaweed *Ulva* spp.	brown seaweed *L. digitata*	red seaweed *P. palmata*	microalgae *C. vulgaris*
proteins		7.8 ± 0.0	10.5 ± 0.0	20.4 ± 0.0	40.3 ± 0.0
lipids		6.8 ± 0.0	10.1 ± 1.2	9.1 ± 0.8	16.3 ± 0.2
carbohydrates	68.1[a]	54.8[b]	44.4[b]	47.6[b]	35.4[b]
C	47.9 ± 0.0	41.7 ± 0.8	36.5 ± 1.6	37.1 ± 0.7	50.1 ± 0.2
H	6.1 ± 0.0	6.3 ± 0.2	5.1 ± 0.1	5.5 ± 0.3	7.1 ± 0.4
N	0.01 ± 0.0	1.7 ± 0.0	2.3 ± 0.0	4.5 ± 0.0	8.8 ± 0.0
S	nd	1.2 ± 1.7	2.2 ± 0.5	1.2 ± 0.1	1.1 ± 1.1
O[c]	44.1	18.6	18.9	28.8	24.9
ash	1.9 ± 0.1	30.5 ± 0.5	35.0 ± 0.4	22.9 ± 0.1	8.0 ± 0.5

[a]Represents the sum of cellulose and hemicellulose. [b]By difference (100-ash-proteins-lipids). [c]By difference (100-C-H-N-S-ash); nd = not detected.

improve the feedstock texture and flow behavior is a novel approach in HTL feedstock pretreatment and also an unexplored topic in the literature.

Microalgae are the most investigated marine biomass for hydrothermal liquefaction, probably due to the fact that microalgae contain higher mass fractions of lipids and proteins and have lower ash content as compared to macroalgae. Higher biocrude yields from microalgae as compared to macroalgae are in general obtained, although large variations are noticed in both cases. For microalgae, the biocrude yields reported in the literature range between 18 wt %[19] and 83 wt %[20] (on dry ash free basis) and for seaweeds between 4 wt %[21] and 36 wt %[22] (on dry ash free basis). The higher biocrude yields from microalgae liquefaction are in general explained by the higher fractions of lipids and proteins in microalgae as compared to seaweeds, but the hydrothermal liquefaction conditions (temperature, reaction time, and catalyst) also play an important role. Temperatures in the vicinity of the critical temperature of water[23−25] and short reaction times (up to 15 min)[26,27] were found to be the most advantageous with respect to biocrude yield. Alkaline catalysts are advantageous for algae with a high content of carbohydrates such as macroalgae, because it reduces char formation and increases the biocrude yield.[19,28] The most frequent solvent used for the extraction of algae-derived biocrude is dichloromethane, but acetone, chloroform, or diethyl ether was also reported.

This work investigates the technical feasibility of using seaweeds (green, brown, and red) and microalgae to improve the processability of wood aqueous slurries. The main reason for using algae as wood slurries stabilizers is that macro- and microalgae contain polysaccharides with thickening and water binding properties. These properties could prevent feedstock dewatering and solids settling. Four different algae species are compared in terms of thickening properties, water holding capacity, and the ability to improve wood slurries pumpability as well as the variation of these properties in alkaline conditions. The impact of wood and algae coprocessing on the biocrude yield, elemental composition, and boiling point distribution is also studied.

2. MATERIALS AND METHODS

2.1. Raw Material. Brown seaweeds, *L. digitata* (cultivated in open ocean), and red seaweed, *P. palmata* (wild harvested), were provided by Ocean Rainforest, Faroe Islands. The algae were collected in March 2016. Green seaweed *Ulva* spp. and microalgae *Chlorella vulgaris* were obtained from commercial sources (Porto-Muiños S.L. and Algomed). Fresh algae were dried at room temperature for 3 days and then in an oven at 60 °C. Willow (genus *Salix*) was collected at Ny Vraa Bioenergi I/S, Tylstrup, Denmark. Trees were harvested at two years old, in winter 2014. The chemical composition of the algae is given in Table 1. Willow consists of 53.3 wt % cellulose, 14.8 wt % hemicellulose, 20.3 wt % lignin, and 1.9 wt % ash, on dry basis.[29]

The seaweed and the willow were milled using a laboratory scale cyclone mill to obtain a powder that passed through a 60 mesh (250 μm). The size distribution of the willow and the seaweed powders is given in Table 2. For the analysis of lipid content, microalgae and seaweed powders were further milled with a Retsch CryoMill to a particle size below 100 μm to facilitate the extraction (the extraction procedure is described in section 2.2).

Table 2. Size Distribution of Willow and Algae Powders

		size distribution (wt %)		
	d_{50} (mm)	0.250−0.125 mm	0.125−0.050 mm	<0.050 mm
willow	0.130	38.0	23.0	25.2
seaweeds	0.115	38.7	34.7	20.3

2.2. Analytical Methods. *Proximate Analysis.* The ash content of biomass was measured at 575 °C according to the standard procedure ASTM E1755-01.[30]

Elemental and Chemical Analysis. The carbon, hydrogen, nitrogen, and sulfur content of the biomass and the biocrude oils was measured with a vario MACRO cube Elementar analyzer. Measurements were performed in duplicate, and the average values are reported. The oxygen content was determined by difference. The content of protein in algal biomass was derived from the elemental analysis using the nitrogen-protein conversion factor (N-factor) of 4.58.[31] The N-factor was determined as an average of 10 marine microalgae species with a standard deviation of 0.11. The content of lipid in algal biomass was determined by extraction with a chloroform−methanol mixture in a Soxhlet extractor.[32,33] Approximately 2 g of algae was weighed into a 37 mm × 130 mm single thickness cellulose thimble. The lipids were extracted with 350 mL of solvent (chloroform−methanol 2:1 v/v) for 5−6 h until a total of 16−18 cycles were completed. The solvent was removed in a rotary evaporator at 35 °C, and afterward the samples were dried for 1 h at 105 °C. The content of lipid was determined gravimetrically. Lipid content was performed in duplicate, and mean values are reported. The carbohydrates were determined by difference. The results presented in Table 1 are similar to the values reported in the literature; the seaweeds are rich in carbohydrates (between 44 and 55 wt %) and less abundant in proteins (between 8 and 22 wt %) and lipids (between 7 and 10 wt %).[22,34] Microalgae have

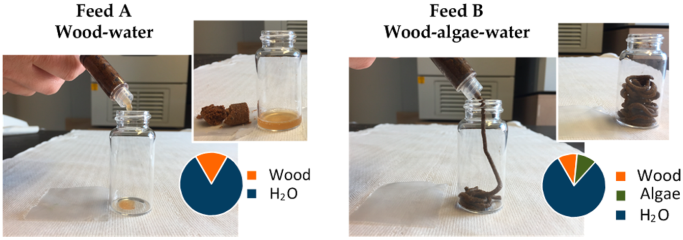

Figure 1. Syringe test applied to a mixture containing 15 wt % wood and 85 wt % water (feed A) and a mixture containing 10 wt % wood, 10 wt % brown seaweed, and 80 wt % water (feed B).

higher fractions of proteins (40 wt %) and lipids (16 wt %) and a lower fraction of carbohydrates (35 wt %) as compared to seaweeds.[19,23]

Thermogravimetric analysis (TGA) was performed with a PerkinElmer STA6000 TG/DSC instrument in nitrogen atmosphere. The samples were heated from 50 to 1000 °C with a heating rate of 10 °C/min. The gas flow rate was 20 mL/min.

Functional Properties of Biomass. The water holding capacity (WHC) of biomass was determined by the centrifugation method as described by Sosulski[35] and Yaich et al.[36] Wood and algae solutions with 12 wt % biomass loading were prepared in preweighed centrifuge tubes. The samples were left to rest at room temperature for 60 min followed by centrifugation at 3000*g* for 25 min at 25 °C. The supernatant liquid was removed, and the tubes were placed mouth down at an angle of 15−20° in a drying oven at 50 °C for 25 min. The percentage of water absorbed was determined gravimetrically and was expressed as the amount of water retained by 1 g of dry solid sample.

The viscosity of the algal slurries was measured with a rotational viscometer Brook RV-DV II-Pro, according to the standard procedure ASTM D2196-86,[37] at 20 °C. Appropriate spindles were used according to the viscosity range measured.

2.3. Slurry Preparation. The wood−algae mixtures were prepared by first mixing the algae powder with the liquid agent (water or NaOH 1 M) followed by the addition of wood. The mixtures were left to rest for 60 min before any test.

2.4. Slurry Stability Tests. The stability of the wood, algae, and wood−algae slurries was evaluated according to the syringe test[38] and the centrifugation test. The syringe test evaluates if dewatering occurs when the slurry is passed through an orifice. The test sample is loaded into a 12 cm^3 syringe with outlet diameter of 3.38 mm and inlet to outlet diameter ratio of 4.7. Dewatering of the slurry is visually monitored while the slurry is discharged. Mixtures that pass through the syringe homogeneously are considered stable, and those that separate into two phases, that is, a liquid phase that is discharged and a solid cake that remains in the syringe tube, are considered unstable. Examples of stable and unstable slurry evaluated with the syringe test are illustrated in Figure 1. The centrifugation test reproduces the conditions used to determine the water holding capacity of biomass (3000*g*, 10 min). Stable and unstable slurries according to the centrifugation test are illustrated in Figure 2. Comparative studies showed that there is a high probability for successful feedstock pumpability if both the syringe and the centrifugation tests are passed. The comparison between the laboratory scale pumpability tests and the performance of a high pressure piston pump is based on the experience gained from operating the continuous bench scale HTL plant installed at Aalborg University, described elsewhere.[10] The continuous HTL system includes a high pressure piston pump that pressurizes the feedstock to 35 MPa.

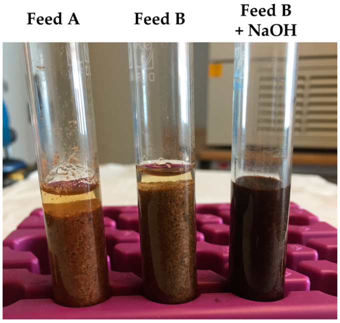

Figure 2. Samples after centrifugation at 3000*g* for 10 min; feed A contains 15 wt % wood and 85 wt % water, feed B contains 10 wt % wood, 10 wt % brown seaweed, and 80 wt % water, and feed B+NaOH contains 10 wt % wood, 10 wt % brown seaweed, and 80 wt % solution NaOH 1 M.

2.5. Hydrothermal Liquefaction Experiments. HTL experiments were carried out in 10 mL stainless steel tubular batch reactors at 400 °C for 15 min. In a typical run, approximately 7 g of feedstock was loaded into the reactor. The biomass was mixed with NaOH 1 M solution to obtain feeds containing 15 wt % wood-based slurries, 20 wt % wood-seaweed slurries, and 30 wt % wood-microalgae mixture. Detailed composition of the feedstock used for the HTL experiments is given in Table 6. The reactor was purged with nitrogen for oxygen removal and prepressurized with 2 MPa of nitrogen. All experiments were performed in duplicate. Two reactors were inserted simultaneously into a preheated fluidized sand bath (model: Techne SBL-2D) and reached the final temperature in about 2 min. After 15 min, the reactors were removed from the sand bath and rapidly cooled in a water bath followed by products deparation according to Figure 3. After being cooled, the reactor content was poured into a vessel and thoroughly rinsed with acetone. The liquid poured from the reactor was mixed with the acetone used to wash the reactor and filtered for solids separation. The solids were further washed with distilled water to dissolve the water-soluble inorganics and dried overnight at 105 °C. The acetone filtrate was evaporated under reduced pressure in a rotary evaporator to remove the acetone. The biocrude was redissolved with dichloromethane (DCM), and the mixture was transferred into

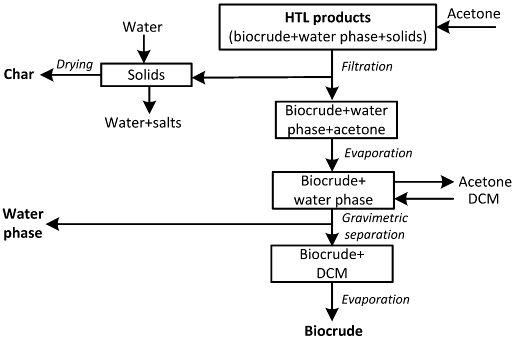

Figure 3. Schematic representation of the HTL product separation procedure.

a separation funnel. A layer of water phase separated from the biocrude–DCM mixture, which was then removed, and the biocrude–DCM mixture was poured into a preweighed collection tube. The DCM was evaporated at atmospheric pressure until the sample reached a constant weight. The biocrude was analyzed for moisture content and elemental analysis. The biocrude yield was expressed as the ratio between the biocrude on dry basis and the biomass on dry ash free basis.

3. RESULTS AND DISCUSSION

3.1. Utilization of Algae as Wood Slurries Stabilizers.

The difference in density between wood and water is the main reason for wood slurries separation. Wood particles separate either by settling or by floating as shown in Figure 4 (left). Small wood particles (<100–200 μm) have a large number of open, accessible pores that are rapidly filled with liquid, causing the wood particle density to increase and thereby settling. The sinking of small wood particles is possible due to the fact that the density of the wood cell wall is higher than the density of water, 1.5 g cm^{-3}.[39] Coarse particles contain a larger number of internal inaccessible pores; thus the density of these particles will not increase significantly when immersed in water. These particles will have a tendency to float. To avoid settling or floating wood particles, the viscosity of the liquid phase can be increased. This will restrict the mobility of wood particles and will ensure a uniform distribution of the solids in the slurry. Slurry dewatering that occurs under high pressure conditions due to the low interactions between the biomass and the liquid phase can be avoided by adding materials with a high water binding capacity. Usually, materials with water binding capacity also have thickening properties. Examples of such materials are some carbohydrates contained in algae. Algae addition into wood slurries may cause both viscosity and water holding capacity increases, and consequently improve the wood slurries stability (see Figure 4, middle and right).

The ability of algae to develop viscosity, change the slurry texture, and prevent dewatering might be related to the presence of hydrocolloids in algae. Hydrocolloids are long-chain hydrophilic polysaccharides that form dispersions and have a common property: thickening. Some hydrocolloids are also able to provide stickiness or to form gels.[40] Polysaccharides such as ulvans (green seaweeds), alginates (brown seaweeds), fucoidans (brown seaweeds), carrageenan (red seaweeds), or agar (red seaweeds) are common thickeners and gelling agents used in the food industry and other sectors. In some seaweed species, these hydrocolloids represent the main fraction of polysaccharides, which makes the algae a good source of natural thickeners and gelling agents.[41] For example, alginates may constitute between 10 and 47 wt % of the dry weight of brown algae,[41] carrageenan up to 50 wt % and agar between 20 and 30 wt % of the dry weight of some red seaweeds species,[41,42] and ulvans between 8 and 29 wt % of the green seaweeds.[43] The thickening mechanism is based predominantly on nonspecific entanglement of polymer chains. This requires that the polymers are in contact, and hence their concentration in solution needs to be sufficiently high.[40] Other factors that affect the thickening effect are the polymer chain length, molecular weight, type of solvent, temperature, and time.[44]

In Table 3, wood slurry containing 15 wt % dry matter is compared to algae slurries of identical solid loading in terms of texture, stability under the syringe, and the centrifugation test and viscosity. With respect to the slurry texture, seaweeds and microalgae form with water pastes with homogeneous aspect, unlike wood that forms two-phase, noncohesive mixtures with water. The type of algae also affects the slurry aspect; green seaweeds form yield stress fluids (that flow only when stress is applied), thicker than brown- or red seaweeds slurries that form with water free-flowing, thin pastes. Microalgae slurries with 15 wt % dry matter content even have a lower viscosity than those obtained with brown or red seaweeds. The transition of microalgae from a liquid-like to a paste-like consistency occurs

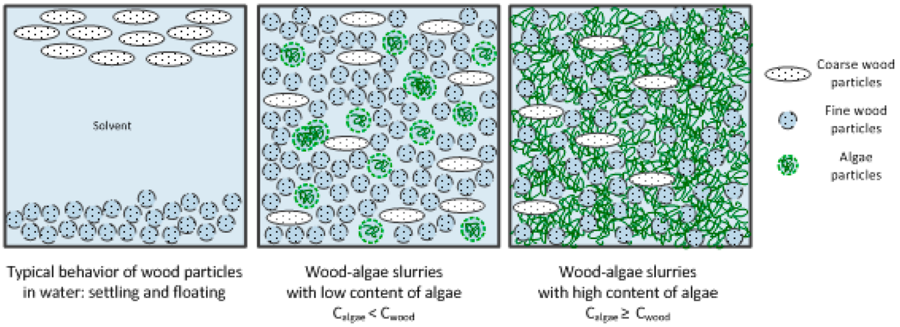

Figure 4. Schematic representation of phase separation in wood aqueous slurries and stabilization with algae hydrocolloids; a high concentration of algae in the slurry is needed to ensure the contact and the entanglement of hydrocolloids.

Table 3. Characterization of Wood and Algae Slurries in Water and NaOH 1 M Solution: Effect of Biomass Type, Biomass Loading, and Solution pH on the Slurries' Stability, Viscosity, and Texture

		slurry texture		dewatering syringe test[c]		dewatering centrifugation test[c]		viscosity[a] (Pa s)	
biomass type	solids dry matter content (wt %)	H_2O	NaOH	H_2O	NaOH	H_2O	NaOH	H_2O	NaOH
wood	15	two-phase material, noncohesive	nonflowing, thick paste, noncohesive	yes	yes	yes	yes		
green seaweed	15	nonflowing, thick paste, cohesive	flowing, thin paste, cohesive	no	yes	yes	yes	22	1.7
brown seaweed	15	flowing, thin paste, cohesive	nonflowing, thick paste, cohesive	no	no	yes	no	29	~300[b]
red seaweed	15	flowing, thin paste, noncohesive	flowing, thin paste, cohesive	no	no	yes	yes	5	30
microalgae	15	flowing, liquid	flowing, liquid			yes	yes	~0.09[b]	~0.16[b]
microalgae	30	nonflowing, thin paste, cohesive	nonflowing, very thick paste, cohesive	no	no	no	no	65	

[a] Dynamic viscosity measured at a shear rate of 2 s^{-1} at 20 °C. [b] Values predicted by extrapolation of the viscosity measurements performed at shear rate values below or above 2 s^{-1}. [c] yes = dewatering occurs, no = dewatering does not occur.

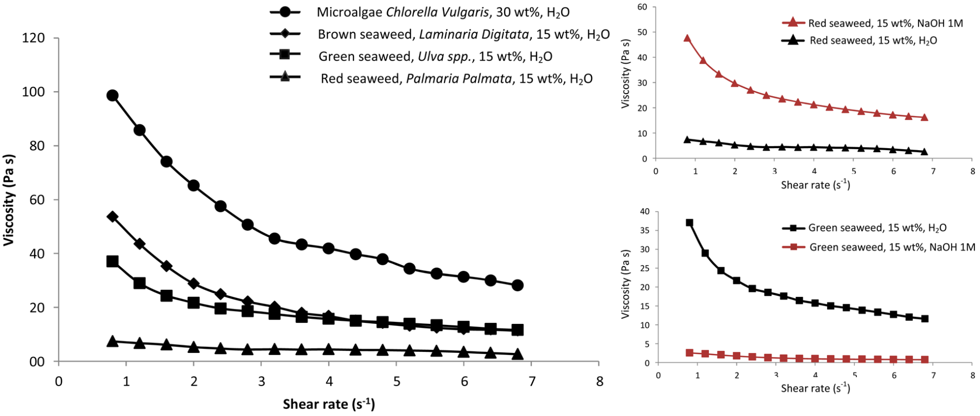

Figure 5. Viscosity of the algae pastes in water and sodium hydroxide solution against the shear rate.

at around 30 wt % dry matter content. At this concentration, the microalgae slurry is a thin instead of a free-flowing paste. With respect to slurry stability (solids dewatering), there is a clear distinction between wood and algae slurries. With water, all algae form stable mixtures (according to the syringe test), while the wood slurry separates when passed through the syringe, as shown in Figure 1. Under centrifugal forces, 15 wt % wood, 15 wt % seaweed, and 15 wt % microalgae slurries undergo dewatering, while the 30 wt % microalgae slurry resists dewatering, as shown in Table 3. The presence of NaOH prevents brown seaweed slurries dewatering under centrifugation despite the fact that for both brown and red seaweed slurries the viscosity increases in the presence of NaOH. A thickening effect is also noticed for the 30 wt % microalgae slurry in the presence of NaOH. For the green seaweeds, alkaline conditions have a negative impact on the slurry stability and also a thinning effect. The results in Table 3 show that, unlike wood, algae form cohesive mixtures (stick together) and are less prone to dewatering. In general, alkaline conditions determine an increase of algae slurries viscosity and improve the stability of the brown seaweeds slurry. The results in Table 3 can be summarized by two main observations: (1) algae slurries have better stability than wood slurries, and (2) the most stable feeds are the 30 wt % microalgae and the 15 wt % alkaline brown seaweed slurries.

The viscosity−shear rate profiles of the 15 wt % seaweed slurries and the 30 wt % microalgae slurry are shown in Figure 5. All algae slurries show a shear thinning (pseudoplastic) flow behavior, typical for most thickeners above the critical overlap concentration.[45] Figure 5 (left-hand side) shows that the 30 wt % microalgae slurry has the highest viscosity followed by the brown seaweed, green seaweed, and red seaweed slurries. From Figure 5 (right-hand side) and Table 3, it can be noticed that NaOH increased the viscosity of all algae pastes, except the green seaweed. For brown seaweed and microalgae, the slurry viscosity in alkaline conditions increases more than 10-fold as compared to neutral conditions, while for the red seaweed the slurry viscosity increases about 6-fold. Green seaweed *Ulva* spp. shows a significant decrease in viscosity in the presence of alkalis, 12−14-fold lower than in neutral conditions. The variation of slurries viscosity with the algae type may be related to the chemical structure, molecular weight, chain length, and linearity of the algae polysaccharides. Ulvans, the main polysaccharides of green seaweeds, are water-soluble and develop low viscosity due to the branched structure and short chain length.[43] The decrease of green seaweed slurry viscosity in 1 M NaOH solution may be related to the formation of the sodium form of ulvans that are not able to form gels.[43] Brown seaweeds are rich in alginates (gelling agent) and fucoidan (viscosifier). Fucoidan is soluble in both water and alkaline solutions,[46] but for alginates only the sodium salt is water-soluble.[44] The addition of alkalis to an algae aqueous solution generates sodium-alginates,[47] which may explain the increase of brown seaweed viscosity in NaOH solution. Red seaweeds are abundant in agar and carrageenans, well-known and exploited gelling agents. Agar is not soluble in cold water, while of the three types of carageenans (kappa, iota, and lambda) only the lambda carrageenan and the sodium salts of kappa and iota are soluble in cold water.[48] Like brown seaweed, the formation of sodium salts of carrageenan may explain the increase of the red algae slurries viscosity in NaOH solution. The thickeners in microalgae are not well described in the literature; thus it is not clear which are the compounds that develop viscosity in *Chlorella vulgaris* slurries.

The next question of this study was how much wood can be coprocessed with algae without affecting the algae slurry stability. For this purpose, brown seaweeds were mixed with wood in different ratios, to prepare mixtures with 20 wt % dry matter content. The slurries stability was evaluated according to the syringe test. As shown in Figure 6, the minimum ratio at which wood-brown seaweed slurries are stable is 1/1, which was defined as the critical algae-to-wood ratio (R^*). Below this point, the mixtures undergo separation, and above the critical ratio the slurries stability and consistency do not change. Using the algae-to-wood ratio of 1/1, mixtures of wood and other algae types in both water and NaOH solution were prepared.

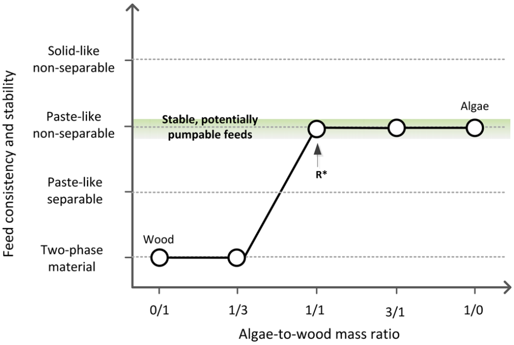

Figure 6. Variation of feed stability (according to the syringe test) with the increase of algae mass fraction; a study case for mixtures of willow and brown seaweed *Laminaria digitata*; total dry matter of wood–algae slurries is 20 wt % and of wood slurry is 15 wt %.

The results in Table 4 show trends similar to those observed for the pure algae pastes (Table 3): all wood–algae mixtures are stable according to the syringe test, except the wood–green seaweed mixture. There are also important differences between the single-component and the two-component wood–algae slurries. One of them is the observed instability of the wood–microalgae slurry in water, when subjected to the centrifugation test. Apparently, the presence of wood particles in microalgae pastes reduces the ability of microalgae to bind the water. However, in the presence of NaOH, the stability of the wood–microalgae slurry is regained. Another difference is the improved stability of the red seaweed slurry in NaOH solution when coprocessed with wood. This might be related to the fact that wood absorbs the liquid in the system. Therefore, the concentration of the algae in the solvent increases, enabling the hydrocolloids entanglement.

Table 4. Effect of Algae Type and Solution pH on the Stability of Wood–Algae Slurries According to the Syringe and the Centrifugation Test

biomass	R^a	solids dry matter content (wt %)	dewatering syringe test^b		dewatering centrifugation test^b	
			H_2O	NaOH 1 M	H_2O	NaOH 1 M
wood–green seaweed	1/1	15	yes	yes	yes	yes
wood–brown seaweed	1/1	20	no	no	yes	no
wood–red seaweed	1/1	20	no	no	yes	no
wood–microalgae	1/1	30	no	no	yes	no

^{a}R: wood/algae mass ratio. ^{b}yes = dewatering occurs, no = dewatering does not occur.

Figure 7 shows the water holding capacity (WHC) of the algae measured in neutral and alkaline conditions. The amount of water held by 1 g of algae represents the sum of capillary water, water bound to the polysaccharides, and water trapped in the fiber matrix.[49] Wood and green seaweed *Ulva* spp. show similar WHC values. Also, for both of them, the WHC decreases in alkaline conditions. Brown and red seaweed species have similar WHCs in neutral conditions and lower as compared to green seaweed and wood. In alkaline conditions, the WHC of brown seaweed increases by 28% and by 8% for red seaweed, relative to the values in neutral conditions. The microalgae show the lowest WHC capacity that increases with 32% in alkaline conditions. Because microalgae have unicellular structure and no porosity, it can be assumed that all water held by microalgae is chemically bound. This is in contrast to wood,

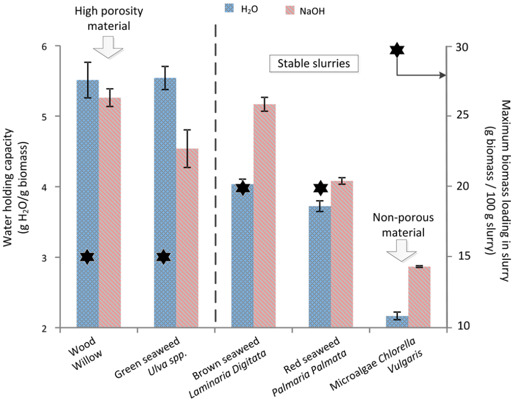

Figure 7. Water holding capacity of wood and algae measured by the centrifugation method and the maximum biomass loading of the wood–algae–water slurries with the composition given in Table 5; materials with high WHC yield slurries with low solids content.

which has a highly porous structure and establishes mainly weak interactions with water.[50] Therefore, seaweeds fall between these two extremes, and it can be considered that their WHC is a combination of water absorbed by physical means and water bound chemically.

From the above, it can be concluded that the water holding capacity of biomass is not a good parameter to predict the ability of biomass to form stable, pumpable slurries. However, the water holding capacity can be used to approximate the maximum biomass loading of the slurry. Considering that the WHC of the biomass represents the maximum amount of water or solution that can be absorbed by 1 g of biomass, the amount of biomass that can absorb 100 g of water can be derived (equals 100/WHC). From here, the theoretical maximum dry matter content in slurry (C^*) prepared with 100 g of water can be calculated according to eq 1:

$$C^*\ (\text{wt }\%) = \frac{m_{\text{biomass}}}{m_{\text{biomass}} + m_{\text{H2O}}} \times 100 = \frac{100/\text{WHC}}{100/\text{WHC} + 100} \times 100 \qquad (1)$$

According to this definition, a slurry with the maximum dry matter concentration C^* contains no free water (all of the water being absorbed by the solid phase). This determines a change of the slurry aspect from paste-like to very thick paste or solid-like consistency. Slurries with dry matter content bellow the critical C^* values are more likely to be pumpable. In Table 5, the calculated C^* values are compared to the experimental C^* values determined by visual observation of the slurry aspect.

Table 5. Theoretical and Experimental Maximum Biomass Loading of Single Component Wood and Algae Slurries Prepared with Water[a]

		C^* (wt %)	
	WHC ($g_{\text{H2O}}/g_{\text{biomass}}$)	calcd with eq 1	exp
willow	5.5 ± 0.3	15.4	15.0
green seaweed	5.5 ± 0.2	15.4	15.0
brown seaweed	4.0 ± 0.1	20.0	20.0
red seaweed	3.7 ± 0.1	21.3	20.0
microalgae	2.2 ± 0.1	31.3	35.0

[a] The experimental values were obtained by visual observation of the point where the mixture consistency changes from paste-like to solid-like.

3.2. Hydrothermal Liquefaction of Wood−Algae Slurries.

Alkaline wood−algae slurries were converted under supercritical water conditions. A reference feed containing wood only was also converted. In Table 6, the chemical composition of the feeds, the product distribution, and the biocrude elemental composition are given. With respect to feed composition, the wood slurry biomass loading was increased by 5% by coprocessing with seaweeds and by 15% by coprocessing with microalgae. However, the organic fraction of the wood-seaweed slurries is only slightly increased as compared to the wood slurries, while in the microalgae−wood feed the organic matter fraction is 63−75% higher than that in the wood−seaweed slurries. This clearly underlines the advantage of utilizing microalgae as costream for wood over macroalgae. The microalgae are advantageous due to the low ash content and the lack of a porous structure, which contributes to the increase of the organic matter fraction and the biomass loading in the feedstock.

Coprocessing of wood with macroalgae is detrimental for biocrude yield. As shown in Table 6, the lowest biocrude yields were obtained from wood−seaweed mixtures with the lowest value for the willow−red seaweed, 22 wt % oil yield as compared to 29 wt % from willow alone. The highest biocrude yield was obtained from the willow−microalgae feed, 42 wt %. Also, the carbon recovery in biocrude has lower values for willow−green seaweed and willow−red seaweed derived oils as compared to willow based oil. Despite the decrease of the biocrude yield for the case of willow−brown seaweed mixture, the carbon recovery value is similar to that of the pure willow case. The highest carbon recovery corresponds to the willow−microalgae mixture due to the higher biocrude yield obtained from this mixture. The low biocrude yields from seaweeds can be explained by the fact that they contain high fractions of carbohydrates that are converted into water-soluble compounds, solid, and gaseous products. Studies on model compounds showed that, in general, the carbohydrates have low conversion into biocrude: 5 wt % from algae carbohydrates (280 °C, no catalyst),[51] 15 wt % from corn starch (350 °C, no catalyst),[52] or between 8 and 20 wt % from glucose (350 °C, without and with Na_2CO_3).[19] Higher conversion of glucose and xylose into biocrude was obtained at supercritical conditions, between 28 and 30 wt % (400 °C, with Na_2CO_3).[53] Most of the polysaccharides are converted into water-soluble compounds (61 wt %), gas phase (25 wt %), and solids (9 wt %).[51] During HTL conversion, the polysaccharides are broken into various polar soluble compounds such as carboxylic acids, ketones, or alcohols. These will remain in the water phase product or will be further converted into gaseous product. The presence of alkalis may reduce the formation water-soluble compounds probably due to decarboxylation reactions that are promoted in alkaline conditions. At the same time, a reduction of solid products formation and an increase of the biocrude yield from carbohydrates are noticed when alkalis are used.[19,54] Proteins, a major constituent of microalgae, generate slightly higher biocrude yields, between 16 and 30 wt %.[51,52] A large fraction of the proteins, between 35 and 80 wt %, will form water-soluble compounds, and only small amounts will be converted into gases or solids.[55,52] The highest conversion into biocrude corresponds to lipids, 80 wt %. The oil yield from lipids may decrease in the presence of alkalis due to the formation of soluble compounds.[55] Thus, the high biocrude yield from microalgae containing feedstock can be explained by the higher protein and lipid content in microalgae and lower fraction of carbohydrates (see Table 1). Temperature also impacts the conversion of algae into biocrude. A study showed that the biocrude yield from various streams of microalgae can increase from 18−45 wt % to 46−58 wt % by increasing the liquefaction temperature from 250 to 375 °C.[23] In the current study, an even higher temperature of 400 °C was used to benefit from the special properties of water at supercritical conditions such as high dielectric constant and high ionic product. These properties enhance the dissolution of biocrude molecules into the liquid phase and suppress the radical reactions that favor char formation.[56]

The elemental distribution of biocrude oils is given in Table 6. Willow-based oil shows the highest carbon content and relative low oxygen. The highest oxygen content was identified in the willow−green seaweed biocrude, which in consequence leads to the lowest carbon content. Relative high content of

Table 6. Feed Composition, Average Yields of the Biocrude, Water-Soluble Organics, and Solids (wt %), and Biocrude Characterization[a]

	willow	willow+green seaweed	willow+brown seaweed	willow+red seaweed	willow+microalgae
Feed Composition					
total biomass (wt %, db)	15.3	20.0	20.0	20.0	30.0
organic matter (wt %, daf)	15.0	16.8	16.3	17.5	28.5
NaOH (wt % of total feed)	3.4	3.2	3.2	3.2	2.8
water/biomass ratio	5.7	4.0	4.0	4.0	2.3
algae/wood ratio	0.0	1.0	1.0	1.0	1.0
Product Yields (wt %, db)					
biocrude	28.5 ± 1.0	24.3 ± 1.0	25.5 ± 0.9	21.6 ± 2.1	41.8 ± 0.1
char	6.6 ± 1.3	16.2 ± 1.7	10.5 ± 0.7	12.5 ± 0.4	9.2 ± 0.5
WSO + gas (by diff.)	64.9	59.5	64.0	65.9	49.0
Biocrude					
C (wt %, db)	81.0 ± 1.0	71.3 ± 5.3	79.5 ± 1.0	79.8 ± 1.9	74.0 ± 1.5
H (wt %, db)	7.8 ± 1.6	6.7 ± 0.9	7.6 ± 0.6	7.8 ± 0.4	8.0 ± 0.1
N (wt %, db)	1.2 ± 0.0	2.1 ± 0.2	2.0 ± 0.0	3.1 ± 0.3	4.8 ± 0.0
S (wt %, db)	0.06 ± 0.0	0.18 ± 0.0	0.23 ± 0.0	0.31 ± 0.0	0.26 ± 0.0
O[b]	9.9	19.7	10.7	9.0	12.9
carbon recovery (%)	48.2	38.7	48.0	40.6	63.1

[a] HTL conditions: 400 °C, 15 min reaction time, solvent NaOH 1 M solution. [b] By difference (100-C-H-N-S); WSO = water-soluble organics.

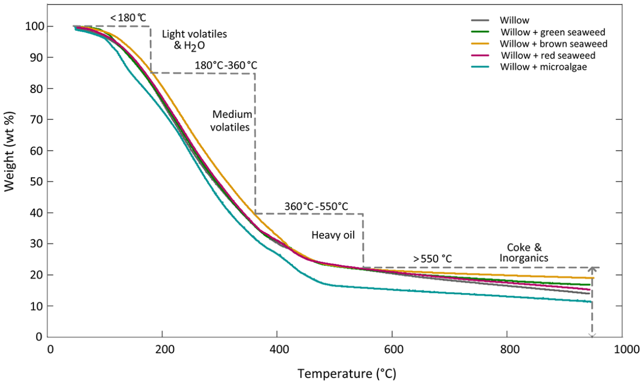

Figure 8. TGA curves of HTL biocrude oils obtained from willow and willow–algae liquefaction (TGA performed in nitrogen atmosphere, with gas flow rate 20 mL/min, and heating rate 10 °C/min).

Table 7. Boiling Point Distribution of the Biocrude Oils Obtained from Willow and Willow–Algae Liquefaction (wt %)

distillate range		willow	willow+green seaweed	willow+brown seaweed	willow+red seaweed	willow+microalgae
gasoline	<180 °C	18.4	18.3	14.3	17.4	22.4
jet and diesel fuel	180–360 °C	45.6	45.8	46.0	46.3	45.6
fuel oil	360–550 °C	14.2	14.2	17.7	14.3	16.2
coke and ash	>550 °C	21.8	21.7	22	22	15.8

oxygen was also measured in the willow–microalgae mixture, which also showed the highest nitrogen fraction 4.8 wt % as compared to 1.1 wt % in the wood-based biocrude. Sulfur and nitrogen were found in all algae derived biocrude oils. Sulfur is mainly originating from sulfated carbohydrates specific for algae and the nitrogen from proteins. The presence of sulfur and nitrogen heteroatoms in algae biomass is a common drawback in using them for biocrude production.

Figure 8 shows the mass loss of the oil samples with temperature, and Table 7 shows the mass fraction of the distillate ranges. As can be noticed from Figure 8, the degradation of the oils occurs in one step, beginning around 100 °C. Until 550 °C, between 78 and 84 wt % of the biocrude is volatilized. The remaining nonvolatile fraction, between 16 and 22 wt %, represents the coke and the inorganic matter. About one-half of the biocrude was evaporated between 180 and 360 °C. This distillate range corresponds to the jet and diesel fuels, suggesting the potential use of the biocrude oils in transportation sector. However, this would require the removal of oxygen, sulfur, and nitrogen heteroatoms that can be achieved by intermediate hydrotreating of the biocrude.[57] Despite the differences in the chemical composition of willow and seaweeds, the biocrude oils derived from these feedstocks have very similar distillation curves. This suggests that

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carbohydrates and proteins generate compounds with similar boiling properties. Previous studies showed that carbohydrates and proteins generate various types of cyclic ketones and phenols with boiling point below or around 180 °C.[19,53] Lipids are converted in compounds like hexadecane or heptadecane, which have the boiling point around 300 °C.[19] High boiling point compounds are also derived from lignin. The biocrude derived from the willow−microalgae mixture has a slightly higher fraction of volatiles with boiling point below 180 °C and between 360 and 550 °C as compared to the oils derived from willow and willow−seaweed slurries. The reason for this deviation is unclear, but one explanation could be the higher content of lipids that favor the formation of oil compounds with high boiling point and probably different structures of carbohydrates in microalgae that favor the formation of oil compounds with low boiling point. A detailed analysis of the composition of biocrude oils and the distillate fractions is necessary for better understanding the differences between microalgae and seaweeds derived biocrudes.

4. CONCLUSIONS

Wood slurries are one of the most difficult feedstocks to handle in continuous HTL. Solids dewatering, particles settling, and low biomass loadings are the main disadvantages of woody biomass. These challenges can be tackled by coprocessing wood with algae. The most suitable algae to improve wood slurries pumpability are brown seaweeds and microalgae mixed with wood in an algae-to-wood ratio of 1/1 or higher. The results indicate that wood−brown seaweeds mixtures with 20 wt % biomass loading and wood−microalgae mixtures with 30 wt % biomass loading could be suitable for continuous processing in HTL systems. Added benefits of coprocessing wood and microalgae are increased biomass loading and increased biocrude yield. The main disadvantage of using algae as cosubstrate is the introduction of sulfur and nitrogen heteroatoms into the biocrude. The high ash content of seaweeds is also a major drawback because it reduces the fraction of organic matter in the feedstock. Coprocessing of wood and algae is a novel approach in lignocellulosic biomass pretreatment for continuous HTL.

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Notes

The authors declare no competing financial interest.

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Paper D

Effect of biomass pretreatment on the product distribution and composition resulting from the hydrothermal liquefaction of short rotation coppice willow

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Effect of biomass pretreatment on the product distribution and composition resulting from the hydrothermal liquefaction of short rotation coppice willow

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HIGHLIGHTS

- Study of the effect of pretreatment method on product distribution and composition.
- Willow – ideal crop & biomass feedstock for biofuels production.
- Alkaline pretreatment enhances biocrude productivity, improves quality.
- Biocrude quality: reduced oxygen content, but increased aromatic content.

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ABSTRACT

A major challenge for the implementation of hydrothermal liquefaction (HTL) as a continuous process is the formulation of lignocellulosic feedstock, which is prone to phase separation into water and biomass parts when pressurized. One approach to remedy such phase separation is to reduce the dry matter content; however, as this approach is detrimental to process cost efficiency, designing an appropriate pretreatment step to ensure pumpability at high dry matter content is preferable. This paper evaluated the effect of various pretreatment methods on product distribution and composition resulting from the HTL of willow and proposes short rotation coppice as an alternative biomass feedstock for biofuels production. Alkaline–thermal pretreatment, besides making high dry matter pumpable feedstock slurries, also led to an increase in the production of the bio-crude product with an oxygen content lower than 8 wt% and a higher concentration of aromatics and phenolic compounds.

1. Introduction

Hydrothermal liquefaction (HTL) is a thermochemical process that utilizes the properties of water at temperatures higher than 553 K and pressures of up to 35 MPa (Elliott et al., 2015; Toor et al., 2011) to convert the main components of lignocellulosic materials (cellulose, hemicellulose and lignin) into its monomers through a series of complex chemical reactions, which are still not fully understood. This process is still under development and will have to compete with a crude oil price below US $50 per barrel and unconventional oil and gas as well as other biofuel technologies. The environmental effects of second-generation (2G) biofuel technologies are internalized in the cost, whereas those of fossil fuels are not; thus, competition arises with other biofuel technologies. In this context, a continuous HTL process is a prerequisite for commercializing the technology.

For this purpose, the efficient preparation of biomass feedstocks with high dry matter content has been a challenge because of the difficulty of injecting the biomass feedstock into the HTL reactors at high pressures (Daraban et al., 2015; Elliott et al., 2015; Lappa et al., 2016). The phase separation between the biomass particles and aqueous phase can be avoided by reducing the particle size to microns with or without the addition of an oil component (Berglin et al., 2012; Daraban et al., 2015); however, such fine milling of woody biomass is energy intensive. To avoid excessive reductions in the particle size, chemical pretreatment can be employed to destroy the lignocellulosic matrix and dissolve the substrate. Acid, neutral or alkaline pretreatment can be applied for this purpose.

Liquid hot water (LHW) pretreatment or auto-hydrolysis is usually carried out in aqueous medium at 453–473 K aiming to break down the hemicellulose into sugars and organic acids to create a

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paste product with 20–25% biomass loading (Goudriaan and Naber, 2015; Goudriaan and Peferoen, 1990). The produced organic acids decrease the pH of the liquid phase, thus favoring the degradation of the hemicellulose and sugar conversion into furfurals. Lignin rearrangements in the lignocellulosic matrix and reductions in cellulose degree of polymerization and crystallinity after this kind of pretreatment have also been reported (Mosier, 2013; Mosier et al., 2005). However, these changes are not sufficient to dissolve the woody biomass to an extent that allows for the formation of homogeneous pumpable feedstock slurries, which is why Shell failed to produce a pumpable woody feedstock for the hydrothermal upgrading (HTU) process.

Using acids as a medium to create pumpable feedstocks is not desired from a material cost perspective (high amounts of alkalis are required to neutralize the acidic feed) and due to the mismatch of reaction conditions between the pretreatment and HTL conversion stage (e.g., the LBL process developed by the Lawrence Berkeley National Laboratory). In contrast, alkaline conditions are imperative to enhance bio-crude yield and reduce char formation by avoiding the re-polymerization of the cellulose and hemicellulose degradation products. Alkaline hydrothermal (AHT) pretreatment has a considerable impact on biomass, dissolving the lignocellulosic substrate and converting the biomass–water mixture into a pumpable paste or liquid (Daraban et al., 2015). Under alkaline conditions, all lignocellulosic biomass components are affected. The main decomposition products are organic acids resulting from carbohydrates and phenolic compounds derived from lignin (Hendriks and Zeeman, 2009; Ramirez et al., 2013; Sjostrom, 1993).

In this study, LHW and AHT pretreatments have been proposed as methods to prepare pumpable wood pastes to address the pumpability issue in HTL continuous systems. Thus, the effect of biomass degradation on the ensuing HTL product distribution and chemical composition is investigated. To this end, willow has been subjected to pretreatment methods—neutral and alkaline media with and without thermal treatment—and then tested under supercritical water conditions. The main objective in this work is to identify an effective pretreatment method aligned with the overall process scheme for continuous HTL processing, favoring the production of bio-crude characterized by chemical compounds that can be easily upgraded in a subsequent refinery stage.

Short rotation coppice (lignocellulosic biomass), including willow, miscanthus, poplar or switchgrass could be considered alternative feedstocks to wood for biofuels production. These perennial crops do not require a considerable amount of fertilizer to grow; thus, the land used is protected. The crops could also be used for wastewater cleaning, balancing of nutrients or phytoextraction of hazard metals, such as cadmium (Cd) from agricultural soils (Greger and Landberg, 2015). Additionally, willow can be harvested on cycles as short as two to three years and represents a suitable crop to be grown on marginal lands. A fast growing, low fertilizer intake and high density biomass such as willow would represent an important biomass feedstock for biofuels production and it is the aim of this study to investigate how this short rotation crop could be formulated (pre-treated) for high-pressure pumpability purposes and delivery of a petroleum substitute product through HTL.

2. Materials and methods

2.1. Materials

Samples of willow—genus *Salix*—were collected at NyVraa Bioenergi I/S in Tylstrup, Denmark. Trees were harvested at two years old and were cut into chips with a width of 14 mm and length of 20–70 mm. The elemental and ash content of willow is given in Table 1. All chemicals used in this study, including sodium hydroxide (NaOH), acetone, dichloromethane (DCM) and the gas standards were purchased from Sigma Aldrich. Distilled water was used in all experiments.

2.2. Pretreatment

Four pretreatment methods were investigated in this work, which resulted in four pretreated feedstocks for the HTL processing. Feedstock A represented a mixture of milled willow and water, whereas Feedstock C was a mixture of milled willow and NaOH solution with a mass fraction of 0.1. Willow was milled to a particle size smaller than 0.10 mm using a laboratory scale FOSS Cyclotec™ mill. Feedstocks B and D, the LHW and AHT pretreated feeds respectively, were prepared in a 400 mL stainless steel autoclave. In each batch, 10 g of willow chips were mixed with 40 g of water for the LHW pretreatment or with sodium hydroxide solution in the case of AHT pretreatment. The pretreatment temperature of 453 K was reached in 25 min, whereupon the willow was pretreated for 2 h. All four mixtures contained a wood mass fraction of 20% on a dry basis. The pH of the pretreated feedstocks was measured prior to the liquefaction process. Feedstocks A and B were characterized by an acidic pH (pH = 4.00 and 3.00, respectively), whereas Feedstocks C and D were alkaline (pH = 13.50 and 12.50, respectively).

2.3. Hydrothermal liquefaction

HTL experiments were conducted in 10 mL stainless steel tubular batch reactors. In a typical run, approximately 7 g of prepared feedstock was loaded into the tubular reactor. The reactor was purged with nitrogen (N_2) for air removal, pre-pressurized with approximately 2 MPa N_2 and then inserted into a pre-heated fluidized sand bath. The initial pressure was necessary to maintain all compounds in the liquid phase while heating the reactors from room temperature to the desired HTL conditions; however, it does not affect the final pressure in the reactor. After each experiment, the reactor was removed from the fluidized sand bath and quenched in ice water. All experiments were performed in triplicate. Each feedstock was converted at 673 ± 2 K and 32–33 MPa under three HTL reaction times: 0, 10 and 20 min.

After the HTL conversion, the gas products were collected in small bottles fitted with crimp butyl caps similar to the ones described by (Glatzel and Well, 2008). After gas collection, the water phase was poured out of the reactor and any solids were filtered out. Afterwards, the reactor was thoroughly rinsed with acetone to collect a mixture of bio-crude and solids. The mixture was further filtered for separation of the solids, which were dried at 378 K for 24 h. The bio-crude–acetone mixture was evaporated in a rotary evaporator to remove the acetone. Any component characterized by a boiling point below the atmospheric equivalent temperature (AET) of 330 K was lost from the bio-crude during the solvent evaporation. The remaining product—a mixture of bio-crude and residual water—was further mixed with hydrochloric acid (HCl)—5.12 vol%—and centrifuged to separate the oil phase from the residual water (and also to break down any formed emulsions). Following centrifugation, the residual water and acid were separated from the bio-crude gravimetrically. Thus, the HTL process produced four products: the bio-crude, aqueous phase, solids and gases.

The yields of the bio-crude and solid fractions were calculated with Eqs. (1) and (2), respectively. The gas yield was quantified by GC analysis. Eqs. (3) and (4) represent the carbon and hydrogen balance, respectively. In these equations, $C_{product}$ and $H_{product}$ represent

Table 1
Elemental, water and ash contents of Willow and HTL products derived from conversion of willow-based feeds at a reaction time of 10 min.

Properties	Willow	Feed A		Feed B		Feed C		Feed D	
		Biocrude	Solids	Biocrude	Solids	Biocrude	Solids	Biocrude	Solids
Elemental analysis (wt% db)									
C	47.9 ± 0.03	69.2 ± 0.5	69.1 ± 2.0	69.1 ± 4.7	76.2 ± 4.2	74.7 ± 1.9	25.7 ± 5.6	73.9 ± 5.9	30.1 ± 3.1
H	6.0 ± 0.01	8.3 ± 0.2	3.8 ± 0.6	8.8 ± 0.1	3.5 ± 0.2	9.6 ± 0.03	1.4 ± 0.5	9.2 ± 0.1	1.95 ± 0.03
N	0.01 ± 0.02	1.7 ± 0.1	0.8 ± 0.2	1.5 ± 0.1	0.7 ± 0.1	1.4 ± 0.03	0.0 ± 0.0	1.4 ± 0.2	0.0 ± 0.0
Bound water (wt%)	0.00	11.5 ± 5.5	0.00	9.6 ± 0.8	0.00	10.8 ± 1.6	0.00	16.95 ± 1.1	0.00
Ash/metals content (wt%)	1.90 ± 0.08	n.d.	0.30	n.d.	0.22	n.d.	2.55	n.d.	2.69
Ash composition (mg/g)	n.d.	n.d.		n.d.		n.d.		n.d.	
Al			0.086		0.034		0.026		0.079
Ca			1.300		0.639		0.812		1.185
Fe			0.351		0.371		0.141		0.807
K			0.123		0.423		0.401		0.522
Mg			0.166		0.149		0.108		0.166
Na			0.155		0.179		23.852		23.347
P			0.648		0.251		0.171		0.667
S			0.121		0.104		0.030		0.084

the amount of carbon and hydrogen (in grams), respectively, determined by using the elemental content measured according with the applied analyses as described in the next section. The carbon and hydrogen balances reveal how much of the initial carbon and hydrogen, respectively, present in willow end up in the HTL products. The *C wt%* and *H wt%* for the aqueous phase was not calculated.

$$Yield_{biocrude} = Weight_{biocrude}/Weight_{dry\ willow} \times 100 \quad (1)$$

$$Yield_{solids} = Weight_{solids}/Weight_{dry\ willow} \times 100 \quad (2)$$

$$C\ wt\% = (C_{product}/C_{feed}) \times 100 \quad (3)$$

$$H\ wt\% = (H_{product}/H_{feed}) \times 100 \quad (4)$$

2.4. Feed and product analyses

The elemental content of willow was measured according to the ASTM D5373 method, whereas the ash content was determined following the ASTM D3174 method.

Components in the gaseous product such as carbon dioxide (CO_2), methane (CH_4), propane and butane, were analyzed on an Agilent model 7890A gas chromatograph (GC) equipped with a thermo-conductivity detector (TCD) and two columns—HP-Molesieve (30 m long, 0.32 mm ID, 25 μm film thickness) and HP-PLOT/Q (30 m long, 0.53 mm ID, 40 μm film thickness). Hydrogen (H_2) was separated in a ShinCarbon ST column installed on a Chrompack CP9002 GC-TCD. The detector and injector temperature was 573 K, whereas the oven temperature was constant at 353 K. The mole fractions of the gas products were determined from single point calibration obtained by analysis of gas standards of known composition.

The aqueous phase and bio-crude samples were extracted with dichloromethane (DCM) and analyzed by gas chromatography–mass spectrometry (GC–MS). No internal standard was used to calibrate these samples. The peak area (%) was used instead to represent the comparative and semi-quantitative content of each component in the bio-crude and aqueous phase samples. The applied GC–MS was a Thermo Scientific Trace 1300 GC equipped with a single quadrupole MS. The analyses were performed in electron ionization (EI) mode, with compounds being separated in an Agilent HP 5-ms column (30 m long, 0.25 mm ID, 0.25 μm film thickness). The detector temperature was 573 K, while the injector was held at 553 K and a split ratio of 20:1 was applied. The following program was used for analyzing the HTL products: 313 K isothermal for 3 min, 313–598 K at a temperature ramp of 5 K/min, and held at 598 K for 3 min. The liquid phase resulting from the thermal pretreatments (LHW and AHT) of willow was analyzed by GC–MS using the same program and solvent for extraction as in the case of the HTL aqueous phase. The detected compounds were identified by searching for compounds with similar mass spectra in the 2014 National Institute of Standards and Technology (NIST) library.

Moreover, infrared (IR) data was obtained at room temperature for the solid products on a Perkin-Elmer Spectrum One instrument coupled with a horizontal ATR accessory (MIRacle, Pike Technologies) with a diamond crystal as the internal reflection element.

Furthermore, the elemental analysis of bio-crude oils was performed according to the ASTM D5291 procedure, whereas the elemental content of solids was determined following the ASTM D5373 method. The percentages of residual water were measured in the bio-crude samples by Karl Fischer titration following the ASTM E203 method.

Additionally, the ash composition of solid samples was analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The small sample size was the reason for not being able to carry this type of analysis for bio-crude samples.

3. Results and discussion

Pretreatment efficiency on biomass deconstruction depends on the slurry pH and pretreatment temperature. The changes occurring in the raw biomass structure while subjected to the four pretreatment methods considered in this study are addressed in Section 3.1. A first novelty in this study is to bring to light what kind of chemical compounds should be expected in the HTL products after a certain pretreatment was applied to the biomass feedstock prior to the HTL process and how easily is it to upgrade the resulting bio-crude to a finished fuel. More details in Sections 3.2 and 3.3. A reaction time study was conducted to determine how the product distribution and composition is affected, as this influence becomes critical for process optimization when processing the biomass in continuous mode (Section 3.4).

3.1. Effect of pH and thermal treatment on the raw biomass prior to HTL

The feedstock slurries prepared for HTL conversion varied in composition according to the pretreatment method employed. There were no changes in the biomass structure or composition occurring in Feedstock A with the exception of some possible dissolution of extractives, which could explain the decrease in pH. The pH of this slurry decreased from neutral to a value of approximately 4.00 only by soaking the willow particles in distilled water. This value might vary as the raw biomass changes according to a study published in Nature (Campbell and Bryant, 1941), becoming either more acidic or closer to neutral pH depending on the type of species involved.

When heat was applied to such a feedstock (LHW pretreatment)—Feedstock B—sugars and derived organic acids were generated by hemicellulose hydrolysis. Qualitative GC–MS data revealed the production of furfurals and 5-methyl-2-furaldehyde, which have likely resulted from the hydrolysis of hemicellulose and subsequent reactions involving its monomers, including xylose, mannose, and glucose. Phenol, 2-methoxy-phenol and 2,6-dimethoxy-phenol have been identified as well, which may be a result of lignin degradation during the pretreatment. Complete dissolution of lignin was not achieved in Feedstock B (pH = 3.0), likely because of the low pretreatment temperature or reaction time or even the acidic conditions, which were not strong enough to break down the lignin backbone.

In contrast, the dissolution of lignin and polysaccharides was promoted in alkaline conditions. In the case of cold alkaline pretreatment—Feedstock C—some of the hemicellulose compounds dissolved, resulting in a feed with increased viscosity and water-holding capacity.

The most dramatic alteration of the willow structure occurred during the AHT pretreatment, in which approximately 70% of the initial solid matter was dissolved in the alkaline solution. The result was a slurry with a paste consistency and a complex mixture of biomass-derived compounds. Hemicellulose and cellulose generated a range of organic acids, whereas lignin provided a large spectrum of phenolic compounds, including 2-methoxy-phenol, 4-ethyl-2-methoxy-phenol, 2,6-dimethoxy-phenol, and 5-tert-1,2,3-benzenetriol.

The major components of biomass started to degrade under alkaline and thermal pretreatment at 453 K with the formation of monomers and smaller compounds depending on the pH of the medium (either acidic or basic). The resulting compounds are expected to undergo various conversion pathways depending largely on the reaction medium. These variations make it important to study the effect of a pretreatment method when processing biomass for biofuel production; this effect on product distribution and composition is addressed in the following two sections.

3.2. Effect of slurry pH and thermal treatment on the HTL product distribution and elemental content

HTL conducted in an acidic medium promotes char formation and suppresses bio-crude production. These effects were also observed in this study as the bio-crude yield resulting from the conversion of Feedstock B (pH = 3.00) was the lowest (see Table 3). This low conversion could be explained by the increased concentration of organic acids produced during the thermal pretreatment, which favored formation of gases and solids (see Table 3). Unlike Feedstock B, Feedstock A generated a higher bio-crude yield, likely because of smaller particle size of biomass, which increased the surface area for water attack and also due to a decreased concentration of organic acids.

In contrast, alkalis, such as NaOH, or potassium carbonate (K_2CO_3), are used in the HTL process as char reduction agents and bio-crude yield enhancers (Karagoz et al., 2005; Yin et al., 2011a,b), promoting retro-aldol reactions/cleavage and condensation reactions (Mazaheri et al., 2010) and preventing

Table 2
Mass, carbon and hydrogen balances of HTL products resulting from conversion of the four feedstocks at three reaction temperatures: 0 min, 10 min and 20 min.

		Feed A			Feed B			Feed C			Feed D		
		0 min	10 min	20 min	0 min	10 min	20 min	0 min	10 min	20 min	0 min	10 min	20 min
Mass balance (wt% db)	Solids	14.2 ± 1.1	15.5 ± 0.9	19.0 ± 1.7	20.3 ± 0.1	21.6 ± 2.3	22.6 ± 1.9	26.0 ± 4.0	31.8 ± 0.4	32.7 ± 1.8	40.5 ± 4.7	37.1 ± 4.9	40.3 ± 2.2
	Biocrude	49.8 ± 2.1	34.5 ± 4.4	38.4 ± 2.3	29.3 ± 4.0	28.5 ± 2.6	30.1 ± 4.3	39.0 ± 5.3	31.0 ± 0.2	29.8 ± 0.6	44.2 ± 3.9	43.0 ± 1.9	40.2 ± 6.4
	Gas*	19.6 ± 1.3	21.4 ± 3.4	24.5 ± 4.0	15.2 ± 2.9	14.9 ± 4.4	16.7 ± 0.3	11.2 ± 0.3	15.2 ± 0.8	19.0 ± 5.0	14.6 ± 0.7	17.8 ± 3.6	16.1 ± 1.6
Carbon balance (wt% db)	Solids	19.1 ± 1.3	22.4 ± 1.9	26.9 ± 0.9	30.4 ± 0.4	32.8 ± 4.6	35.7 ± 1.6	18.4 ± 4.0	18.4 ± 4.1	17.8 ± 2.0	26.1 ± 0.9	22.2 ± 1.3	26.1 ± 1.9
	Biocrude	69.0 ± 2.4	49.7 ± 4.9	55.1 ± 5.6	41.4 ± 5.3	39.3 ± 5.4	43.5 ± 7.0	56.6 ± 1.8	48.2 ± 1.3	46.5 ± 0.9	61.7 ± 1.7	58.6 ± 1.2	58.8 ± 3.3
	Gas*	12.3 ± 1.0	14.8 ± 1.4	15.7 ± 2.1	9.6 ± 1.4	10.7 ± 3.3	13.0 ± 0.8	7.3 ± 0.1	10.9 ± 0.4	14.8 ± 4.2	9.7 ± 0.4	12.5 ± 2.5	11.7 ± 0.9
Hydrogen balance (wt% db)	Solids	8.1 ± 0.6	9.8 ± 1.1	11.9 ± 1.5	10.8 ± 1.1	11.9 ± 1.6	11.9 ± 0.4	9.9 ± 1.6	7.9 ± 3.0	7.8 ± 0.4	15.0 ± 0.7	12.9 ± 1.4	12.7 ± 2.1
	Biocrude	68.0 ± 2.9	47.1 ± 5.3	55.1 ± 2.2	39.8 ± 5.1	39.4 ± 3.0	43.0 ± 5.3	57.5 ± 2.8	49.1 ± 0.1	47.5 ± 1.8	64.7 ± 6.0	65.3 ± 2.4	62.7 ± 11.3
	Gas*	4.9 ± 1.3	10.3 ± 1.7	7.4 ± 0.9	4.1 ± 1.0	9.8 ± 3.2	13.6 ± 1.7	9.3 ± 0.7	14.0 ± 1.7	18.0 ± 2.8	11.8 ± 0.3	14.3 ± 2.7	16.8 ± 2.4

db = dry basis.
[*] Gas measured by GC.

Table 3
Classification of the chemical compounds detected by GC–MS in bio-crude products derived from the conversion of the four feedstock slurries under supercritical water conditions (673 K, 32–33 MPa, 10 min).

	Chemical compound	Formula	MW	Peak area (%)			
				Feed A	Feed B	Feed C	Feed D
Alcohols	3-Penten-2-ol	$C_5H_{10}O$	86	2.94	6.85	4.98	3.39
	4-Methyl-2-pentanol	$C_6H_{14}O$	102	0	3.09	2.30	1.75
	5-Octen-1-ol	$C_8H_{16}O$	128	0.67	0.75	1.47	1.49
	2-Methyl-1-hexadecanol	$C_{17}H_{36}O$	256	1.55	1.06	1.58	1.45
Ketones	Cyclopentanone	C_5H_8O	84	0.98	0.86	0.43	0.46
	2-Methyl-cyclopentanone	$C_6H_{10}O$	98	0	1.73	1.77	1.51
	4-Hydroxy-4-methyl-2-pentanone	$C_6H_{12}O_2$	116	6.47	1.45	2.78	2.69
	3-Methyl-cyclohexanone	$C_7H_{12}O$	112	0	0	1.89	1.34
	2-Methyl-2-cyclopenten-1-one	C_6H_8O	96	2.07	0.90	0.42	0.48
	2,3-Dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	110	0.68	0.49	0.36	0.51
	3-Methyl-2-cyclopenten-1-one	C_6H_8O	96	3.65	0	0	0
	3,4-Dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	110	0.96	0.35	1.00	0.47
	2,3-Dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	110	0.97	0.56	0.43	0.70
	3,4-Dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	110	0.87	0.49	0	0.47
	2,3-Dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	110	3.65	1.48	1.01	1.24
	2,3,4-Trimethyl-2-cyclopenten-1-one	$C_8H_{12}O$	124	0.56	0.33	1.11	1.22
	3-Isopropyl-2-cyclopenten-1-one	$C_8H_{12}O$	124	0.57	0.37	0	0.82
	2,3,4,5-Tetramethyl-2-cyclopenten-1-one	$C_9H_{14}O$	138	0.42	0	0.55	0.75
	3-Isopropyl-2-cyclopenten-1-one	$C_8H_{12}O$	124	0.58	0	0	0
	2,2-Dimethylcyclohexyl methyl ketone	$C_{10}H_{18}O$	154	0.99	1.65	3.43	3.44
Phenols	Phenol	C_6H_6O	94	1.98	0.65	0.66	0.83
	m-Cresol	C_7H_8O	108	0.88	0.5	0.55	0.79
	p-Cresol	C_7H_8O	108	1.51	0	0.52	0.63
	2-Methoxy-phenol	$C_7H_8O_2$	124	2.01	0.78	1.26	1.84
	2,3-Xylenol	$C_8H_{10}O$	122	0.38	0.63	0.60	0.72
	2-Methoxy-4-methyl-phenol (creosol)	$C_8H_{12}O_2$	138	1.25	1.67	3.04	2.69
	2,3,6-Trimethyl-phenol	$C_9H_{12}O$	136	0	0	0.93	0.84
	4-Ethyl-2-methoxy-phenol(*p*-ethylguaiacol)	$C_9H_{12}O_2$	152	0.90	0.38	0.59	0.47
	2,6-Dimethoxy-phenol	$C_8H_{10}O_3$	154	0.85	0	0.47	0.51
	2-Methoxy-4-propyl-phenol	$C_{10}H_{14}O2$	166	0.39	0	0	0
	4-Methoxy-3-(methoxymethyl)-phenol	$C_9H_{12}O_3$	168	0.56	0.46	0	0.46
	Butylated hydroxytoluene	$C_{15}H_{24}O$	220	2.11	6.71	11.06	10.86
Esters	2-Propenoic acid, 3-(1-acetyl-2,2-dimethylcyclopentyl)-,methyl ester	$C_{13}H_{20}O_3$	224	0.41	0.36	0.82	1.04
	Terephthalic acid, bis(2-ethylhexyl)ester	$C_{24}H_{38}O_4$	390	23.32	11.01	0	0
Others	2-Chloro-2-methyl-butane	$C_5H_{11}Cl$	106	8.43	22.50	17.70	13.11
	2,5,8-Trimethyl-1,2,3,4-tetrahydro-1-naphthol	$C_{13}H_{18}O$	190	0.32	0	0	0
	9-Hexadecenoic acid	$C_{16}H_{30}O_2$	254	0.65	0.42	0.63	0.65
	(*Z*)-9-Octadecenamide	$C_{18}H_{35}NO$	281	6.31	8.56	2.89	10.46
Total				80.84	77.04	67.23	70.08

re-polymerization reactions (Li et al., 2015; Liu et al., 2014; Minowa et al., 1998). In Table 3, the solid yield for the results from alkaline pretreatment was higher if compared to the results from the acidic study as it contained the ash which was formed mainly of Na. Analysis of ash by ICP included in Table 1 confirmed this fact. More than 23 mg/g Na was measured in the ash of solids resulting from Feeds C and D as compared to only 0.15–0.18 mg/g in the case of solids from Feeds A and B, most likely derived from willow (1.9 wt% ash). Some of the Na derived from the alkaline agent is expected to end up in the bio-crude composition as well, but no ICP analysis can support this statement, as the sample size for these samples was not enough to conduct this type of analysis. The AHT pretreatment also led to a decrease in the gas yield from approximately 19.6–24.5 wt% to 14.6–17.8 wt% (Table 3).

Feedstock D produced a bio-crude yield higher than 40 wt%, which could be explained by the increased reaction rates during the HTL process due to biomass dissolution. Additionally, the liquid homogeneous phase created by this pretreatment method could also have played a role in the enhancement of the oil productivity and be related to the decomposition of lignin to low-molecular-weight (LMW) compounds in the liquid phase. This alkaline solution might have shifted the reactions toward the formation of oil compounds rather than going under condensation or re-polymerization reactions. However, this was not the case of Feedstock C, as the bio-crude yield was about the same as it was in the case of Feedstock B. This might be related to the initial slurry alkalinity as reported by (Yin et al., 2011a,b), which can change the reaction pathway during hydrothermal conversion such that the reactions can involve both alkaline and acidic pathways. Thus, an increase in the alkalinity of solutions might lead to a decrease in the bio-crude yield.

Moreover, the solvent used in the extraction of the liquid product is important because the polarity of certain components, such as hydroxy-methyl-furfural (HMF), is weaker than those of e.g. carboxylic acids, and thus, certain components are more soluble than others and can be more easily extracted as bio-crude. The applied extraction solvent—in this case, acetone—could have had an influence on the bio-crude yields. The aqueous phase comprised of many compounds similar to the ones in the bio-crude product (see Section 3.3). Furthermore, some low molecular components with boiling points lower than 330 K might had been lost from the bio-crude during solvent evaporation. The applied separation procedure might have had an effect on bio-crude yields as well.

An alkaline reaction medium (attached to a thermal treatment or not of the raw biomass) is preferable when comparing the elemental content in the bio-crudes and solids (see Table 1). The carbon content in the bio-crudes increased from 69 wt% (Feed A and B) to 75 wt% (Feed C and D), whereas in the solids decreased from

70 wt% (Feed A and B) to 30–25 wt% (Feed C and D). Solid formation occurs during the HTL process because of re-polymerization and condensation reactions. Carbohydrate conversion into solids is enhanced in acidic media and suppressed in the presence of NaOH. The hydrogen content in these products followed a similar path. The nitrogen content does not depend on the reaction medium and/or pretreatment method. Nitrogen content in bio-crude is dependent on the biomass composition, as it is derived from willow.

Carbon and hydrogen balances showed that about 60% and 65% of the initial carbon and hydrogen, respectively present in willow was transferred to the bio-crude when subjected to an alkaline and thermal treatment. The situation was similar in the case of bio-crude derived from Feed A.

Performing an AHT pretreatment on the raw biomass to produce a pumpable feedstock slurry for continuous HTL seems to be a plausible option because it enhances the bio-crude productivity. However, recycling of sodium from the solid fraction has to be considered for reduction of processing costs. Willow pretreatment by fine milling led to similar results, so a study on processing costs could reveal which one of these two options is better for continuous HTL. In addition, the effect of such a pretreatment on the composition of bio-crude is of high interest in the upgradability of the product to a finished fuel; this topic is discussed in the next section.

3.3. Effect of slurry pH and thermal treatment on the HTL product composition

GC/MS results of the bio-crude fractions revealed a significant difference in chemical composition as a function of the reaction medium. Thus, the volatile compounds detected by GC–MS were distributed in the same classes of compounds, but their relative abundance varied with the reaction medium, and in the case of experiments conducted in acidic medium, their relative abundance varied significantly with the thermal treatment of the raw biomass as well.

The majority of the chemical compounds identified in the bio-crude products were oxygenates: ketones, phenols and alcohols. More details about the nature of these compounds is given in Table 2.

A major difference in composition was represented by the near complete disappearance of the esters from the composition of bio-crude products resulting in an alkaline medium. This might be related to the neutralization of the organic acids resulting from hydrolysis of polysaccharides during alkaline pretreatment. The di-ester of terephthalic acid was identified in the composition of bio-crude products obtained from conversion of Feeds A and B. The presence of these high molecular weight (HMW) organic esters is expected to increase the total acid number (TAN) of the bio-crude products. Such compounds are undesirable because of the difficulty of storing products with a high TAN number and because of the downstream processing; de-esterification of two ester groups is typically achieved in two steps (Furimsky, 2013). Another effect of the reaction medium was an increase in the relative abundance of phenolic compounds and alcohols in bio-crude products as the pH of the feed slurry became alkaline. This fact was also noticed by (Ogi et al., 1985) and (Akhtar et al., 2010). Such a behavior would be preferable as the formation of heavy organic acids is inhibited under these conditions. Furthermore, alcohols and ketones are easy to upgrade because they require only one hydrogen molecule to convert into hydrocarbons. Most of the phenolics in bio-crude samples were substituted phenols, and they are more difficult to handle during a hydro-deoxygenation process compared to simple phenols (Furimsky, 2013).

The pH measurements of the HTL aqueous products indicated that a large fraction of the alkaline agent (NaOH) added to the feedstock prior to conversion was found in the water phase product; the pH values for cases C and D were 9.65 and 9.50, respectively, whereas the values for cases A and B were 3.75 and 3.95, respectively. This result indicates that any organic acid produced after the pretreatment process was neutralized by the NaOH. This fact was also confirmed by the GC–MS analysis, where the distribution of the classes of compounds depended on the reaction medium and the thermal treatment applied to the raw biomass. The distribution showed a slightly different classification of the compounds as compared to the bio-crude product, comprising of alcohols, ketones and aldehydes, phenols, furans and carboxylic acids (see Supplemental Material).

The aqueous products resulting from conversion under an acidic medium (Aqueous phase Feed A) were rich in furans, acids, ketones and phenolic compounds, in contrast to the products resulting from alkaline conversion (Aqueous phase Feed C), which were predominantly composed of ketones and small percentages of alcohols and phenolic compounds. This result highlights that under the action of an alkaline agent, furfurals and acids, which are typically formed in acidic medium, might be directed to form ketones and alcohols. The phenolic compounds were also affected by alkalinity; their percentage area decreased in aqueous products obtained from alkaline conversion. Moreover, the aldehydes present in Aqueous phase Feed A vanished when an alkaline agent was employed in the HTL process. Their disappearance could be explained by the Cannizzaro reaction, by which they form alcohols through disproportionation. When a thermal treatment was applied to the feedstock slurry (Feedstock B) prior to HTL conversion, the furan abundance in the aqueous product increased while the relative abundance of phenolic compounds and ketones decreased, suggesting an enhancement in the hydrolysis of hemicellulose under the thermal treatment to form furfurals.

A challenge in the continuous processing of such biomass feedstock slurries to produce biofuels would be to optimize the process such that the majority of these organic compounds in the HTL aqueous products become part of the bio-crude product. Gravimetrical separation of the aqueous and bio-crude products or by using membranes would be the preferable options from an industrial point of view and not by employing a solvent, which would increase the operation costs.

Another important aspect in terms of continuous operation is the recycling of the water phase because it contains the majority of the alkaline agent. Zhu et al. (2015) demonstrated that aqueous phase recirculation enhanced the bio-crude yield when converting barley straw through HTL in a batch process but also increased the solid residues with the number of recycling cycles, highlighting that the dissolved organic compounds in the aqueous phase could play a role in re-polymerization reactions to form solids.

Pedersen et al. (2016) demonstrated that recirculation of the aqueous phase can also impact the quality of the bio-crude in terms of the effective carbon-to-hydrogen (C/H) ratio, which increased when processing a mixture of aspen wood and glycerol continuously under supercritical water conditions. Water is a commodity that is expected to become expensive in the future; thus, recirculation of aqueous products in such a process and recovery of the alkaline agent are necessary to minimize operation costs.

The gaseous products obtained from conversion of all four feedstocks consisted mainly of CO_2 (see Fig. 1). CO_2 accounted for more than 75% of the produced gases in the case of gas derived from conversion of feedstocks in acidic medium. The higher concentrations of CO_2 in the gas produced from Feed A and Feed B indicate that the acidic medium promoted decarboxylation reactions involving organic acids derived from the lignocellulosic biomass. (Eager et al., 1981) found that CO_2 could be released from carbohydrates

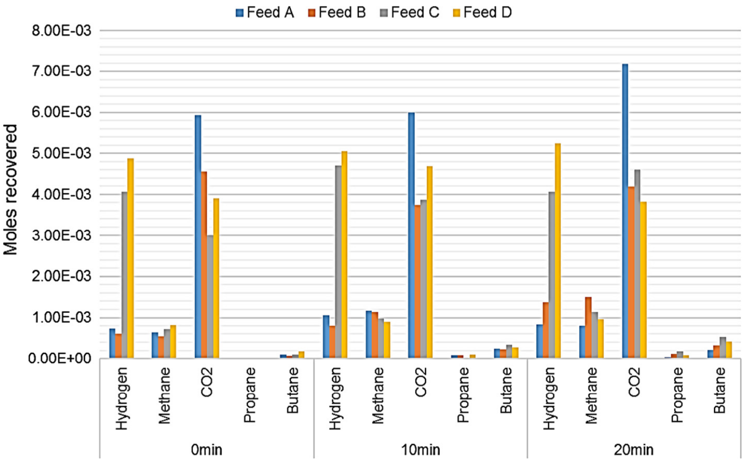

Fig. 1. Gas composition as function of the HTL reaction time.

during the formation of certain intermediates. These reactions appear to be inhibited when a thermal treatment is applied (Feedstock B); the solid yield increased significantly, indicating that re-polymerization reactions are favored. Residual carbon could also be formed through the disproportionation of carbon monoxide (CO) into carbon and carbon dioxide ($2CO \leftrightarrow C + CO_2$).

Analysis of the gas phase produced in alkaline conditions illustrates that dehydrogenation reactions are enhanced. The presence of higher concentrations of hydrogen in the gas phase obtained from alkaline-pretreated feeds might be due to the higher fractions of CO generated and converted to H_2 and CO_2 through the water gas shift reaction. Ethane, ethylene, propylene and CO are other gases expected to result from the HTL process, but they could not be quantified in this study.

The IR data of solid fractions showed that the peaks for the C–C ring stretch (1570 cm^{-1}), C–O stretch (1420 cm^{-1}) and C–C ring bend or aromatic C–H bend (870 cm^{-1}) were more intense in the case of solid particles procured from alkaline feedstock slurries. All of these bands indicate the aromatic character of the ‘alkaline’ solids.

3.4. Effect of reaction time on the HTL product distribution and composition

Reaction time plays an important role in the optimization of the HTL process. The results indicated that a longer reaction time indeed affects the product distribution: the bio-crude production was negatively affected, whereas the solid and gas production increased. This result demonstrates that re-polymerization and gasification reactions are favored at longer reaction times. As the reaction time is prolonged, water-soluble compounds are also subjected to re-polymerization and/or gasification reactions. The observation that the bio-crude production is the highest at shorter reaction times (in this case, 0 min) demonstrates that the compounds from the biomass convert into oil compounds first and then either become soluble in the aqueous phase or produce the gases and solids with the increasing reaction time. Thus, it will be important from an optimization perspective to identify the stage at which these compounds start to become soluble into the aqueous phase or react to form gases and solids.

The change in composition with increasing reaction time will impact the subsequent step (upgrading); thus, knowing the types of compounds in the bio-crude becomes significant. The elemental composition of the bio-crude products exhibited a slight increase in the hydrogen contents at longer reaction times, whereas the oxygen content was reduced. As addressed in the previous sections, hydro-deoxygenation is a preferred route in the upgrading stage of the bio-crude products. As a result, the occurrence of such reactions during HTL conversion is desired.

In the case of solids, the analysis of elemental distribution did not suggest that the reaction time had any impact; the composition remained fairly constant. The IR spectra exhibited peaks for the same functional groups as explained in the previous section.

The final pH of aqueous products was not influenced by the reaction time either. The composition of gaseous products was influenced by the reaction time, as the contents of all gas components increased with longer reaction times in all cases (see Fig. 1). Carbon and hydrogen balance showed that as the reaction time was prolonged, more of the initial carbon and hydrogen in the biomass was transferred to solids and gases. Compared to all other gas components identified by GC analysis, propane was not formed at 0 min, or the concentration was so low that the equipment could not detected. Propane might have likely formed at longer reaction times only.

In terms of composition, a longer reaction time had an influence on the component distribution. If the relative abundance for alcohols and alkanes increased in the case of bio-crude samples resulting in an acidic medium, an opposite effect was observed for the samples derived in an alkaline medium. A similar effect was observed for phenolic compounds and ketones. In the case of organic compounds in aqueous phase derived from Feedstocks A and B, a longer reaction time favored the formation of ketones and acids while the relative abundance for furans, aldehydes, alcohols and phenolics decreased. In the case of water soluble organics derived from Feedstocks C and D, the reaction time was only observed to impact the relative abundance of ketones, which decreased, whereas the relative abundance for alcohols and phenolics increased.

From a bio-refinery perspective, a shorter reaction time during the HTL process is preferable as the bio-crude production is enhanced, but it might negatively influence the quality. Having a process that can convert biomass residues in short reaction times would be ideal if the bio-refinery was placed adjacent to the petroleum refinery so that the liquid product being separated from the residual streams (gases and solids) could be directly transferred to the upgrading unit in the petroleum refinery. In such a situation, organic compounds soluble in the aqueous phase, such as furans, ketones and phenolics, could also be hydro-deoxygenated and converted into hydrocarbons, but this case will most likely be impossible to apply in the future because of many challenges that must be considered, including building the bio-refinery next to an oil refinery, transportation of biomass to the bio-refinery (an extremely expensive step), and efficient and immediate separation of the liquid product from the residual streams. Additionally, water is undesirable in an oil refinery.

4. Conclusions

The effect of biomass pretreatment on the HTL product distribution and composition was evaluated in this work to identify an effective pretreatment method of short rotation coppice aligned with the overall process scheme for continuous HTL processing. The AHT pretreatment was the most effective on the bio-crude production and composition, improving the yield and reducing the production of oxygenates, but increasing its aromatic character. Recovery of the alkaline agent from the solid and/or aqueous phases, recycling of the aqueous phase, and utilization of gaseous and solid products are challenges that remain to be addressed in the near future.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2017.01.056.

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Paper E

Continuous hydrothermal co-liquefaction of aspen wood and glycerol with water phase recirculation

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HIGHLIGHTS

- Biocrude compounds from woody biomass can be classified into two groups: cyclopentenones and oxygenated aromatics.
- Biocrude quality can be predicted based on the feedstock model compound composition.
- Elemental composition is almost invariant to feedstock composition.
- Reaction scheme from model compound, through intermediates, to biocrude is proposed.
- Residual oxygen in the biocrude is mainly positioned in ketones and phenolic alcohols.

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ABSTRACT

Hydrothermal liquefaction is a promising technology for the conversion of a wide range of bio-feedstock into a biocrude; a mixture of chemical compounds that holds the potential for a renewable production of chemicals and fuels. Most research in hydrothermal liquefaction is performed in batch type reactors, although a continuous and energy-efficient operation is paramount for such process to be feasible. In this work an experimental campaign in a continuous bench scale unit is presented. The campaign is based on glycerol-assisted hydrothermal liquefaction of aspen wood carried out with the presence of a homogeneous catalyst at supercritical water conditions, 400 °C and 300 bar. Furthermore, in the experimental campaign a water phase recirculation step is incorporated to evaluate the technical feasibility of such procedure. In total, four batches of approximately 100 kg of feed each were processed successfully at steady state conditions without any observation of system malfunctioning. The biocrude obtained was characterized using several analytical methods to evaluate the feasibility of the process and the quality of the product. Results showed that a high quality biocrude was obtained having a higher heating value of 34.3 MJ/kg. The volatile fraction of the biocrude consisted mostly of compounds having number of carbon atoms in the C_6–C_{12} range similar to gasoline. In terms of process feasibility, it was revealed that total organic carbon (TOC) and ash significantly accumulated in the water phase when such is recirculated for the proceeding batch. After four batches the TOC and the ash mass fraction of the water phase were 136.2 [g/L] and 12.6 [%], respectively. Water phase recirculation showed a slight increase in the biocrude quality in terms on an effective hydrogen-to-carbon ratio, but it showed no effects on the product gas composition or the pH of the water phase. The successful operation demonstrated the technical feasibility of a continuous production of high quality biocrude.

1. Introduction

Hydrothermal conversion of biomass in hot-compressed water is a viable, scalable, and energy-efficient thermo-chemical route for converting biomass into synthetic solid, liquid, or gaseous fuels and chemicals. At near and supercritical water conditions, biomass fragments into a bulk liquid phase, better known as biocrude. It consists of low molecular weight and deoxygenated chemical species compared to the original biomass macromolecules. The biocrude may be further processed into platform chemicals or infrastructure-compatible fuels. Hydrothermal conversion of

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biomass has been widely studied experimentally, mostly in batch reactors and less so in continuous systems, and has been reviewed in the many process aspects, such as near-critical water synthesis properties [1,2], the effects of various process conditions [3], effects of biomass composition [4–7], process developments [8–10], and upgrading of the biocrude [11–13].

Although the vast majority of research is carried out in batch reactors, development of continuous operation and technology upscaling of near-critical water technologies has been ongoing since the mid-seventies – but has not yet reached commercialization [9]. The continuous process was first demonstrated at a bench scale system at the Pittsburgh Energy Research Center (PERC) which was later scaled to the Albany plant, Oregon [14]. The production facility utilized a recycle concept in which wood (Douglas fir) was slurried in recycled process water and initially in anthracene oil and eventually in recycled biocrude as it became available. The following three aspects of the process were identified as critical: (1) the energy intensive pre-drying and grinding step required for wood flour preparation, (2) wood–biocrude–water slurries could not be fed at concentrations greater than 10% without causing system plugging, (3) high recycle ratios of biocrude (up to 19:1) required excessive heat [15]. Many process improvements have since been done, and it is believed that the critical aspects can be overcome or greatly reduced to an extent for the process to become feasible. One aspect of the process optimization is to maximize the biocrude whilst decreasing the amount of solid byproducts. During liquefaction, reactive biomass fragments rearrange to biocrude compounds through condensation, cyclization, and re-polymerization, and for prolonged process severity a solid fraction insoluble in most solvents is formed, which is generally termed char.

In a lignocellulosic context, char formation results primarily from two counteracting mechanisms; (1) dehydration reactions of free sugars favored at intermediate temperatures, high feed concentrations [16], and acidic conditions [17] and (2) radical formation during lignin degradation leading to retrogressive char formation [18]. Char formation from carbohydrates can be suppressed by applying high heating rates to reach high reaction temperatures, preferably above supercritical conditions, and alkaline conditions [16,19,20]. Lignin radical formation purely a thermal effect, hence supercritical conditions tends to enhance lignin char formation [21]. Means of overcoming these counteracting thermal effects includes the addition of a reducing agent such hydrogen or carbon monoxide, or by the addition of a stabilizing co-solvent acting as a radical scavenger through hydrogen donation. Alcohols may undergo thermal scission causing hydrogen abstraction in the form of $^{\cdot}$H, $^{\cdot}$OH, or $^{\cdot}CH_2OH$ radicals, amenable to cap lignin radicals and hence preventing lignin repolymerization [22–24]. Low molecular weight co-solvents such as phenol [25], propanol [26], ethanol [27,28], methanol [29], and glycerol [30,31] have been applied, and are preferable in order to obtain low molecular weight product compounds, when transport fuel precursors are targeted.

Among co-solvents, glycerol is of particular interest since it is already produced in large quantities. Today, glycerol is mainly a refined bio-based by-product from biodiesel production, and its market value has been declining since the market entry of biodiesel production, making it economically interesting. Xiu et al. investigated in batch the potential of utilizing crude glycerol, the unrefined by-product, as a co-substrate in hydrothermal processing of swine manure. It was found that crude glycerol enhanced both the yield and the quality of the biocrude based on the elemental composition [32–37]. In the same studies it was attempted to understand the conversion chemistry involved through model studies using pure glycerol, methanol, and fatty acids as model co-substrates, but the reaction mechanisms of the different organic compounds in the crude glycerol on the biocrude production were not fully established. Moreover, in house, but yet unpublished, model studies in batch reactors have shown that by hydrothermally liquefying aspen wood in the presence of glycerol or crude glycerol, char formation can be significantly reduced whilst maintaining a high yield of high quality biocrude [38].

The objective and novelty of the present study is to investigate and demonstrate continuous co-liquefaction at bench scale conditions of aspen wood and glycerol as a co-solvent as a viable route to process lignocellulose at high organic concentrations in the feed. The technical feasibility of process water phase recirculation is incorporated to evaluate benefits and eventual complications of such procedure. The process is evaluated based on system performance, recirculation effects on phase characteristics, and a product assessment to examine the quality of the obtained biocrude.

2. Materials and methods

2.1. Materials

Supercritical co-liquefaction of aspen wood and glycerol was demonstrated in the continuous bench scale reactor unit (CBS1) at the Department of Energy Technology, Aalborg University. In total, four batches of approximately 100 kg of feed each were processed, all prepared from the same recipe. Table 1 shows the properties of the aspen wood. Glycerol (99.5%), potassium carbonate (K_2CO_3), and carboxymethyl cellulose (CMC) were purchased from Brenntag Nordic A/S.

2.2. Process feed composition

Table 2 shows the feed composition used in the experimental campaign. Aspen wood and glycerol were mixed in nearly 50/50 ratios in recycled water phase together with K_2CO_3 and CMC. In the absence of product water phase, the feed for Batch #1 was prepared using distilled water.

2.3. Description of the Continuous Bench-Scale Unit (CBS1)

A process flow diagram (PFD) of the CBS1 is presented in Fig. 1. Pretreatment and feed slurry preparation is done in a stand-alone mixer, where aspen wood, glycerol, water phase and catalyst are mixed. Steady state conditions at the preset operating conditions are reached by circulating hot-compressed water (HCW) through

Table 1
Elemental and chemical analysis of aspen wood used in continuous hydrothermal liquefaction.

Elemental and chemical analysis[a] *(%, daf)*	
C	50.39 (±0.86)
H	6.19 (±0.08)
N	0.19 (±0.02)
S	N.D.
O (by difference)	43.23 (±0.08)
Fibre mass composition (%, db)[b]	
Cellulose	47.14 (±0.86)
Hemicellulose	19.64 (±0.11)
Lignin	22.11 (±0.17)
Extractives (by difference)	6.63 (±0.01)
Ash[c]	0.46 (±0.02)

daf = dry, ash-free. N.D. = Not Determined.

[a] Ultimate analysis was carried out in a Perkin Elmer 2400 Series II CHNS/O system.

[b] Fibre composition was determined by the Van Soest method in a FOSS Fibertec M6 unit.

[c] Ash content measured by heating a sample to 850 °C and held isothermally for 2 h.

Table 2
Feed slurry composition of the four batches.

Feed composition						
Compound	Aspen wood	Glycerol	Water phase	K_2CO_3	CMC	SUM
Mass fraction [%]	16.9	15.7	62.3	4.2	0.8	100

the plant. Once reached, the water is replaced by a batch of the prepared feed and continuous biocrude production commences. After each batch of approximately 100 kg, HCW is again recirculated to maintain process conditions. The feed barrel is reloaded with new premixed feed and processed continuously, and so on. Small amounts of CMC are added to the feed slurry (0.8% on a mass basis) to prevent feed slurry sedimentation while processing a batch. In a single stage, the feed slurry is pressurized to process pressure (300 bar) by a high pressure piston pump. Hereafter the feed is heated in two serial heaters to process temperature (400 °C) with a heat ramp in the range of 200–400 °C/min. Two 5 L, heat-traced, serial reactors accommodate the reaction residence time. Reactor effluent phases are pre-cooled in a concentric-tube heat exchanger prior entering two parallel high-pressure filters. Depressurization and feed slurry mass flow is controlled by serial capillary tubes of various lengths and various diameters. Finally, the product phases are cooled to ambient conditions in a secondary cooler before separation.

2.4. Process conditions for liquefaction experiments

Process conditions were kept constant at 400 °C and 300 bar. Mass flow rate was approximately 9 kg/h for Batch #1 and approximately 14 kg/h for Batch #2, #3, and #4. During each batch run, mass balance samples were collected to evaluate process yields. In total, 14 mass balances were collected over the four batches.

2.5. Product separation procedure

Product phases (water phase and biocrude phase) were separated gravimetrically in a separation funnel. In contrast to small scale lab-experiments, using only a gravimetric separation procedure alleviates the need for expensive solvents and provides a more realistic picture of economically viable yields. The biocrude and water phases were left to settle (30–60 min) before the water phase was tapped from the bottom of the funnel. Biocrude yields were measured right after the gravimetric separation. Product gases were collected and analyzed online for H_2, CO_2, CO, CH_4, and O_2.

2.6. Methods for biocrude and water phase analyses

Prior to biocrude analyses, the biocrude was centrifuged in a Sigma 6-16 HS centrifuge (2153 RCF) for 60 min to extract free water. Bound water was determined by Karl Fischer titration using a TitroLine 7500 KF. Elemental composition was measured using a Perkin Elmer 2400 Series II CHNS/O system (ASTM D5291). Calorific values were measured using an IKA C2000 oxygen combustion calorimeter (ASTM D2015). Qualitative analyses of all biocrude samples were carried out on a Thermo Scientific Trace 1300 ISQ GC–MS system, using a TG-SQC column (Length: 15 m, i.d.: 0.25 mm, film: 0.25 μm film). Prior to analysis, all samples were diluted in diethyl ether (DEE) and subjected to the following oven temperature profile: 40 °C was held for 3 min, then ramped to 325 °C at 8 °C/min and finally kept at this temperature for 4 min. Injector and ion source temperatures were 280 °C, split ratio was 1:20, and flow rate of the carrier gas (helium) was 1.0 mL/min.

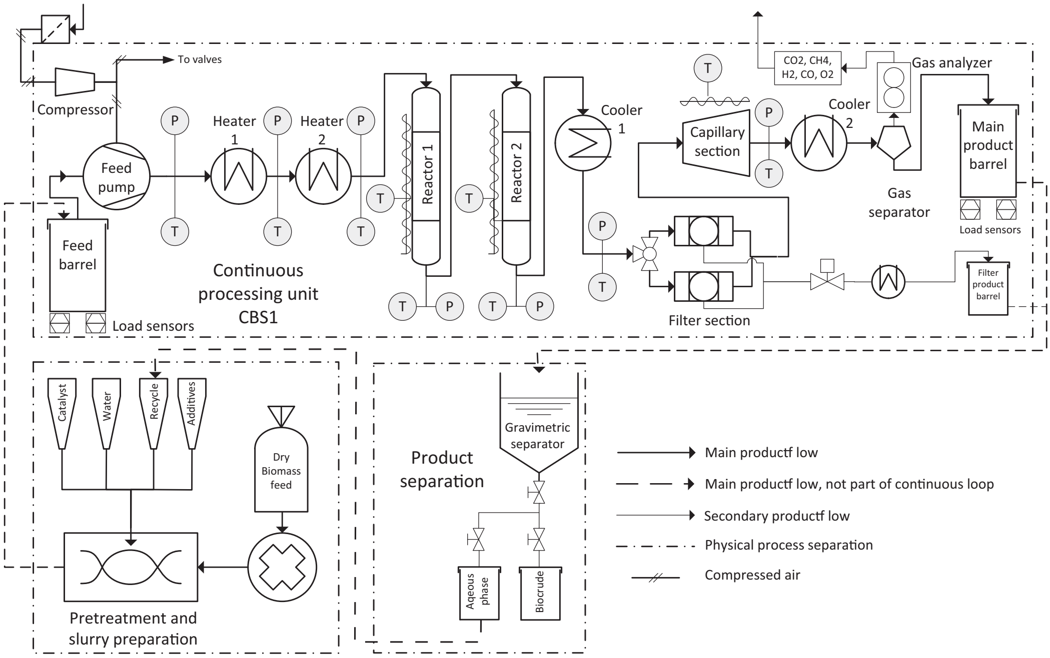

Fig. 1. PFD of the CBS1 unit.

Compounds were identified by mass spectra comparison with the NIST mass spectral data library. Identification of all compounds by GC–MS is challenged by the complexity of the mixture and due to the fact only the volatile fraction is identifiable (roughly 50% of the bulk biocrude). The identification of the reported compounds on the specific instrument was confirmed by a round robin test. Total organic carbon (TOC) and potassium analyses of the water phases were performed on a Hach Lange Spectrophotometer with RFID.

Energy Recovery (ER), Carbon Recovery (CR), and the effective hydrogen-to-carbon ratio (H/C_{eff}) were calculated according to Eqs. (1)–(3):

$$ER = \frac{\text{HHV of biocrude} \cdot \text{mass of biocrude}}{\text{HHV of feedstock} \cdot \text{mass of feedstock}} \tag{1}$$

$$CR = \frac{\text{mass of C in the biocrude}}{\text{mass of C in the feedstock}} \tag{2}$$

$$H/C_{eff} = \frac{H - 2O}{C} \tag{3}$$

3. Results and discussion

3.1. CBS1 performance

The performance and process stability in terms of process temperature, pressure, and mass flow rate of the CBS1 system is illustrated in Fig. 2. The figure displays trend curves for a typical batch run, operating at a flow rate of approximately 14 kg/h. It is readily observed that process conditions remains stable throughout the entire batch. Small pressure fluctuations in the beginning and in the end of a batch are observed, but these are explained by viscosity changes when feed is pumped into the system instead of HCW, and vice versa. The tiny oscillations in the pressure profile are due to the use of a piston pump.

For each mass balance sample roughly 20 kg of product (biocrude and water phase) was loaded into the funnel and left to separate gravimetrically before the water phase was tapped off at the bottom of the funnel. Fig. 3 clearly shows a resulting hydrophobic supernatant biocrude. The yields of biocrude were based on this initial gravimetric separation, where bound water was not included. Furthermore, later centrifugal runs of the biocrude samples revealed yet unsettled water which naturally introduced unaccounted experimental errors on the biocrude yields. Fig. 3 shows the yield calculations based on the mass balance samples obtained from the four batches. Due to significant yield variations within each batch, effects of water phase recirculation on the biocrude yields are somewhat inconclusive. As a result it is concluded that the separation procedure was not adequate for producing reliable yield results and a more robust and standardized separation procedure is under evaluation. Based on analysis of variations (ANOVA) calculations, it can only be concluded that yields from Batch #3 are statistically higher than the yields from Batch #4 (on a 95% confidence interval). During the liquefaction process water-soluble organics (WSO) are formed and contained in the aqueous phase. For Batch #1, for which the feed slurry was prepared using demineralized water, it appears from Table 3 that the total organic carbon (TOC) content of the aqueous phase reaches a value of 54.1 g/L. after the first batch. Due to the recirculation procedure adopted, commenced after Batch #1, it is observed that the TOC of the aqueous phase increases almost linearly to 136.2 g/L after the last batch. As the fraction of WSO in the aqueous phase increases, the biocrude and aqueous phase separation weakens since WSO act as co-solvents, leading ultimately to a single phase mixture, as it was found by Oasmaa et al. in a study on pyrolysis biooil separation [39]. As the amount of WSO increases, biocrude compounds become more soluble in the aqueous phase which could explain the tendency to a lower biocrude yield. The yield fluctuations also cause fluctuations in the energy

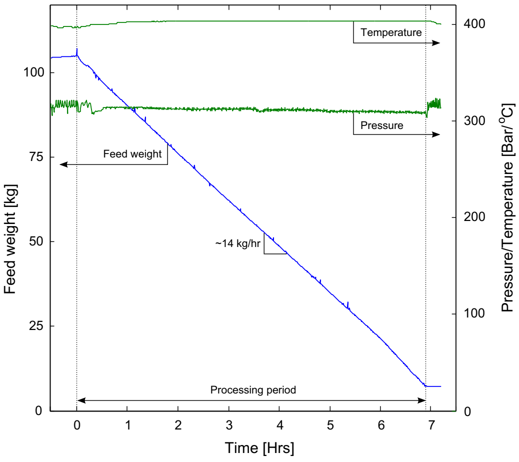

Fig. 2. Process conditions, temperature, pressure, and feed barrel weight during a continuous batch run.

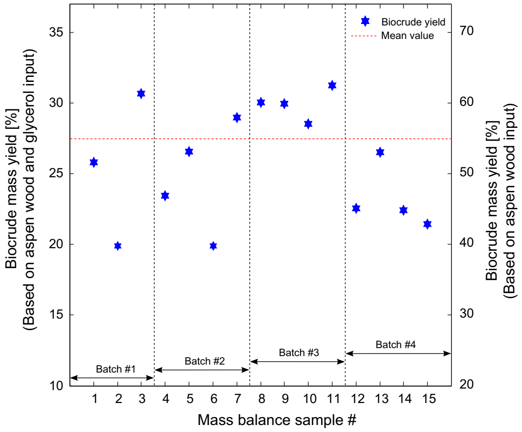

Fig. 3. Biocrude yields obtained from mass balance samples during the four batches. Mean value of all the mass balance samples are presented. In the plot; display of a typical supernatant biocrude and water phase sample. The hydrophobic biocrude readily separates gravimetrically.

Table 3
Aqueous phase analyses: mass fraction of ash, total organic carbon (TOC), pH and potassium (K) content of the four different batches.

	Batch #1	Batch #2	Batch #3	Batch #4
Ash [%]	6.20	9.41	10.7	12.6
TOC [g/L]	54.1	96.9	106.3	136.2
pH	5.28	5.91	6.02	5.35
K [g/L]	27.2	50	56.4	61.7

(ER) and carbon recovery (CR) in the biocrude. In the present experiments, biocrude ER and CR ranges from 39% to 62% and 42% to 66%, respectively. Due to the fact that glycerol forms mostly WSO or gaseous products, the ER and CR are generally penalized when including the co-solvent fraction in the ER and CR calculations, which is only measured with respect to the biocrude.

Table 3 also shows that accompanying the accumulation of WSO in the aqueous phase, ash is likewise observed to accumulate as an equal amount of K_2CO_3 is added for each batch. Starting at an aqueous phase ash content of 6.2%, resembling that of the original feed composition, the ash content is increasing linearly to a final value of 12.6% after three recycles. Tracing the potassium in the water phase, it is observed that potassium accumulates linearly in the water phase. The mass fraction of potassium to the total water phase is almost half of the mass fraction of the TOC to the total water phase. It is also evident that after four batches (3 recycles) steady state values of the water phase has yet not been reaches. During hydrothermal processing of glycerol, glycerol is mainly converted into WSO and hence the observation of WSO accumulation is likely to be a contribution from the high amount of glycerol added for each batch. Möller and Vogel investigated hydrothermal conversion of glycerol at 400 °C [16]. Even after 60 min, more than 10% of the glycerol was unconverted. During the present experiments, product analysis showed intact glycerol, but it was not clear how much glycerol was actually converted during processing. For continuous industrial operation with water phase recycling, ash accumulation presents an operational challenge to be addressed, as failing to do so may lead to operational malfunction. It has yet not been investigated, if the WSO containing water phase possess similar effects as glycerol on retardation of char formation. If so, glycerol may gradually by phased out as a feed additive as a work around for limiting the accumulation of WSO and still obtaining a stable process. The polarity of water as a solvent is known to diminish as it approaches near and supercritical water conditions, leading to solubility reduction for some salts, causing precipitation and ultimately plugging of the system. For the experiments reported here plugging was not experienced, nor did the campaign show signs of impending blockage, which would manifest itself as an increased pressure drop across the system.

Table 3 shows that after conversion the water phase is noticed to be acidic despite of the significant addition of alkaline catalyst. Lignocellulose and glycerol are known to form acidic compounds under hydrothermal processing, especially under alkaline conditions, which first neutralizes the K_2CO_3, then later acidifies the water phase [16,40]. Over the four batches the water phase pH appears almost invariant to the recirculation of aqueous phase.

To investigate if the aqueous recirculation affects the quality of the obtained biocrudes, an effective hydrogen-to-carbon ratio (H/C_{eff}) was calculated as a quality measure. Fig. 4 shows the results. Like for the biocrude yields, some variations within the individual batches are noticed blurring a clear trend to be observed. However, when excluding Batch #1, it seems as the quality in terms of H/C_{eff} is increasing as water phase is recirculated. The improvement in biocrude quality by aqueous phase recycling has also been demonstrated by Elliott et al. [10]. A hypothesis is that WSO act as hydrogen-donors. By aqueous phase recirculation, the concentration of WSO increases, which in turn increases the concentration of hydrogen-donors.

Gas phase composition was monitored continuously for carbon dioxide, hydrogen, methane, carbon monoxide, and oxygen throughout each batch. Fig. 5 displays typical gas trends. Initially, oxygen is diluted by producer gases and ultimately vanishes. It must be stated that the gas composition measured prior and in between batches is not precise, since gas detectors are calibrated only in a narrow band resembling process gas composition. It is noticed that the volume fractions CO_2 and H_2 reach steady state values of approximately 62% and 30%, respectively, and hence being the most abundant gases. The volume fractions of CH_4 and CO are 4–5% and 2–3%, respectively. During each mass balance samples, product gases are involuntarily exposed to surrounding conditions, allowing air to enter the gas stream. This is observed by an increased oxygen concentration, followed by decreasing product gases. After each mass balance sample steady state process conditions are reestablished as soon as the system is resealed. The gas mass flows were registered to approximately 0.6–0.7 kg/h, amounting to a mass fraction of approximately 12–15% of the input organic fraction. In terms of energy and carbon recoveries, this corresponds to approximately 2.4% and 8.8% in the gas phase.

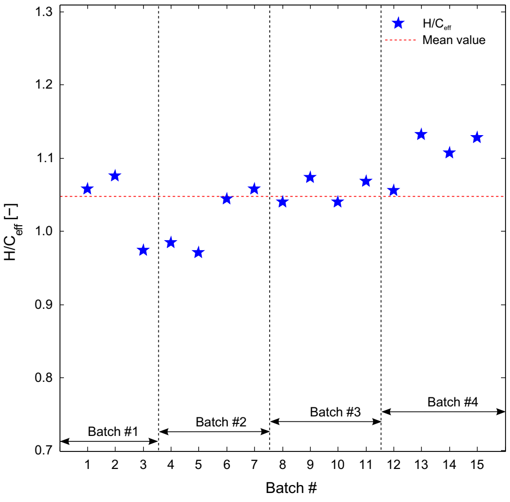

Fig. 4. H/C_{eff} of the biocrude obtained from mass balance samples during the four batches. Mean value of all the mass balance samples are presented.

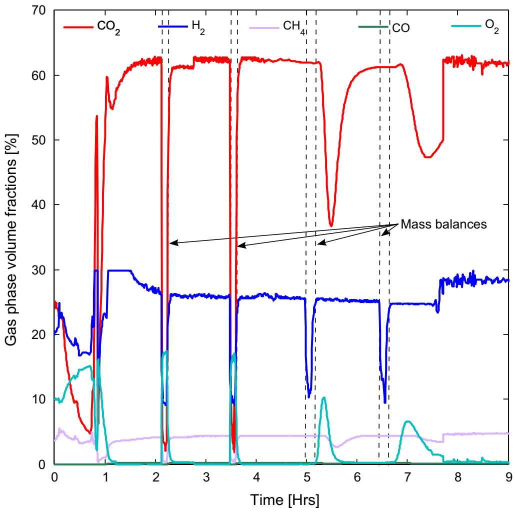

Fig. 5. Continuous process gas composition. Initiations of mass balances are indicated in the figure.

Table 4
Normalized gas composition of CO_2, CO, CH_4, and H_2.

	Gas phase volume fractions [%]			
	CO_2	CO	CH_4	H_2
Batch #1	62.1	2.9	4.6	30.5
Batch #2	62.1	2.9	4.6	30.5
Batch #3	60.8	2.7	4.5	32.0
Batch #4	63.6	3.3	4.2	28.8

At best, the carbon balance across input and output phases was established at a 96% closure.

Gas compositions obtained from the four batches are presented in Table 4, where the gas compositions have been normalized to exclude oxygen. It appears that the gas compositions are relatively invariant over the four runs and hence not affected by the water phase recirculation, although ashes and WS are observed to accumulate. The significant and insignificant shares of H_2 and CO, respectively, relative to uncatalyzed hydrothermal processing of lignocellulosic materials, indicate alternative chemical pathways [41–43]. Alkali catalysts have previously been found to enhance water–gas shift reactions, which can explain the high and low shares of H_2 and CO, respectively [44]. Steam reforming reactions may also be secondary contributors, but they proceed usually at much higher temperatures and in the presence of a transition metal catalyst [45]. A more speculative explanation is hydrogen abstraction reactions catalyzed by alkaline conditions. Glycerol deprotonation derives dihydroxyacetone, glyceraldehyde, and lactic acid, commonly observed WSO compounds, in addition to gaseous hydrogen [46].

3.2. Analyses of the biocrude

The biocrude was analyzed for determining the system performance in terms of biocrude quality. Table 5 compiles the bulk analysis obtained. First of all, it is observed that the mass fraction of oxygen in the biocrude (15.8%) is significantly lower as compared to that of the feedstock (47%, aspen wood plus glycerol). Secondly, the course of deoxygenation resulted in a hydrophobic, easily separable biocrude, with an increased gross calorific value (34.3 MJ/kg). The hydrophobicity of the biocrude is quantified by the low mass fraction of bound water in the biocrude (3.8%). It is further observed that the ash content of the biocrude is fairly high. The recycling effect of the ash content in the biocrude was not evaluated, but following the trends of the water phase, it is expected to increase from each aqueous phase recycle. A mass fraction of 0.48% of undesirable inorganics poses a potential challenge, as inorganics mount a concern from a downstream point of view. A significant part of the inorganics is alkali metals, carried over by the high amount of K_2CO_3 added for each batch cycle. If the biocrude is to be refined, inorganics may decompose and deposit in refinery hardware or even poison expensive refining catalysts. If the biocrude is to be combusted directly, inorganics can cause corrosion, wear, and deposit in pumps, injectors, burners, turbines, *etc.* Hence, if the aqueous phase is to be recycled, procedure amendments have to be implemented. Accumulation of inorganics is of particular concern, which is why an inorganic removal step of the aqueous phase may have to be implemented downstream. A supercritical salt separator has previously been proposed as a means for precipitation various salts with high separation efficiency [47]. Furthermore, the accumulation of WSO in the aqueous phase must be investigated in greater details to understand, (1) the impact of WSO on the conversion mechanisms in terms of yields and product quality and (2) the impact of WSO on the phase separation of the aqueous phase and the biocrude.

Table 5
Elemental mass analysis, higher heating value (HHV), mass fractions of ash and bound water of the biocrude, and biocrude ash composition.

Elemental analysis [% (daf)]		Metals [mg/g]	
C	75.2	Al	0.054
H	8.2	Cr	0.035
N	0.5	Fe	0.037
S	0.3	K	1.78
O	15.8	Mg	0.136
HHV [MJ/kg]	34.3	Zn	0.01
Ash content [%]	0.48	P	0.015
Bound water [%]	3.8	Ca	0.97
		S	0.1

The volatile fraction of the biocrude was further characterized to investigate the chemical composition. Table 6 presents the identified compounds by GC–MS analysis together with their

Table 6
List of compounds identified in the biocrude by gas chromatography–mass spectroscopy. The table includes compound name, formula, relative peak area, and number of carbon atoms (C#). No standards were used for compound verification.

RT (min)	Identified compound	Chemical formula	Peak area (%)	C#
2.06	Cyclopentanone	C_5H_8O	0.30	5
2.59	3,5,5-Trimethyl-2-hexene	C_9H_{18}	0.39	9
2.94	2-Methyl-cyclopentanone	$C_6H_{10}O$	2.28	6
3.37	Ethylbenzene	C_8H_{10}	0.39	8
3.56	p-Xylene	C_8H_{10}	0.62	8
3.87	2,5-Dimethyl-cyclopentanone	$C_9H_{16}O$	0.86	9
4.04	3,4-Dimethyl-3-penten-2-one	$C_7H_{12}O$	1.51	7
4.38	2-Methyl-2-cyclopenten-1-one	C_6H_8O	1.58	6
5.04	1-Cyclohexylethanol	$C_8H_{16}O$	2.84	7
5.19	1,2-Dimethyl-cyclohexene	C_8H_{14}	1.26	8
5.56	3-Methyl-2-cyclopenten-1-one	C_6H_8O	1.83	6
6.93	2,3-Dimethyl-2-cyclopenten-1-one	$C_7H_{12}O$	4.33	7
7.37	2,3,4-Trimethyl-2-cyclopenten-1-one	$C_8H_{12}O$	4.32	8
7.65	p-Cresol	C_7H_8O	1.75	7
8.12	2,3-Dimethyl-phenol	$C_8H_{10}O$	2.71	8
8.50	2-Ethyldienecyclohexanone	$C_8H_{14}O$	1.34	8
8.81	3,5-Dimethyl-phenol	$C_8H_{10}O$	4.69	8
9.15	2,4,6-Trimethyl-3-cyclohexen-1-carboxaldehyde	$C_{10}H_{16}O$	1.25	10
9.35	4-Methyl-1-(1-methylethyl)-cyclohexene	$C_{10}H_{18}$	1.32	10
9.44	4-Methyl-1-(1-methylethyl)-cyclohexene	$C_{10}H_{18}$	1.73	10
9.62	2,4,6-Trimethyl-3-cyclohexen-1-carboxaldehyde	$C_{10}H_{16}O$	1.62	10
9.82	4-Ethyl-3,4-dimethyl-2,5-cyclohexadien-1-one	$C_{10}H_{14}O$	1.31	10
10.14	2,4,6-Trimethyl-3-cyclohexen-1-carboxaldehyde	$C_{10}H_{16}O$	1.50	10
10.71	2,6-Dimethoxytoluene	$C_9H_{12}O_2$	1.49	9
11.07	2,3-Dihydroxy-3-methyl-1H-inden-1-one	$C_{11}H_{12}O_3$	2.05	10
11.33	Duroquinone	$C_{10}H_{12}O_2$	0.86	11
11.71	2,6-Dimethyl-1,4-benzenediol	$C_8H_{10}O_2$	1.62	8
12.13	4-Ethylcatechol	$C_8H_{10}O_2$	1.92	8
12.42	2,5-Dimethyl-1,4-benzenediol	$C_8H_{10}O_2$	1.47	8
12.76	5-Methoxy-2,3-dimethyl-phenol	$C_9H_{12}O_2$	3.67	9
12.90	4-Ethylguaiacol	$C_9H_{12}O_2$	2.54	9
13.68	2,3,5-Trimethyl-1,4-benzenediol	$C_9H_{12}O_2$	4.21	9
13.97	3-Tert-butyl-4-hydroxyanisole	$C_{11}H_{16}O_2$	1.52	11
14.19	4-Butoxybenzyl alcohol	$C_{10}H_{16}O$	0.93	10
14.81	2,3,5,6-Tetramethyl-1,4-benzenediol	$C_{10}H_{14}O_2$	1.52	10
15.30	2,6-Dimethoxy-4-(2-propenyl)-phenol	$C_{11}H_{14}O_3$	2.61	11
16.32	6-Tert-butyl-2,4-dimethylphenol	$C_{12}H_{18}O$	1.20	12
16.44	Benzaldehyde, 3-hydroxy-4-methoxy-2-(2-propenyl)-	$C_{11}H_{12}O_3$	0.81	12
16.63	4-(2,4,4-Trimethyl-cyclohexa-1,5-dienyl)-but-3-en-2-one	$C_{13}H_{18}O$	0.64	13
18.82	Methyl dehydroabietate	$C_{21}H_{30}O_2$	0.36	21
19.79	10,18-Bisnorabieta-5,7,9(10),11,13-pentene	$C_{18}H_{22}$	0.74	18
20.82	Retene	$C_{18}H_{18}$	1.55	18

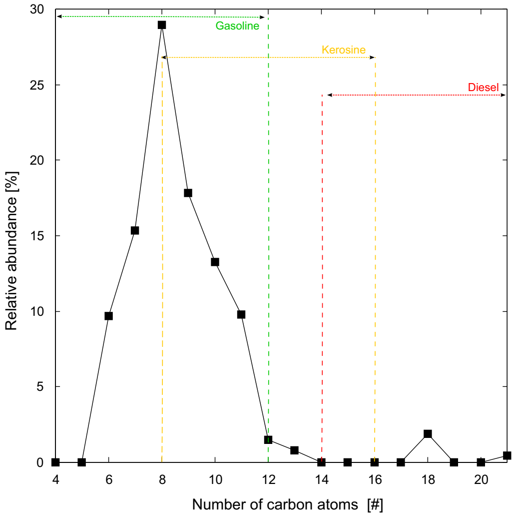

Fig. 6. Relative distribution (by relative peak area) in numbers of carbon atoms in the compounds obtained from the identified in the biocrude. The relative abundance is calculated based on summed relative peak areas. The ranges of number of carbon atoms in conventional fuels are included.

chemical formulas, relative peak area, and number of carbon atoms (C#). It is readily observed that the biocrude is a complex mixture of chemical compounds for which the majority of compounds are oxygenated cyclic structures having carbon atoms in the range of C_6–C_{21}. Unsaturated hydrocarbons compounds with higher number of carbon atoms, including fused ring structures, were also identified but in minor quantities. The major denominators for all of the compounds are cyclic C_5 or aromatic C_6 backbones, substituted with various functional groups (ketonic, aldehyde, phenolic). Ketonic functionalities are mainly observed on pentane and pentene backbones having only single heteroatoms, and are believed to be formed by condensation reactions between Retro-Aldol derived carbohydrate intermediates. A broad collection of aromatics are also observed having mainly phenolic functionalities with single, double or even triple heteroatom formulas. Despite the fact that the compound mixture is complex and diverse, the range of numbers of carbon atoms is relatively narrow. The distribution of number of carbon atoms based on the identified compounds has been calculated semi-quantitatively by total ion count. The distribution is plotted in Fig. 6, together with the common number of carbon atom ranges of conventional gasoline, kerosene-type jet fuel, and diesel. It appears that the majority of compounds lump into the C_6–C_{12} region, mainly representing gasoline range and 'low cut' jet fuel. Based only on carbon range, the diesel range is hardly represented in the biocrude.

4. Conclusion

Continuous co-liquefaction of aspen wood and glycerol at supercritical water conditions was demonstrated successfully. High organic content feeds were prepared and processed for which a water phase recycling procedure was implemented. High process stability in terms of temperature, pressure, and mass flow rate was obtained and steady state conditions were achieved throughout all experiments. High hydrophobicity of the resulting biocrudes allowed for a simple, but commercially realistic, gravimetric separation between biocrudes and water phases. Unfortunately, significant yield variations obtained from mass balance samples within each batch obscured the identification of clear effects of the water phase recirculation on the biocrude yields, but a slight decreasing tendency is observed. Conversely the biocrude yield trend, the biocrude quality in terms of an effective hydrogen-to-carbon ratio was observed to increase slightly when the water phase is recirculated. Gas phase yields and compositions were found almost invariant to the water phase recirculation. Some process inconveniences were observed with respect to water phase recirculation; TOC and ash contents of the water phase were observed to increase significantly with water phase recirculation, which may eventually lead to system failure due to salt precipitation. Moreover, the mass fraction of ash in the biocrude was found relatively high (0.48%). From the biocrude analysis it was found that the major biocrude compounds were cyclic C_5 or aromatic C_6 backbones, substituted with various oxygenated functionalities. The number of carbon atoms range of the biocrude compounds is distributed mainly in the C_6–C_{12} range similar to gasoline. In conclusion, the experimental campaign demonstrated an auspicious platform for continuous operation of hydrothermal liquefaction for the production of high quality biocrudes.

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