



Continuous Hydrothermal Liquefaction of Mexican *Sargassum* Seaweed—An Analysis of Hydrocarbon Fractions and Elemental Composition

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Abstract: Hydrothermal liquefaction (HTL) is often mooted as a promising and sustainable processing methodology for converting biomass into usable products, including bio-oils, which can potentially alleviate humanity's reliance on fossil fuels. To date, most HTL development work with novel biomasses has been undertaken at the laboratory scale in batch processes, and the results have been extrapolated to the theoretical continuous flow processes required for industrial uptake. Here, we assess the use of a novel continuous flow HTL system, applying it to *Sargassum* (seaweed) material and generating a bio-oil, which is assessed against typical crude oil fractions.

Keywords: *Sargassum*; hydrothermal liquefaction

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1. Introduction

Marine blooms of *Sargassum* seaweed in the Great Atlantic *Sargassum* Belt (GASB) stretch over 8000 km between the Gulf of Mexico and the West Coast of Africa. Every year, millions of tonnes are washed ashore on otherwise pristine tropical beaches, where they decompose to release potent gases, including hydrogen sulphide. The economic impacts on tourism and fishing across the Caribbean, in particular, are both widespread and considerable. In the marine environment, the blooms starve light to other marine phototrophic organisms and reduce oceanic oxygen, killing fish and smothering coral reefs. Substantial spatial and temporal variation in the beaching of *Sargassum* material over a prolonged growth season leads to unwanted waste biomass of unpredictable quality and quantity, often sent to landfills or reburied in situ or close by.

One approach for the low-cost but potentially useful bioprocessing of this variable marine biomass is hydrothermal liquefaction. Hydrothermal liquefaction (HTL) has gained increasing attention in recent years as a technology that uses the water present in the feedstock as a versatile reaction medium, which functions as a solvent, reactant, and catalyst for a cascade of organic reactions.

HTL is a biomass-to-bio-liquid conversion route carried out in water at a moderate temperature of 280–370 °C and high pressure (10–25 MPa) that has a liquid bio-crude as the main product, along with gaseous, aqueous, and solid phase by-products. Unique physio-chemical properties of sub-critical and super-critical water produce water and bio-oil as the main products. The dielectric constant decreases from 78.5 Fm⁻¹ at 25 °C and 0.1 MPa to 14.07 Fm⁻¹ at 350 °C and 25 MPa [1].

Marine macroalgae (seaweeds) offer a sustainable source of renewable biomass, which requires no land or freshwater to cultivate or harvest [2] and can potentially be grown in any place (even on land in specific reactors), provided the availability of suitable water, sunlight, CO₂, and nutrients [3,4]. Such biomasses can be considered excellent

natural substitutes for fossil crude oil in producing liquid fuels and petrochemicals [5]. The GASB provides an opportunity to take advantage of unwanted, dangerous, and environmentally destructive seaweed to develop stable industrial processes today, which can be integrated with more stable and reliable cultivated material.

Challenges for continuous HTL have been highlighted [6]. Compared with batch systems, continuous HTL holds better control, consistency, and scaleup for commercial production systems, yet reactor configurations require precise control over the temperature, pressure, and rheology of feedstocks throughout the system. Process design engineering offers a multi-parametric approach for assessing technology scalability using simultaneous variable interactions and appraisal, favouring continuous commercial systems. The identification of continual hydrothermal liquefaction systems comprises the following components and features: a high-pressure and medium-temperature biomass feedstock entry port; an externally heated high-pressure and high-temperature reactor where hydrothermal liquefaction occurs; a cooling zone; a depressurisation, separation, and product collection zone at ambient pressure and temperature [7]. Several factors influence both the yield and quality of biocrude, which is considered to be the most highly sought component of HTL products. These are feedstock chemical composition, size, and homogeneity; solvent used, reaction temperature, pressure, and residence time; and catalyst composition and application. Improvements in process efficiency might address the translation of these factors into commercial and economic viability, reducing capital costs in continuous high-pressure equipment and more efficient biocrude upgrading processes [8]. Recently, PuriFire Labs developed a system to address these issues. Here, we investigate its application to processing *Sargassum* seaweed continuously at 350 °C and 180 bar. Oil hydrocarbon fractions were separated from aqueous and char and analysed for petroleum and elemental quantitative analysis.

2. Materials and Methods

Figure 1 presents the flow chart of *Sargassum* processing.

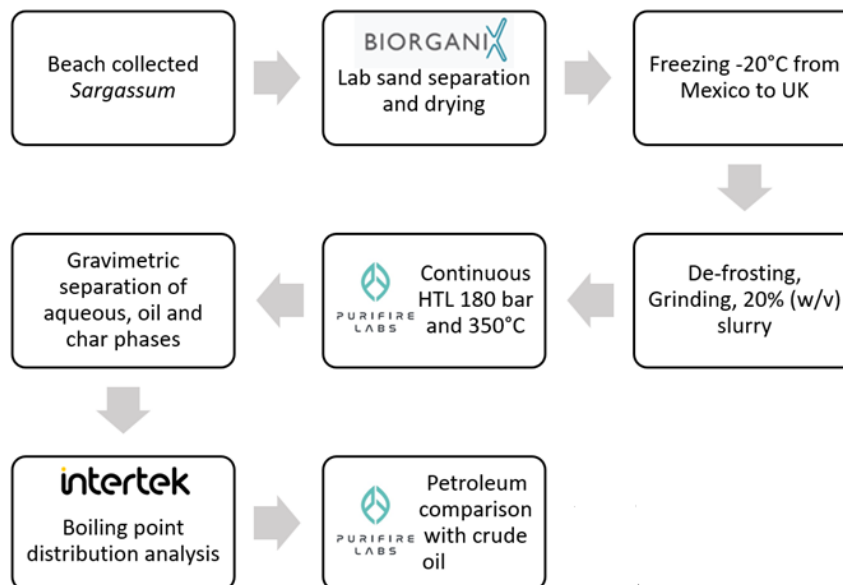


Figure 1. *Sargassum* processing procedures.

Naturally beached *Sargassum* seaweed was collected from the beach in Cancún (June 2020) in the municipality of Benito Juárez, state of Quintana Roo, where the biochemical and elemental composition of pelagic *Sargassum* biomass had previously been identified [9]. Samples were sent to the Biorganix laboratory in Saltillo, Mexico, where they were

cleaned from sand and non-*Sargassum* debris and sundried for 48 h at temperatures between 25 and 35 °C during the day and 18 and 25 °C at night time, with a constant flow of air from a ventilator.

Samples were shipped to the UK and kept at −20 °C until preparation for HTL at PuriFire Labs Limited. Batched samples of seaweed (5 kg) equilibrated to ambient room temperature were particulated through a Buffalo heavy-duty meat mincer comprising a variable thread auger and 5 mm die holes, resulting in uniform particle sizes of less than 1–2 mm. Fresh water was added to separate any residual sand and form a 20% seaweed solids slurry, which was fed into the HTL reactor.

The PuriFire Labs' plug flow is a continuous, thermally isolated 3 L volume reactor operated at 350 °C. The reactor comprised a circulatory coolant system as a fluidic, convective heat exchanger on either side of the inlet and outlet to the HTL reactor chamber. The HTL processing system is a single hydraulically fed pump via a feedstock intake chamber. The reactor had a constant pressure of 180 bar and continuous throughput into and out of the reactor at a flow rate of 2 Litres per hour. 3 kW thermostatic electrical heating elements maintained the reactor at 350 °C (+/−3 °C). Control valves and pressure sensors provided operational process control feedback during experimentation to ensure reaction condition control over temperature, pressure, and volumetric throughput parameters. A complete description of the hydrothermal liquefaction reactor can be found in patent publication GB2609399A [10].

Experiments occurred over a 12 h duration, including a reactor heat-up time of 3 h. Upon initiation, the continuous HTL reactor system was primed with 20 L of slurry mixture until the reactant outputs converted from a heated seaweed slurry into a reacted biocrude and aqueous composition. Output reactant products were stored at ambient pressure and temperature. The HTL-derived oil phase was gravimetrically separated from the aqueous output product in a 15 L container and stored in borosilicate glass bottles. Char, as a micro-particulate solid suspension, was uniformly distributed within the aqueous output products and separated gravimetrically from the remaining aqueous fraction over 48 h. Aqueous top fractions were decanted, and suspended solids in mixed fractions were filtered in Whatman grade 1 and air-dried.

18 L seaweed slurry was run sequentially over three days at 180 bar and 350 °C to obtain 200 mL of pooled oil for laboratory analysis. Daily operation of 8 h upon reaching operational pressure and temperature produced an output of 4 L aqueous fraction, 280 g char, and between 30 and 60 mL of biocrude. Variability in operational output was a function of non-automated experimental operator control. To allow for variance and maintenance of pressure at 180 bar as a function of changes in feedstock rheology, the feedstock throughput flow rate was periodically checked and adjusted with manual control of the back pressure regulation valve, hydraulic pumping rate, and flow rate between 1 and 2 L/h. Oil coated the internal reactor and tubing during operation; hence, there was a lag phase between reactor operation and post-reactant yield of oil.

Samples of HTL oil were sent to Intertek Sunbury, an independent UKAS accredited petroleum testing laboratory, for petroleum analysis. Samples of oils were analysed for incremental boiling point distribution (ASTM D7169), elemental analysis for carbon, hydrogen, and nitrogen, oxygen content, quantitative analysis of organic samples by inductively coupled plasma-mass spectrometry, sulphur content by elemental analyser and determination of specific energy by gross heat of combustion.

3. Results

Yield analysis (Table 1) showed that 200 mL of biocrude oil, 800 g char, and 12 L aqueous output were collected from 15 L of seaweed slurry or 3 kg of dried seaweed equivalent. Upon completion of the experiment, the reactor was disassembled, and unreacted seaweed contents were removed. Biocrude that had coated to internal tubing was also quantified. A further 160 mL of biocrude, 150 g char, and 2 L aqueous output was recovered from within the reactor and appending tubing system. Additional yield

resulted in a biocrude total yield of 12% from 3 kg of seaweed dry weight. Our continually produced a yield of 12% compared with averaged batch system biocrude yields of 20% from benchtop batch experiments. Water was lost as steam from the back pressure regulator valve during operation and as a reaction medium for HTL.

Table 1. Processing parameters of *Sargassum* compared to high-ash, low-lipid algal biomass in batch hydrothermal liquefaction processing.

Parameter	Input	Output	Yield %	Batch Comparison % [8]
Water (L)	15	-	-	0.085
Algal dry weight (kg)	3	-	-	0.015
Retention time (min)	20	-	-	90
Reactor size (L)	3	-	-	0.1
Temperature (°C)	350	-	-	340
Pressure (Bar)	180	-	-	300
Biocrude yield (mL)	-	360	12	17.7
Char yield (g)	-	950	32	20.6
Aqueous yield (L)	-	14	93	51.8

Table 1 compares continual hydrothermal liquefaction processing to a batch experiment using a high-ash, low-lipid algal species comparable to Mexican *Sargassum*. The batch system operated at a similar temperature but 120 bar higher pressure. Pressure vessel wall thickness and mass of stainless steel increase significantly with larger pressure vessels compared with batch laboratory reactor systems. Continual bio-crude yield of 12% was comparable with the batch study at 17.7% [11].

Boiling point analysis is presented in Figure 2, elemental analysis in Figures 3 and 4. Elemental analysis of biocrude oil was carbon 61.8%, hydrogen 8.3%, nitrogen 2.7%, and oxygen 20.8%. The sulphur content was 0.42% mass. Metal analysis comprised arsenic 251,000 ng/g, cadmium 47 ng/g, chromium 500 ng/g, copper 1700 ng/g, lead 241 ng/g, manganese 1140 ng/g, nickel 3440 ng/g, vanadium 3500 ng/g, zinc 109,000 ng/g, magnesium 61 mg/kg, and sodium 913 mg/kg. The sulphur content was 0.42% mass, with a higher heating value of 28.48 MJ/kg.

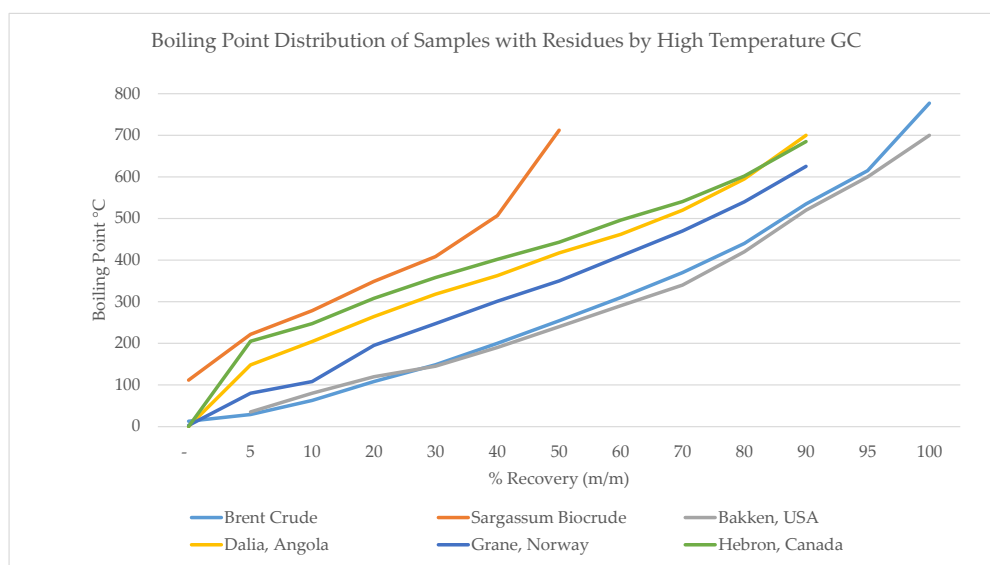


Figure 2. Boiling point distribution (ASTM D7169) of HTL oil from Mexican *Sargassum* seaweed compared to other common petroleum fractions.

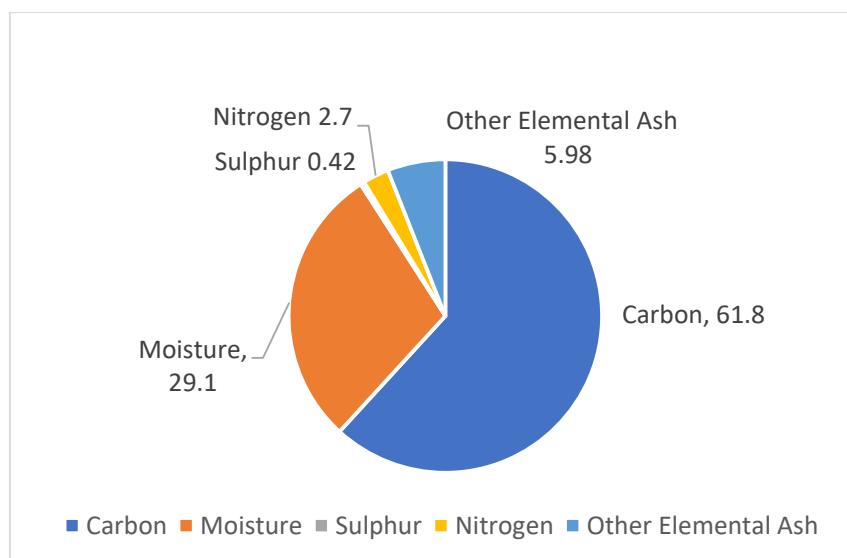


Figure 3. Major elemental composition of *Sargassum* HTL biocrude oil (%).

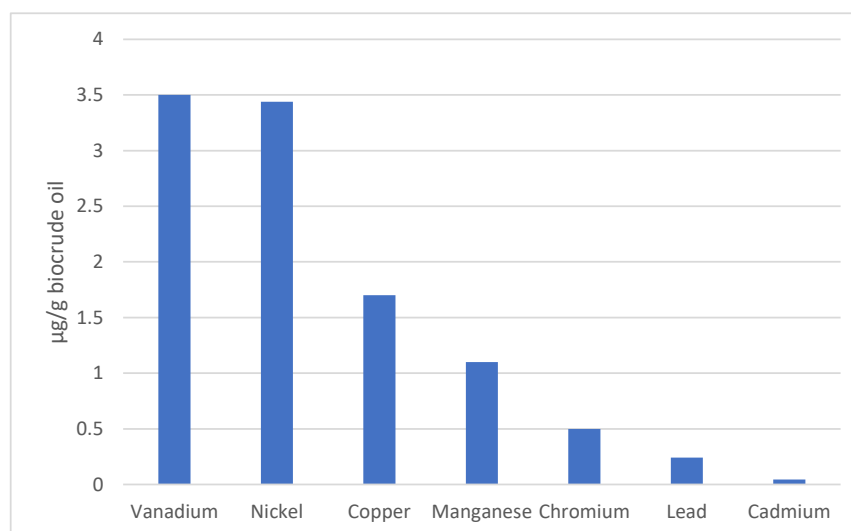


Figure 4. Minor metal analysis of *Sargassum* HTL biocrude oil.

4. Discussion

The results indicate the successful formation of a hydrocarbon crude-like organic bio-oil mixture from the HTL of Mexican *Sargassum* seaweed at a sufficient scale to test for several commercial grade tests for petroleum analysis. Yield analysis comparison of continuous biocrude production at 12% was less than the batch systems at ~20% using this reactor configuration. However, this comes with the caveat that process systems engineering development continues to upgrade and adjust reactor refinements in response to discoveries on system engineering optimisation that are only likely to improve further yields in subsequent embodiments. These modifications include valve development, tubular length and morphology, insulation, and circulatory reactor coolant mechanism arrangement for temperature control. These factors influence key parameters of HTL operation, namely heating rate, holding temperature, cooling rate, flow control, and pressure stabilisation with variable throughput in and out of the reactor. A quantitative multi-parametric variance analysis will form part of future work. Multi-parametric variance analysis will help identify extraneous confounding variable factors of continuous HTL optimisation.

Residual contents of the 3 L reactor from the preceding days' operation resulted in a volumetric calculation of oil, char, and aqueous fractions that exited the reactor during subsequent daily operation. There was, therefore, a lag phase of filling, reacting, and emptying to a volume of 3 L for the reactor, 3 L for the hydraulic feed intake system, and another 1.5 L for the appending tubular sections. The reactor was maintained at 180 bar pressure during heating up to 350 °C and subsequent cooling back to ambient temperature to ensure that char formation was minimised without compromising the bio-oil.

Nitrogen compounds in crude oils are conventionally classified as basic (derivatives of pyridine) and non-basic (derivatives of pyrrole) [12]. The deleterious effects of nitrogen-containing compounds on oil processing include free radical reactions affecting the thermal stability of oils, the deactivation of hydrocracking catalysts, salt precipitation and potential corrosivity issues, and the increase in total acid number [13]. Caribbean *Sargassum* seaweed contains 18 amino acids, accounting for 3.87 to 5.84% of biomass dry weight [9]. Invasive strains of freshwater-washed European *Sargassum muticum* contained 21% protein and 3% more if not washed [14]. Differences between the protein content of Mexican versus European *Sargassum* strains might be accounted for by high tropical light conditions favouring phototrophic growth over protein accumulation. Using a generic protein conversion factor of 6.25, this study found 2.7% nitrogen, corresponding to 17% protein equivalent if the biocrude was considered a foodstuff. Compared with the 4–6% protein content of Mexican *Sargassum* [9], the 2.9% nitrogen content is deemed high, suggesting preferential allocation of nitrogen into the oil phase rather than the aqueous phase. Such nitrogen compounds are likely oil-soluble derivatives of phenolic nitrogen compounds, including pyrroles and pyridines. Although the seaweed in this study was washed in freshwater to re-humidify prior to size particulation, the water was re-suspended into seaweed slurry; hence, any freshwater-washed protein would be re-allocated again with the slurry formation prior to HTL reaction. Future work might consider approaches for HTL using seawater rather than freshwater as a reaction medium.

To scale HTL with commercial-scale seaweed bioprocessing, the resuspension and washing of seaweed in freshwater is unrealistic; hence, there is a need to use seawater. Seawater as an alternative to freshwater did not significantly influence the biocrude yield and quality in the HTL of red macroalgal feedstocks, showing a promising potential of producing biocrude through the hydrothermal liquefaction technique in the context of marine biorefinery [15]. However, with sodium being high (913 mg/kg) in the biocrude oil already, betraying the marine origin of the biomass, the inclusion of additional salt water in the processing stage will need to be balanced against the increased reactor/refinery maintenance costs incurred by its corrosive nature.

One of the major limitations of using macroalgae to produce biofuels is their high ash content (up to 50%), which reduces the yield and quality of the generated bio-oils and restricts their use in direct combustion and gasification processes [16,17]. Considering the high levels of nitrogen and ash in Mexican *Sargassum*, a preceding thermal pre-treatment process, catalytic zeolite deactivation precursor, or pre-exposure to ion exchange resins might be a useful remediation procedure for further studies.

Figure 2 shows the boiling point distribution curve compared to other world petroleum samples recovered from ASTM D7169 assays. *Sargassum* biocrude shows the greatest similarity with Hebron crude from Canada, a heavy crude oil. Differentiators between this study and Canadian crude oil are percentage recovery, accounted for by higher viscosity and particle agglomeration in the heterogenous complexity of the crude oil in this sample.

The sulphur content in the seaweed-derived biocrude oil sample was 0.42% mass. The sulphur content of crude oils varies from less than 0.05 to more than 10% weight by volume but generally falls in the range of 1–4%. Crude oil with less than 1% sulphur is low or sweet; that with more than 1% is referred to as high or sour [18]. The International Maritime Organisation reduced the limit on sulphur content in shipping fuel oils from 3.5% in 2012 to 0.5% in 2020. The low presence of sulphur in this biocrude samples suggests positive implications for the capability of upgrading into shipping transport fuels.

However, detrimentally, the viscosity of this sample was high, comparable to tar and bitumen in rheology and viscosity. Flowability, pumpability, and pipeline transport of biocrude oil are important considerations when commercialising *Sargassum* biocrude into industrial production. To reduce viscosity, it may be necessary to perform the protein extraction of the seaweed before using the protein extracted seaweed remnants for subsequent HTL. Protein extraction requires an additional pre-treatment process that would add to both CAPEX and OPEX costs. Seaweed biorefinery systems have been considered as a viable processing pathway. Several potential mechanical and chemical pathways might be a pulsed electric field, cold plasma microwave treatment, ultra-low temperature pre-treatment, dialysis and/or ion exchange resin anion and cation exchange. The extent of using seaweed originating from the GASB as an ingredient in the biorefinery process extends beyond solely the production of biocrude. Green chemistry for integrated chemical, salt, nutrient, mineral, and protein extractions using filtration, centrifugation, ion exchange resin columns, and dialysis has been proposed in natural and industrially produced seaweed production systems [19].

Oxygen content was high at 20.8%, substantially higher than that typically found in crude oils (typically less than 2%) but lower than that observed in typical pyrolysis oils, which often range between 35 and 50% [20]. Oxygen removal by hydrogenation will help further increase the energy density and improve oil stability during transport and storage. However, it will require a sustainable source of hydrogen, which is currently unavailable.

Further work would consider other solvents to recover all heterogeneous components, which might require additional organic analytical chemistry. Fractions of short carbon chain volatile organic compounds might have been lost to the atmosphere in sample preparation, as detected by characteristic petroleum odours near the reactor. Upscaling process engineering to higher levels of volumetric throughput and control of the oil recovery phase would improve lower chain carbon compound retention. The implications of heterogeneity in the organic mixture suggest that further development into downstream process chemistry could potentially isolate interesting bio-derived chemicals from output products of HTL from seaweed. The aqueous and char phases were beyond the scope of study for this project. However, the aqueous phases might also be a source of fufurals, carboxylic acids, and other soluble and insoluble sugars for upgrading into value-added by-products.

Arsenic has been identified previously as accumulated in *Sargassum* and has been highlighted as a concern particularly for fertiliser-derived products. Unsurprisingly, heavy metals were found in the crude oil following conversion, although at levels generally considered acceptable to the oil industry. Arsenic, however, at 0.25 mg/L, is potentially of concern for any catalytic-derived process (causing deactivation) and, at the very least, may incur a waste processing charge.

5. Conclusions

ASTM D7169 is an internationally recognised method of petroleum analysis that includes assessment criteria, reproducibility, and repeatability under the laboratories' quality management system. The performance of the method is measured against other labs regularly.

A high-energy hydrocarbon fuel mixture was successfully produced following the continuous low-cost HTL conversion of beach-harvested *Sargassum* seaweed from Mexico. Preliminary analysis following extraction of the organic biocrude oil shows the potential for its use as an alternative to fossil-derived crude oils and highlights opportunities and limitations for processing.

To develop commercialisation, considerations should be given to the logistics of harvesting offshore floating *Sargassum* compared to beach-harvested *Sargassum*. Only once ashore does the detrimental environmental decomposition effects of *Sargassum* accumulation become a societal menace. Therefore, offshore prevention may be a better alternative than beach-harvested remediation. This process would encompass a multi-parametric

collection, distribution, and processing scope of work that would benefit from further analysis of techno-economic and life-cycle analysis investigations.

With tens of millions of tonnes of unwanted, problematic *Sargassum* biomass washed up on the shores of the West Coast of Africa and the Caribbean every year, this work highlights the potential for its conversion and that of biomasses like it into a usable fuel to alleviate our reliance on fossil-derived crude oil reserves.

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Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

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