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Characterization of the aqueous fractions from hydrotreatment and hydrothermal liquefaction of lignocellulosic feedstocks

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ABSTRACT

In this study the aqueous phases resulting from the hydrothermal liquefaction (HTL) of biomass and the hydrotreatment (HT) of fast pyrolysis bio-oils were analyzed via TC, COD, GC-MS, GC-FID, HPLC, and ICP-OES to determine the organic and inorganic species present and the quantitative amounts of each. This work is necessary to address a significant knowledge gap in the literature related to the aqueous phases from thermochemical processes. Results showed that water from the hydrotreatment of eight different bio-oils contained less than 1 wt% total carbon, in many cases less than 0.2%. Negligible organic carbon was observed. HTL samples contained between 1 and 2 wt% carbon. Due to the large volume of water added to the HTL feedstock and the dilute samples generated, this accounts for 34–45% of the total carbon sent to the reactor. The majority of this carbon was present as acids, with glycolic acid and acetic acid having the highest concentrations. Alcohols, specifically methanol and ethanol, were also present. Numerous ketones were observed, consisting of mainly acetone and cyclopenta-ones. The amount of the total carbon identified and quantified in the HTL samples ranged from 64 to 82%. Inorganic species present in the HT samples were sodium, silicon, and sulfur. The highest levels of sulfur were observed in the grasses and agricultural residue (corn stover). The HTL samples exhibited much higher inorganic content, with very high levels of sodium and potassium. Alkali and alkali earth metals, as well as sulfur, were also present at levels high enough to raise concerns for the use of catalysts in downstream upgrading or reforming processes.

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1. Introduction

As the global use of petrochemical fuels increases, the unsustainable nature of the current utilization trends is receiving greater attention. The concerns being raised cover a

wide range of topics, including environmental, political, and economic [1–3]. In particular, the use of petrochemical fuels for the transportation industry has been highlighted. According to the most recent reports, 70% of all the petroleum consumed by the United States was used to produce liquid

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transportation fuels [4]. In light of this data, the use of renewable biomass feedstocks capable of generating infrastructure compatible liquid transportation fuels is receiving serious consideration [5]. In addition to biological conversion pathways such as fermentation to produce alcohols, thermochemical processes such as hydrothermal liquefaction (HTL) and fast pyrolysis (FP) have become a cornerstone of biofuels research [6].

The direct liquefaction of biomass to produce an intermediate known as bio-oil (when used for pyrolysis products) or biocrude (when referring to HTL products) has seen extensive research in the last several decades [7–10]. Two methods in particular have become the focus for the primary processing step, namely hydrothermal liquefaction and fast pyrolysis. Hydrothermal liquefaction is a process where the biomass is combined with water to form a slurry that is then pumped into a reactor operated in a condensed phase at medium temperature (280–370 °C) and high pressure (10–25 MPa) with residence times typically in the range of 5–60 min [11]. The outlet stream includes the biocrude, solids consisting of primarily ash with small quantities of char, non-condensable gases, and a distinct aqueous byproduct that is easily separated from the non-polar organic fraction (biocrude). Fast pyrolysis is a process where the biomass is rapidly heated (e.g. 2 s) to ~500 °C in an inert environment at ambient pressures. The resultant outlet stream contains a liquid aerosol, char, and non-condensable gases [12]. The solids are removed from the product stream and the liquids are then condensed to give the final bio-oil product. Although the water content of the oil can be between 15 and 30%, a separate aqueous fraction is generally not formed [13]. Regardless of the primary conversion pathway used, the resultant bio-oil/biocrude must undergo an upgrading process known as catalytic hydroprocessing (also referred to as hydrotreatment) that includes catalytic hydrodeoxygenation (HDO) and hydrocracking (HC) [8]. This step is necessary to reduce the oxygen and other heteroatom content of the bio-oil and make it compatible with petroleum refinery infrastructure for final processing into liquid fuels. Hydrotreating (HT) for pyrolysis bio-oil is often done as a two or three step process where the oil is passed over a noble metal catalyst at ~220 °C, followed by a second catalyst bed containing cobalt and molybdenum operated at 400 °C. The outlet product stream is a mixture of upgraded fuel, non-condensable gases, and a separate aqueous fraction [8]. HTL biocrude is thermally stable and can be hydrotreated in a single step. The aqueous yields when hydrotreating FP bio-oils can range from 40 to 60%, while they are much lower for HTL biocrudes at 10–15%. Hence the largest source of aqueous byproducts for the FP/upgrading pathway is after the HT stage, while for HTL/upgrading the largest source is immediately after the HTL step.

Although extensive research has been conducted on direct liquefaction and upgrading processes, the focus of the research is almost exclusively the quantity and quality of the bio-oil produced [7–10]. Very little data exists in the published literature examining the quantitative characterization of the organic compounds present in the aqueous phases formed during HTL of lignocellulosic materials or the HT of bio-oils. Villadsen's group in Denmark has developed an HPLC-TOF-MS analytical method that has shown the presence of

specific fatty acids in the aqueous phase, along with pyrazine/pyridine, cyclopentanones, cyclopentenones, acids, amides, and furans [9]. However, the aqueous phases analyzed were primarily from the HTL of DDGS, with no lignocellulosic feedstocks used. This lack of data was highlighted in a report from Argonne National Laboratory where a key gap in the existing water footprint analysis was attributed to limited data availability, and “In particular, information on wastewater characterization of the new developing processes is limited in the public domain.” [14]. And as mentioned in the conclusions of Villadsen's paper, “Only very few studies have previously analyzed organic compounds in the aqueous phase from HTL bio-oil production.” [9].

To advance process economics and minimize environmental impact, the wastewater streams generated by the conversion process must be treated for discharge, anaerobically digested to produce methane, or catalytically upgraded/reformed into useful products prior to treatment. The use of catalytic hydrothermal gasification (CHG) has shown great promise in the ability to convert organic carbon present in HTL aqueous streams to a medium BTU gas containing methane, CO, and CO₂. As reported by Doug Elliot's team at the Pacific Northwest National Laboratory (PNNL), chemical oxygen demand (COD) of the aqueous fraction from HTL of an algal feedstock was reduced by 98.8–99.8% under CHG [15]. The product gas had very little hydrogen or other higher hydrocarbons. The organic compounds present in the aqueous fraction from the HTL of lignocellulosic feedstocks can differ significantly from those found when using algal feedstocks, however. In addition to CHG, research is underway at PNNL to develop new processes capable of upgrading the aqueous phase organic compounds to liquid fuel range hydrocarbons, as well as reforming these compounds to provide some of the hydrogen required for bio-oil upgrading [16]. Maximizing the efficiency of the catalysts used in these processes requires characterization data not only of the types of compounds present, but their exact identity and quantity.

In order to begin filling a substantial knowledge gap in the published literature, refine and develop HTL process models and techno economic analyses (TEA), and enable the further development of aqueous phase upgrading and reformation research, aqueous samples from two different thermochemical conversion processes were quantitatively characterized. Hydrothermal liquefaction samples processed at various conditions and using either whole pine forestry residuals or corn stover as the feedstock were examined. Also studied were the aqueous fractions from the hydrotreatment of 8 different bio-oils generated from the fast pyrolysis of clean pine, whole pine, tulip poplar, hybrid poplar, corn stover, switchgrass, and 2 blends of the pure feedstocks.

2. Materials and methods

2.1. Hydrothermal liquefaction (HTL)

Hydrothermal liquefaction was conducted on four corn stover (C Stover) and four loblolly pine (L pine) forest product residual feedstocks at a nominal reactor temperature of 350 °C and a nominal pressure of 20.7 MPa (3000 psi) using a continuous

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