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Effect of Geographical Location on the Variation in Products Formed from the Hydrothermal Liquefaction of *Ulva intestinalis*

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Supporting Information

ABSTRACT: Hydrothermal liquefaction (HTL) of macroalgae offers a promising route to advanced biofuel production, although the distinct biochemical compositions of different macroalgae species can lead to widely different product yields and compositions. On the basis of this, there is an implicit assumption that there exists a universal optimal feedstock species for a bioenergy-based biorefinery, which could be exploited across a wide region. However, no studies to date have examined the effect of this large geographical variation on a single macroalgae species for biofuel production. In this study, 24 samples of *Ulva intestinalis* were collected along 1200 km of Swedish coastline and assessed as a feedstock for HTL. Significant variation in composition was observed between samples from Baltic and Atlantic regions, but substantial variation also existed between sites within close proximity. This was reflected in the HTL biocrude oil yields, which varied between 9 and 20% (14−28% dry and ash-free basis) across the sample set. In a number of cases, greater variation was seen for adjacent sites than for sites at opposite ends of the sampling spectrum. Biocrude oil yields in this study also differed substantially from those previously obtained for *U. intestinalis* from the United Kingdom and Vietnam. Localized environmental conditions affected the HTL product composition significantly, in particular, the elemental distribution within the sample set. The variability observed in this study suggests that no single species will be dominant within a macroalgal biorefinery concept, but rather a species would need to be selected to match the needs of the exact local environment.

1. INTRODUCTION

To limit global temperature increases to 2 °C, the vast majority of the energy sector must be decarbonized by 2075.[1] However, liquid fuels are likely to continue to play a major role in the transport sector long into the future,[2] and "drop-in" biofuels or crude oil alternatives compatible with current transport and refinery infrastructure are a crucial step in the transition to cleaner energy sources.[3] The use of terrestrial crops as feedstocks for biofuel production has been explored extensively, but concerns about utilization of arable land[4] as well as general availability have spurred a search for alternative marine feedstocks.[5]

Macroalgae are a fast-growing and important global resource. With production of aquatic plants reaching 30.5 million tonnes in 2015 harvested for commercial use[6] and cultivation increasing on average 8% per year,[7] it constitutes a promising source of biomass for food, pharmaceuticals and agriculture. As production volumes continue to grow, macroalgae has the potential to be used as an alternative to terrestrial biofuel feedstocks.[8]

A number of processing techniques have been examined for the conversion of macroalgae to liquid fuels, including biodiesel production,[9−11] fermentation to bioethanol and biobutanol,[12−14] and anaerobic digestion.[15] In recent years, thermochemical processing techniques, such as pyrolysis[16] and hydrothermal liquefaction (HTL),[17] have been examined as a route to produce high energy content oils as precursors for biofuel production. Of these, HTL has a number of advantages over pyrolysis: it is a low-temperature technique, using water at subcritical conditions (280−370 °C), and is ideally suited to inherently high-moisture feedstocks, thereby avoiding the substantial energetic penalty of feedstock drying. HTL also generates biocrude oils with lower oxygen content, higher energy content,[18] and higher thermal stability[19] compared to pyrolysis oils. HTL biocrude oils can be upgraded directly to biofuels through hydrotreating,[20] although oils have the potential to be co-refined with fossil crude oils in existing refineries in the future.[19,21,22] Upgrading options and refining protocols are dependent upon biocrude oil composition.

The exact composition and properties of biocrude oils are influenced by HTL reaction conditions but are most strongly influenced by the composition of the feedstock.[23] The earliest

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studies on the HTL of macroalgal biomass focused on individual feedstock species,[24−27] but recent reports have demonstrated the vast difference in products obtainable from different species growing in one place.[28] However, even within a single species, compositions can be influenced substantially by localized environmental conditions, such as salinity, temperature, and nutrient availability, and there is some evidence that certain biochemical components can vary widely between different geographical locations.[29−33] For example, brown macroalgae grown in more turbulent conditions typically have elevated levels of alginate,[34] and salinity has been shown to increase fatty acid levels in the green alga *Ulva pertusa* and the brown alga *Sargassum piluliferum*.[35] Cultivation of macroalgae downstream from aquaculture, such as salmon farms, has been shown to induce accumulation of higher levels of nitrogen[30] and phosphorus,[36] while biomasses grown in contaminated waters also exhibit bioaccumulation of heavy metals,[37] which could potentially be exploited as a route to environmental remediation of marine environments. Aside from direct increases in contaminant levels as a result of biosorption, the presence of metals has also been shown to affect the expression of polyunsaturated fatty acids (PUFAs).[38] All of these fluctuations have the potential to affect biomass reactivity and suitability as a feedstock for HTL.

Large-scale cultivation of macroalgae for fuel and food production in Sweden has recently been explored.[39,40] The waters of the Swedish coastline are divided into two distinct regions: high-salinity and nutrient-rich in the North Sea on the western coast and shallower, more brackish waters in the Baltic Sea in the east.[40] Within these regions, there are also variations in both biotic and abiotic factors that give rise to eutrophication, although the Helsinki Convention has led to overall improvements in water quality in recent decades.[41,42] These variations give rise to potential differences in macroalgal productivity and composition, which, in turn, could significantly affect the efficency of the HTL process. In this investigation, the suitability of a single species, *Ulva intestinalis*, was assessed as a feedstock for a macroalgal HTL biorefinery through the conversion of biomass harvested from a range of locations around the coast of Sweden.

2. MATERIALS AND METHODS

2.1. Materials and Apparatus. Fresh macroalgal biomass samples were collected in late summer over 22 days at eight sites along the Swedish coast. Three samples were collected at each site, 50−7000 m apart (several hundred meters for the majority of sites). The samples were dewatered using a salad spinner and frozen in a portable freezer shortly after collection. Prior to analysis, all samples were freeze-dried and milled to a homogeneous powder. Freeze-dried samples were stored at −80 °C prior to compositional analysis and, subsequently, stored at ambient conditions prior to being processed by HTL.

Sampling locations in graphs and tables are referred to using abbreviations: Tjärnö (TJÖ), Tjörn outside Göteborg (GBG), Helsingborg (HBG), Trelleborg (TBG), Åhus (ÅHS), Karlskrona (KKR), Västervik (VSV), and Stockholm (STH). Locations are summarized in Figure 1.

Batch reactors were fabricated according to the literature precedent using stainless-steel Swagelok tube fittings.[43−45] The reactor body consisted of a length of stainless-steel 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.[45] In a typical reaction, the reactor was loaded with 3 g of biomass and 15 cm^3 of freshly deionized water, heated within a vertical tubular furnace set to 700 °C until the specified reaction temperature was reached (345 °C, approximately 11 min), then removed from the furnace, and allowed to cool to room temperature.

Figure 1. Map of sampling sites. Atlantic sites are represented by yellow markers, and Baltic sites represented by blue markers. Three samples were obtained at each site, with sampling locations located approximately 50−7000 m apart.

After cooling, gaseous products were released via the needle valve into an inverted, water-filled measuring cylinder to measure the gaseous fraction volume. The gas phase is typically composed of 96−98% CO_2.[45,46] 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 the gaseous product was determined using the following equation:

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

Following this, the aqueous phase was decanted from the reactor contents and filtered through a Fisher qualitative filter paper predried 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. The 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 biocrude 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 biocrude oil. The filtrate was collected; the solvent was removed *in vacuo* (40 °C, 72 mbar) until no further solvent evaporation was observed visually; and biocrude oil 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. The biocrude oil yield was determined using the following equation:

$$\text{yield}_{\text{biocrude oil}} = m_{\text{biocrude oil}}/m_{\text{dry biomass}} \times 100\% \quad (3)$$

The char yield was calculated from the mass of the retentate collected on the filter paper after drying overnight in an oven at 60 °C.

The solid yield was determined using the following equation:

$$\text{yield}_{\text{solid}} = m_{\text{solid}}/m_{\text{dry biomass}} \times 100\% \quad (4)$$

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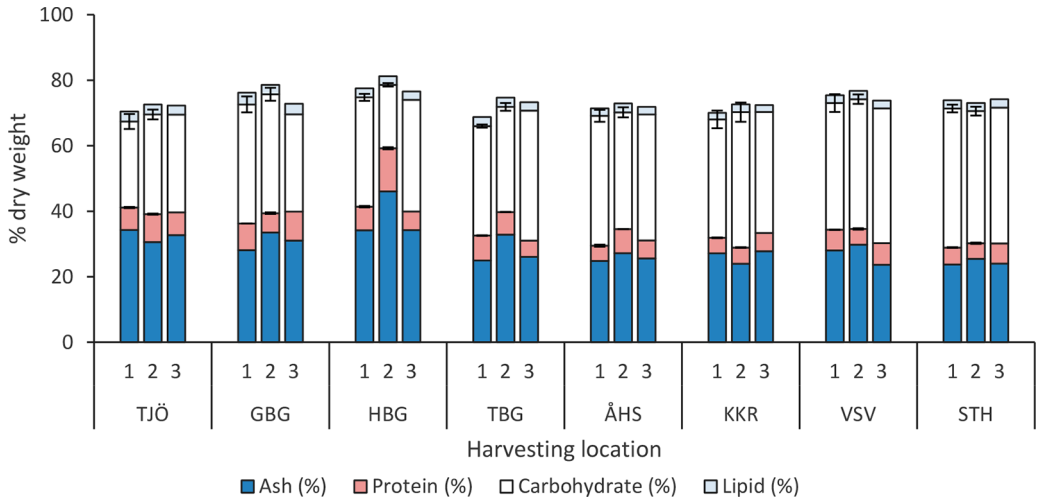

Figure 2. Total biochemical mass balance for *U. intestinalis* collected from three sampling sites across eight locations around the coast of Sweden. Error bars are derived from duplicate analysis of the protein content and triplicate analysis of total carbohydrate.

Inevitable material losses occurred during workup, predominantly through evaporation of light organics from the aqueous and biocrude oil phases during filtration and solvent removal. The shortfall in the mass balance has thus been designated "volatiles".

2.3. Biomass and Product Characterization. For the macroalgal biomass, lipid quantification was carried out on freeze-dried biomass using *in situ* transesterification with gas chromatography with flame ionization detection (GC−FID) as described previously.[47] Analysis was carried out in triplicate. Monosaccharide quantification was carried out using acid hydrolysis as described by Bikker et al.,[48] without neutralization. Samples were diluted and kept at 4 °C, and analysis was performed in triplicate within approximately 48 h. High-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC−PAD) was used for detection as described previously,[47] with minor modifications, incorporating a gradient of increasing sodium acetate content to separate sugar acids.[49] The total carbohydrate content was calculated as the sum of all monosaccharides and sugar acids, with correction for the addition of water during hydrolysis of polysaccharides. The crude oil protein content was calculated from the biomass nitrogen content using a conversion factor of 5 as established previously.[50]

Biomass ash was quantified by heating a 500 mg sample of biomass in a Carbolite muffle furnace at 550 °C for 5 h. The mass remaining at the end of the experiment was taken to be the ash.

For macroalgal biomass, biocrude oil, and char, elemental (CHN) analysis was carried out externally at the London Metropolitan University on a Carlo Erba Flash 2000 elemental analyzer to determine the CHN content (elemental analyses were carried out at least in duplicate for each sample, and average values are reported). From this, a higher heating value (HHV) was calculated using the equation set out by Channiwala and Parikh from elemental composition. HHVs calculated using the Channiwala and Parikh equation[51] were found to be in line with values determined experimentally using an IKA C1 bomb calorimeter (within ±5%).[28]

The aqueous-phase products were analyzed for total carbon (TC) and total nitrogen content (TN) using a Shimadzu TOC-L TOC analyzer fitted with a TNM-L total nitrogen analyzer unit and an ASI-L autosampler.

Further elemental analysis was carried out using inductively coupled plasma optical emission spectrometry (ICP−OES). Samples were digested in 4 mL of aqua regia at 95 °C for 1 h and then left to digest at ambient temperature for 24 h before being made up to 20 mL with 10% NaOH solution in deionized water to a pH of approximately 3. The resulting solution was filtered through a 0.45 μm filter membrane prior to analysis. ICP−OES was carried out externally by Yara U.K, Ltd. using an Agilent 700 series inductively coupled plasma optical emission spectrometer.

To determine experimental error and test the repeatability of experimental results, three repeat HTL runs of *U. intestinalis* collected in Göteborg were carried out to determine the standard deviation in mass balances at different reaction temperatures. All elemental analyses (CHN) were carried out in duplicate, and average values were used.

2.3.1. Statistical Analysis. Statistical analysis (two-tailed *t* test, regression) was conducted using Microsoft Excel's built-in data analysis module as well as the XLSTAT add-in for nonparametric testing (Mann−Whitney's *U* test).

3. RESULTS AND DISCUSSION

3.1. Geographical Variation in Biomass Biochemical Composition. Three seaweed samples, sampled no less than 50 m apart, were collected at each of the eight locations around the coast of Sweden. The biochemical composition of the macroalgae tested displayed some geographical variation (Figure 2). The Atlantic region (Tjärnö and Göteborg) has higher salinity compared to the more brackish waters of the Baltic (the remaining six sampling locations, with Helsingborg at the border of the two regions), which is one factor that may influence composition. Indeed, samples from Atlantic sites had elevated lipid, protein, and ash levels and reduced carbohydrate content compared to the Baltic sites. Protein and lipid contents have previously been found to increase in more saline environments,[29,35] and a negative correlation between the total carbohydrate content and water salinity has also been reported.[29]

The overall biochemical composition differed substantially from that observed for *U. intestinalis* harvested in the U.K. and other regions.[28] Most notably, protein and lipid levels were significantly lower (4.6−13.2% protein, cf. 20.9% for U.K. *U. intestinalis*, and, similarly, 2.0−3.6% lipid, cf. 5.9% in the U.K.). The U.K. macroalgae were harvested during spring, when protein and lipid levels are at their highest for many species;[52] therefore, these differences could also be attributable to seasonal as well as other geographical and environmental factors. A further evaluation of the environmental condition at collection sites correlated to biomass composition will be presented separately.[49]

The elemental compositions of the samples displayed some variation, with total carbon contents ranging from 22.2% in Helsingborg to a maximum of 29.4% observed for Västervik

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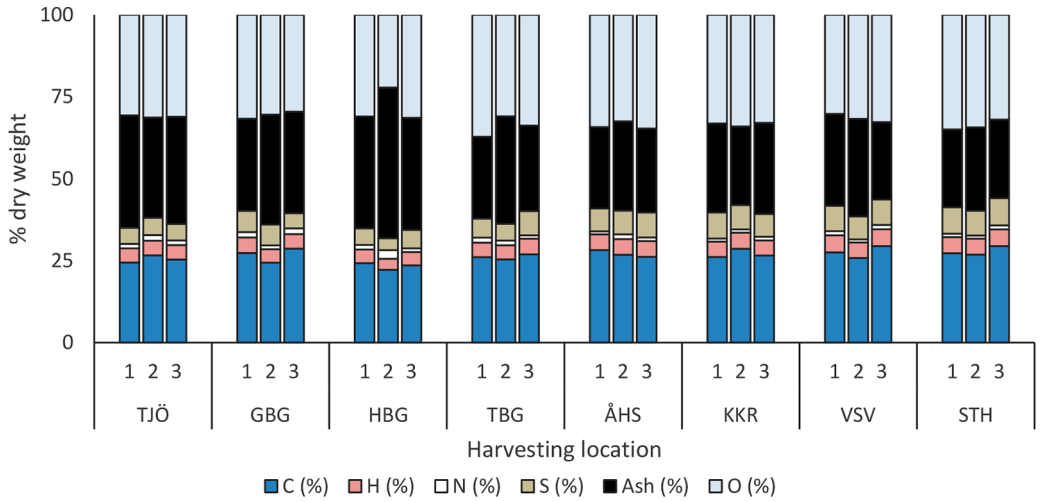

Figure 3. Elemental composition of *U. intestinalis* collected from three sampling sites across eight locations around the coast of Sweden. Carbon, hydrogen, and nitrogen analyses were carried out in duplicate; error was negligible.

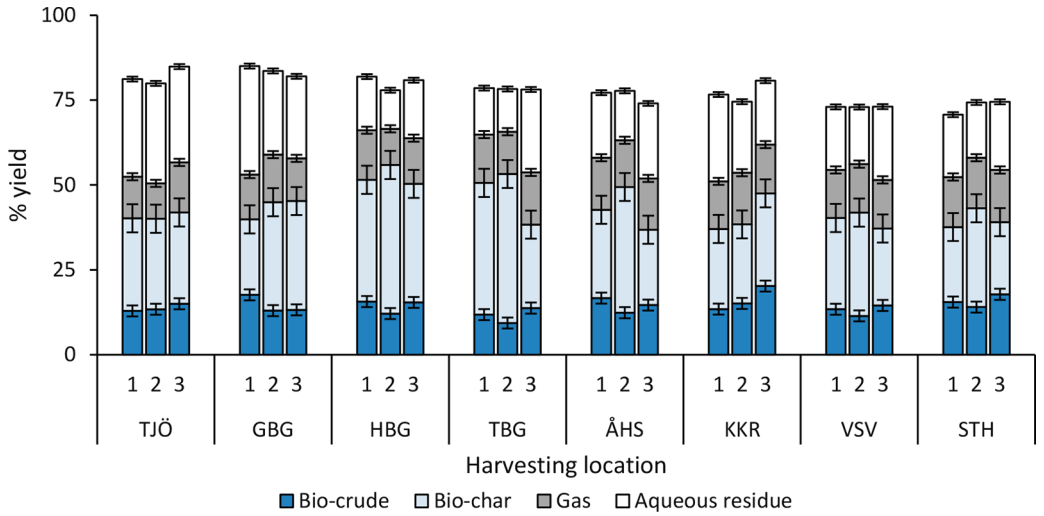

Figure 4. Mass balance of product fractions obtained from the HTL of 24 samples of *U. intestinalis* from three sampling sites across eight locations around the coast of Sweden. The remaining fraction of the mass is assigned to volatile losses from the aqueous and biocrude oil fractions upon work up. Mass yields quoted on a dry basis. Error bars represent the standard deviation of the product mass fractions obtained from three repeat runs of HTL using the GBG3 feedstock.

and Stockholm (Figure 3). The largest standard deviation for carbon content within any one sampling location was 2.2% for Göteborg. The sulfur content increased toward the northernmost sampling points in the Baltic region (Västervik and Stockholm), with statistically significant differences between the Atlantic and Baltic (p = 0.010), and the highest sulfur content was observed to be 8.3%. A significant difference between Atlantic and Baltic sites was also found for the nitrogen content (p = 0.022); an elevated nitrogen content was observed for Atlantic sites, although the difference was modest.

3.2. Variation in Biocrude Oil Production and Quality. HTL was carried out on all 24 collected samples across the eight locations (Figure 4). The reaction conditions were selected on the basis of previous work[28] to give optimal biocrude oil production. Mass closures of 70−85% were observed, in line with those previously seen for similar feedstocks,[53] with losses attributed to the evaporation of light volatiles from the aqueous fraction during water removal to calculate yields and during solvent evaporation from the biocrude oil products.

Biocrude oil ranged from 9% for a sample from Trelleborg to a maximum of 20% observed for one of the biomasses from Karlskrona, still somewhat more modest than yields obtained from the same species, *U. intestinalis*, collected in the U.K.[28] The majority of the biocrude yields were similar, falling between 13 and 17%, with a small number of outliers. The biocrude oil yields on a dry and ash-free basis (daf) are given in Table 1.

It is well-established that lipids and proteins are preferentially converted to biocrude oil,[43] and the depleted lipid and protein contents of the autumn-harvested Swedish biomass compared to the lipid-rich spring *Ulva* crop in the U.K. would also make a difference. Despite significant differences observed between the biomass compositions of Atlantic and Baltic samples, no statistically significant differences between biocrude oil yields obtained from Atlantic versus Baltic macroalgae were identified (p > 0.05). The variation in biocrude oil yields generated from samples within each location was, in some cases, greater than the variation between samples collected from geographically remote sites. Yields

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Table 1. Biocrude Oil Yields from Swedish *U. intestinalis*, Reported on a Dry and Ash-Free Basis (%, daf)

location	yield (%, daf)		
	1	2	3
Tjärnö	19.6	19.3	22.3
Göteborg	24.5	19.5	19.1
Helsingborg	23.8	22.4	23.4
Trelleborg	15.7	13.9	18.6
Åhus	22.2	17.0	19.7
Karlskrona	18.4	19.9	28.0
Västervik	18.6	16.3	19.0
Stockholm	20.3	18.8	23.4

ranging from 13 to 20% were obtained for the three Karlskrona samples, while identical biocrude oil yields of 13% were observed for multiple feedstocks sampled across both the Atlantic and Baltic regions (Tjärnö, Göteborg, Karlskrona, and Västervik).

Total material recoveries in the aqueous-phase products ranged from 11.4 to 32.0%, with substantial variation within sampling sites: for the three biomasses collected in Trelleborg, aqueous-phase yields ranged from 12.6 to 24.5%, with a similar level of variation observed for Åhus (14.6−22.1% aqueous product yield). Previous studies have suggested that biomass carbohydrates are preferentially converted to aqueous-phase products,[54] such as a range of water-soluble polar organics.[26] However, a direct correlation between carbohydrate levels and aqueous-phase yields was not observed in this case.

In recent years, there has been some focus on attempting to rationalize the reactivity of different macroalgal feedstocks across species[18,28,55] to supplement the investigations of biomass reactivity using model compounds.[43,56,57] As a result of substantial species-related differences between individual protein, lipid, and carbohydrate types within each broad compound class, simple and clear-cut correlations enabling the prediction of biocrude oil yields based on biochemical composition have thus far been elusive.[28,55] It was hypothesized that, for a single species, fluctuations in environmental conditions would induce changes in the relative quantities of biochemical components, but the individual protein, lipid, and carbohydrate types would remain constant. This could potentially enable the derivation of a more strongly predictive model for biocrude oil production based on biomass biochemical breakdown. Lipids have been previously found to be linked to biocrude oil yields;[28] however, regression analysis could not confirm any statistically significant correlations between the levels of lipid, protein, carbohydrate, or total ash and biocrude oil production ($p > 0.05$). Alkali and alkaline earth metals in biomass ash have been variously attributed as having a catalytic or inhibitive effect on biocrude oil formation, although mechanisms are still poorly understood.[58] The fluctuating content of alkali and alkaline earth metals, such as Ca, Mg, and K, as well as other metallic species across the locations sampled could play a role in directing biocrude oil production and counteract the effect of an increasing lipid content.

Biocrude oil nitrogen and sulfur contents were found to be strongly correlated with biomass nitrogen and sulfur levels (Figure 5). The levels of both elements appeared to follow a similar pattern, peaking at Helsingborg (the first sampling location in the Baltic region) and decreasing steadily as the sampling location moved north toward Stockholm, albeit with a small increase at Västervik. The Sound (Öresund), with Helsingborg at its narrowest point, attracts some of the highest marine traffic intensity in the Baltic region,[59] with emissions of SO_x and NO_x potentially leading to elevated sulfur and nitrogen levels in seawater and concomitant N and S increases in biomass. The lowest nitrogen and sulfur levels were observed for biocrude oil produced from biomass obtained in Stockholm, lower than the Atlantic biocrude oils (somewhat surprising, given the high level of industrial and shipping activity in the Baltic region compared to the Atlantic). Sulfur levels in the biocrude oils (ranging from 0.9% for Stockholm to 4.4% for Helsingborg) fall in line with those observed for many fossil crude oils (0.05−5%), although sulfur levels of over 0.5% are undesirable, and oils with sulfur levels exceeding this require hydrodesulfurization prior to refining and use. Both the sulfur and nitrogen contents of the biocrude oils derived from biomass harvested in Helsingborg exhibited the highest level of variability, with a factor of 2 difference between the highest and lowest N values (3 cf. 6%). These exceed the nitrogen contents typically observed in fossil crude oils (0.5−2.1%,[60] although values under 1% are more typical[61]). Nitrogen in crude oils is highly unfavorable in terms of fuel properties, because they can denature petroleum cracking catalysts, inhibit hydrodesulfurization, and contribute to NO_x emissions upon combustion,[60] and hydrotreatment would be necessary before biocrude oils could be co-processed with crude oils or used as fuel. In terms of nitrogen and sulfur contents, biocrude oils derived from biomass harvested in Stockholm would be optimal for co-refining and fuel use, closely followed by Karlskrona and Västervik.

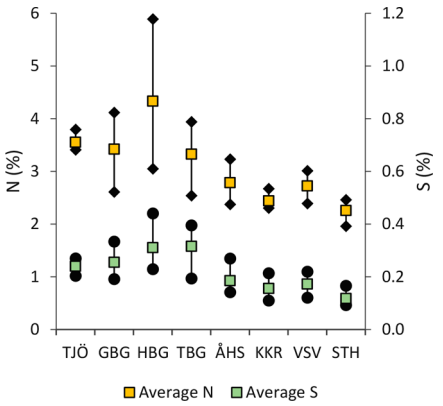

Figure 5. Biocrude oil nitrogen and sulfur levels. The markers represent average values for each sampling location, and the bars represent the highest and lowest values for biocrude oil N and S obtained for each location.

Contrastingly, the biocrude oils with the lowest nitrogen and sulfur contents exhibited the lowest energy density (Figure 6). Biocrude oil energy contents fell within the range of 24.4−33.2 MJ kg^{-1}, corresponding to approximately 55−75% of the energy density of a typical crude oil (ca. 42−44 MJ kg^{-1}). Most of the biocrude oils analyzed had energy contents exceeding 30 MJ kg^{-1}, although three of the Baltic biocrude oils, two derived from biomass originating in Stockholm and one from Karlskrona, had markedly depleted HHVs, more similar to those obtained for pyrolysis bio-oils.[62] Between 29.1 and 55.5% of the total energy content of the biomasses was recovered in the biocrude oil fraction.

Analysis of the biocrude oil compositions by gas chromatography/mass spectrometry (GC/MS) revealed

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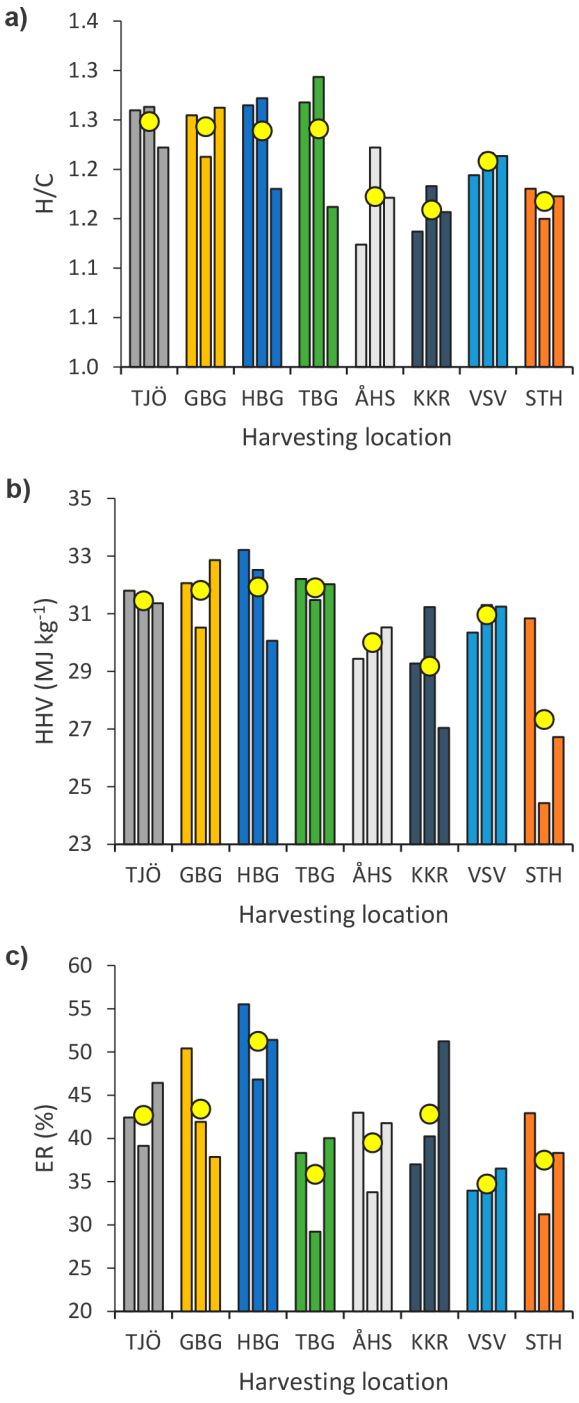

Figure 6. Characteristics of the biocrude oil produced through HTL processing of *U. intestinalis* from three sampling sites across eight locations around the coast of Sweden: (a) biocrude oil H/C ratios, (b) HHVs, and c) energy recovery (ER) in the biocrude oil products. Bars represent the values obtained for individual biocrude oils, and yellow markers denote averages for each location.

broad similarities between the samples across all locations. Phenols made up a substantial proportion of compounds identified, with phenol, *m*-cresol, *p*-cresol, 4-aminophenol, and 2,6-dimethylphenol present in all samples, alongside isomers of methyl- and dimethylcyclopenten-1-one. All samples also contained a substantial contribution from (*Z*)-9-octadecenamide. 5-Methylfurfural was observed in several of the samples, appearing more frequently in the biocrude oils derived from

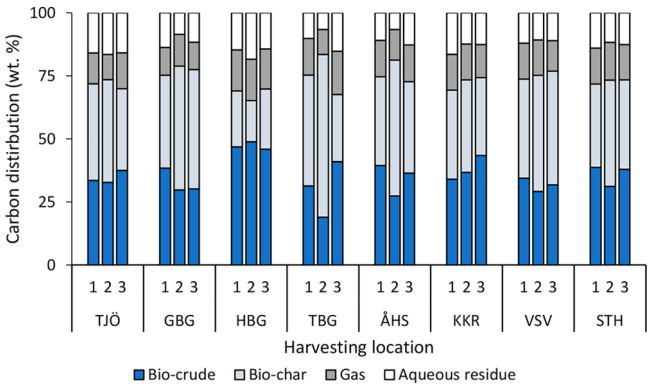

Figure 7. Carbon distribution (weight percent) between the product phases of HTL of *U. intestinalis* from three sampling sites across eight locations around the coast of Sweden.

the Baltic macroalgae, while 1-tetradecanol was more prevalent in Atlantic biocrude oils. Notably, limonene was observed in one of the Helsingborg biocrude oils and two of the biocrude oils from macroalgae harvested in Trelleborg, suggesting some terpene production. A full summary of the biocrude oil compositions and GC/MS chromatograms are provided in the Supporting Information.

Ultimately, there are high levels of variability in both the yields and properties of the biocrude oils. There is as much variation over a small, localized environment as over a large geographic range, and even for a single species, differences in marine environments can lead to significant fluctuations in HTL outcomes and biocrude oil properties.

3.3. Elemental Distribution. Overall, carbon was recovered predominantly in the biocrude oil and solid char product phases, with a maximum of 18.4% recovered in the aqueous phase and 17.2% as CO_2 in the gas phase (Figure 7). The most substantial variation was seen for Trelleborg, with between 19 and 41% of carbon recovered in the biocrude oil and 27−65% in the solid char for the three samples. Because the total carbon content of the biocrude oils was generally relatively consistent, this variation was attributable predominantly to the variation in the biocrude oil yields obtained.

The distribution of biomass metals between different product phases was assessed using ICP−OES. In all cases, the metals partitioned predominantly between the solid and aqueous phases (Figure 8), with biocrude oil metals constituting only a small fraction of overall recovery.

Although the proportion of total metals recovered in the biocrude oil was small, biocrude oil metal levels nonetheless significantly exceeded those found in fossil crude oils. The balance of metal distributions between the biocrude oil and aqueous-phase products is affected by HTL reaction parameters, with more severe reaction conditions (increasing temperatures and holding times) driving the partitioning of metals into the biocrude oil.[63]

Biocrude oil metal levels were highly variable, both within and between sampling sites, while the most abundant elements, alongside S and N, measured in the biocrude oil were Al, Ca, Fe, K, Mg, and Si. Although common crude oil metal contaminants, such as cadmium and vanadium, are present at lower levels than those observed in fossil crude oil, Ca levels are comparable to superheavy crude oils,[64] which could impact upgrading procedures and limit the blend levels that can be used in co-refining. High iron levels of up to 415 ppm were

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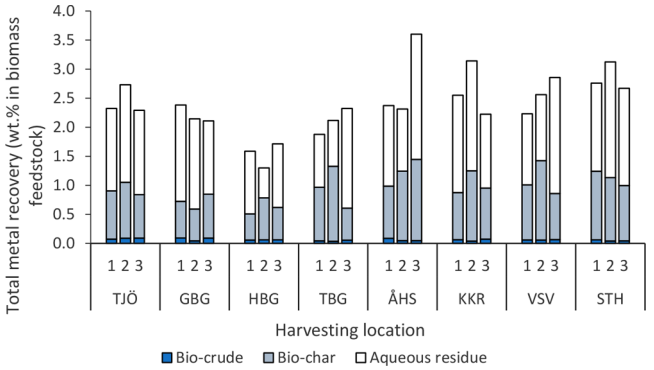

Figure 8. Partitioning of biomass metals between HTL product phases, presented as a proportion of the total metal content of the macroalgae feedstock.

observed, which have been shown to cause rapid plugging of catalyst beds and catalyst degradation by highly stable iron porphyrin structures during hydrotreatment of microalgal biocrude oils.[65] The magnesium content was highly variable, falling between 30 and 733 ppm for the three Göteborg biocrude oils. Metal levels are comparable to those observed for microalgal biocrude oil,[63] although Si and Al levels are notably higher. A summary of all the metals detected in the biocrude oil can be found in Table S1 of the Supporting Information.

The aqueous product is also rich in dissolved minerals and micronutrients, such as Na, K, Ca, and Mg, as well as nitrogen and phosphorus, which are essential for plant and algae growth. A number of studies have addressed the possibility of nutrient recovery through the utilization of diluted HTL aqueous phases as a growth media for microalgal cultures.[66−71] HTL aqueous-phase growth media has given rise to biomass productivity comparable to or even exceeding[66,68,70] that observed in standard growth media, although growth has been found to be limited by toxic organic compounds, such as phenol.[71]

Essential elements for plant growth are presented in Figure 9. A full breakdown of the metal concentrations in the aqueous products is presented in Table S2 of the Supporting Information. Dissolved micronutrient concentrations are high, and aqueous phases would require dilutions of around 100−300× to obtain concentrations suitable for cultivation of microalgae, although, notably, the aqueous-phase sulfur levels obtained are up to 700× higher than those used in a typical microalgal growth medium.[68] Certain species of microalgae express higher levels of triacylglycerol under conditions of sulfur starvation;[72] therefore, the high-sulfur aqueous phases may not be optimal for production of microalgae for biodiesel. A recent study found that a growth medium derived from HTL products performed better with the addition of trace metals, such as Co and Mo, resulting in higher biomass yields and an increase in maximum specific growth rates for *Chlorella sorokiniana*.[68]

Substantial variation in aqueous nutrient levels was observed both within and between locations: calcium levels between 131 and 546 ppm were observed for the Tjärnö aqueous phases, while potassium levels fluctuated between 575 and 3872 ppm for the Västervik sample set. Crucially, the concentrations of nutrients beneficial to plant growth (K, Mg, and Ca) are high, whereas levels of toxic metals, such as arsenic and lead, are limited (0−14 ppm As and a maximum of 1 ppm for Pb)

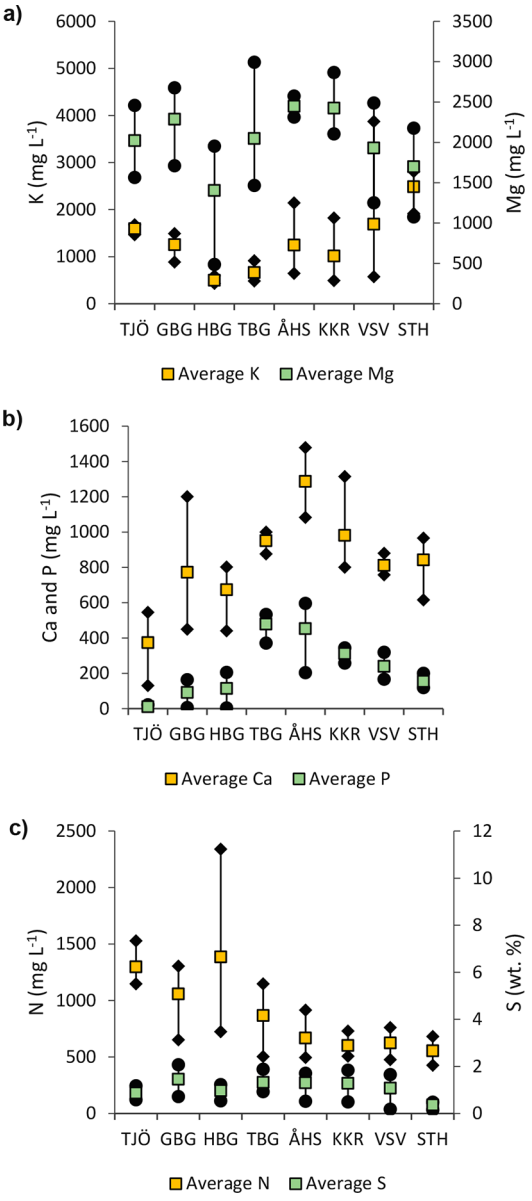

Figure 9. Partitioning of key elements suitable for plant growth in the aqueous phase (K, Mg, Ca, P, N, and S).

across all locations and will be further diminished at the dilutions necessary for aqueous-phase utilization as a growth medium. The variation and unpredictability of metal and nutrient recoveries within some locations could create problems in streamlining the utilization of the aqueous phase as a growth medium within a biorefinery.

The total nitrogen content of up to 2340 mg L^{-1} were seen in the aqueous phase. Nitrogen in HTL aqueous phases tends to be in the form of ammonium rather than nitrate. This may be beneficial in terms of utilization for microalgae cultivation, because ammonium may be a more efficient source of nitrogen for aquatic plants than nitrate, especially under light-limited conditions.[73] The aqueous-phase nitrogen content was variable (427−2340 mg L^{-1}) and somewhat elevated for aqueous phases derived from Atlantic macroalgae with respect to Baltic samples, although the highest N content observed was for a feedstock from Helsingborg.

Phosphorus is an important and increasingly expensive worldwide resource and could constitute a significant source of

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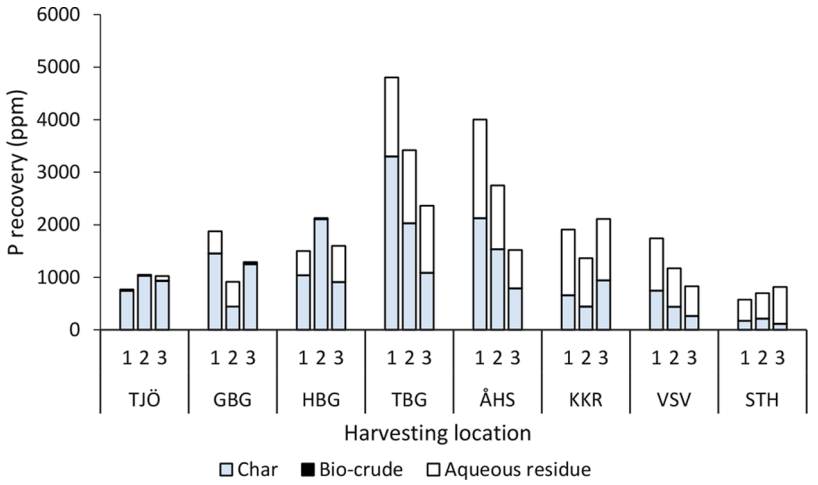

Figure 10. Partitioning of P between the product phases for the HTL of *U. intestinalis* from three sampling sites across eight locations around the coast of Sweden.

value within a HTL biorefinery. Previous work has demonstrated that the vast majority of P in the aqueous phase is as bioavailable phosphate.[66] Although the aqueous-phase products contain up to 596 ppm of phosphorus that could be used for microalgal or higher plant cultivation at the conditions examined, biomass phosphorus is recovered predominantly in the solid-phase products. Precipitation of metal phosphates (e.g., $CaPO_3$) is a key route of metal partitioning to the solid products.[74] Phosphate recovery from solid-phase products may be possible, as previously demonstrated for pyrolysis char,[75] and used for fertilizer production. The aqueous-phase phosphorus content was highly variable, with higher levels on average for Baltic macroalgae. Notably, the aqueous-phase phosphorus content of the Tjärnö biomasses was substantially lower than the remaining samples (a maximum of 22 ppm observed across the three samples), while the biomasses in Trelleborg and Åhus yielded aqueous phases with the highest dissolved phosphorus (204−596 ppm). Trelleborg and Åhus are situated in one of the main agricultural areas of Sweden, and it is expected that leaching of nutrients from fertilizer use may reach coastal areas and be available for seaweeds, translating to higher nutrient levels in aqueous-phase HTL products.

A substantial proportion of biomass phosphorus is also recovered in the solid char products (Figure 10), with phosphorus contents of up to 8504 ppm (Trelleborg). Phosphorus recovery is feasible for HTL char (having previously been demonstrated for pyrolysis char[75]) and could constitute a highly lucrative process within a HTL biorefinery. Although biomass phosphorus levels are approximately similar for Tjärnö and Stockholm, the distribution of phosphorus between the aqueous and solid phases differs: phosphorus is recovered predominantly in the solid phase for Tjärnö, and the aqueous products are recovered predominantly in the solid phase for Stockholm. This may be linked to the fluctuating levels of other dissolved inorganic species, which can form phosphate salts with varying water solubility.

4. CONCLUSION

Recent studies have demonstrated a large variation in the yields and composition of products formed from the HTL of different species of macroalgae. In this study, the effect of geographic location on a single species of macroalgae harvested across a large area was examined. While *U. intestinalis* has previously been demonstrated as one of the most suitable macroalgae species for biocrude oil production in the United Kingdom, this does not necessarily translate worldwide, with reduced biocrude oil production observed for the same species sampled across Sweden. All samples of the Swedish *U. intestinalis* produced broadly similar yields of biocrude oil; however, environmental variations led to large fluctuations in the elemental composition and metal content, with knock-on effects for the uniformity of HTL mass distributions, even within a highly localized area. A significant difference in the composition of the aqueous and solid phases was also observed. Geographic variability plays a huge role in the yields and composition of the HTL products, and it is probable that there will not be one suitable species for a macroalgal biorefinery; rather, feedstock suitability will need to be assessed and optimized individually for each growing location.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.8b02374.

Detailing the breakdown of metals across each phase and the GC/MS data of the biocrude oil fraction (PDF)

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Notes

The authors declare no competing financial interest.

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DEDICATION

The authors thank their dear friend and colleague Viktor Andersson, previously at Chalmers University of Technology, for discussions within their joint project. May he rest in peace. This paper is dedicated to Viktor Andersson, and the authors believe he would have been proud of the outcome of the project.

REFERENCES

(1) Intergovernmental Panel on Climate Change (IPCC). *Climate Change 2007 Synthesis Report Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; IPCC: Geneva, Switzerland, 2007.

(2) Fulton, L. M.; Lynd, L. R.; KörneR, A.; Greene, N.; Tonachel, L. R. The need for biofuels as part of a low carbon energy future, Biofuels. *Biofuels, Bioprod. Biorefin.* **2015**, *9*, 476−483.

(3) National Renewable Energy Laboratory (NREL).. Can "drop-in" biofuels solve integration issues? *Contin. Mag.* **2013**, *5*, 8−13.

(4) Cassman, K. G.; Liska, A. J. Food and fuel for all: Realistic or foolish? *Biofuels, Bioprod. Biorefin.* **2007**, *1*, 18−23.

(5) Jung, K. A.; Lim, S.-R.; Kim, Y.; Park, J. M. Potentials of macroalgae as feedstocks for biorefinery. *Bioresour. Technol.* **2013**, *135*, 182−90.

(6) Food and Agriculture Organization of the United Nations (FAO).. FAO Yearbook: Fishery and Aquaculture Statistics. 2015. *FAO Annu. Yearb.* **2017**, 1−230.

(7) Food and Agriculture Organization of the United Nations (FAO). *The State of World Fisheries and Aquaculture. Contributing to Food Security and Nutrition for All*; FAO: Rome, Italy, 2016; http://www.fao.org/3/a-i5555e.pdf.

(8) Chen, H.; Zhou, D.; Luo, G.; Zhang, S.; Chen, J. Macroalgae for biofuels production: Progress and perspectives. *Renewable Sustainable Energy Rev.* **2015**, *47*, 427−437.

(9) Aresta, M.; Dibenedetto, A.; Carone, M.; Colonna, T.; Fragale, C. Production of biodiesel from macroalgae by supercritical CO_2 extraction and thermochemical liquefaction. *Environ. Chem. Lett.* **2005**, *3*, 136−139.

(10) Suganya, T.; Renganathan, S. Optimization and kinetic studies on algal oil extraction from marine macroalgae *Ulva lactuca*. *Bioresour. Technol.* **2012**, *107*, 319−326.

(11) Suganya, T.; Nagendra Gandhi, N.; Renganathan, S. Production of algal biodiesel from marine macroalgae *Enteromorpha compressa* by two step process: Optimization and kinetic study. *Bioresour. Technol.* **2013**, *128*, 392−400.

(12) Huesemann, M. H.; Kuo, L. J.; Urquhart, L.; Gill, G. A.; Roesijadi, G. Acetone-butanol fermentation of marine macroalgae. *Bioresour. Technol.* **2012**, *108*, 305−309.

(13) Wargacki, A. J.; Leonard, E.; Win, M. N.; Regitsky, D. D.; Santos, C. N. S.; Kim, P. B.; Cooper, S. R.; Raisner, R. M.; Herman, A.; Sivitz, A. B.; Lakshmanaswamy, A.; Kashiyama, Y.; Baker, D.; Yoshikuni, Y. An engineered microbial platform for direct biofuel production from brown macroalgae. *Science (Washington, DC, U. S.)* **2012**, *335*, 308−313.

(14) Van der Wal, H.; Sperber, B. L. H. M.; Houweling-Tan, B.; Bakker, R. R. C.; Brandenburg, W.; López-Contreras, A. M. Production of acetone, butanol, and ethanol from biomass of the green seaweed *Ulva lactuca*. *Bioresour. Technol.* **2013**, *128*, 431−437.

(15) Sutherland, A. D.; Varela, J. C. Comparison of various microbial inocula for the efficient anaerobic digestion of *Laminaria hyperborea*. *BMC Biotechnol.* **2014**, *14*, 7.

(16) Song, L.; Hu, M.; Liu, D.; Zhang, D.; Jiang, C. Thermal cracking of *Enteromorpha prolifera* with solvents to bio-oil. *Energy Convers. Manage.* **2014**, *77*, 7−12.

(17) Elliott, D. C.; Hart, T. R.; Neuenschwander, G. G.; Rotness, L. J.; Roesijadi, G.; Zacher, A. H.; Magnuson, J. K. Hydrothermal Processing of Macroalgal Feedstocks in Continuous-Flow Reactors. *ACS Sustainable Chem. Eng.* **2014**, *2*, 207−215.

(18) Singh, R.; Balagurumurthy, B.; Bhaskar, T. Hydrothermal liquefaction of macro algae: Effect of feedstock composition. *Fuel* **2015**, *146*, 69−74.

(19) Hoffmann, J.; Jensen, C. U.; Rosendahl, L. A. Co-processing potential of HTL bio-crude at petroleum refineries—Part 1: Fractional distillation and characterization. *Fuel* **2016**, *165*, 526−535.

(20) Tews, I. J.; Zhu, Y.; Drennan, C. V.; Elliott, D. C.; Snowden-Swan, L. J.; Onarheim, K.; Solantausta, Y.; Beckman, D. *Biomass Direct Liquefaction Options: TechnoEconomic and Life Cycle Assessment*; Pacific Northwest National Laboratory: Richland, WA, 2014; DOI: 10.2172/1184983.

(21) López Barreiro, D.; Prins, W.; Ronsse, F.; Brilman, W. Hydrothermal liquefaction (HTL) of microalgae for biofuel production: State of the art review and future prospects. *Biomass Bioenergy* **2013**, *53*, 113−127.

(22) Jensen, C. U.; Hoffmann, J.; Rosendahl, L. A. Co-processing potential of HTL bio-crude at petroleum refineries. Part 2: A parametric hydrotreating study. *Fuel* **2016**, *165*, 536−543.

(23) Akhtar, J.; Amin, N. A. S. A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. *Renewable Sustainable Energy Rev.* **2011**, *15*, 1615−1624.

(24) Elliott, D. C.; Sealock, L. J., Jr.; Butner, S. R. Product Analysis from Direct Liquefaction of Several High-Moisture Biomass Feedstocks. In *Pyrolysis Oils from Biomass*; Soltes, E. J., Milne, T. A., Eds.; American Chemical Society (ACS): Washington, D.C., 1988; ACS Symposium Series, Vol. *376*, Chapter 17, pp 179−188, DOI: 10.1021/bk-1988-0376.ch017.

(25) Anastasakis, K.; Ross, A. B. Hydrothermal liquefaction of the brown macro-alga *Laminaria saccharina*: Effect of reaction conditions on product distribution and composition. *Bioresour. Technol.* **2011**, *102*, 4876−83.

(26) Zhou, D.; Zhang, L.; Zhang, S.; Fu, H.; Chen, J. Hydrothermal Liquefaction of Macroalgae *Enteromorpha prolifera* to Bio-oil. *Energy Fuels* **2010**, *24*, 4054−4061.

(27) Li, D.; Chen, L.; Xu, D.; Zhang, X.; Ye, N.; Chen, F.; Chen, S. Preparation and characteristics of bio-oil from the marine brown alga *Sargassum patens* C. Agardh. *Bioresour. Technol.* **2012**, *104*, 737−742.

(28) Raikova, S.; Le, C. D.; Beacham, T. A.; Jenkins, R. W.; Allen, M. J.; Chuck, C. J. Towards a marine biorefinery through the hydrothermal liquefaction of macroalgae native to the United Kingdom. *Biomass Bioenergy* **2017**, *107*, 244−253.

(29) Nielsen, M. M.; Manns, D.; D 'este, M.; Krause-Jensen, D.; Rasmussen, M. B.; Larsen, M. M.; Alvarado-Morales, M.; Angelidaki, I.; Bruhn, A. Variation in biochemical composition of *Saccharina latissima* and *Laminaria digitata* along an estuarine salinity gradient in inner Danish waters. *Algal Res.* **2016**, *13*, 235−245.

(30) Sanderson, J. C.; Dring, M. J.; Davidson, K.; Kelly, M. S. Culture, yield and bioremediation potential of *Palmaria palmata* (Linnaeus) Weber & Mohr and *Saccharina latissima* (Linnaeus) C.E. Lane, C. Mayes, Druehl & G.W. Saunders adjacent to fish farm cages in northwest Scotland. *Aquaculture* **2012**, *354*−*355*, 128−135.

(31) Marinho, G. S.; Holdt, S. L.; Birkeland, M. J.; Angelidaki, I. Commercial cultivation and bioremediation potential of sugar kelp, *Saccharina latissima*, in Danish waters. *J. Appl. Phycol.* **2015**, *27*, 1963−1973.

(32) Handå, A.; Forbord, S.; Wang, X.; Broch, O. J.; Dahle, S. W.; Størseth, T. R.; Reitan, K. I.; Olsen, Y.; Skjermo, J. Seasonal- and depth-dependent growth of cultivated kelp (*Saccharina latissima*) in close proximity to salmon (*Salmo salar*) aquaculture in Norway. *Aquaculture* **2013**, *414*−*415*, 191−201.

(33) Broch, O. J.; Ellingsen, I. H.; Forbord, S.; Wang, X.; Volent, Z.; Alver, M. O.; Handå, A.; Andresen, K.; Slagstad, D.; Reitan, K. I.; Olsen, Y.; Skjermo, J. Modelling the cultivation and bioremediation potential of the kelp *Saccharina latissima* in close proximity to an exposed salmon farm in Norway. *Aquac. Environ. Interact.* **2013**, *4*, 187−206.

(34) McHugh, D. J. *A Guide to the Seaweed Industry*; Food and Agriculture Organization of the United Nations (FAO): Rome, Italy,

DOI: 10.1021/acs.energyfuels.8b02374
Energy Fuels XXXX, XXX, XXX−XXX

2003; FAO Fisheries Technical Paper 441, http://www.fao.org/3/a-y4765e.pdf (accessed April 19, 2018).
(35) Floreto, E. A. T.; Teshima, S. The fatty acid composition of seaweeds exposed to different levels of light intensity and salinity. *Bot. Mar.* **1998**, *41*, 467−481.
(36) Chopin, T.; Yarish, C.; Wilkes, R.; Belyea, E.; Lu, S.; Mathieson, A.-T. Developing *Porphyra*/salmon integrated aquaculture for bioremediation and diversification of the aquaculture industry. *J. Appl. Phycol.* **1999**, *11*, 463−472.
(37) Souza, P. O.; Ferreira, L. R.; Pires, N. R. X.; Filho, P. J. S.; Duarte, F. A.; Pereira, C. M. P.; Mesko, M. F. Algae of economic importance that accumulate cadmium and lead: A review. *Rev. Bras. Farmacogn.* **2012**, *22*, 825−837.
(38) Collén, J.; Pinto, R.; Pedersén, M.; Colepicolo, P. Induction of oxidative stress in the red macroalga *Gracilaria tenuistipitata* by pollutant metals. *Arch. Environ. Contam. Toxicol.* **2003**, *45*, 337−342.
(39) Thomas, J.-B. E.; Nordström, J.; Risén, E.; Malmström, M. E.; Gröndahl, F. The perception of aquaculture on the Swedish West Coast. *Ambio* **2018**, *47*, 398−409.
(40) Pechsiri, J. S.; Thomas, J.-B. E.; Risén, E.; Ribeiro, M. S.; Malmström, M. E.; Nylund, G. M.; Jansson, A.; Welander, U.; Pavia, H.; Gröndahl, F. Energy performance and greenhouse gas emissions of kelp cultivation for biogas and fertilizer recovery in Sweden. *Sci. Total Environ.* **2016**, *573*, 347−355.
(41) Baltic Marine Environment Protection Commission, Helsinki Commission (HELCOM). *Convention*; HELCOM: Helsinki, Finland, 2018; http://www.helcom.fi/about-us/convention (accessed May 3, 2018).
(42) Rosenberg, R.; Elmgren, R.; Fleischer, S.; Jonsson, P.; Persson, G.; Dahlin, H. Marine Eutrophication Case Studies in Sweden. *Ambio* **1990**, *19*, 102−108.
(43) Biller, P.; Ross, A. B. Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical con tent. *Bioresour. Technol.* **2011**, *102*, 215−25.
(44) Wagner, J.; Bransgrove, R.; Beacham, T. A.; Allen, M. J.; Meixner, K.; Drosg, B.; Ting, V. P.; Chuck, C. J. Co-production of bio-oil and propylene through the hydrothermal liquefaction of polyhydroxybutyrate producing cyanobacteria. *Bioresour. Technol.* **2016**, *207*, 166−174.
(45) Raikova, S.; Smith-Baedorf, H.; Bransgrove, R.; Barlow, O.; Santomauro, F.; Wagner, J. L.; Allen, M. J.; Bryan, C. G.; Sapsford, D.; Chuck, C. J. Assessing hydrothermal liquefaction for the production of bio-oil and enhanced metal recovery from microalgae cultivated on acid mine drainage. *Fuel Process. Technol.* **2016**, *142*, 219−227.
(46) Xu, Y.-P.; Duan, P.-G.; Wang, F. Hydrothermal processing of macroalgae for producing crude bio-oil. *Fuel Process. Technol.* **2015**, *130*, 268−274.
(47) Mayers, J. J.; Vaiciulyte, S.; Malmhäll-Bah, E.; Alcaide-Sancho, J.; Ewald, S.; Godhe, A.; Ekendahl, S.; Albers, E. Identifying a marine microalgae with high carbohydrate productivities under stress and potential for efficient flocculation. *Algal Res.* **2018**, *31*, 430−442.
(48) Bikker, P.; van Krimpen, M. M.; van Wikselaar, P.; Houweling-Tan, B.; Scaccia, N.; van Hal, J. W.; Huijgen, W. J. J.; Cone, J. W.; López-Contreras, A. M. Biorefinery of the green seaweed *Ulva lactuca* to produce animal feed, chemicals and biofuels. *J. Appl. Phycol.* **2016**, *28*, 3511−3525.
(49) Olsson, J.; Raikova, S.; Mayers, J. J.; Chuck, C.; Nylund, G.; Albers, E. Environmental effects on potentially valuable components of *Ulva intestinalis* along the Swedish coast. Manuscript in preparation.
(50) Angell, A. R.; Mata, L.; de Nys, R.; Paul, N. A. The protein content of seaweeds: A universal nitrogen-to-protein conversion factor of five. *J. Appl. Phycol.* **2016**, *28*, 511−524.
(51) Channiwala, S. A. A.; Parikh, P. P. P. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel* **2002**, *81*, 1051−1063.
(52) Khairy, H. M.; El-Shafay, S. M. Seasonal variations in the biochemical composition of some common seaweed species from the coast of Abu Qir Bay, Alexandria, Egypt. *Oceanologia* **2013**, *55*, 435−452.
(53) Anastasakis, K.; Ross, A. B. Hydrothermal liquefaction of four brown macro-algae commonly found on the UK coasts: An energetic analysis of the process and comparison with bio-chemical conversion methods. *Fuel* **2015**, *139*, 546−553.
(54) López Barreiro, D.; Beck, M.; Hornung, U.; Ronsse, F.; Kruse, A.; Prins, W. Suitability of hydrothermal liquefaction as a conversion route to produce biofuels from macroalgae. *Algal Res.* **2015**, *11*, 234−241.
(55) Chow, M. C.; Jackson, W. R.; Chaffee, A. L.; Marshall, M. Thermal Treatment of Algae for Production of Biofuel. *Energy Fuels* **2013**, *27*, 1926−1950.
(56) Teri, G.; Luo, L.; Savage, P. E. Hydrothermal Treatment of Protein, Polysaccharide, and Lipids Alone and in Mixtures. *Energy Fuels* **2014**, *28*, 7501−7509.
(57) Biller, P.; Riley, R.; Ross, A. B. Catalytic hydrothermal processing of microalgae: Decomposition and upgrading of lipids. *Bioresour. Technol.* **2011**, *102*, 4841−8.
(58) Díaz-Vázquez, L. M.; Rojas-Pérez, A.; Fuentes-Caraballo, M.; Robles, I. V.; Jena, U.; Das, K. C. Demineralization of *Sargassum* spp. macroalgae biomass: Selective hydrothermal liquefaction process for bio-oil production. *Front. Energy Res.* **2015**, *3*, 1−11.
(59) Swedish Institute for the Marine Environment (SIME). *Mapping Shipping Intensity and Routes in the Baltic Sea*; SIME: Göteborg, Sweden, 2014; http://havsmiljoinstitutet.se/digitalAssets/1506/1506887_sime_ais_report_2014_5.pdf (accessed May 9, 2018).
(60) Ward, O. P.; Singh, A.; Van Hamme, J. D.; Voordouw, G. Petroleum Microbiology. In *Encyclopedia of Microbiology*; Elsevier: Amsterdam, Netherlands, 2009: pp 443−456, DOI: 10.1016/B978-012373944-5.00171-1.
(61) Ball, J. S.; Whisman, M. L.; Wenger, W. J. Nitrogen Content of Crude Petroleums. *Ind. Eng. Chem.* **1951**, *43*, 2577−2581.
(62) Trinh, T. N.; Jensen, P. A.; Dam-Johansen, K.; Knudsen, N. O.; Sørensen, H. R.; Hvilsted, S. Comparison of Lignin, Macroalgae, Wood, and Straw Fast Pyrolysis. *Energy Fuels* **2013**, *27*, 1399−1409.
(63) Jiang, J.; Savage, P. E. Metals and Other Elements in Biocrude from Fast and Isothermal Hydrothermal Liquefaction of Microalgae. *Energy Fuels* **2018**, *32*, 4118−4126.
(64) Wu, B.; Zhu, J.; Li, X. Distribution of calcium, nickel, iron, and manganese in super-heavy oil from Liaohe Oilfield, China. *Pet. Sci.* **2014**, *11*, 590−595.
(65) Jarvis, J. M.; Sudasinghe, N. M.; Albrecht, K. O.; Schmidt, A. J.; Hallen, R. T.; Anderson, D. B.; Billing, J. M.; Schaub, T. M. Impact of iron porphyrin complexes when hydroprocessing algal HTL biocrude. *Fuel* **2016**, *182*, 411−418.
(66) Biller, P.; Ross, A. B.; Skill, S. C.; Lea-Langton, A.; Balasundaram, B.; Hall, C.; Riley, R.; Llewellyn, C. A. Nutrient recycling of aqueous phase for microalgae cultivation from the hydrothermal liquefaction process. *Algal Res.* **2012**, *1*, 70−76.
(67) Jena, U.; Vaidyanathan, N.; Chinnasamy, S.; Das, K. C. Evaluation of microalgae cultivation using recovered aqueous co-product from thermochemical liquefaction of algal biomass. *Bioresour. Technol.* **2011**, *102*, 3380−3387.
(68) Edmundson, S.; Huesemann, M.; Kruk, R.; Lemmon, T.; Billing, J.; Schmidt, A.; Anderson, D. Phosphorus and nitrogen recycle following algal bio-crude production via continuous hydrothermal liquefaction. *Algal Res.* **2017**, *26*, 415−421.
(69) Garcia Alba, L.; Torri, C.; Fabbri, D.; Kersten, S. R. A.; Wim Brilman, D. W. F. Microalgae growth on the aqueous phase from hydrothermal liquefaction of the same microalgae. *Chem. Eng. J.* **2013**, *228*, 214−223.
(70) Selvaratnam, T.; Reddy, H.; Muppaneni, T.; Holguin, F. O.; Nirmalakhandan, N.; Lammers, P. J.; Deng, S. Optimizing energy yields from nutrient recycling using sequential hydrothermal liquefaction with Galdieria sulphuraria. *Algal Res.* **2015**, *12*, 74−79.
(71) López Barreiro, D.; Bauer, M.; Hornung, U.; Posten, C.; Kruse, A.; Prins, W. Cultivation of microalgae with recovered nutrients after hydrothermal liquefaction. *Algal Res.* **2015**, *9*, 99−106.

DOI: 10.1021/acs.energyfuels.8b02374
Energy Fuels XXXX, XXX, XXX−XXX

(72) Cakmak, T.; Angun, P.; Demiray, Y. E.; Ozkan, A. D.; Elibol, Z.; Tekinay, T. Differential Effects of Nitrogen and Sulfur Deprivation on Growth and Biodiesel Feedstock Production of *Chlamydomonas reinhardtii*. *Biotechnol. Bioeng.* **2012**, *109*, 1947−1957.
(73) Harrison, P. J.; Hurd, C. L. Nutrient physiology of seaweeds: Application of concepts to aquaculture. *Cah. Biol. Mar.* **2001**, *42*, 71−82.
(74) Elliott, D. C.; Hart, T. R.; Schmidt, A. J.; Neuenschwander, G. G.; Rotness, L. J.; Olarte, M. V.; Zacher, A. H.; Albrecht, K. O.; Hallen, R. T.; Holladay, J. E. Process development for hydrothermal liquefaction of algae feedstocks in a continuous-flow reactor. *Algal Res.* **2013**, *2*, 445−454.
(75) Atienza-Martínez, M.; Gea, G.; Arauzo, J.; Kersten, S. R. A.; Kootstra, A. M. J. Phosphorus recovery from sewage sludge char ash. *Biomass Bioenergy* **2014**, *65*, 42−50.

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