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Thermolysis of microalgae and duckweed in a CO_2-swept fixed-bed reactor: Bio-oil yield and compositional effects

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ABSTRACT

Microalgae and duckweed were grown and harvested over a three-month period in CO_2-sparged helioreactors and open earthen ponds, respectively. The biomass feedstocks were thermolyzed in a thermogravimetric analyzer (TGA) and fixed-bed reactor to produce a fuel precursor coined "bioleum". Analysis of the thermolysis kinetics revealed an increase in the activation energy with heating rate for both aquatic species. Activation energies were lower than literature-reported values for lignocellulosics, corroborated by TGA thermolysis of pinewood. Thermolysis of microalgae resulted in higher bioleum and energy yields than for duckweed, reflecting differences in the biomass composition. The algal bioleum properties resemble those of crude petroleum except for higher nitrogen and oxygen content and acid number. Speciation identified 300+ compounds in the oil phase, with similar amounts of hydrocarbons and oxygenates, while acetic acid was the major species in the aqueous phase. The compounds were classified according to their degree of aromaticity, oxygenation, and nitrogenation.

1. Introduction

The last decade has seen an increased interest in the development of new liquid fuels from biomass, due principally to the concern about the nearly exclusive reliance on petroleum as a feedstock, a depleting resource with undesirable environmental characteristics. In this regard, liquid fuel precursors derived from aquatic plants (e.g. algae and duckweed) constitutes a possible, low water-intensity alternative for supplanting at least a fraction of fossil fuels for transportation.

The cultivation and processing of microalgae have long promised, but as yet unrealized advantages at a commercial scale, such as of low cost growth and production (Brennan and Owend, 2010). Algae, if they could be grown at rates extrapolated from small scale studies, would require much less land for their cultivation compared to food crops due to their ostensibly higher areal energy yields. In the yet to be demonstrated full-scale production of ca. 10 g/m^2/day, microalgae would require much less land than terrestrial crops to produce the same quantity of biodiesel feedstock (Clarens et al., 2010). In principle, microalgae can be cultivated in non-arable areas, in fresh, brackish, and salt water, and even waste water, require only simple nutrients, and can utilize waste CO_2. They promise faster growth rates and productivities than any agricultural feedstock, wood or plant. Duckweed (*Lemna* sp.) also offers several advantages, similar to those of algae, namely fast growth rates compared to terrestrial plants (Cheng and Stomp, 2009), no displacement of food crops, and fertilization with simple nutrients. Duckweed has the added advantage that it can be easily recovered from the cultivation medium by a simple, mechanical separation, while algae requires energy-intensive processes to recover the crop from the aqueous medium, then must be dried, typically using evaporation, to the desired moisture level.

In recent years, the conversion of algae has been examined for three different routes. The first route involves the conversion of algae to a diesel-like liquid fuel. Algal biodiesel is made by the extraction of algal lipids followed by transesterification with an alcohol (Brennan and Owend, 2010). While the latter step has matured for a variety of seed oils, the extraction step remains challenging for algae. Moreover, this route requires the cultivation of algae strains selected for high lipid content. The second route is applicable to all types of biomass; gasification to syngas, followed by Fischer-Tropsch conversion to fuel range alkanes. However, gasification and gas-to-liquid conversion are neither energy efficient nor carbon efficient and can provide attractive economic returns only at very large scale, which is problematic for the biomass-based fuels that are grown over wide areas because of collection and transportation costs. The third route involves pyrolysis or thermolysis followed by upgrading of the bio-oil (which we have termed "bioleum"). This process has the advantage of producing

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a relatively high yield of bio-oil without the need for cultivating special strains (e.g. high content of triglycerides and a specific composition of fatty acids) or using constrained growth conditions. Since pyrolysis also obviates the lipid extraction step, pyrolysis and its hydrothermal and solvolytic variants are potentially economically attractive (Brown et al., 2010).

Pyrolysis is the thermal decomposition of an organic compound by heat in the absence of oxygen, usually at rather high temperatures (e.g., >800 K). Most of the studies in this area have been carried out employing cellulosic feedstocks, such as wood, agricultural crops and waste, switchgrass, among others (Balat, 2008; Ingram et al., 2008), which are mainly composed of cellulose, hemicelluloses and lignin. The chemical composition of aquatic species consists mainly of carbohydrates, proteins and lipids. Only a few researchers have studied the pyrolysis of microalgae in a reactor system (Demirbas, 2006; Miao et al., 2004). One group studied the effect of temperature (252–550 °C) on the pyrolysis of bio-oil of different moss and *Chlorella protothecoides* in a slow pyrolytic reactor. In this study, it was found that the yield of bio-oil increased with the temperature, where the optimum bio-oil yield for the microalgae was 55.3% at 502 °C (Demirbas, 2006). Miao et al. (2004) studied the fast pyrolysis of three microalgae strains in a fluidized bed and found that the chemical composition of the feedstock has a strong effect in the bio-oil yield. Under the same pyrolytic conditions the bio-oil yield was 18% for autotrophic *C. protothecoides*, 24% for *Microcystis aeruginosa*, while the bio-oil yield of heterotrophic *C. protothecoides* was 3.4 times higher than autotrophic *C. protothecoides*. These results suggest that microalgae containing higher content of lipids will produce higher yields of bio-oil. Recently, the pyrolysis of *lemna minor* in a slow pyrolysis reactor has been studied (Muradov et al., 2010; Whitton and Weber, 2010). The latter approach differed from those reported in the literature because it employed carbon dioxide as a sweeping gas (c.f., Butterman and Castaldi, 2010).

The objective of this integrated study is to grow, harvest, and pyrolyze aquatic plants into fuel precursors in order to assess process viability and to compare biomass feedstocks. We report on the thermochemical conversion of microalgae and duckweed grown at moderate scale aquaculture facilities. We carried out thermolysis of two aquatic plants (viz. microalgae and duckweed) in a thermogravimetric analyzer (TGA) to analyze the effect of different feedstock properties (i.e. composition, particle size, etc.) and operating conditions (i.e. heating rate, sweep gas, etc.) on the thermolysis rate, employing carbon dioxide as the sweep gas. The use of CO_2 as a sweep gas has the advantage over alternatives like steam or N_2 because it can be incorporated into a process that uses flue gas directly, resulting in potential energy savings. The TGA experiments helped in the design of a continuous bench-scale flow thermolysis reactor system. Slow thermochemical degradation in CO_2 atmosphere was performed in a fixed bed configuration in which the main focus was to better understand the thermolysis process through identification of the product distribution and yield. The results are analyzed in terms of overall kinetics and product yields. Finally, some observations are provided on the viability of algae and duckweed versus lignocellulosics for biomass to liquid fuels via pyrolysis.

2. Methods

2.1. Algaculture

The algae, a mixed wild culture, consisting primarily of *Scenedesmus* sp., were grown in two sizes of helioreactors (closed bags configured as either a toroidal or center-baffled racetrack and constructed from 20 mil (ca. 0.5 mm) polyvinylchloride film reinforced with polyester meshing). The larger helioreactors were about 30 m long and 2.5 m wide, contained 25,000 L of growth medium and provided 90 m^2 of illuminated area (see Fig. S1a – Supplemental Material). The smaller helioreactors that were 3 m long and 2 m wide, and contained about 600 L of growth medium. Both sizes of helioreactors were installed on the grounds of the Hornsby Bend Biosolids Management Plant near Austin, Texas.

The algae were produced in sequential, batch growth experiments that took place during the late spring and summer of 2009. The growth medium consisted of outfall wash water from the water treatment plant, nutrified with inorganic nitrate and phosphate salts to achieve concentrations of nitrate and phosphate that averaged about 50 and 1.5 ppm, respectively. Compressed carbon dioxide derived from spray-cooled stack gas from the digester flare of the wastewater treatment plant was demisted and then bubbled into the helioreactors.

To harvest the algae the growth medium was transferred to a large cone bottom tank, where the suspension was acidified to a pH of about 5 by adding mineral acid (HCl). The algae flocculated into a thick paste that settled and dewatered under its own weight. The recovered paste was dried in a convection oven to about 10 wt% moisture and then stored in plastic bags.

2.2. Lemnaculture

The duckweed, primarily Wolffia and Spirodela species were grown in three, adjacent 0.5 hectare ponds located in Katy, Texas (see Fig. S1b and c – Supplemental Material). The ponds were filled to an average depth of 0.6-0.7 m with local ground water and then nutrified with commercial fertilizers. Initially ordinary, pelletized garden fertilizer was used until it was recognized that the ammoniacal nitrogen was present as the chloride salt that impeded the growth of the crop. Subsequently urea was used to increase the concentration of nitrogen to approximately 8 mg/L and “triple superphosphate” to raise the phosphorous concentration to 1 mg/L. The crop was harvested mechanically using nets and then air dried in the sun.

2.3. Biomass characterization

All the samples employed in this set of experiments were ground and then dried at 100 °C for 12 h. An elemental analysis was carried out by Galbraith Laboratories, Inc. (Knoxville, TN). Heating values of the original biomass were estimated from their elemental composition using a standard Dulong correlation (Demirbas, 2006; Channiwala and Parikh, 2002). The chemical composition was determined by standard forage assays carried out by Holmes Laboratory Inc. (dry matter: AOAC 967.03; crude protein: AOAC 990.03; lignin, fiber: Ankom Method, crude fat: AOAC 920.39; cations: AOAC 968.08; phosphorous: AOAC 965.17; ash: AOAC 942.05; sulfur: AOAC 923.01). Table 1 lists the chemical and elemental composition of both aquatic species employed in this work.

2.4. Thermogravimetric analyzer

The dried biomass was pyrolyzed in a thermogravimetric analyzer (TGA). In a typical run, about 10 mg of sample was placed in a ceramic pan and then loaded into the instrument. The sample was heated from room temperature to 800 °C, linearly at rates that varied from 5 to 80 °C/min under an atmosphere of CO_2 (Praxair, UHP grade, 99.9999%). The total mass loss of the sample was measured as a function of the heating rate, particle size, and flow rate. Three repeats were performed for all the variables studied. The evolved products were assayed during experiments in which the feedstocks had been pyrolyzed in the TGA from room temperature