



Research paper

Production of fuel range oxygenates by supercritical hydrothermal liquefaction of lignocellulosic model systems



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ABSTRACT

Lignocellulosic model compounds and aspen wood are processed at supercritical hydrothermal conditions to study and understand feedstock impact on biocrude formation and characteristics. Glucose and xylose demonstrate similar yield of biocrude and biochar, similar biocrude characteristics, and it is hypothesized that reaction mechanisms for the two model compounds are indistinguishable. Glucose and xylose are main sources of substituted cyclopentenones and substantial contributors to oxygenated aromatics mainly in the range of C₆–C₉ number of carbon atoms, and potential, sustainable biogasoline candidates. Lignin yields predominantly aromatic biocrudes having similar C₆–C₉ number of carbon atoms. Model mixtures show good predictability in the distribution of substituted cyclopentenones and oxygenated aromatics, but aspen wood-derived biocrude is more aromatic than predicted by model mixtures. The work extends previous work on the understanding of the chemical mechanisms of lignocellulose liquefaction and the biocrude formation. Potential applications for the biocrudes are identified, where significant sustainability issues for the transport sector can be addressed.

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1. Introduction

Hydrothermal processing of biomass in near-critical water is a viable, scalable and renewable chemical pathway, utilizing the unique properties of hot-compressed water (HCW), to break down the original macromolecules in biomass and convert their fragments into green synthetic liquid (hydrothermal liquefaction, HTL) [1–4] or gaseous fuels (super critical water gasification, SCWG) [5,6]. The processing technology has been identified as a promising energy efficient and sustainable carbon-neutral platform for valorisation of biomasses through bio-fuel production [7]. Hydrothermal processing has successfully been demonstrated to convert a broad range of biomasses into four easily separated phases; a gas phase rich in carbon dioxide and combustible gases (e.g. H₂ and CH₄), a combustible biochar solid phase, a distinct water-soluble organic phase suitable for fine chemical extraction or synthetic gas production, and a bulk, water-insoluble and oxygen-lean fraction commonly termed biocrude, all which comprise an ideal no waste discharge system. The biocrude is a blend of numerous intermediate chemical compounds spanning a broad range from e.g.

oxygenated aromatics, heterocyclic compounds to long chain aliphatic backbones mostly dependent on the feedstock composition. The feasibility of the conversion step of various biomasses into biocrudes has already been proven mostly in batch and less so in continuous processing systems [7], and techno-economic assessments recognize HTL as a profitable process for marketable sustainable liquid fuels, even when followed by a subsequent hydrotreatment step to meet hydrocarbon specs for drop-in applications [8–10]. Several studies have shown that the specific composition of the different types of biomass (wood, grass, vegetable oils, algae etc.) has a major influence on the chemical profile of the biocrude [11–19].

Predictability between feedstock composition and biocrude characteristics is still a topic that needs attention [13,20]. General trends have been observed, such as microalgae resulting mostly in aliphatic structures, mainly due to the high lipid contents, and lignocelluloses resulting in alkylated cyclopentenones and aromatic structures, the latter expected to originate mainly from lignin conversion. The numerous compounds found in the biocrude and the lack of predictability are considered a significant challenge for technology commercialization. Recently, Carrier et al. investigated the conversion of holocellulose, lignin and α -cellulose extracted from fronds (*Pteris vittata* L.) at sub- and supercritical water conditions, and found that the resulting

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compounds can be grouped into two main compound pools; one consisting of oxygenated and substituted 5-membered ring structures, such as ketonic cyclopentanes and cyclopentenes (CPs), and one consisting of oxygenated and substituted aromatics (OA) [12,13]. This is a significant simplification of a highly complex pool of compounds, which further simplifies the identification of downstream applications of the resulting liquids, as these can be characterized by compound families or pools rather than individual compounds. It was further found that the first group of 5-membered derivative compounds originated from the carbohydrates and that the aromatic derivatives originated both from the carbohydrates and lignin. The compounds obtained consisted mainly of oxygenated paraffins, olefins and aromatics and ranged primarily from the C₅ to C₁₀ number of carbon atoms, and had been identified as promising drop-in gasoline candidates [21]. It was also found that the distribution of 5-membered compounds and aromatics was almost invariant to reaction time but sensitive to reaction temperature and feedstock composition, as mentioned above.

Although these observations are indicators of expected product compounds, it is of particular interest to investigate if the distribution of the two primary compound pools can be predicted and produced selectively based on varying the feedstock composition. If this is the case, it provides an opportunity to tailor biocrude composition to the intended downstream purpose by manipulating the feedstock composition.

To the best of our knowledge, a comprehensive study investigating lignocellulosics from a single model compound and model mixtures point of view does not exist. The main objective of this study is thus a novel contribution to the understanding of the chemistry of biocrude formation and the quality of such biocrudes from a model compound viewpoint. It is generally accepted that alkaline conditions and high process severity leads to higher quality biocrude, which justifies processing at supercritical conditions compared to subcritical conditions [7]. Glucose, xylose and alkali lignin as model compounds for cellulose, hemicellulose and lignin, respectively, and their mixtures are processed in an alkaline supercritical water environment to obtain original information on the formation of green fuel range chemicals. It is envisioned that by studying and understanding the biocrude formation of the individual lignocellulose constituents, unique knowledge can be gained towards understanding the relationship between macro-structures (carbohydrates vs. lignin) on the biocrude formation from real biomass feedstock. In this work, an experimental campaign is carried out to investigate:

1. The formation and characterization of the water-insoluble compounds obtained when processing aspen wood under alkaline supercritical water conditions.
2. The formation of biocrude from individual model compounds; glucose, xylose and lignin along with the characterization of the individual biocrudes.
3. The behavior of sugar derived model compounds to understand the biocrude composition to the chemical properties of the input feed.

2. Materials and methods

2.1. Materials

Glucose, xylose, lignin (alkali, low sulfonate), sorbitol, xylitol and ethylene glycol (EG) were all purchased from Sigma–Aldrich ($\geq 98\%$). Glycerol (99.5%) was purchased from Brenntag Nordic A/S. Properties of the aspen wood used are listed in Table 1.

Table 1

^aUltimate analysis was carried out in a Perkin Elmer 2400 Series II CHNS/O system. ^bFibre composition was determined by the Van Soest method in a FOSS 121 Fibertec unit. ^cAsh content measured by heating a sample to 850 °C and hold isothermally for 2 h daf = dry, ash-free. N.D. = Not Detected.

^a Ultimate analysis (wt. %, 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)
^b Fibre Composition (wt. %, db.)	
Cellulose	63.59 (0.86)
Hemicellulose	7.65 (0.11)
Lignin	22.13 (0.17)
Extractives (by difference)	6.63 (0.01)
^c Ash	0.46 (0.02)

2.2. Experimental procedure

All experiments were carried out in rapidly heated, 10 mL batch micro-reactors. For each run, the reactor was loaded with 5 g of pre-mixed solutions reaching an estimated final autogenous reaction pressure of circa 300 bars. All mixtures consisted of 20 wt. % input bio-feedstock, for all combinations of model compounds, mixtures hereof or real biomass mixed in demineralized water. K₂CO₃ was added as an alkaline catalyst amounting to 10 wt. % of the input bio-feedstock (pH 11.5). The reactor was purged with nitrogen before heating, and then heated to 400 °C in a pre-heated fluidised sand bath (Techne SBL-2D) for 15 min (including the heating period) and finally quenched in water. Typical heating and cooling rates for the micro-reactors are 250–450 K/min and >1000 K/min., respectively, conclusively eliminating any heating and cooling rate effects compared to the time spent at final reaction conditions.

Five mixtures (Mix1–5) of glucose, xylose and lignin were investigated to study qualitative effects on the biocrudes from different compositions. The compositions of the five mixtures were chosen in order to frame the composition of a variety of lignocellulosic feedstock obtained from Demirbas et al. [22]. The compositions of the five mixtures are displayed in Table 2.

2.3. Recovery and analysis of biocrude

After the reactor was cooled to room temperature any overpressure was vented through a top valve. No further attention was given to the gas phase in this work. As in most comparable work with micro-reactors, extraction and separation of products from the micro-reactor was found challenging as some products remained partially emulsified in the aqueous phase and had to be extracted by an appropriate water-insoluble solvent to obtain stable and reproducible results. In the adopted procedure, the aqueous phase and easily removable products were poured out of the reactors and filtered to remove any solids. The emulsified aqueous phase was then extracted using diethyl ether (DEE) which led to a phase separation.

Table 2

Composition of the five model compound mixtures investigated. The five mixtures are arranged as four corner and one center point, framing the variety of cellulose, hemicellulose and lignin compositions of lignocellulosic biomass [22].

	Mix1	Mix2	Mix3	Mix4	Mix5
Cellulose/Lignin	1/3	1/3	3	3	8/3
Hemicellulose/Lignin	1/3	3	3	1/3	8/3

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