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## Impact of nitrogenous alkaline agent on continuous HTL of lignocellulosic biomass and biocrude upgrading

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### ABSTRACT

Continuous hydrothermal liquefaction (CHTL) of lignocellulosic biomass with subsequent hydrotreating is carried out to study the effect of NH<sub>3</sub> versus NaOH as alkaline HTL catalyst. Product analysis include Py-GCxGC-MS, simulated distillation and fractional distillation. Ammonia enhances biocrude quality slightly in terms of H/C ratio, density and HHV, but a significant coke formation of 11 wt.% is observed. Furthermore, ammonia pollutes the biocrude with 2.7 wt.% nitrogen, which is observed to inhibit hydrotreating conversion. In comparison, CHTL with NaOH is associated with a 43 wt.% yield of a hydrotreatable biocrude, stable TOC levels during aqueous phase recirculation and mass, carbon and energy balance closure. Hydrotreating eliminates the TAN, reduces oxygen to 2–3 wt.% and produces a promising fuel bio-blendstock with ultra-low sulphur and a diesel fraction equal to 43%.

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### 1. Introduction

Hydrothermal liquefaction (HTL) and pyrolysis are thermochemical processes capable of converting biomass into liquid energy carriers. In particular, HTL enables a feedstock-flexible conversion of non-food biomass to a liquid biocrude intermediate [1–5] that can be hydrotreated to produce drop-in biofuel [6–8]. The greenhouse gas emission savings on a HTL biofuel from wood is estimated to be 70% [9] to 84% [10] relative to the 2005 petroleum baseline. However, with the recent collapse of benchmark oil prices, there is little economic incentive to keep pursuing pathways to biofuel blendstocks or alternatives to fossil resources. The skepticism seems justified, as HTL biocrude production costs around \$70 per barrel were reported in a thorough techno-economic assessment prepared for the U.S. Department of Energy by Tews et al. [9]. But is the price of biofuel equal to that of commodity fuels? And is it fair to determine a price just based on energy content, when the source of this energy has significant impact on the cost to society of using it?

During the last decade the price of liquid biofuels have been dictated by the price of their fossil equivalent and thus crude oil [11]. A margin between fossil and bio has facilitated a business case for e.g. production of hydrogenation derived renewable diesel by

major players such as Neste, Preem, UPM biofuels and Dynamic Fuels [12]. However, hydrogenation of fatty acids and vegetable oils comprise a simpler process relative to thermochemical conversion of solid biomass into biofuels, and the additional complexity of the latter may need incorporation into the price margin before such technologies will be commercial. Contained in the production cost of biofuels is also the cost of curbing CO<sub>2</sub> emissions. In the case of fossil fuels, it is not, yet it is likely that the additional cost associated with removing resulting CO<sub>2</sub> from the atmosphere or dealing with climate changes (or both) will be significantly higher than the additional price tag on biofuels. Recognizing this and acknowledging the recent calls for action [13,14], it is very likely that near future society through legislative framework will create a market for biocrudes that is independent of benchmark crude oil prices. As a result, the price of biofuel will be less affected by the price of benchmark petroleum, but instead regulated by the biocrude availability and the cost competitiveness of the individual biocrude production technologies such as HTL. Significant players on the international political agenda are indirectly supporting the improved incitements for biofuel production by raising awareness to the heavy subsidisation of fossil fuels. In 2009, the G20 nations and APEC called for an end to fossil fuel subsidies. But since then the consumption subsidies to fossil fuels has increased from \$390 billion in 2009 (in 2014 dollars) to \$493 billion in 2014 [13]. Continuing these subsidies adds to the undermining of the competitiveness of renewables, and discourages necessary investments into energy efficiency and

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renewable technology [13–15]. IEA calls for a progressively stronger commitment in the conclusive remarks of their 2015 World Energy Outlook [13]. In support of this and recognizing that even though the competitiveness will not be relative to the cost of fossil energy, there will still be strong motivations to drive down production costs for biofuel technologies in competition with each other, the present study contributes to the development of cost-competitive HTL of biomass for bio-crude production.

### 1.1. Aspects on ammonia as alkaline HTL catalyst

Based on the above reasoning, the effect of using ammonia instead of sodium hydroxide as HTL catalyst in continuous conversion of wood is studied. The catalyst comprises around 15% of the fixed HTL operating costs in the economic assessment by Tews et al. [9], which motivates the study of  $\text{NH}_3$  as a potentially cheaper and/or more effective catalyst compared to NaOH. Secondly, ammonia may potentially act as both hydrogen donor to improve the H/C ratio of the biocrude, and as radical scavenger to reduce polymerization reactions or coke formation. Finally, the dielectric constant of water decreases significantly when entering the supercritical state, which introduces the risk of precipitation of inorganic salts such as NaOH [16,17]. This can be avoided by using ammonia as the alkaline catalyst, since it is completely soluble in supercritical water [18]. A potential downside associated with the use of ammonia during HTL of lignocellulose is the risk of polluting the biocrude by introducing a nitrogenous reagent into a feed very low on nitrogen. The intended product is a pure hydrocarbon biofuel, and nitrogen removal through hydrotreating requires severer conditions and more stoichiometric hydrogen relative to sulphur and oxygen removal [19,20]. The risk of polluting the biocrude with nitrogen may however be of less importance considering the nitrogen that is indigenous to HTL biocrudes from protein rich feedstocks such as algae, manure and municipal waste [2,3,5]. Thus, the findings of this study may also contribute to the knowledge on HTL of such feedstocks.

In a recent study by Albrecht et al. [8] on CHTL and hydrotreating of algae, more than 50 vol.% of ammonia was detected in the gaseous hydrotreating products. From circularity and efficiency considerations, this introduces the potential of applying the ammonia produced during hydrotreatment of nitrogenous biocrudes as alkaline HTL catalyst during production of these. On the other hand Albrecht et al. [8] state that ammonia was observed to pollute the Brønsted acid sites of the presulphided  $\text{CoMo}/\text{Al}_2\text{O}_3$  hydrotreating catalyst and thereby inhibit cracking activity. Thus, numerous aspects including the effect on HTL process stability, biocrude quality and downstream hydrotreatability are to be considered when evaluating the effect of using ammonia versus sodium hydroxide as HTL catalyst in the production of biofuels. In support of this, the current study investigates the effects discovered during the entire path from tree to tank.

### 1.2. Effect of hydrotreatment on biocrude volatility

Hydrotreating of biocrudes result in severe heteroatom removal and this is expected to affect the volatility of the biocrude significantly, which describes an additional hypothesis challenged in this study. Generally, oxygenates are characterized by a higher boiling point than the corresponding hydrocarbon due to the changes oxygen does to intermolecular forces such as hydrogen bonding and van der Waals attractions. To give an example, phenol has a boiling point of 182 °C, whereas the boiling point of benzene is 80 °C [21].

The distillation profile of a particular crude mineral oil is a crucial parameter in order to evaluate its suitability in a given petrochemical process such as e.g. a petroleum refinery that simply put is designed around the distillation profile of a particular group of crude

**Table 1**  
List of equipment used for product analysis.

Analysis	Equipment
Simulated distillation	ASTM D7169 (Cert. Lab.)
Elemental analysis	ASTM D5291 (Cert. Lab.)
Heating value	IKA C2000 Basic
FT-IR	Thermo Sc. Nicolet 380
Density	Anton Paar DMA500
CCR	Perkin Elmer STA 6000
Py-GC/GC-MS	Shimadzu QP-2010
GC/GC columns	DB-5 & DB-17
Gas analysis	Shimadzu GC2010
TAN	Manual titration
TBP distillation	BR Instruments, ASTM D2892

oils [22]. Since biocrude is mostly proposed as a potential route towards petroleum crude oil substitution, it is beneficial to adopt crude oil characterization and evaluation tools. Meanwhile, it is important that the different composition of a biocrude compared to a mineral crude is acknowledged. Within commodity petroleum fuel production, distillation residue is associated with a higher degree of processing and thus costs to produce final products compared to the straight run distillates [19]. Thus, it is extremely important to acknowledge the effect heteroatoms have on a biocrude distillation profile when evaluating the corresponding technology for biofuel production.

## 2. Experimental section

The experimental work includes CHTL at a continuous bench scale unit and subsequent hydrotreating in microbatch reactors. Microbatch HTL was also carried out to further evaluate certain observations, but the microbatch HTL is of minor importance and it is carefully outlined whenever microbatch HTL results are discussed. The methodologies applied are described for each reactor system below. Table 1 comprises the list of equipment used for the various analysis carried out. A 15:5 fractional distillation of the CHTL biocrudes were carried out according to ASTM D2892. 15:5 refers to a 15 theoretical plate, 5:1 reflux distillation. Hoffmann et al. [23] provides more information on the set-up and fractional distillation of HTL biocrudes in general.

### 2.1. Continuous hydrothermal liquefaction

CHTL at a state of the art research facility have been carried out during two campaigns with a total of more than 100 hours of operation. The two campaigns deviate with respect to HTL catalyst, which were aqueous ammonia (ammonia hydroxide) and sodium hydroxide applied in 1 wt.% and 2.5 wt.% slurry concentrations respectively. Potassium carbonate was added and adjusted to stable concentrations around 15 g/l in both campaigns.

Two biocrudes were produced during the continuous campaigns by processing aspen wood with supercritical water in a 17.5% dry matter content slurry at approximately 400 °C, 310 bar and 20–23 kg/h. Briefly described, the semi-continuous HTL bench scale unit CBS1 consists of a high pressure piston pump, two serially connected induction heaters, two 5 L serial reactors, a cooler, a capillary depressurisation system and a 3-phase funnel separator. Further details on the system can be found in Refs. [4,24–26]. Biocrude and aqueous phase products were recycled during production. Recycling of the biocrude phase enhance homogeneity and thus pumpability of the slurry, it improves oil quality and yield, and it reduces the overall heat capacity of the slurry [4]. Likewise, recycling of the aqueous phase improves process stability, biocrude quality and yield, and it reflects an up-scaled process design, in which water phase recycling is a necessity in order to reduce water treatment expenses [4]. Crude

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