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## Review

# Hydrothermal liquefaction of biomass: Developments from batch to continuous process

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## HIGHLIGHTS

- HTL has been evaluated with biomass feedstock ranging from lignocellulosic to algae.
- Continuous-flow processing systems have been demonstrated for HTL of biomass.
- HTL concentrates bioenergy by a high yield of biocrude product.
- Biocrude can be catalytically hydrotreated to liquid hydrocarbon fuel components.
- The byproduct aqueous stream can be processed by CHG to maximize energy efficiency.

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## ABSTRACT

This review describes the recent results in hydrothermal liquefaction (HTL) of biomass in continuous-flow processing systems. Although much has been published about batch reactor tests of biomass HTL, there is only limited information yet available on continuous-flow tests, which can provide a more reasonable basis for process design and scale-up for commercialization. High-moisture biomass feedstocks are the most likely to be used in HTL. These materials are described and results of their processing are discussed. Engineered systems for HTL are described; however, they are of limited size and do not yet approach a demonstration scale of operation. With the results available, process models have been developed, and mass and energy balances determined. From these models, process costs have been calculated and provide some optimism as to the commercial likelihood of the technology.

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## 1. Background on hydrothermal liquefaction

Hydrothermal liquefaction of biomass is the thermochemical conversion of biomass into liquid fuels by processing in a hot, pressurized water environment for sufficient time to break down the solid biopolymeric structure to mainly liquid components. Typical hydrothermal processing conditions are 523–647 K of temperature and operating pressures from 4 to 22 MPa of pressure. Closely related processing in supercritical water conditions (>647 K and >22 MPa) will not be discussed in this review, except in the context of aqueous phase processing. The process is meant to provide a means for treating wet materials without drying and to access ionic reaction conditions by maintaining a liquid water processing medium. The temperature is sufficient to initiate pyrolytic

mechanisms in biopolymers while the pressure is sufficient to maintain a liquid water processing phase.

Hydrothermal processing is divided into three separate processes, depending on the severity of the operating conditions. At temperatures below 520 K, it is known as hydrothermal carbonization. The main product is a hydrochar which has a similar property to that of a low rank coal. In the case of microalgae, the hydrochar is largely produced from the carbohydrate and protein fractions and the lipid fraction is still intact making it possible to extract the lipids prior to hydrothermal carbonization (Heilmann et al., 2011). At intermediate temperature ranges between 520 and 647 K, the process is defined as hydrothermal liquefaction resulting in the production of a liquid fuel known as biocrude. Biocrude is similar to petroleum crude and can be upgraded to the whole distillate range of petroleum derived fuel products. At higher temperatures above 647 K gasification reactions start to dominate and the process is defined as hydrothermal gasification, resulting in the production of a synthetic fuel gas. One of the advantages of

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hydrothermal gasification over liquefaction is the lower amount of organic carbon found in the water phase following gasification leading to high carbon efficiencies (Brown et al., 2010). The overall aim in each case is to generate a product with a higher energy density by removal of oxygen. The current review will focus on the HTL pathway at intermediate conditions to produce a biocrude using continuous-flow reaction systems.

Hydrothermal liquefaction (also known as direct liquefaction) is essentially pyrolysis in hot liquid water. As such, it does not require a catalyst, but a significant amount of research and development on catalytic methods in hydrothermal liquefaction has been undertaken. The most commonly considered “catalyst” has been the use of alkali to modify the ionic medium to favor certain base-catalyzed condensation reactions, which can lead to aromatic oil formation, in preference to acid-catalyzed polymerization reactions, which lead to solid product formation. While HTL proceeds through pyrolytic mechanisms, its biocrude product is much different from fast pyrolysis bio-oil. It is more deoxygenated through, among other reaction pathways, condensation reactions of the light fragments generated from the biomass, resulting in a more hydrophobic phase with less dissolved water. Physically, the biocrude is much more viscous, but is actually less dense than bio-oil.

Analysis of the HTL products from woody biomass show the biocrude product is clearly not a petroleum analog. It is a complex mixture of oxygenated compounds extending over a wide range of molecular weight. More details of the analyses and the composition are described in Elliott’s review (Elliott, 2011). The biocrude products included acids, alcohols, cyclic ketones, phenols, methoxy-phenols (guaiacols from softwood lignin) and more condensed structures, like naphthols and benzofurans. The amount of biocrude chromatographed reflected the amount of distillate product. A large fraction of the chromatographed oil was not included in the quantified identified peaks, either because of poor resolution and peak overlap or because the complex, oxygenated isomers were not found in the standard mass spectrometry libraries. Attempts to understand and organize the means of formation of these complex mixtures have been reviewed previously (Barbier et al., 2012; Behrendt et al., 2008; Peterson et al., 2010).

Direct biomass liquefaction was the terminology used for hydrothermal liquefaction in the 1970–1980s. This early continuous-flow process development work, including laboratory work at Lawrence Berkeley Laboratory (Schaleger et al., 1982) and the Albany Biomass Liquefaction Experimental Facility (Thigpen, 1982), both in the U.S., and the Hydrothermal Upgrading (HTU) plant (Goudriaan et al., 2008) in the Netherlands, was recently described by Elliott (Elliott, 2011). Hydrothermal liquefaction has only been demonstrated on a small scale for short time periods. The largest demonstration of a version of the technology was the operation of the Albany Facility producing 52 barrels of product (approximately 8 m<sup>3</sup>) over the life of the facility.

Although these pilot scale efforts demonstrated continuous-flow operation of HTL, the vast majority of the literature describes small batch reactor tests in the laboratory (Toor et al., 2011). This review will concentrate on the recent research in continuous-flow process development for biomass HTL and related subjects.

## 2. Wet biomass feedstocks—properties and preparation for processing

Most biomass can be processed in HTL because of the hydrophilic nature of biomass and the reasonable ease in forming water slurries of biomass particles at pumpable concentrations, typically 5–35% dry solids. In using lignocellulosic biomass, which is lower in moisture content, recovery and reuse of the water for slurry preparation is imperative. For high-moisture biomass, like algae,

some dewatering is required prior to processing in order to lessen the processing costs of excessive water. Table 1 presents some common feedstock utilized in HTL processing, wet feedstocks are particularly suited for HTL and especially algae biomass has received a lot of attention in the research field recently. Woody biomass requires grinding prior to processing as is discussed in the subsequent section, microalgae, some strains of macroalgae and certain manures and sludges are of suitable small size for direct processing. Table 1 also presents a summary of the HTL results published on the respective feedstock to date. It can be seen that the wet manure and sewage sludge feedstock have not been processed in continuous systems, although results from batch systems are promising for their application in continuous systems (Vardon et al., 2011; Yin et al., 2010). A further advantage of using hydrothermal processing for sludges and manures is the effect of sterilizing bioactive contaminants (Pham et al., 2013).

Algal biomass has been identified as a promising alternative as a resource for renewable fuels due to its higher photosynthetic efficiency and area specific yields (Pienkos and Darzins, 2009; Ross et al., 2008). The development of third generation biofuels from microalgae has seen increasing research efforts over the last decade. Microalgae are microscopic organisms that can grow in fresh, brackish or salt water. The advantage of microalgae compared to terrestrial biomass is its much higher photosynthetic efficiency which results in higher growth rates and improved CO<sub>2</sub> mitigation (Brennan and Owende, 2009). They are especially suited for continuous hydrothermal liquefaction due to the small size (<100µm). Because they grow at concentrations significantly less than 0.1% they need to be dewatered prior to HTL. However, through physical separation methods, they are available as slurries with around 10–20% water post cultivation harvest and dewatering. This means that the additional energy spent to achieve a dry feedstock required for most thermochemical biofuel pathways is not required and nor is additional water added as required for a dry biomass feedstock for HTL. Their pumpability has been demonstrated at large scale (Elliott et al., 2013b; Jazrawi et al., 2013). The particle size has been shown to be in direct correlation to pumpability and pressure control in continuous reactors (Jazrawi et al., 2013).

Macroalgae, also known as seaweed, is a group of eukaryotic photosynthetic marine organisms. Diverse and abundant in the world’s oceans and coastal water, they are typically comprised of a blade or lamina, a stipe, and a holdfast (haptera) for anchoring and support in marine environments. They generally have a low lipid content (McDermid and Stuercke, 2003) but are high in carbohydrates, which are potential biofuel precursors. Adams et al. (Adams et al., 2011) studied the seasonal variation in the chemical composition of a macroalga, *Laminaria digitata*, for thermochemical conversion. They reported that summer harvests contained the highest proportion of carbohydrate and lowest ash content making them most suitable for conversion to biofuels. Macroalgae are generally of larger size than microalgae and only certain species such as those of the genus *Ulva* do not require pre-processing; the majority of macroalgae require grinding or maceration when wet before pumping due to their large size.

Pumping of wet biomass slurries is well-known. For example, the pulp and paper industry moves slurries through their facilities, but only at lower pressures. The use of higher pressure systems at high temperatures leads into processing territory with limited commercial experience, and thus remains a technological challenge (Matsumura et al., 2005). Relevant industrial scale pumping systems have been identified, but have not been demonstrated for this application (Berglin et al., 2012). When considering capital costs for such systems, it is obvious that more concentrated feedstock slurries should require smaller processing systems for equivalent throughput and resulting lower capital costs. Similarly,

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