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Thermochemical conversion of raw and defatted algal biomass via hydrothermal liquefaction and slow pyrolysis

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ABSTRACT

Thermochemical conversion is a promising route for recovering energy from algal biomass. Two thermochemical processes, hydrothermal liquefaction (HTL: 300 °C and 10–12 MPa) and slow pyrolysis (heated to 450 °C at a rate of 50 °C/min), were used to produce bio-oils from *Scenedesmus* (raw and defatted) and *Spirulina* biomass that were compared against Illinois shale oil. Although both thermochemical conversion routes produced energy dense bio-oil (35–37 MJ/kg) that approached shale oil (41 MJ/kg), bio-oil yields (24–45%) and physico-chemical characteristics were highly influenced by conversion route and feedstock selection. Sharp differences were observed in the mean bio-oil molecular weight (pyrolysis 280–360 Da; HTL 700–1330 Da) and the percentage of low boiling compounds (bp < 400 °C) (pyrolysis 62–66%; HTL 45–54%). Analysis of the energy consumption ratio (ECR) also revealed that for wet algal biomass (80% moisture content), HTL is more favorable (ECR 0.44–0.63) than pyrolysis (ECR 0.92–1.24) due to required water volatilization in the latter technique.

1. Introduction

Algae are a diverse group of microorganisms that have garnered increased attention as a feedstock for renewable energy production and pollution remediation. Algae hold promise as a bioenergy feedstock due to their prolific growth rate and lipid productivity, ability to grow in saline and degraded waterbodies, utilization of waste carbon dioxide, and production of fuel precursors and high-value biochemicals (Mata et al., 2009). Furthermore, integration of algal cultivation into wastewater treatment may be advantageous (Pittman et al., 2010) for nutrient capture to support algal growth and mitigate eutrophication in effluent-receiving water bodies. However, despite these benefits, effective dewatering of harvested algal biomass for lipid extraction presents a current limitation to economical and sustainable biofuel production due to the high energy, operating, and capital costs (U.S. Department of Energy, 2010).

Many commercial efforts are underway to maximize economic return and improve energy balances in algal cultivation. Currently, much work is focused on extracting high value chemicals (e.g., nutraceuticals) and energy-dense lipids (e.g., for biodiesel) from algae, but this still leaves behind a large residual of "defatted" biomass. Effective utilization of defatted algal biomass will be necessary to achieve favorable energy balances and production costs (Pan et al., 2010). Several downstream uses have been considered for defatted algal biomass, including animal feed and fertilizer, or as a feedstock for energy production through direct burning, ethanol fermentation, or anaerobic digestion (Mata et al., 2009). Here, we focus on examining the potential of different thermochemical conversion routes for recovering energy dense bio-oil products from raw and defatted algal biomass.

Thermochemical conversion technologies are a promising option for transforming diverse biomass feedstocks into energy dense, transportable liquid fuels that can combusted directly or upgraded into petroleum replacements (Bridgwater, 2011; Duan and Savage, 2011; Brown and Stevens, 2011; Elliott, 2007). Two thermochemical routes, hydrothermal liquefaction (HTL) and slow pyrolysis, were examined in this study to compare the chemical characteristics of bio-oils that can be produced from algal biomass, including defatted biomass.

HTL is ideal for processing high-moisture (i.e., wet) biomass since water is used as the reaction medium under high temperature (250–350 °C) and pressure (5–15 MPa). These conditions produce a highly reactive solvation environment and avoid an energetically costly phase change associated with biomass drying. Complex biomolecules decompose and reform into a variety of compounds that partition into a self-separating bio-oil phase when conditions return to ambient temperature and pressure. HTL has been tested with a wide range of biomass feedstocks including agricultural and forest residues (Minowa et al., 1998), manure, sewage sludge (Suzuki et al., 1988; Vardon et al., 2011), and several

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algal species, including *Spirulina* (Jena et al., 2011; Vardon et al., 2011), *Nannochloropsis* (Biller and Ross, 2011; Brown et al., 2010), and *Chlorella* (Biller and Ross, 2011).

Alternatively, pyrolysis technologies are best suited for the conversion of dry feedstocks (<5% moisture) since moisture must be removed before biomass is heated to high temperatures (400–600 °C) under ambient pressure. The dried biomass is heated in the absence of oxygen to cleave and volatilize biomolecules, which re-condense into an aqueous and bio-oil phase; a carbon-rich solid phase, typically referred to as biochar, is also obtained. Pyrolysis technologies are often classified by their heating rate, with rates of 0.1–1 °C/s referred to as slow pyrolysis, 10–200 °C/s as fast pyrolysis, and >1000 °C/s as flash pyrolysis (Demirbas and Arin, 2002). This study focused on slow pyrolysis due to its potential for producing more energy dense bio-oils that approach petroleum crude oils (Duman et al., 2010; Maggi and Delmon, 1994). Pyrolysis has been studied extensively with lignocellulosic feedstocks and has been scaled to pilot and commercial production levels (Bridgwater, 2011; Brown and Stevens, 2011). Non-traditional feedstocks have also been examined, such as hazelnut shells (Pütün et al., 1999), chicken litter, switch grass (Mullen et al., 2009), and cherry seed (Duman et al., 2010). Pyrolysis of several algal species have also been tested, including *Chlorella* (Demirbaş, 2006; Miao et al., 2004; Peng et al., 2000; Grierson et al., 2009), heterotrophically enhanced *Chlorella* (Miao and Wu, 2004), *Microcystis* (Miao et al., 2004), salt-water *Tetraselmis* (Grierson et al., 2011, 2009), and *Nannochloropsis* residue (Pan et al., 2010).

Bio-oils produced from HTL and slow pyrolysis display diverse chemical properties that are heavily influenced by the source feedstock composition. Algae of varying biochemical composition have been shown to produce bio-oils with distinct chemical characteristics (Grierson et al., 2009; Biller and Ross, 2011; Jena et al., 2011), but to our knowledge no studies have examined how the chemistry of thermochemical bio-oils derived from defatted algal biomass compare to those produced from the parent algae (non-defatted) or other low-lipid algal species with composition similar to defatted algae biomass. This study examined thermochemical bio-oils produced from raw and defatted *Scenedesmus*, a species with a range of lipid contents (10–55%) suitable for biodiesel production (Mata et al., 2009) and amenable for wastewater treatment (Pittman et al., 2010). These bio-oils were also compared with bio-oils produced from thermochemical conversions of *Spirulina*, which has a nutritional profile similar to defatted algal biomass (i.e., high protein, low-lipid) that has been used as a feedstock in recent studies examining HTL (Biller and Ross, 2011; Jena et al., 2011; Vardon et al., 2011). To our knowledge, this is the first study to examine thermochemical conversion of *Scenedesmus* biomass, in raw or defatted form, as well as the first study to directly compare the chemical properties of bio-oils produced from the different algal feedstocks via HTL and slow pyrolysis. The thermochemically-derived bio-oils were also compared with Illinois shale oil, a low-grade petroleum crude. Bio-oils and shale oil were analyzed for bulk properties (e.g., elemental analysis and higher heating value) and physicochemical characteristics (e.g., molecular constituents, functional group allocation, proton speciation, molecular weight distribution, and boiling point distribution). Results were used to determine the influence of feedstock and thermochemical conversion method on bio-oil yield and chemistry and to evaluate the energy balances for algal biomass thermochemical conversions.

2. Methods

2.1. Algal feedstocks and shale oil

Scenedesmus biomass was provided by Stellarwind Bio Energy LLC (Indianapolis, IN) and *Spirulina* biomass was obtained from Cyanotech located in (Kailua-Kona, HI). Algal samples were used in dry powder form (moisture content <5%) and stored at 5 °C prior to processing. *Scenedesmus* biomass was defatted by using hexane in a Soxhlet extraction apparatus. Crude lipids were extracted until the recirculated solvent ran clear (~24 h). Illinois shale oil was obtained from the Illinois State Geological Survey (Champaign, IL).

2.2. Thermochemical conversion

Algal biomass conversions with HTL and pyrolysis were conducted in triplicate batch reactions. Hydrothermal liquefaction was performed in a Parr 4575 500-ml reactor using approximately 250 g of biomass slurry (80 wt.% moisture). Conversion conditions were identical to those previously reported (Vardon et al., 2011), with 30-min HTL reactions taking place at 300 °C, and pressure ranging from 10 to 12 MPa. Slow pyrolysis was conducted using a Thermolyne 79400 tube furnace. Approximately 100 g of dry biomass was loaded into the furnace chamber and heated to 450 °C at a rate of 50 °C/min, with a nitrogen sweep gas flow rate of ~100 ml/min and a reaction time of 2 h. Volatile products were condensed in an ice-chilled collection vessel while the remaining biomass solid (biochar) was collected and weighed separately.

The liquid products obtained from HTL and slow pyrolysis contained a water-insoluble organic phase, suspended solids, and an aqueous phase with dissolved constituents. The combined liquid products were rinsed with dichloromethane (DCM) to separate the aqueous and DCM-soluble organics (Pütün et al., 1999; Peng et al., 2000; Grierson et al., 2011; Biller and Ross, 2011; Brown et al., 2010; Duan and Savage, 2011). A Teflon-coated stainless steel pressurized filtration assembly (Millipore) was then used to remove suspended solids from the DCM and aqueous phases. The filter (Satorious 0.45-μm cellulose membranes) and retained solids were recovered and dried to determine the mass of residual solids. The filtered DCM-soluble organics were then recovered using a separatory funnel and DCM was evaporated under reduced pressure to recover the bio-oil phase.

For slow pyrolysis, the aqueous-phase included water-soluble constituents as well as water formed from biomass decomposition. For HTL, aqueous phase constituents consisted of total dissolved solids that were measured gravimetrically after filtration and evaporation of the aqueous phase at 65 °C for ~12 h to remove water since it served as the reaction medium.

The mass balance yields were calculated as the ratio of the corresponding product phase to the initial dry feedstock mass, including ash. The bio-oil yield accounted for the mass of DCM-soluble organics recovered after filtration and DCM evaporation. For HTL, the aqueous phase yields accounted for the mass of dissolved aqueous constituents remaining after DCM extraction, filtration and water evaporation. For pyrolysis, the aqueous phase yields also accounted for re-condensed water evolved during the conversion process. The solid phase yields accounted for the mass of dried particulates retained after DCM extraction and filtration, plus the pyrolysis biochar residual remaining in the tube furnace. Lastly, the gas-phase yields were calculated based on the resulting mass difference.

2.3. Feedstock and oil analyses

Forage analysis of the algal biomass was performed by Midwest Labs (Omaha, Nebraska) to determine crude protein, neutral detergent fiber (hemicellulose, cellulose, and lignin), acid detergent fiber (cellulose and lignin), lignin and ash content. Elemental analysis of the dried algal feedstocks, bio-oils, and shale oil was conducted by the University of Illinois Microanalysis Laboratory (Urbana, IL). Samples were processed for total carbon/hydrogen/nitrogen using an Exeter Analytical CE-440 Elemental Analyzer. Sulfur was