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Review

Golden Tides: Problem or Golden Opportunity? The Valorisation of *Sargassum* from Beach Inundations

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Abstract: In recent years there have been massive inundations of pelagic *Sargassum*, known as golden tides, on the beaches of the Caribbean, Gulf of Mexico, and West Africa, causing considerable damage to the local economy and environment. Commercial exploration of this biomass for food, fuel, and pharmaceutical products could fund clean-up and offset the economic impact of these golden tides. This paper reviews the potential uses and obstacles for exploitation of pelagic *Sargassum*. Although *Sargassum* has considerable potential as a source of biochemicals, feed, food, fertiliser, and fuel, variable and undefined composition together with the possible presence of marine pollutants may make golden tides unsuitable for food, nutraceuticals, and pharmaceuticals and limit their use in feed and fertilisers. Discontinuous and unreliable supply of *Sargassum* also presents considerable challenges. Low-cost methods of preservation such as solar drying and ensiling may address the problem of discontinuity. The use of processes that can handle a variety of biological and waste feedstocks in addition to *Sargassum* is a solution to unreliable supply, and anaerobic digestion for the production of biogas is one such process. More research is needed to characterise golden tides and identify and develop commercial products and processes.

Keywords: *Sargassum*; Phaeophyceae; beach-cast; seaweed; macroalgae; golden tide

1. Introduction

The number of inundations of beaches by seaweed has been increasing dramatically over recent years with these "seaweed tides" causing economic disruption to tourism, aquaculture, and traditional fisheries [1]. Seaweed inundations of the shoreline can be various described as green, red, or golden tides depending on the colour of the seaweed. Despite the large number of species of seaweeds, two genera are responsible for the majority of shoreline inundation incidents: *Ulva*, a green seaweed causing green tides, and a golden/brown floating or pelagic seaweed, *Sargassum*, causing golden tides, particularly in the Caribbean and West Africa [2].

There are a large number of species of the genus *Sargassum* (>350) [3]; most have a mature phase that grows anchored to the bottom of the sea by a root-like structure, the holdfast. Two species, *S. natans* and *S. fluitans*, are holopelagic and the predominate species in golden tides. They both reproduce vegetatively and never attach to the seafloor during their lifecycle [4]. Both species are golden brown and characterised by numerous blades, a highly branched thallus, and air bladders [5]. Typically *S. natans* has a delicate fine leaf structure, whereas *S. fluitans* has large lanceolate (lance like) leaves with *S. fluitans* having "thorns". *S. natans* has smooth stems, but each species exhibits a diversity of morphological forms with variation in blade and bladder shape [2,5,6].

Pelagic *Sargassum* (Gulfweed) has been described as a floating jungle or golden floating rainforest as it is important for a diverse range of invertebrates, fishes, sea turtles, birds, and mammals, with over

145 species of invertebrates and 100 species of fishes being associated with it [2,7]. The National Marine Fisheries Service has designated floating mats of *Sargassum* as an essential fish habitat [5]. *Sargassum* is not only of ecological importance, but has a global role in ocean sequestration of carbon, with the *Sargassum* of the Sargasso Sea being a net sink of CO_2, representing ~7% of the global net "carbon pump" [2].

The amount of Pelagic *Sargassum* in the ocean is huge, and thus the potential for golden tides is as well. The Sargasso Sea, so called due to the abundance of *Sargassum,* is the greatest aggregation of seaweed in the world with a total biomass of 10 million tonnes [5]. Around 1 million tonnes of *Sargassum* leaves the Gulf Mexico via the Florida Straits and enters the Sargasso Sea area of the Atlantic Ocean annually [7]. However, the Sargasso Sea and Gulf of Mexico are not the only sources of the golden tides in the Caribbean; a new source has been identified from the Northern Equatorial Recirculation Region (NERR) [4,6]. During the inundation of the Caribbean in 2015, ~10,000 wet tonnes of seaweed was being dumped on beaches of the Caribbean islands daily [8]. However, inundations are not restricted to the Caribbean, but also occur on the beaches of the Gulf of Mexico, the Atlantic Coast of the USA, and the shoreline of western Africa from Morocco (South of Casablanca) to the Gulf of Guinea [4,9,10]. Prior to 2011 there had been no reports of golden tides on the shores of northwest Africa [1,10]. The exact reason for the *Sargassum* inundations of recent years are not fully known, although climate change and coastal sea eutrophication are implicated [1,10,11], and it is not known if the major golden tides of 2011–2015 will continue to happen every year [12].

Deposits of *Sargassum* occur naturally and regularly on beaches, albeit in smaller quantities than the major golden tides of 2011–2015. They play a role in stabilising beaches and providing nutrients for beach and dune plants [13,14]. The organisms they carry can be important sources of food for beach fauna [12]. In locations where small deposits of *Sargassum* have been left on the beach, it is eventually washed away or buried by wave action and the smell of decomposition reduced by rain [12]. Beach-cast *Sargassum* is not considered injurious to human health [12,15], although there have been some reports of minor skin and eye irritations [16,17]. Leaving *Sargassum* where it is may be a viable approach for small deposits, avoiding the cost and potential negative impacts of beach cleaning, such as sand removal and destruction of habitat. However, large deposits may not be acceptable to beach users, and may have negative environmental effects, smothering organisms such as turtle hatchlings [2,15].

Tourism was worth $29.2 billion in on-shore spending in the Caribbean in 2014, and contributed over 80% of the regional GDP. Tourists are reported to be avoiding resorts affected by golden tides [18], and Sir Hilary Beckles, the Vice Chancellor of the University of the West Indies, has described the inundation of Caribbean and Mexican Gulf beaches as "an international crisis" and "the greatest single threat" to the Caribbean [8,19]. However, the removal of *Sargassum* from beaches or the prevention of it reaching the beaches could be very costly. It has been estimated that it would take at least $120 million to clean up the *Sargassum* inundations across the Caribbean based on the $5 million spent on the clean-up of beaches in Mexico [8,19]. Galveston Island spends $3.5 million annually on maintaining 32 miles of public beach by moving *Sargassum* from the main strand to less tourist-sensitive back areas of the beach to compost [20]. The prevention of seaweed reaching the beaches could also be costly, with 300-m floating booms estimated to cost $80,000 to protect some of the beaches of St. Vincent and the Grenadines [21].

There are over 90 patents that refer to *Sargassum*, and it has been used for both fertiliser and animal feed [2]. Wild harvesting and cultivation of pelagic *Sargassum* in the Sargasso Sea for biofuel has been proposed [22–25]. However, commercial extraction of *Sargassum* from the Sargasso Sea is considered to pose a threat to the ecosystem, and currently there is no commercial extraction of *Sargassum* from the Sargasso Sea [2]. Although there have been some recommendations on how to remove *Sargassum* from beaches [12,20], there appears to be limited commercial exploitation with *Sargassum* only being used as a traditional local fertiliser, soil conditioner, and animal feed [15]. One of the key recommendations of the Caribbean Sea Commission [26] for addressing the threat of the *Sargassum* seaweed is to support research into commercial uses of *Sargassum.* The further exploitation of biomass is considered one of the best options for increasing renewable energy [27], and *Sargassum* collected from golden tides may be a potential source of bioenergy [12].

Sargassum muticum is a member of the *Sargassum* genus and an invasive species in Europe. Attempts to eradicate *S. muticum* have failed [28], and methods are being researched for its valorisation to encourage harvesting and control [29,30]. *S. muticum* has been suggested as a source of biochemicals, nutraceuticals, and pharmaceuticals [30,31]; a biorefinery feedstock [29]; and a biofuel feedstock [32–34]. The research and lessons learnt on *S. muticum* may be of value in seeking methods for the valorisation of the pelagic *Sargassum* species, *S. natans* and *S. fluitans*.

2. *Sargassum* Composition and Potential Uses of Compounds

Sargassum species and floating mats of *Sargassum* contain a wide range of biologically active compounds: sulphated polysaccharide, phenolics, plastoquinone, phlorotannins, fucoxanthin, fucoidan, sargaquinoic acid, sargachromenol, steroids, terpenoids, and flavonoids [16,35]. Various extracts from *Sargassum* species, including *S. natans*, showed significant therapeutic potential, suggesting *Sargassum* could provide novel functional ingredients for pharmaceuticals for the treatment and prevention of several disorders [35,36].

The ultimate composition and Higher Heating Value of *S. natans* is similar to that of *S. muticum* (Table 1).

Table 1. Ultimate analysis of *S. muticum* and *S. natans*.

	Ash	C	H	O	N	S	HHV	LHV
			% dw				$kJ{\cdot}g^{-1}{\cdot}dw$	
S. muticum [1] (Summer)	33.3	30.1	4.2	28.1	3.6	0.8	12.0	
S. natans [2]	32.5	28.9	6.2	27	4	1.4	12.2 *	9.7

[1] [34]; [2] [37]; * Calculated from LHV using the method of Demirel [38].

The heating values of both species are somewhat less than that of the terrestrial energy crops of 17–20 $kJ{\cdot}g^{-1}{\cdot}dw$ [39] due to the high ash content. Adjusting for the ash content, the HHV of the volatile solids (VS) of both species is ~18 $kJ{\cdot}g^{-1}$. The typical HHV of complex carbohydrates is 17.2 $kJ{\cdot}g^{-1}{\cdot}dw$ and 21 $KJ{\cdot}g^{-1}$ dw for typical proteins [40]. The protein content can be estimated from the HHV data to be ~11% of volatile solids and ~7% of the dry weight (dw) for both species.

2.1. Proteins

Brown seaweeds typically contain 3%–16% protein depending on the species and season [41,42]. The protein content of a biomass can be estimated from the nitrogen present by multiplying the N content by a factor (N factor).The N factor is based on the proteins present in the biomass. A great many commonly occurring proteins contain ~16% nitrogen and a factor of 6.25 has been most commonly used for foods [40] and is also widely used in algal literature [43]. However, there is a wide variation in the composition of protein in foods [40] and in particular algae [44,45]. Biomass may also contain a proportion of nitrogen that is not associated with proteins, but with compounds such as DNA, pigments, and free amino acids [44,46], and thus the commonly used multiplier of 6.25 causes the protein content to be overestimated [44,47]. Factors for common foods vary between 5.2 and 6.3 [40] and for algae 3.75–6.4 [44,48]. Overall N factors have been suggested for general use with algae of 5 [41], 4.78 [49], and 4.44 [44], and an average N factor for brown algae of 4.56 has been suggested in an extensive recent study by Angel et al. [41]. Using this latest N factor of 4.56, a protein content of 18% can be calculated for *S. natans*. The average protein content of *S. fluitans* is 12.8% [42]. Oyesiku and Egunyomi [16] found the protein content of pelagic mats of *S. natans* and *S. fluitans*, floating off the coast of Nigeria, to be 15.4%.

Although both *S. natans* and *S. fluitans* are known to obtain a large proportion (~44%) of their nitrogen requirement from "ubiquitous" epiphytic cyanobacteria [50], there are considerable differences in the C:N ratio of pelagic seaweed depending on the availability of nutrients [5]. The average C:N ratio of *Sargassum* from the open ocean is 47, whereas in neritic water it is 27 [5]. The C:N for floating mixed *Sargassum* mats floating close to the coast of Nigeria can be estimated from the data of Oyesiku and Egunyomi [16] to be around 23. Although Lapointe et al. [5] found no significant difference between the C:N ratio of *S. natans* and *S. fluitans*, the C:N ratio found by Wan et al. [37] for *S. natans* was only 7. Milledge and Harvey [34] found the C:N ratio of *S. muticum* to be 8. The C:N ratio of *S. muticum* can vary between 6 and 20 depending on location and season [32,51,52]. A high C:N ratio could be advantageous for the production of biofuels, but a low C:N ratio may be advantageous in the production of fertilisers and animal feeds.

Although seaweeds contain all 22 amino acids, they are generally rich in aspartic and glutamic acids, but limited in lysine, threonine, tryptophan, cysteine, and methionine [42] Although nutritional studies have shown that algal proteins are generally comparable to vegetable proteins [53], the imbalance of amino acids may limit the applicability of *Sargassum* as a foodstuff. A recent extensive review has found that the proteins, peptides, and amino acids from seaweed have shown positive bioactive effects in the treatment of diabetes, cancer, and AIDS, and the prevention of vascular diseases [54]. Considerable further research is required to identify polypeptides from pelagic *Sargassum* and their potential therapeutic benefits.

2.2. Polysaccharides

Sargassum can contain up to 68% polysaccharides [42], with the polysaccharide content of floating mats of *Sargassum* being 57% [16]. The polysaccharide composition of brown seaweed is different to that of terrestrial plants, with the major polysaccharides of brown algae being laminarin, mannitol, alginate, fucoidan, and cellulose [55,56].

2.2.1. Alginates

Alginates are a major component of the cell wall of brown algae, accounting for up to 40% of the dry weight [56]. They are U.S. Food and Drug Administration (FDA) approved polymers, and represent some of most important biomaterials for diverse applications, not only in the food and cosmetics industries, but also in the textile industry and for biomedical applications [57]. Worldwide annual alginate production has been estimated at 30,000 tonnes [58], and the uses of alginates have been extensively reviewed by Rehm [58], Bixler et al. [59], Holdt and Kraan [54], and Sun and Tan [57]. *S. muticum* has been used for alginate production [60,61], but the yield is relatively low, 5%–11% compared to 16%–30% for commercially exploited brown algae [62,63]. Although there appears to have been some past exploitation of pelagic *Sargassum* for the production of hydrocolloids, the quality of alginic acid from *Sargassum* does not make it a viable source of commercial alginates, and there appears to be no current major commercial exploitation [64,65].

2.2.2. Sulphated Polysaccharides

The sulphated polysaccharides of seaweeds are chemically very different from those of land plants, with those in brown seaweed being mainly sulphated fucans (fucoidans), with other sulphated polysaccharides containing galactose, xylose, glucose, and other simple sugars also being found [66,67]. *S. muticum* contains 8% dry weight as fucans [68], with fucose being the dominant sugar in *S. muticum* sulphated polysaccharides [69]. Fucans have been classified as non-toxic. They have been shown to "aid" insoluble antioxidants, and they have been proposed as alternatives to the anticoagulant heparin [67]. Fucans can also inhibit the virus infection of cells and parasite invasion, showing antimalarial activity as well as inhibiting another widespread parasite, *Toxoplasma gondii* (the disease vector for toxoplasmosis) [67].

The structure of fucans can vary with the algal species, life-stage, and environment with the antioxidant capacity of the fucans related to their molecular mass and sulphate content [67]. Sulphated polysaccharides having a molecular mass <30 kDa have been shown to be the most biologically active, and sulphated polysaccharides of 26–35 kDa from *Sargassum* species have been shown to block carcinogens and display antiviral properties. Fucoidans from seaweeds can have a wide range of molecular masses, extending from 8 to at least 627 kDa [61]. The molecular biology, biochemistry, and enzymology of fucan and fucoidan production in brown seaweeds and *Sargassum*, in particular, is a relatively underexplored area with considerable promise for future commercialisation [30]. *S. natans* has a sulphur content of 1.4% dw, and could contain a number of sulphated carbohydrates that may have potential commercial value. However, this relatively high sulphur content in *Sargassum* can have negative environmental impacts, with rotting *Sargassum* producing foul smelling and toxic hydrogen sulphide [26]. The organic sulphur in *Sargassum* can be completely lost from seaweed biomass as hydrogen sulphide under anaerobic conditions [34], and considerable care in the postharvest handling will be required to preserve sulphated carbohydrates.

2.3. Lipids

Macroalgal biomass typically has low lipid content, 0.3%–6% [24,70,71], and the lipid content of *Sargassum* is also low. *S. muticum* has a lipid content <1.3% [72,73] and *S. natans* has a lipid content of 1% [74], but the lipid content of the mixed biota of floating *Sargassum* mats was found to be 2.5% [16].

Humans and animals lack the requisite enzymes to synthesise polyunsaturated fatty acids (PUFAs) of more than 18 carbon atoms and must obtain them from food; they are, therefore, often known as essential fatty acids. A group of essential fatty acids known as omega-3s (a group of unsaturated fatty acids where a carbon double bond is in the third position from the methyl or omega end) are attracting a lot of attention currently, as they exhibit anti-inflammatory and antioxidant activity and other health benefits [74–76]. Seaweeds are rich in polyunsaturated fatty acids (PUFAs), although there is considerable variation in the lipid profile between species [30,42].

Van Ginneken et al. [74] found that *S. natans* lipids contained 50% PUFAs, and the biomass was particularly rich in docosahexaenoic acid (DHA) (C22:6) at 1 $mg \cdot g^{-1}$. DHA is used as a supplement in infant formulas and as an adult dietary supplement. It is essential for the proper functioning of human brains as adults, and for the development of the nervous system and visual abilities during the first six months of life [75].

Turner et al. [77] found that all species of organism, both heterotrophic and autotrophic, from floating *Sargassum* mats were rich in PUFAs, 16%–62% of the total fatty acid composition, but there was considerable variation in the fatty acid composition between species found within the floating mats. Levels of 20:5 (*n*3), 22:5 (*n*3), and 22:6 (*n*3) were significantly higher in the particulate matter, containing microalgae, found within the floating seaweed mats, compared to the *Sargassum* spp. or epiphytic algae. The predominant PUFAs in the tissue of invertebrates and vertebrates within the *Sargassum* mats were 18:2(*n*6), 20:4 (*n*6), 20:5(*n*3), 22:5(*n*3), 22:6(*n*3). In PUFAs the cis double bonds are the most frequently separated from each other by a single methylene group (methylene-interrupted polyenes). However, non-methylene-interrupted fatty acids have been found in low levels in *Sargassum* that may have anti-proliferation activity against cancer cells, but considerable more research is required [78–80]. *Sargassum* mats could be a potential valuable source of a wide variety of PUFAs for both animal and human nutrition, although the yields per unit of dry biomass could be low ~0.5%.

Despite the high concentration of PUFAs in seaweed, the main fatty acid of many seaweeds is the saturated fatty acid palmitic acid (16:0) [81]. Palmitic acid makes up 41% of the fatty acids in *S natans* [74]. In *S. muticum*, palmitic acid constitutes 21.5% of the total fatty acids, and has been shown to have antimicrobial activity against bacteria and diatoms [82]. The free fatty acids extracted from *Sargassum pallidum* have considerable antimicrobial activity against bacteria, yeast, and fungi, with glycolipids and neutral lipids demonstrating "moderate" activity [83]. The exact mechanism of antimicrobial action is unknown, but specific algal fatty acids may initiate lipid peroxidation and inhibit fatty acid synthesis within bacteria [83].

2.3.1. Sterols

The use of sterols in managing high cholesterol levels and cardiovascular health is extremely topical [84,85]. A wide range of sterols (C16–C30) have been described in *Sargassum* spp. [86], and sterols from *Sargassum* spp. have been shown to have potent natural cholesterol-lowering activity [87,88].

2.3.2. Carotenoids

Most brown seaweeds contain the carotenoid pigment fucoxanthin, which has important antioxidant, anti-inflammatory, anti-obesity, anti-tumour, and UV-preventative activities [89–91].

Gammone et al. [92] have recently reviewed the effect of various carotenoids (including fucoxanthin) on human health, and in particular cardiovascular health; Maeda [93] has reviewed the use of fucoxanthin for obesity and diabetes therapy; and Zorofchian et al. [94] have reviewed the anticancer and anti-tumour potential of fucoxanthin.

Despite fucoxanthin being the main carotenoid produced by brown seaweeds, and its demonstrated benefits for human health, the biosynthetic pathway of fucoxanthin in seaweed is poorly understood; considerably more research is required to fully characterise the biochemistry and molecular biology of the enzymes that synthesise fucoxanthin, together with their structure and subcellular location [95,96]. However, fucoxanthin could be a major potential commercial product from *Sargassum* [97].

2.3.3. Terpenoids and Phenolics

A number of terpenoids and phenolic compounds have been found in *Sargassum* [16]. A group of phenolic terpenoids, merodIterpenoids (plastoquinones, chromanols, and chromenes), are found almost exclusively in the *Sargassaceae* and exhibit anti-tumour activity [98]. The phenolic compounds in brown algae play a primary role in the structure of cell walls and are generally considered to be a chemical defence against grazers, bacteria, fungi, and other epiphytes [99,100]. *Sargassum* spp. have been suggested as a sustainable source of bioactive phenolic compounds [101]. However, phenols in *Sargassum* may also be problematic as they can impart not only undesirable flavours but also can inhibit anaerobic digestion (AD) for the production of biogas [102,103].

2.4. Inorganic Compounds

Seaweeds generally contain high amounts of ash (inorganic material) (9%–44% dw), with brown seaweeds also being generally rich in iodine (>1.2% dw) relative to terrestrial plants and both red and green macroalgae [42]. *S. natans* typically has ~30% ash [37].

The high ash content of *Sargassum* can provide minerals and trace elements that are beneficial in both fertiliser and animal feed [16,65,104]. In addition to macro- and micro-nutrients, seaweeds contain many growth-promoting hormones [105]. Growth of coastal plants increases with the use *Sargassum* as a fertiliser as it is a useful source of N, P, and K [13,16], and the use of *Sargassum* as a fertiliser is suggested as a positive, natural, and efficient method of dealing with golden tides [13]. However, the high ash content of *Sargassum* may be problematic for biofuels, especially direct combustion and gasification [71].

Iodine was extracted from kelp in Ireland from the seventeenth century [54], but the use of seaweed for the production of iodine has petered out due to competition from cheaper iodine from mineral deposits [106]. The iodine content of the biomass of floating *Sargassum* mats is relatively low 0.04 $mg \cdot g^{-1} \cdot dw$ compared to previously exploited species such as *Laminaria japonica* [16,54], thus the commercial extraction of iodine from *Sargassum* would not appear to be a commercial viable target. However, the addition of *Sargassum* to the diet could be a useful supplementary source of iodine.

Seaweed can accumulate heavy metals from the environment, with metal concentrations in the seaweed biomass reaching values many times higher than their corresponding concentrations in seawater [107–109]. *Sargassum* can contain high levels of arsenic (20–231 $\mu g \cdot g^{-1} \cdot dw$) with inorganic arsenic accounting for up to 80% of the total arsenic content, and there have been a number of health advisories around the world warning against eating too much *Sargassum*, especially *S. fusiforme* [110]. The arsenic content of *S. fluitans* (20 $\mu g \cdot g^{-1}$) is the lowest found for any *Sargassum* spp. studied [110]. However, care should be taken in incorporating *Sargassum* into the diet of both humans and animals to avoid increased heavy metal intake. Heavy metals in fertilisers may also accumulate in the soil, and high heavy metal content in seaweed may limit its value as a fertiliser [111].

The ability of both living and dead macroalgae to sequester heavy metals could be useful in the treatment of wastewater, with algae, especially the brown seaweeds, shown to be excellent biosorbents for heavy metals [112]. The high sorption capacity of brown seaweed and *Sargassum* is believed to be related to the polysaccharide composition of the cell wall [109,113]. *Sargassum* spp. including *S. natans* and *S. fluitans* have been shown to be effective biosorbents for a range of heavy metals including cadmium, lead, and gold [61,114,115]. *Sargassum* spp. have also been suggested as a low-cost biosorbent for the treatment of wastewater from industries that use dyes and phenolic compounds due to their high absorption capacity for phenolic compounds and industrial dyes such as methylene blue [60,116,117].

3. Processing *Sargassum*

There has been discussion on how to collect *Sargassum* to minimise damage to beaches [12,20], but there appears to be little information on the post-harvest processing of golden tides.

3.1. Cleaning and Sorting

Beach-cast *Sargassum* is composed not only of *S. natans and S. fluitans*, but is a varied biota of epiphytes, bacteria, microalgae, and invertebrates, together with any marine pollution that has become entrapped. Once on the beach the organic material within the golden tide will begin to decompose. The decomposition and pollution, together with variable and undefined composition, may make golden tides unsuitable for food, nutraceutical, and pharmaceutical use, and considerable sorting and cleaning may be required for other applications. Sand in the biomass may also be problematic, having been shown to increase technical problems and reduce biomethane conversion efficiency in the pilot scale anaerobic digestion of seaweed [118]. The collection of *Sargassum* immediately offshore from the beach, such as that proposed in Guadeloupe [119], may eliminate much of the decomposition, but the variability of the feedstock and potential for pollutants being present will remain.

3.2. Preservation

The seasonal nature of golden tides will require a method of preserving *Sargassum* to provide a continuous supply, and the seasonal macroalgal growth is considered one of the major hurdles to the exploitation of seaweed for biofuel [120,121]. There are numerous methods used in food and agriculture to preserve organic materials, but two methods used to preserve large volumes of material are drying and ensiling.

3.2.1. Drying

The removal of water from the algal biomass by evaporation is very energy-intensive, requiring an energy input of ~2.6 $MJ \cdot kg^{-1}$ to heat water from 20 to 100 °C and evaporate it at atmospheric pressure [122]. Dewatering (the mechanical removal of water) generally uses less energy than evaporation, and thus it would appear preferable to minimise the water content of the harvested algae prior to drying. Although coal-fired driers have been used in Ireland for the production of seaweed-meal products [123], the use of fossil fuels to dry seaweed will be costly, have a negative energy balance, and produce unwanted greenhouse gas [32,124]. However, the cost of conventional drying could be reduced if 'waste' heat is available from power generation or large-scale refrigeration plant.

Sun-drying is the main method of drying seaweed [125–127]. Clearly this approach does not require fossil fuel energy, but is both weather- and volume-dependent. Sun-drying in tropical locations may take 2–3 days in sunny weather, but could take up to seven days in rainy seasons [127]. Despite these limitations, solar methods are the least expensive drying option [128], but large areas are required as only around 100 g of dry matter can be produced from each square metre of surface [129].

Solar drying can cause considerable denaturisation of organic compounds in seaweed [130–133]. Freeze drying tends to cause less damage to organic materials, but is more expensive than solar or conventional drying, and is typically used for products such as premium instant coffee to give better flavour [134,135]. Freeze drying has been used for algae, particularly microalgae, such as *Dunaliella*, but is considered too expensive for the large-scale commercial recovery of algae, and its use is confined primarily to research and some high-value seaweed products [132,133,136,137].

3.2.2. Ensilage

An alternative preservation method is ensiling. It is routinely used for the storage of forage for animal feed. In ensilage lactic acid fermentation under anaerobic conditions converts water-soluble carbohydrates into organic acids, mainly to lactic acid. As a result the pH decreases and the moist crop is preserved [138]. Typically, ensiling conditions are achieved from spontaneous anaerobic lactic acid fermentation that is initiated by bacteria naturally present in the crop [139,140]. Dewatering and demineralisation are inherent features of ensiling [141] that may be of benefit for downstream processes such as anaerobic digestion, pyrolysis, and gasification.

Despite its widespread use in terrestrial agriculture there has been little research on how to preserve seaweed biomass year-round in order to satisfy continuous demand [142–144]. However, "an understanding of ensiling of seaweed is absolutely crucial for a substantial seaweed biofuel industry" [144]. There was some research into the ensilage of seaweed in the 1950s [142], and more recently in both Ireland and the United Kingdom [124,144]. A recent study of ensiling *Sargassum muticum* concluded that ensiling is an energy-efficient method of preserving seaweed for biofuel, and in particular biogas production, as energy losses are low (<8%) and methane yields are not significantly reduced [34]. However, ensilage may cause changes to the composition of the biomass and the degradation of some organic compounds, and thus may not be suitable as a method of preservation for production of some high-value compounds, but lactic acid fermentation may yield novel pickled seaweed food products [143]. During ensilage virtually all the organic sulphur was removed from *Sargassum muticum* [34]. Low-sulphur feedstocks are favoured for both gasification and AD, and thus ensilage may yield downstream process benefits in biofuel production, but ensilage would not appear be an appropriate storage method if sulphated carbohydrates are the commercial target. The production of H_2S during ensilage will also have both operational and health and safety implications.

Although the pH values achieved in ensiling *Sargassum* (4.9–5.1) are similar to commercial grass silage produced in the Netherlands (4.5 to 5.8: average of 5.1), the pH achieved in seaweed ensilage may be insufficient to completely inhibit clostridial fermentation and the production of butyric acid, due to the high water content of seaweed silage relative to typical terrestrial forage crops [34,144,145]. Dewatering seaweed, as with drying, may also be advantageous prior to ensiling. Grass silage at a TS of 25% produces very little effluent, and thus potential pollution [146]. The United Kingdom's Ministry of Agriculture, Fisheries, and Food (MAFF) [147] has recommended that, in order to minimise effluent production, wilting to at least 25% dry matter prior to ensilage is required. Such wilting processes prior to ensilage also increases the concentration of sugars, which enhances the ease with which fermentation of the biomass occurs, whilst also reducing odours [147,148]. However, only rapid wilting (<24 h) offers benefits as slow wilting can lead to rotting and increased organic material losses [148]. The requirement to rapidly wilt seaweed prior to ensilage could have considerable influence on the operation, economics, and energy balance of macroalgal ensilage.

4. Biochar, Biofuels, and Biorefineries

Sargassum has traditionally been recovered from beaches for use as both a fertiliser and animal feed [2], and this could remain a useful method of exploitation of golden tides. Although both fertiliser and animal feed can exploit the entire biomass, new markets will need to be found to exploit the potential volumes produced from inundations. Considerably more research will be required to establish whether the fertilisers and animal feeds from golden tides can meet relevant international quality and animal health standards. Transport costs could also considerably influence the economic competitiveness of these relatively low-value products [149].

4.1. Biochar

Another potential agricultural product could be biochar, defined as a solid material obtained from the carbonisation of biomass used to improve soil properties [150]. The differences between charcoal and biochar are primarily in the end uses, with charcoal being used as a fuel and biochar as a nonfuel [151]. Since the turn of the century biochar has received considerable attention, both from scientists and policy makers, as a soil enhancer to potentially increase agricultural yields and simultaneously sequester carbon to help mitigate climate change [152,153]. Biochar is produced by pyrolysis, the thermal decomposition of the organic component of dry biomass by heating in the absence of air [154,155]. The distribution between solid, liquid, and syngas depends on the biomass and the pyrolysis temperature and time. Lower temperatures (around 400 °C) tend to produce more solid char (slow pyrolysis) [122,156]. The properties of the biochar are dependent not only on the pyrolysis conditions, but also on the feedstock [157]. Biochar has been produced experimentally from brown seaweeds including *Sargassum* spp., and has different properties to ligno-cellulosic biomass with relatively low carbon content and surface area, but with a high content of essential trace elements and exchangeable cations, particularly potassium [158]. The char from the pyrolysis of algae has been found to be an effective soil ameliorant and fertiliser [159], but the blending of seaweed and ligno-cellulosic chars could produce a soil ameliorant that has high fixed C, together with a high mineral content, which may further enhance crop productivity [158]. The energy required for the pyrolysis of *Sargassum* could be provided by the syngas and bio-oil produced [32]. However, pyrolysis requires dry feedstock, and there is insufficient energy within *Sargassum* for drying, but the use of solar drying could result in a positive energy balance. Biochar will also have the advantage of reduced transport costs compared to dried seaweed fertiliser [160].

4.2. Biofuel

One way in which the extraction of energy from macroalgae can be categorised is according to whether an initial drying step is required or not. This leads to two distinct groups of processes:

(1) Energy extraction methods requiring dry macroalgae

- (i) direct combustion
- (ii) pyrolysis
- (iii) gasification (conventional)
- (iv) trans-esterification to biodiesel

(2) Energy extraction methods for wet macroalgae

- (v) hydrothermal treatments
- (vi) fermentation to bioethanol or biobutanol
- (vii) anaerobic digestion

The methods of energy extraction from macroalgae have been recently reviewed and it was concluded that it is probably too early, at the current stage of biofuel development, to select definitively what method or combinations of methods for exploiting energy from macroalgae will be commercially exploited [71].

Direct combustion is, historically and currently, the main method by which energy from dry biomass resources is realised, providing heat or steam for household and industrial uses and for the production of electricity [161]. Macroalgal combustion does not appear to have been greatly explored [162,163]. However, the high energy required to dry seaweed, the relatively low thermal values, and the high ash and sulphur content can cause fouling and corrosion of boilers, and unacceptable emissions could preclude direct combustion as an economic method of exploiting seaweed [71,162,163].

The higher lipid content of some microalgae compared to macroalgae has focused much of the published research work on the production of biodiesel from the microalgal lipids via trans-esterification [122,164,165]. Macroalgal biomass typically has lower lipid content, 0.3%–6% compared to microalgae, which can have 10%–70% [24,70,166,167]. Macroalgae would, therefore, not appear to be a suitable feedstock for the production of biodiesel via trans-esterification.

4.3. Anaerobic Digestion

Both gasification and anaerobic digestion have been suggested as promising methods for exploiting bioenergy from biomass [168]. A recent study that analysed four methods of microalgal bioenergy production found that anaerobic digestion produces more net energy than supercritical gasification, the latter requiring higher energy input and having a negative return on energy investment [122,169]. This conclusion is supported by a related study that has demonstrated that anaerobic digestion of "algal residues" can have a higher net energy return and much lower GHG emissions than gasification [170].

Seaweed-derived biogas was used industrially in the 19th century, and currently AD is perhaps closest to industrial exploitation [56,71,120,171]. Not only is it a relatively simple process from an engineering/infrastructure standpoint, but it has the potential to exploit the entire organic carbon content of macroalgae and can readily tolerate high moisture content without incurring additional process energy penalties. It is also readily scaled up [118]. A report for the Crown Estates has concluded that AD at a small, distributed scale was economically feasible for the co-digestion of seaweed with food waste [171]. The gasification of seaweed with wood-based biomass was also considered economically feasible. Conversely, the large-scale anaerobic digestion or gasification of seaweed alone was considered extremely challenging economically, and will require seaweed to be delivered to the processing plant at below £300 per tonne [171,172]. However, the biomass from golden tides has no cultivation cost, with the only costs prior to AD being for collection, sorting, and transport. The economics of the AD of seaweed could also be improved if it is part of a process that yields high-value products [173]. The residue remaining after the anaerobic digestion of seaweed, or digestate, is also considered to have considerable potential as fertiliser and could be an additional income source from the disposal of *Sargassum* [118].

The biomethane potential of *Sargassum* spp. is low at ~0.13 $L \cdot CH_4 \cdot g^{-1} \cdot VS$ [33,34,52], and considerably below that typical of seaweed at 0.2 $L \cdot CH_4 \cdot g^{-1} \cdot VS$ [121,174,175] and ~30% of that from common commercially exploited feedstocks [176–180]. There is considerable conjecture about the reasons for the relatively low practical methane yields compared to the theoretical values [33,71,103,120,181], and more research is needed to find the cause of low methane yields and how to overcome them.

4.4. Biorefineries

A biorefinery concept that attempts to commercialise all the components of seaweed has been suggested as a more appropriate approach for the further exploitation of seaweed, rather than an approach based solely on the production of biofuel [166,182,183]. During the First World War, Hercules was producing 54 chemicals from seaweed; it closed shortly after the war when demand fell and alternative supplies became available [184]. As has been discussed previously, *Sargassum* has the potential to produce a wide range of high-value biochemicals, nutraceuticals, and pharmaceuticals.

Despite this, there are still very few compounds commercially produced from seaweed, and the main product remains hydrocolloids [30,59,185–187]. Considerable more research is required to develop a commercially viable biorefinery for *Sargassum*.

5. Co-Production

The potential of the "failure" of golden tides to arrive in any year will require processes that are capable of exploiting other local biomass, or process plants could remain idle for long periods, considerably impacting on commercial viability. The ability to process two or more biomass feedstocks may also be advantageous—for example, the co-digestion of seaweed and another feedstock can enhance anaerobic biodegradability. Recent studies found that co-digestion of *Sargassum* spp. with glycerol or waste cooking oil containing little nitrogen increased methane production by 19%–56% compared to the individual materials digested separately [34,188].

6. Conclusions

Although *Sargassum* has considerable potential as a source of biochemicals, feed, food, fertiliser, and fuel, variable and undefined composition together with the possible presence of marine pollutants may make golden tides unsuitable for food, nutraceuticals, and pharmaceuticals, and could limit their use in feed and fertiliser.

Discontinuous and unreliable supply of *Sargassum* also presents considerable challenges. Low-cost methods of preservation such as solar drying and ensiling may address the problem of discontinuity. The use of processes that can handle a variety of biological and waste feedstocks in addition to *Sargassum* is a solution to unreliable supply, and anaerobic digestion for the production biogas is one such process.

More research is needed to characterise golden tides and to identify and develop commercial products and processes.

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