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Biocrude yield and productivity from the hydrothermal liquefaction of marine and freshwater green macroalgae

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HIGHLIGHTS

- Hydrothermal liquefaction is an effective biocrude production method for macroalgae.
- Biocrude yield is highly influenced by biomass organic carbon content.
- Assessment of biocrude productivities is an effective species selection tool.
- Marine macroalgae have higher biocrude productivities due to higher growth rates.

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ABSTRACT

Six species of marine and freshwater green macroalgae were cultivated in outdoor tanks and subsequently converted to biocrude through hydrothermal liquefaction (HTL) in a batch reactor. The influence of the biochemical composition of biomass on biocrude yield and composition was assessed. The freshwater macroalgae *Oedogonium* afforded the highest biocrude yield of all six species at 26.2%, dry weight (dw). *Derbesia* (19.7% dw) produced the highest biocrude yield for the marine species followed by *Ulva* (18.7% dw). In contrast to significantly different yields across species, the biocrudes elemental profiles were remarkably similar with higher heating values of 33–34 MJ kg^{-1}. Biocrude productivity was highest for marine *Derbesia* (2.4 g m^{-2} d^{-1}) and *Ulva* (2.1 g m^{-2} d^{-1}), and for freshwater *Oedogonium* (1.3 g m^{-2} d^{-1}). These species were therefore identified as suitable feedstocks for scale-up and further HTL studies based on biocrude productivity, as a function of biomass productivity and the yield of biomass conversion to biocrude.

1. Introduction

The decline in fossil fuel reserves and increasing greenhouse gas emissions necessitate the development of alternative and sustainable energy sources. Phototrophic biomass has been identified as a primary feedstock for energy capture and the production of renewable liquid fuels (Perlack et al., 2005). Critical factors in the selection of a biofuel feedstock are productivity, scalability and a continuous supply of biomass. Given these criteria, macroalgae are particularly suitable as they are highly productive, are produced at scale and can be delivered as a continuous feedstock supply (Chopin and Sawhney, 2009). Furthermore, macroalgae can be grown within a broad range of environments, from the open ocean through to land-based tanks and ponds production systems, and do not require arable land for cultivation thereby avoiding the highly contentious food *versus* fuel debate (Pimentel et al., 2009). Notably, production systems can also be integrated into an industrial ecology framework where the culture of algae in wastewater provides bioremediation applications in agriculture (Mulbry et al., 2008), mineral processing (Saunders et al., 2012), and aquaculture (de Paula Silva et al., 2008; Mata et al., 2010). The combination of biomass production with these established industries enables macroalgae to become a bioresource for the production of renewable fuels and co-products (Ragauskas et al., 2006). However, the application of algae for renewable fuels is also dependent on the biochemical composition of the biomass, as this directly affects the quantity and quality of the fuel (Rowbotham et al., 2012). The culture medium and environmental conditions affect the biochemical properties of macroalgae significantly and interactively (Saunders et al., 2012; Angell et al., 2014), and hence the subsequent conversion of algal biomass to energy (Bruhn et al., 2011) and renewable fuels (Rowbotham et al., 2012).

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Renewable fuels can be produced through the refining of a liquid biocrude produced through the thermochemical conversion of biomass, either through hydrothermal liquefaction (HTL) or pyrolysis (Rowbotham et al., 2012). HTL is a medium temperature process (200–374 °C), carried out under sufficient pressure to maintain water in a liquid state. Under subcritical conditions, water participates in a series of complex reaction cascades with macromolecules including hydrolysis, fragmentation, aromatisation, dehydration and deoxygenation to produce lower molecular weight compounds resulting in liquid biocrude, solid biochar, aqueous and gaseous fractions (Toor et al., 2011). For algal biomass, HTL offers several advantages over pyrolysis through the use of wet biomass thereby avoiding energy losses associated with drying, and also through enhanced reaction rates and an efficient separation of products (Peterson et al., 2008). In addition, HTL delivers a high-energy biocrude (30–40 MJ kg^{-1}) that is lower in oxygen and moisture content compared to pyrolysis biocrude and, therefore, provides a more stable product (Peterson et al., 2008; Bridgwater, 2012). This biocrude can subsequently be refined to deliver a diversity of 'drop-in' renewable fuels ranging from petroleum to aviation fuel (Larson, 2006).

The combination of high biomass productivities for macroalgae, comparable to highly productive terrestrial crops (Larson, 2006; Kraan, 2013), and efficient conversion processes such as HTL (Aresta et al., 2005), provides a new focus on high-energy fuels derived from algal biomass. The first critical step in assessing and selecting species of macroalgae for the production of biomass and subsequent conversion to advanced high energy biofuels is the quantitative comparison of biomass productivity and biochemical composition (Neveux et al., accepted for publication). The second step is to quantify the conversion of this biomass to biocrude through the HTL process and assess the quality of this biocrude. The third and final step is to quantify and compare biocrude productivities, specifically the mass of biocrude produced per unit area of culture per unit of time.

Therefore, the aim of this study was to provide a direct comparison of the yield and elemental composition of biocrude and co-products resulting from HTL of marine and freshwater macroalgae, and then compare their biocrude productivities. To do this, four marine and two freshwater green macroalgae were cultivated in outdoor tanks simultaneously (Neveux et al., accepted for publication). These species were selected based on a combination of their ability to be cultured in land-based systems, high productivities, resistance to contamination and a high tolerance to environmental fluctuations (de Paula Silva et al., 2008; Lawton et al., 2013; Angell et al., 2014). This approach differs substantially from previous studies, where macroalgal biomass was collected from natural environments or cultivated under laboratory conditions and enables a true comparative assessment of macroalgae originating from different environments in terms of biocrude production.

2. Methods

2.1. Algae collection

Six species of green macroalgae (Chlorophyta) were selected for this study including four species of marine macroalgae, *Derbesia tenuissima* (Crouan), *Ulva ohnoi* (Hiraoka and Shimada), *Chaetomorpha linum* (Kutzing), *Cladophora coelothrix* (Kutzing) and two species of freshwater macroalgae, *Cladophora vagabunda* (Hoek), *Oedogonium* sp. (Lawton et al., 2013), hereafter referred to by origin and genus, e.g. marine *Cladophora*. Refer to Neveux et al. (accepted for publication) for details. All species were maintained as stock cultures in outdoor tanks at the Marine & Aquaculture Research Facilities Unit (James Cook University, Townsville). In these tanks, macroalgae species underwent fundamental changes in terms of composition and morphology compared to their natural environment (data non-reported), due to the changes of the environmental conditions. For this reason, macroalgae were cultivated in experimental conditions for a period of 3 weeks for acclimation, prior to the start of the experiment.

2.2. Algae culture

The experimental culturing of algae was conducted in an outdoor tank-based recirculation system, where productivity of marine and freshwater species was compared on a dry weight basis. Each species was cultured in triplicates at 2 g L^{-1} (fresh weight) in 50 L tanks, with a 0.25 volume d^{-1} water exchange rate. Experimental culturing of algae was carried on for 3 cycles of 6 days and biomass was restocked at 2 g L^{-1} for each new cycle while the excess biomass was discarded. After 18 days, all biomass in each tank was harvested using a fish net (2 mm screen) and the biomass productivity was calculated on a dry basis. This biomass was freeze-dried, ground to a mean particle size of <500 μm and stored in air-tight vials. Proximate, biochemical and ultimate analysis were performed on the dry biomass and the results are listed in Table 1. Refer to Neveux et al. (accepted for publication) for details on macroalgae culture and analyses.

2.3. Hydrothermal processing

Hydrothermal liquefaction of macroalgae was performed on each of the three replicates of the six species, for a total of 18 runs. HTL was performed using a custom-built stainless steel reactor system, assembled from commercially available components (Swagelok Company, Australia) and the setup is illustrated in Fig. 1. A slurry (6.6 wt.% solids) composed of 1 g of dry, powdered algae and 14 mL of distilled water was loaded in the 20 mL stainless steel tube reactor for each run. The reactor was subsequently fitted with a gasket and attached to the pressure-head, specifically engineered to handle pressures up to 250 bar at 350 °C. The head-space of the system was purged with nitrogen 3 times, then pressurized with nitrogen to 90 bar at ambient temperature, to ensure that the aqueous phase would remain liquid at high temperatures and to minimise the transport of vapour from the reactor into the connecting tubing, after the reactor was heated and began to generate steam pressure. A vapour reducer (50 mm length of tubing, 1.75 mm internal diameter; clearance between tube and thermocouple of 0.165 mm) served to dampen pressure spikes and inhibit diffusive interchange between the reactor and the cold tubing. The reactor was subsequently immersed in a pre-heated fluidized sand bath (Techne, model SBL-2D) set to 350 °C to initiate the HTL process. Typically, the internal temperature (determined by an internal thermocouple) rose on average to 262 °C (119 bar) within 1 min, 310 °C (131 bar) within 2 min and 325 °C (138 bar) within 3 min of reaction time. Internal reaction temperatures between 330 °C and 341 °C (maximum temperature) (140–170 bar) were maintained for a further 5 min (total of 8 min reaction time) before the reactor was quenched in an ice/water bath for 1 min to cool the reactor to room temperature.

2.4. Products separation and analysis

Use of the batch reactor system described above did not permit analysis of the gas produced by the reaction as this phase was vented inside a fume hood immediately following the reaction quench and prior to disassembly. In contrast, the condensed phases were separated and analysed. The reaction mixture (minus gas product) was diluted with dichloromethane (DCM) and distilled