



Process development for hydrothermal liquefaction of algae feedstocks in a continuous-flow reactor



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ABSTRACT

Wet algae slurries can be converted into an upgradeable biocrude by hydrothermal liquefaction (HTL). High levels of carbon conversion to gravity separable biocrude product were accomplished at relatively low temperature (350 °C) in a continuous-flow, pressurized (sub-critical liquid water) environment (20 MPa). As opposed to earlier work in batch reactors reported by others, direct oil recovery was achieved without the use of a solvent and biomass trace components were removed by processing steps so that they did not cause process difficulties. High conversions were obtained even with high slurry concentrations of up to 35 wt.% of dry solids. Catalytic hydrotreating was effectively applied for hydrodeoxygenation, hydrodenitrogenation, and hydrodesulfurization of the biocrude to form liquid hydrocarbon fuel. Catalytic hydrothermal gasification was effectively applied for HTL byproduct water cleanup and fuel gas production from water soluble organics, allowing the water to be considered for recycle of nutrients to the algae growth ponds. As a result, high conversion of algae to liquid hydrocarbon and gas products was found with low levels of organic contamination in the byproduct water. All three process steps were accomplished in bench-scale, continuous-flow reactor systems such that design data for process scale-up was generated.

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1. Introduction

Hydrothermal liquefaction (HTL) of biomass provides a direct pathway for liquid biocrude production. This liquid product is a complex mixture of oxygenated hydrocarbons and, in the case of algae biomass, it contains substantial nitrogen as well. Hydrothermal processing utilizes water-based slurries at medium temperature (350 °C) and sufficient pressure (20 MPa) to maintain the water in the liquid phase. The processing option is particularly applicable to wet biomass feedstocks, such as algae, eliminating the need to expend energy to dry the feed before processing, as is required in other thermochemical conversion processes.

Elliott recently reviewed the early work in hydrothermal processing of wet biomass for both liquid and gas production [1]. Recent reports in the literature that have described HTL and its application to algae have been primarily related to batch reactor tests (see the long list in Chow et al. [2]). There have been reports of continuous-flow reactor tests for hydrothermal gasification of algae, both sub-critical liquid phase [3] and super-critical vapor phase [4]. Here we report the preliminary results of continuous-flow reactor studies of hydrothermal liquefaction with wet algae feedstocks. Subsequent

hydrotreatment of the HTL product oil demonstrated continuous-flow production of hydrocarbon fuel components while catalytic treatment of the aqueous phase in a separate continuous-flow reactor demonstrated fuel gas production from the dissolved organics. The generation of a relatively clean aqueous byproduct suggests the potential for recycle with dissolved nutrients to the algae growth medium.

1.1. Background

The use of hydrothermal processing (high-pressure, high-temperature liquid water) has received relatively limited study [1]. Although process development of hydrothermal liquefaction of biomass for fuel production can be traced to the work related to the Albany, Oregon, Biomass Liquefaction Experimental Facility, significant development has languished in the U.S. for the last three decades. HTL was recently included in the National Advanced Biofuels Consortium [5] program of work following a resurgent project at PNNL with ADM and Conoco-Phillips [6]. This article provides additional results of liquefaction using wet algae slurries.

Recently algae biomass has received a very high level of interest as a renewable biomass resource for fuel production because of the relatively high growth rates attained [7]. The primary focus has been the recovery of the fatty acid triglycerides produced by the

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algae as a feedstock for biodiesel production. However, not all algae are high fatty acid producers, and those that are, must be grown under controlled conditions, which are less than optimal growth conditions in order to maximize fatty acid production. An alternative algae utilization strategy is to grow algae in a wild and/or mixed culture at optimum growth conditions in order to maximize total biomass without consideration of fatty acid production. An appropriate biomass conversion process to utilize such algae without drying is desired to minimize parasitic energy requirements. Hydrothermal liquefaction can be used in this application for biocrude production from algae [8], utilizing both the lipid components but also the balance of the biomass structure as source material for oil production. The conversion of both biomass biopolymers (carbohydrates and protein) as well as lipid structures to a liquid oil product at hydrothermal conditions is expected [9].

Yokoyama's group at the National Institute for Resources and Environment in Japan (Dote et al. [10] and Minowa et al. [11]) published the first reports of hydrothermal liquefaction of microalgae (*Botryococcus braunii* and *Dunaliella tertiolecta*) using a batch reactor fed with high concentration dry matter algae mass, 50 wt.% and 78.4 wt.%, respectively. At 300 °C they reported oil yield of 37 wt.% and 57–64 wt.%, respectively for the two algae types. There has recently been a spike in reports on hydrothermal liquefaction of wet algae biomass. Ross et al. [12] at the University of Leeds in the UK, also a Chinese group [13] and a European group [14], groups at the University of Illinois [15] and Georgia [16], and Savage's group at the University of Michigan [17] have revisited HTL of algae. In their work similar processing conditions have been evaluated with different algae, *Chlorella vulgaris* and *C. pyrenoidosa*, *Nannochloropsis oculata*, *Scenedesmus dimorphus*, *Porphyridium cruentum*, *Desmodesmus sp.* as well as *Chlorogloeopsis fritschii* and *Spirulina* cyanobacteria. These reports develop a consensus that a wide range of microalgae can be processed by this route into a complex mixture oxygenated hydrocarbons that is liquid at or near room temperature at a high mass yield, including not only the lipid structures but the other biomass as well. Thus far the reports of all these groups have been limited to batch reactor testing. Although they have investigated the range of operating conditions in more detail than the earlier work, the results are still of limited value for developing an industrially useful continuous-flow process. In addition, the use in most cases of small batch reactors led the investigators to the use of solvents for the recovery of their oil products, thus complicating the determination of the oil yield and distorting its composition and properties by the inclusion of solvent-extractable, water-soluble components. A very recent report now available [18] describes continuous-flow operations of algae HTL. However, in those tests a low concentration of algae in water slurry, 1 to 10 wt.% of *Chlorella* or *Spirulina*, was evaluated and the operators chose to recover the biocrude by a solvent extraction.

The work at PNNL has focused on bench-scale testing in a continuous-flow reactor system in which the biocrude was recovered by gravity separation without the requirement of solvent handling. The work has been performed as part of the National Alliance for Advanced Biofuels & Bioproducts (NAABB), whose mission is to lay the technical foundations for a scalable, responsible and affordable renewable biofuel industry based on algae feedstocks [19]. The results reported here were performed as part of NAABB as an outgrowth of the original scope of work on hydrothermal gasification [20].

2. Methods and material

The equipment and procedures described below were used for testing the hydrothermal liquefaction of wet algae slurries as well as hydrotreating of the biocrude produced and the catalytic hydrothermal gasification of the organics left in the byproduct water stream.

2.1. Hydrothermal processing

A continuous-flow reactor system was originally designed for obtaining engineering data for the catalytic hydrothermal gasification (CHG) process and has been described in the literature previously [20]. The system essentially consists of the high-pressure pump feeding system, product recovery system, the 1-liter stirred tank preheater and the 1-liter tubular catalytic reactor. The mineral separation and sulfur stripping were done via two 1-liter high-pressure vessels in line between the preheater and the tubular reactor. The system was based on a throughput of 1.5 l of slurry per hour and was typically operated over a test period of 6–10 h. The process flow diagram is shown in Fig. 1. The modifications implemented for handling minerals and sulfur in the algae feedstocks are indicated in the outline labeled "NEW."

Essentially the same reactor system was used for HTL except with the omission of the catalyst bed in the tubular reactor and plumbing modifications to allow biocrude liquid product separation from the aqueous byproduct stream and the collection of both. The HTL configuration is shown in Fig. 2.

The algae feedstock preparation method was designed to ensure a relatively homogeneous feed for the reactor. The feedstocks were acquired as dewatered paste and the small cellular structure of the algae allowed simple mixing involving only stirring and minor amounts of dilution to form a uniform puree-like consistency as the feedstock. This contrasts strongly with the difficulty of forming a pumpable slurry for lignocellulosic feedstocks for hydrothermal processing [1]. For the CHG tests with the HTL aqueous byproduct, no feedstock preparation was required.

The pumping subsystem consists of a modified Isco 500D dual syringe pumps. Using the Isco pumps, the feeding rates were measured directly by the screw drive of the positive displacement syringe pump. The Isco pumps could pump either the algae slurries or the aqueous feed.

In the first two HTL tests, only the 1-liter continuous-flow stirred tank reactor (CSTR) was used. In the latter two tests the initial heat-up of the slurry was in an oil-heated tube-in-shell heat exchanger, which heated the feed to 133 °C. The final heat-up to reaction temperature was in the CSTR itself, which was reduced to a 400 ml vessel by insertion of a spacer. The reactor, an Inconel vessel equipped with internal stirring propellers, functioned as a back-mixed reactor and additional residence time was provided by a subsequently heated plug-flow portion of the reactor. This combination of CSTR and plug-flow was used in these tests as a result of conservative approach based on plugging problems experienced previously with a plug-flow only reactor system with lignocellulosic feedstocks. When the temperature in the initial preheater was maintained below 200 °C, there was no plugging detected with algal feedstocks.

In the CHG tests, the preheated feed from the CSTR passed through the solid separator as well as a sulfur stripping bed before entering the up-flow, fixed catalyst bed in the 1-liter tubular reactor. The catalyst used was ruthenium metal, 7.8% on a partially graphitized carbon extrudate.

As a result of the liquefaction chemistry, it was possible to separate the mineral matter from the liquid stream. In the HTL process, the organics in the algae were pyrolyzed and liquefied while certain inorganic components, such as calcium phosphates, formed and precipitated as solids. A vessel was placed in the process line following the reactor to capture and remove the solids at reaction conditions, temperature and pressure. The design of the separator was a combination settler, filtration unit wherein the solids fell to the bottom of a vessel and the liquids passed overhead through a filter to the reactor. The solids could be removed by batch from the bottom of the vessel as they built up over time. We found that by using this in-line system, a solid-free bio-oil product would more readily become separated from the water phase.

In the CHG configuration, the in-line filtration and sulfur scrubber system served to protect the catalyst bed in the tubular reactor from

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