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Research paper

Towards a marine biorefinery through the hydrothermal liquefaction of macroalgae native to the United Kingdom

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ABSTRACT

Hydrothermal liquefaction (HTL) is a promising biomass conversion method that can be incorporated into a biorefinery paradigm for simultaneous production of fuels, aqueous fertilisers and potential remediation of municipal or mariculture effluents. HTL of aquatic crops, such as marine macro- or microalgae, has significant potential for the UK owing to its extensive coastline. As such, macroalgae present a particularly promising feedstock for future UK biofuel production. This study aimed to bridge the gaps between previous accounts of macroalgal HTL by carrying out a more comprehensive screen of a number of species from all three major macroalgae classes, and examining the correlations between biomass biochemical composition and HTL reactivity. HTL was used to process thirteen South West UK macroalgae species from all three major classes (Chlorophyceae, Heterokontophyceae and Rhodophyceae) to produce bio-crude oil, a bio-char, gas and aqueous phase products. Chlorophyceae of the genus *Ulva* generated the highest bio-crude yields (up to 29.9% for *U. lactuca*). Aqueous phase phosphate concentrations of up to 236 mg L^{-1} were observed, obtained from the Rhodophyta, *S. chordalis*. Across the 13 samples, a correlation between increasing biomass lipids and increasing bio-crude yield was observed, as well as an increase in biomass nitrogen generally contributing to bio-crude nitrogen content. A broader range of macroalgae species has been examined than in any study previously and, by processing using identical conditions across all feedstocks, has enabled a more cohesive assessment of the effects of biochemical composition.

1. Introduction

The increasing unreliability of crude oil supplies, coupled with the causal link between fossil fuel use, CO_2 emissions and climate change, has led to extensive research into alternative liquid fuel sources compatible with the existing transport infrastructure. The production of first- and second-generation biofuels has been fraught with concerns over effective and ethical utilisation of arable land and fresh water [1], leading to a shift in focus from terrestrial to marine biomass feedstocks. Marine biomass, such as micro- and macroalgae, typically have higher biomass yields [2,3], owing to their higher photosynthetic efficiencies with respect to terrestrial crops (approx. 6–8%, *c.f.* approx. 1.8–2.2%) [4]. Although cultivation and harvesting of biomass constitutes a roadblock to widespread commercialisation of fuel production technologies [3], micro- and macroalgal fuel production systems also have the potential to be integrated with industrial and municipal waste remediation [5], aquaculture [6–9] or biomining of metals [10] to create an added-value biorefinery.

Investigations into micro- and macroalgae utilisation for biofuel production have spanned anaerobic digestion [11], fermentation [12] and conversion to biodiesel [13,14], with thermochemical processing techniques, such as hydrothermal gasification (HTG), pyrolysis and hydrothermal liquefaction (HTL) attracting attention in more recent years [15]. HTL in particular is ideally suited to wet feedstocks such as micro- and macroalgae, significantly lowering the prohibitive energy requirements associated with feedstock drying [16], and boosting the HHV of the resulting bio-crudes [17] with respect to pyrolysis bio-oils.

HTL utilises water at sub-/near-critical conditions (200–380 °C) as both a solvent and a reactant for a complex cascade of reactions, converting algal biomass into a bio-crude oil, alongside a nutrient-rich aqueous phase, a solid char and gaseous products. HTL of microalgae has been explored in great detail in recent years [18,19] but energy-

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Abbreviations

AP	Aqueous phase
ER	energy recovery
HHV	higher heating value
HTG	hydrothermal gasification
HTL	hydrothermal liquefaction

intensive cultivation and harvesting on an industrial scale remains a major setback to obtaining good energy returns on investment (EROI) [16]. Macroalgal biomass has comparatively lower associated production costs [20] and, as such, has been the subject of a range of recent HTL investigations.

Since the first documented liquefaction of *Macrocystis* sp. [21], a number of different macroalgae species have been examined across all three major classes (Heterokontophyceae, Rhodophyceae and Chlorophyceae – brown, red and green seaweeds) [4,13,22–30]. A comprehensive mechanistic study of microalgae conversion using HTL by Biller and Ross [31] found that biochemical components contributed to bio-crude formation in the order lipids > proteins > carbohydrates, proposing a simple additive model for predicting bio-crude yield from biochemical composition. In a similar study examining specifically low-lipid algae, Yang et al. [32] confirmed that proteins made a greater contribution to bio-crude oil yields than polysaccharides, albeit at the expense of inflated nitrogen content. While this serves as a useful proxy for macroalgae, which tend to contain low lipid and high carbohydrate levels, no macroalgae-specific verification of this relationship has been published to date. Conversely, Elliott et al. have suggested that the oil generated from liquefaction of *Saccharina* spp. is more similar in composition and properties to lignocellulosic HTL bio-crude than the microalgal equivalent [33], despite the almost complete absence of any lignin in the macroalgal feedstock.

A number of investigations [31,34,35] have looked into rationalising HTL reactivity through the use of individual and multiple model compounds. Neveux et al. [27] attempted to use the model proposed by Biller and Ross [31] to predict the bio-crude yields of marine and freshwater Chlorophyceae, but experimentally obtained bio-crude yields did not fit the proposed additive conversion framework. The group speculate that Biller and Ross's model was not an accurate descriptor of the process due to its failure to account for bio-crude generated through secondary reactions between biochemical compounds, in addition to individual additive conversion yields from each biochemical fraction. The occurrence of secondary reactions was confirmed by Jin et al. [36]. In addition to bio-crude oil, hydrothermal liquefaction of marine biomass also generates a range of aqueous products, including water-soluble light organics, ammonia and phosphates. The composition of the aqueous products is dependent on the composition of the feedstock and exact conditions used. The aqueous phase products from HTL of microalgae have been demonstrated to be as effective in promoting growth in microalgal cultures as the industry standard growth media 3N-BBM + V [37]. The recovery of nutrients could prove to be a crucial step in the development of a viable biorefinery, particularly if finite resources, such as phosphorus, are able to be recycled. To date, there has been no assessment of phosphate recovery in the aqueous phase products of macroalgal HTL.

In light of these findings, this investigation aimed to identify optimal conditions for both bio-crude production and nutrient partitioning into the aqueous phase from hydrothermal liquefaction of UK macroalgae species. A comprehensive screening of a range of seaweed species prevalent on the South West coast of the UK was subsequently carried out, and biomass biochemical compositions linked to product yields and properties in order to rationalise reactivity. Based on this, specifications for an ideal biomass feedstock were sought, with the ultimate aim of developing a theoretical model of a South-West UK-based biorefinery for the production of bio-crude oil and fertilisers for terrestrial or microalgal crops.

2. Methods

2.1. Materials and apparatus

Fresh macroalgal biomass samples were collected from Paignton, Devon (specifically, Broadsands Beach 50°24′24.9″N 3°33′16.2″W, Oyster Cove 50°25′04.1″N 3°33′20.9″W and Saltern Cove 50°24′57.9″N 3°33′24.4″W). Prior to analysis, all samples were freeze-dried and milled to < 1.4 mm diameter. Samples were stored in sealed vials at −18 °C. Macroalgal species used were *Ascophyllum nodosum* (AN), *Chondrus crispus* (CC), *Fucus ceranoides* (FC), *Fucus vesiculosus* (FV), *Himanthalia elongata* (HE), *Laminaria digitata* (LD), *Laminaria hyperborea* (LH), *Pelvetia canaliculata* (PC), *Rhizoclonium riparium* (RR), *Sargassum muticum* (SM), *Solieria chordalis* (SC), *Ulva intestinalis* (UI) and *Ulva lactuca* (UL). A more detailed description of the collection and preparation of the biomass samples is included in the supplementary information.

Batch reactors were fabricated according to literature precedent using stainless steel Swagelok® tube fittings [31,38,39]. The reactor body consisted of a length of tubing capped at one end, and connected at the other to a pressure gauge, thermocouple, needle valve, and relief valve. The total internal volume of the reactors was *ca.* 50 cm^3.

2.2. Procedure

Reaction procedures have been reported previously [39]. In a typical reaction, the reactor was loaded with 4 g biomass and 20 cm^3 freshly deionized water, and heated within a vertical tubular furnace set to 400 °C, 550 °C, 700 °C or 850 °C until the specified reaction temperature was reached (300–350 °C, 5–47 min), then removed from the furnace and allowed to cool to room temperature.

After cooling, gaseous products were released *via* the needle valve into an inverted, water-filled measuring cylinder to measure gaseous fraction volume. The gas phase is typically composed of 96–98% CO_2, observed experimentally for liquefaction of *A. nodosum* at 345 °C, and confirmed by Raikova et al. [39,40]. Hence, gas phase yields were calculated using the ideal gas law, approximating the gas phase as 100% CO_2, assuming an approximate molecular weight of 44 g mol^{-1} and a volume of 22.465 dm^3 mol^{-1} gas phase at 25 °C. The yield of gaseous product was determined using the following equation:

$$\text{yield}_{\text{gas}} = (V_{\text{gas}} \times 1.789 \times 10^{-3}) / (m_{\text{dry biomass}}) \times 100\% \quad (1)$$

Following this, the aqueous phase was decanted from the reactor contents and filtered through a Fisher qualitative filter paper pre-dried overnight at 60 °C. The product yield in the water phase was determined by leaving a 2.5 g aliquot to dry in a 60 °C oven overnight, and scaling the residue yield to the total aqueous phase mass. Aqueous phase residue yield was determined using the following equation:

$$\text{yield}_{\text{AP residue}} = m_{\text{residue}}/m_{\text{dry biomass}} \times 100\% \quad (2)$$

To separate the remaining bio-crude oil and char phase, the reactor was washed repeatedly using chloroform until the solvent ran clear, and filtered through the same filter paper used to separate the aqueous phase (after drying for a minimum of 1 h). The filter paper and collected char were washed thoroughly with chloroform to remove all remaining bio-crude. The filtrate was collected, and solvent removed *in vacuo* (40 °C, 72 mbar) until no further solvent evaporation was observed visually, and bio-crude samples were left to stand in septum-sealed vials venting to the atmosphere *via* a needle for a further 12 h to remove residual solvent. Bio-crude yield was determined using the following equation:

$$\text{yield}_{\text{bio-crude}} = m_{\textit{bio}\text{-crude}}/m_{\text{dry biomass}} \times 100\% \quad (3)$$