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

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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 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 phyto-extraction 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 (N₂) for air removal, pre-pressurized with approximately 2 MPa N₂ 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 $673 \pm 2\text{K}$ 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 equations (1) and (2), respectively. The gas yield was quantified by GC analysis. Equations (3) and (4) represent the carbon and hydrogen balance, respectively. In these equations, $C_{product}$ and $H_{product}$ represent 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 (CO₂), methane (CH₄), 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 (30m long, 0.32mm ID, 25µm film thickness) and HP-PLOT/Q (30m long, 0.53mm ID, 40µm film thickness). Hydrogen (H₂) 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 μ m 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 to 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**d**, resulting in a feed with increased viscosity and water-holding capacity.

The most dramatic alteration of the willow structure occurred**red** 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**d** a range of organic acids, whereas lignin provided**d** 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**ed** 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.*, 2011), promoting retro-aldol reactions/cleavage and condensation reactions (Mazaheri *et al.*, 2010) and preventing 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.*, 2011), 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 hydroxymethyl-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 have 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**d** while the relative abundance of phenolic compounds and ketones decreased**d**, 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. Gravimetric 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. (*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. (*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 CO₂ (see Figure 1). CO₂ 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 CO₂ 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 CO₂ could be released from carbohydrates 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 H₂ and CO₂ 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 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 Figure 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 0min, 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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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.	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	7	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	8.8±0.1	0.7±0.1	1.4±0.03	0.0±0.0	1.4±0.2	0.0±0.0
				1.5±0.1					
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		23.85		23.347
P			0.648		0.251		2		0.667
S			0.121		0.104		0.171		0.084
							0.030		

Table 2 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	C5H10O	86	2.94	6.85	4.98	3.39
	4-methyl-2-pentanol	C6H14O	102	0	3.09	2.30	1.75
	5-octen-1-ol	C8H16O	128	0.67	0.75	1.47	1.49
	2-methyl-1-hexadecanol	C17H36O	256	1.55	1.06	1.58	1.45
Ketones	Cyclopentanone	C5H8O	84	0.98	0.86	0.43	0.46
	2-methyl-cyclopentanone	C6H10O	98	0	1.73	1.77	1.51
	4-hydroxy-4-methyl-2-pentanone	C6H12O2	116	6.47	1.45	2.78	2.69
	3-methyl-cyclohexanone	C7H12O	112	0	0	1.89	1.34
	2-methyl-2-cyclopenten-1-one	C6H8O	96	2.07	0.90	0.42	0.48
	2,3-dimethyl-2-cyclopenten-1-one	C7H10O	110	0.68	0.49	0.36	0.51
	3-methyl-2-cyclopenten-1-one	C6H8O	96	3.65	0	0	0
	3,4-dimethyl-2-cyclopenten-1-one	C7H10O	110	0.96	0.35	1.00	0.47
	2,3-dimethyl-2-cyclopenten-1-one	C7H10O	110	0.97	0.56	0.43	0.70
	3,4-dimethyl-2-cyclopenten-1-one	C7H10O	110	0.87	0.49	0	0.47
	2,3-dimethyl-2-cyclopenten-1-one	C7H10O	110	3.65	1.48	1.01	1.24
	2,3,4-trimethyl-2-cyclopenten-1-one	C8H12O	124	0.56	0.33	1.11	1.22
	3-isopropyl-2-cyclopenten-1-one	C8H12O	124	0.57	0.37	0	0.82
	2,3,4,5-tetramethyl-2-cyclopenten-1-one	C9H14O	138	0.42	0	0.55	0.75
	3-isopropyl-2-cyclopenten-1-one	C8H12O	124	0.58	0	0	0
	2,2-dimethylcyclohexyl methyl ketone	C10H18O	154	0.99	1.65	3.43	3.44
Phenols	Phenol	C6H6O	94	1.98	0.65	0.66	0.83
	m-cresol	C7H8O	108	0.88	0.5	0.55	0.79
	p-cresol	C7H8O	108	1.51	0	0.52	0.63
	2-methoxy-phenol	C7H8O2	124	2.01	0.78	1.26	1.84
	2,3-xyleneol	C8H10O	122	0.38	0.63	0.60	0.72
	2-methoxy-4-methyl-phenol (creosol)	C8H12O2	138	1.25	1.67	3.04	2.69
	2,3,6-trimethyl-phenol	C9H12O	136	0	0	0.93	0.84
	4-ethyl-2-methoxy-phenol(p-ethylguaiacol)	C9H12O2	152	0.90	0.38	0.59	0.47
	2,6-dimethoxy-phenol	C8H10O3	154	0.85	0	0.47	0.51
	2-methoxy-4-propyl-phenol	C10H14O2	166	0.39	0	0	0
	4-methoxy-3-(methoxymethyl)-phenol	C9H12O3	168	0.56	0.46	0	0.46
Esters	Butylated hydroxytoluene	C15H24O	220	2.11	6.71	11.06	10.86
	2-propenoic acid, 3-(1-acetyl-2,2-dimethylcyclopentyl)-,methyl ester	C13H20O3	224	0.41	0.36	0.82	1.04
	Terephthalic acid, bis(2-ethylhexyl)ester	C24H38O4	390	23.32	11.01	0	0
Others	2-chloro-2-methyl-butane	C5H11Cl	106	8.43	22.50	17.70	13.11
	2,5,8-trimethyl-1,2,3,4-tetrahydro-1-naphthol	C13H18O	190	0.32	0	0	0
	9-hexadecenoic acid	C16H30O2	254	0.65	0.42	0.63	0.65
	(Z)-9-octadecenamide	C18H35NO	281	6.31	8.56	2.89	10.46
Total				80.84	77.04	67.23	70.08

Table 3 Mass, Carbon and Hydrogen balances of HTL products resulting from conversion of the four feedstocks at three reaction temperatures: 0min, 10min 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;													

Figure 1 Gas composition as function of the HTL reaction time