

Review

Macroalgae-Derived Biofuel: A Review of Methods of Energy Extraction from Seaweed Biomass

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Abstract: The potential of algal biomass as a source of liquid and gaseous biofuels is a highly topical theme, but as yet there is no successful economically viable commercial system producing biofuel. However, the majority of the research has focused on producing fuels from microalgae rather than from macroalgae. This article briefly reviews the methods by which useful energy may be extracted from macroalgae biomass including: direct combustion, pyrolysis, gasification, trans-esterification to biodiesel, hydrothermal liquefaction, fermentation to bioethanol, fermentation to biobutanol and anaerobic digestion, and explores technical and engineering difficulties that remain to be resolved.

Keywords: seaweed; macroalgae; algae; bioenergy; pyrolysis; gasification; liquefaction; fermentation; anaerobic digestion

1. Introduction

Algae are a diverse range of aquatic “plants”, comprising both unicellular and multi-cellular forms, which generally possess chlorophyll, but are without true stems and roots. The algae can be divided by

size into two groups: macroalgae commonly known as “seaweed” and microalgae, microscopic single cell organisms ranging in size from a few micrometres (μm) to a few hundred micrometres [1]. Unlike terrestrial crops cultivated for biofuel, algae do not require agricultural land for cultivation and many species grow in brackish or salt water avoiding competition for land and fresh water required for food production [2–4]. The potential biomass yield of algae per unit area is also often higher than that of terrestrial plants [5–7] with, for example, brown seaweeds grown “under cultured conditions” having yields of $\sim 13.1 \text{ kg dry weight m}^{-2}\cdot\text{yr}^{-1}$ compared to $\sim 10 \text{ kg dry weight m}^{-2}\cdot\text{yr}^{-1}$ from sugarcane [8,9]. Algae, therefore are considered as among the most potentially significant future sources of sustainable biofuels [10], and have been described as potential sunlight-driven cell factories for the conversion of carbon dioxide to biofuels and chemical feedstocks [3]. Nevertheless despite their obvious potential, there are no economically-viable commercial-scale quantities of fuel from either micro- or macroalgae [11–13].

In the case of microalgae, part of the problem lies in the low values calculated for energy return on investment (EROI) (1–3) compared to that for petroleum and diesel (4–5) [14]. This is now being addressed by a raft of research initiatives aimed at considering the full spectrum of products that might be obtained from microalgae in addition to biofuel, in so-called “biorefineries” [2]. By contrast in the case of macroalgae there has been a paucity of research directed towards producing fuels or developing feedstocks for fuels [12,15]. However, the use of macroalgal feedstocks for non-fuel uses is currently 100 times bigger in wet tonnage terms than that for microalgae [16]. Today the global utilisation of (non-fuel) products obtained from macroalgae is a multi-billion dollar industry [17], with Asia being the main market [18,19]. Current uses of seaweeds include human foods, fertilisers, cosmetics ingredients and phycocolloids [20]. Alginates, agars, and carrageenans (E400, E406 and E407, respectively), three major phycocolloids, are widely used in the food industry and have a combined annual production of 86,000 tonnes [21,22]. Worldwide 221 species of macroalgae are known to be exploited by humankind with 66% of the species used as food [23]. However, the majority of algal biomass comes from a relatively small number of species [24] with five genera, *Laminaria* (reclassified as *Saccharina* for some species), *Undaria*, *Porphyra*, *Euchema*, and *Gracilaria*, representing 76% of the total tonnage for cultured macroalgae [25].

This review draws on available literature resources to unravel the opportunities and limitations for exploiting macroalgae as a source of biofuel, particularly from the perspective of EROI, and highlights areas where further research effort and investment needs to be directed in order to realise their potential as sustainable biofuel resources.

2. Macroalgal Production Process Operations

The process operations used for algal-derived fuel production can be grouped into four main areas:

- i. cultivation including “seed” production;
- ii. harvesting;
- iii. post-harvest treatments including cleaning, size reduction, preservation and storage;
- iv. energy extraction.

Any future successes of macroalgal-derived fuel will be dependent on achieving an optimised, energy efficient process in each of these four areas. As is the case with microalgae the development of new and

improved methods for both seaweed cultivation and harvesting techniques will be vital for economic and energetic viability of biofuel from macroalgae [26,27]. In the case of macroalgae the seasonal nature of seaweed growth and culture is of particular concern for commercial-scale biofuel production, and methods of storage or preservation must be developed to enable its use in year-round fuels manufacturing processes. However, there has been little research on how to preserve seaweed biomass year round in order to satisfy continuous process demand [28–30].

3. Energy Extraction from Macroalgal Biomass

One way in which 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
 - i. hydrothermal treatments;
 - ii. fermentation to bioethanol or biobutanol;
 - iii. anaerobic digestion.

A summary of the potential methods of energy extraction is given in Table 1.

Table 1. Methods of energy extraction from macroalgal biomass.

Method	Utilises entire organic biomass	Requires biomass drying after harvesting	Primary energy product
Direct combustion	Yes	Yes	Heat
Pyrolysis	Yes	Yes	Primarily liquid by fast pyrolysis
Gasification	Yes	Yes ^b (conventional)	Primarily Gas
Biodiesel production	No	Yes ^c	Liquid
Hydrothermal treatments	Yes	No	Primarily Liquid
Bioethanol production	No ^a	No	Liquid
Biobutanol production	No ^a	No	Liquid
Anaerobic digestion	Yes	No	Gas

^a Polysaccharides require hydrolysis to fermentable sugars. Some of the sugars produced from the breakdown of seaweed polysaccharides are not readily fermented; ^b Supercritical water gasification (SCWG) an alternative gasification technology can convert high moisture biomass; ^c No current commercial process for the wet trans-esterification of wet macroalgal biomass

3.1. Energy Extraction Methods Requiring Dry Macroalgae

Many processes for the manufacture of fuels from biomass, such as direct combustion, pyrolysis, gasification and current commercial biodiesel production, require a dry feedstock and drying is required prior to energy extraction. The inclusion of a drying stage in macroalgae-to-fuels processes will have a significant impact on EROI since the water content of macroalgae (80%–90%) is generally higher than that of many terrestrial crops (sugarcane ~75%, grain maize 14%–31%) [8,15,31,32]. The energy to heat water from 20 to 100 °C and evaporate it at atmospheric pressure requires an energy input of approximately $2.6 \text{ MJ}\cdot\text{kg}^{-1}$ or over $700 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$ [13]. The removal of water from the algal biomass by evaporation can, therefore, be very energy intensive, and establishing either a low energy drying methodology or a biomass-to-fuel conversion technology that can tolerate a wet feedstock are vital to ensure the future applicability of this potentially attractive sustainable feedstock.

3.1.1. Dewatering and Drying Macroalgae

Sun-drying is the main method of drying seaweed [12,33,34]. 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 and could take up to 7 days in rainy seasons [33]. Despite these limitations, solar methods are the least expensive drying option [35], but large areas are required as only around 100 g of dry matter can be produced from each square metre of sun-drier surface [36].

Finding a more controllable and cost-effective method of large-scale seaweed drying, compared to that of sun-drying, is clearly key to establishing a viable seaweed-to-fuels processing industry [33]. Coal-fired driers have been used in Ireland for the production of seaweed meal products to achieve a moisture content ~10%, but this approach is uneconomic for biofuel production [37]. The energy to dry a seaweed with a moisture content of 88% has been calculated to be $0.7 \text{ MJ}\cdot\text{kg}^{-1}$ higher than the Lower Heating Value (LHV) of dry seaweed [37].

The dewatering (the removal of water by mechanical methods from the algal biomass, such as pressing and centrifugation) or drying of seaweed biomass to 20%–30% will increase “shelf-life” and reduce transportation costs [37]. Reducing the moisture content of the seaweed is beneficial as it prevents the growth of these spoilage-causing microorganisms and slows down detrimental enzymatic reactions [33]. However, certain species of seaweed are inherently more resistant to degradation. For example, brown seaweed is more stable than green seaweed, attributed to the presence of polyphenols, and can be stored at ambient temperature for hours or even days without starting to deteriorate [37].

Dewatering (the mechanical removal of water) generally uses less energy than evaporation to remove water and it would appear preferable to minimise the water content of the harvested algae prior to drying.

3.1.2. Direct Combustion of Macroalgae

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 or for the production of electricity [38]. However, in the case of macroalgae, combustion does not appear to have been greatly explored [39,40]. Dry macroalgae are easy to ignite, but have a low thermal value typical of carbohydrate-rich biomass ($14\text{--}16 \text{ MJ}\cdot\text{kg}^{-1}$) [41].

The moisture content of biomass can reduce the heat available compared to that from dry biomass by 20% [38] and the direct combustion of biomass is “feasible” only for biomass with a moisture content of less than 50% [42,43]. Nevertheless, it has been suggested that the relatively simple process of direct combustion of dried seaweed (*Ulva*) could avoid the “additional technological problems” of producing liquid fuels from macroalgae (see below) [44].

Another issue associated with direct combustion routes to energy from biomass is that of the solid inorganic residues or ash produced. These residues often lead to fouling of the boilers, which impacts detrimentally on overall process efficiency. Consequently, direct combustion processes are restricted to using biomass streams that have a low ash content [38]. Wood has a typical ash content of 0.5%–2% [45,46], but the ash content of algae can be high ranging from 3.5% to 46% [24,25,41] with that of *Laminaria* typically being 33% [47]. The higher ash content of seaweed results in its biomass having a higher heating value (HHV) that is lower than that of the terrestrial energy crops (cf. 14–16 compared to 17–20 MJ·kg⁻¹) [41]. The chemical composition of the seaweed ash resulting from combustion could also be problematic. Macroalgae have a high alkali index, *i.e.*, the amount of alkali metal oxide in the fuel per unit of energy expressed as kg alkali GJ⁻¹, of 16–82 kg alkali GJ⁻¹. This range of values for macroalgae is considerably above the level, 0.17 kg alkali GJ⁻¹, recommended to prevent potential fouling of combustion/boiler systems [41]. Consequently, without pre-treatment to remove ash-generating components, it is difficult to envisage seaweed being used in combustion systems without encountering problems due to failure [41]. Indeed, the high ash and alkali contents were found to be the main challenges in the direct combustion of *Ulva lactuca* [48,49]. Furthermore seaweed has high sulphur (1%–2.5%) and nitrogen (1%–5%) contents relative to many other types of biomass [50–52]. This unusual biomass chemistry for seaweed could also hinder its utilisation as a direct combustion fuel, since harmful and corrosive nitrogen and sulphur containing emissions will need to be controlled [40].

Fluidised bed boilers have been suggested as the best method to combust materials with a high volatiles content, high ash and low thermal value fuels such as seaweed [39,40]. However, in order to combust seaweed in a fluidised bed it has been demonstrated that the particle size has to be ground down to <0.18 mm in order to minimize “heat-transfer resistance” [39]. The necessity to grind down the biomass feed consequently adds to the energy demands of the process, with the amount of energy required to grind the biomass to a diameter of less than 1 mm (2%–3% of the heating value) being almost double that compared to the energy required for coal pulverisation (0.9%–1.2% of the heating value) [53]. The energy requirements for biomass pulverisation increase significantly (>20% of the heating value) for fibrous and or moist biomass [53], something potentially problematic for non-dried seaweed.

Co-Combustion of Macroalgae

The co-combustion of biomass in coal-fired plants is generally considered to be an especially attractive option for biomass exploitation [38,42,45]. The co-generation of heat and electricity can significantly improve the economics of biomass combustion, but requires that there is a local demand for heat [38]. A Life Cycle Assessment of co-firing of coal and solar-dried microalgae found that, although Green House Gas (GHG) emissions could be reduced by co-firing with microalgae grown using the power plant CO₂ emissions, it was more expensive and the depletion of natural resources greater than with using coal alone [54]. Combustion and co-firing of seaweed have yet to be evaluated

widely [41], however the conclusion reached by Kadam [54] for combustion of microalgae, namely that it could have environmental benefits, but may be uneconomic, could also be true for the potential of macroalgal direct combustion. Indeed, a study of the thermochemical behaviour of macroalgae concluded that the direct combustion of seaweed biomass does not appear an attractive option due to its low calorific value and relatively high moisture, ash and chlorine content [41].

3.1.3. Pyrolysis

An alternative thermolytic technique for the conversion of biomass to fuel is pyrolysis. This may be defined broadly as the thermal decomposition of the organic components of dry biomass by heating in the absence of air [42,45,55]. Pyrolysis processes can be classified by temperature and process time as; slow, fast and flash [55,56]. Slow pyrolysis is characterised by long residence times (from minutes to days for solids) at low reactor temperatures ($<400\text{ }^{\circ}\text{C}$) with very low rates of heating ($0.01\text{--}2\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$) [57], and results in higher yields of char rather than the liquid or gaseous fuel products [35,56]. Fast and/or flash pyrolysis covers a range of newer technologies operating with temperatures above $500\text{ }^{\circ}\text{C}$ and short vapour residence times of a few seconds or less [42,56], and has potential for the commercial production of biofuel from biomass [35,55].

Pyrolysis can produce high volumes of fuel materials relative to the volume of biomass feed and the process can be optimised to favour the production of bio-oil (the liquid product, the composition of which depends on feedstock and pyrolysis protocol employed), syngas or solid char [58] depending on the desired product phase. Pyrolysis can also be used in the presence of solvents to deliver biofuels with different characteristics: for example, in the pyrolysis of *Enteromorpha prolifera* at $300\text{ }^{\circ}\text{C}$ in the presence of vacuum gas oil (VGO), mainly hydrocarbons are produced, whereas in the presence of ethanol, mainly oxygenated products predominate [59].

Fast pyrolysis is capable of achieving greater liquid product and gas yields of around 70%–80%, compared to 15%–65% achieved through slow pyrolysis [35,43]. Bio-oil is generally thought of as a more attractive end product than either char or syngas as it has a higher energy density and is easily transported and stored [60]. Following an extensive review of thermochemical conversion of microalgae, it was concluded that if liquid or gaseous products are the main target, fast pyrolysis is recommended with a heating rate of $1\text{--}200\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$ [61]. The optimum pyrolysis reaction range for *Chlorella*, in terms of the proportion of biomass converted, was found to be close to the conditions used in flash pyrolysis [62].

Research on the pyrolysis of microalgae has achieved reliable and promising outcomes [61]. The pyrolysis of dry *Chlorella* has been found to give higher yields and better quality bio-oil (higher calorific value) than that from macroalgal or moss biomass [63]. The maximum bio-oil yield from pyrolysis of dry *Chlorella* was found to be between 50.8% and 57.9% of the weight of the original dry biomass [58,63–65]. The HHV of *Chlorella* and the microalgal bio-oil were $23.6\text{ MJ}\cdot\text{kg}^{-1}$ and $39.7\text{ MJ}\cdot\text{kg}^{-1}$, respectively [63]. Therefore the yield of bio-oil energy is 85% of the initial energy in the microalgal biomass in the conversion of 50.8% w/w of biomass to bio-oil. A new experimental microwave assisted method of pyrolysis has been laboratory tested on *Chlorella* yielding up to 22% bio-oil [66].

By contrast fast pyrolysis of macroalgae has been reported to produce a lower yield of bio-oil equivalent to $\sim 76\%$ of the energy content of the biomass [49,67]. Importantly, the lipid content of

microalgae is believed to influence the energy balance of pyrolysis with higher lipid content microalgae having an improved energy balance [62], therefore the energy balance of pyrolysis of microalgae may be more favourable than for macroalgae.

Effect of Metals in Seaweed Pyrolysis

The metals in the ash of seaweed have been shown to produce a significant catalytic effect on pyrolysis, and ash content (especially potassium salts) strongly influences the product yields and bio-oil properties [41,68].

Overall yield of bio-oil derived from the pyrolysis of seaweed is lower than that from lignocellulosic biomass something that has been attributed to the high ash content of seaweed and the presence of metal ions [68,69]. High potassium content caused high char yields and reduced bio-oil yields [67,68], but copper ions have been shown to promote the onset of pyrolysis in algininate polymer and *Laminaria digitata* [70]. In addition, high inorganic content (e.g., Mg, K and S) has been found to vastly increase the specific surface areas of the char produced from *Laminaria digitata* ($1490 \text{ m}^2 \cdot \text{g}^{-1}$) compared to land-based biomass such as oilseed-rape straw ($\sim 950 \text{ m}^2 \cdot \text{g}^{-1}$) [71]. In another study, pre-treatment of *Saccharina japonica* with sulphuric acid was undertaken in order to remove inorganic contaminants that may have an influence on the pyrolysis process itself. Implementing this strategy was found to increase the fatty acid composition of the resulting bio-oil, but inhibited the formation of large char chunks that were found to hinder the continuous pyrolysis of the untreated macroalgae in a fluidised bed [72].

Clearly, the high concentration of metals and inorganic ions coupled with the high moisture content of seaweeds make them far from “ideal feedstocks” for combustion or pyrolysis. However, metal concentration and calorific value vary throughout the year and by harvesting when metal concentrations are at their lowest and HHV at its highest, July in the UK for *Laminaria digitata*, the biofuel potential could be maximised [50]. While this seasonality does alleviate some of the issues surrounding the use of seaweeds as energy sources, it raises the problem of storage since fuels are required year-round, not just during a specific month.

Refining of Oils from Pyrolysis

The oils resulting from pyrolysis of biomass are typically complex mixtures of highly oxygenated organic compounds, which are generally polar, viscous, corrosive (due to their low pH as a result of the formation of organic acids with water) [73], unstable and unsuitable for use in conventional fuel engines unless refined [74]. Oxygenated components generally make up around 50% of such oils and may be subject to polymerisation over time, which leads to an increased viscosity and phase separation [75]. Increasing the heating rate of pyrolysis processes has been found to lower the oxygen and sulphur contents of the resulting bio-derived oils, along with a respective increase in carbon and hydrogen [76]. Indeed, the properties of fast biomass pyrolysis-derived oils have been reported to be more suitable for refining to liquid fuels [58]. Oil from the pyrolysis of microalgae has been reported to have a lower oxygen content and viscosity and higher heating value than oils obtained following pyrolysis from wood or other terrestrial plant material [58,64,66]. The bio-oil produced from fast pyrolysis of *Chlorella protothecoides* and *Microcystis aeruginosa* had lower oxygen content than that derived from wood, and had a distribution of straight-chain alkanes that was similar to diesel fuel, making it more suitable

for fuel-oil use than oils derived from fast pyrolysis of lignocellulosic materials [58]. However, in contrast oils from pyrolysis of seaweeds showed a lower heating value (23.08–32.46 MJ·kg⁻¹) than that of oil obtained from lignocellulosic biomasses [68,77]. Oxygen content has been found to be reduced in bio-oils through the use of catalysts during pyrolysis of *Laminaria japonica*, such as zeolites, but this approach also led to a decrease in the overall yield of bio-oil and increased the amount of gaseous products [78]. Pyrolysis oils from both microalgae and macroalgae also contain nitrogen compounds (which on combustion generate harmful NO_x gases), which must be removed and hence incur additional fuel refining costs [69,79].

Energy Return on Investment Considerations

In a comparative study of land-based biomass-to-liquid fuel, which looked at pyrolysis, gasification and bioethanol manufacture *via* fermentation, pyrolysis was found to have the lowest cost per U.S. gallon of gasoline equivalent of the three methods studied, with pyrolysis costs being 40%–60% lower [80]. However, this was a study of low moisture content feedstocks (moisture ~25%), and the additional costs of drying and handling wet materials, such as seaweed, will considerably increase the costs of pyrolysis and gasification fuels relative to that of ethanol produced by fermentation. Although pyrolysis is carried out at atmospheric pressure and is a well-established and “simpler” (in terms of technological complexity) process than hydrothermal liquefaction [81], the ability of the latter to use wet biomass would appear to give it an advantage over pyrolysis. Yanik *et al.* [68] in a study of the pyrolysis of lignocellulosic and seaweed biomass concluded that the production of fuels by pyrolysis is not viable from seaweed. Ross *et al.* [41] in a study of the direct combustion and pyrolysis of macroalgae concluded that: the most suitable conversion technologies for macroalgae will most likely be those which are most tolerant to the ash components in the fuel, and hydrothermal and or digestion methods may be more suitable for exploitation of these seaweed for fuels. As with direct-combustion the need to dry the macroalgae prior to pyrolysis may preclude it as an energetically and economically viable method of producing bioenergy. A recent review of the energy extraction from microalgal biomass has indicated that pyrolysis can use as much, or more, energy than is generated as biofuels [13].

To offset a potentially unfavourable EROI one option might be to situate pyrolysis in the context of a biorefinery and generate additional revenue streams from pyrolysis by-products. Pyrolysis char for instance can be used for the production of carbon nanotubes and agrochemicals or further upgraded to a hydrogen-rich fuel [75]. The chars from the pyrolysis of algae have been found to be effective soil ameliorants and fertilisers and could be an additional revenue stream [82]. However, recent studies have suggested that while biomass-derived chars applied to plants may lead to increased growth they may also reduce the plants ability to survive both biotic and abiotic stress [83].

3.1.4. Gasification

Gasification is the conversion of organic matter by partial oxidation at high temperature (800–1000 °C) mainly into a combustible gas mixture (syngas) [38,42,45,84]. The syngas has a calorific value of 4–6 MJ·m⁻³ [42], and is a mixture of hydrogen (30%–40%), carbon monoxide (20%–30%) methane (10%–15%), ethylene (1%), nitrogen, carbon dioxide and water vapour [38,45]. The gas can be burnt to produce heat or converted to electricity and heat in combined gas turbine systems [38,42].

The syngas produced from gasification can also be used to produce methanol and hydrogen as a fuel for transport and other uses [42,45], but the cost of methanol produced from methane from biomass has been estimated at 1.5–4 times higher than from fossil fuel gas [85].

The gasification processes involves a number of stages: initially pyrolysis occurs in a reaction producing char, which is then gasified in the presence of a gasifying agent such as O₂ or H₂O to produce syngas. Importantly, the amount of syngas produced through further gasification of the char is considerably greater than that produced through conventional pyrolysis at 800–900 °C [86]. Nickel compounds, olivine and dolomite have typically been employed as cracking catalysts to enhance gasification.

The gasification of dry lignite and woody biomass can have high yields with up to 90% of the original chemical energy in the biomass being recovered as energy in syngas [87], with the net energy return, including energy inputs, for pyrolysis operation of dry land agricultural biomass waste ranging from 42%–53% [80].

Conventional biomass gasification processes require dry feedstock [88], but supercritical water gasification (SCWG) is an alternative gasification technology for the conversion of high moisture biomass. It is suggested that SCWG processes can be net energy positive in a well-engineered systems [89], but the presence of water can alter the composition of the gases produced [90]. Catalytic supercritical water gasification of *Ulva lactuca* has produced a methane-rich gas [49]. A study of SCWG of *S. latissima* harvested during various months found that seaweed harvested in July produced gas with the highest calorific value, due to the lower ash content and the higher carbohydrate content [91]. Upon addition of NaOH in the SCWG of the macroalgae, *Saccharina*, there was a three-fold increase in H₂ production, along with an increase in methane, decrease in C₂–C₄ yields and the elimination of CO and CO₂ from the syngas [92]. The origins of these observations are believed to be due to the removal of CO₂ through reactions that form Na₂CO₃, a process that disrupts the water-gas shift equilibrium together with a similar scenario for increased methane production through alkaline catalysed decarboxylation of acetate groups of the primary sugar components of seaweed. Similarly, the addition of alumina-supported ruthenium (Ru/Al₂O₃) catalysts was found to double the H₂ and CH₄ yields from SCWG of *S. latissima* compared to the uncatalysed reaction with an increase of the gasification efficiency from 58% to 92% [91]. CO and C₂–C₄ yields correspondingly decreased whilst CO₂ yield increased. However, subsequent reuse of the regenerated catalyst led to a decrease in the yields of H₂ and CH₄, although, after reuse of the catalyst three times the H₂ and CH₄ yields were still above those from the uncatalysed processes. Analysis of the spent catalysts showed the build-up of surface sulphur and calcium. The addition of CO₂ during the steam gasification of *S. japonica* at 700 °C has been shown to increase the yield of CO in the resulting syngas by 20% [93].

Pre-treatment of macroalgae with water and acid may be employed to remove Mg, K, Na and Ca salts and other mineral matter by up to 90% [94] which can lead to high char levels, but conversely alkaline species can catalytically aid the steam gasification of macroalgae to H₂ at temperatures above 700 °C [95]. Higher syngas yields from steam gasification of macroalgae are possible due to their high content of inorganic elements than land based biomass such as Japanese Cedar and Apple branch, however the latter materials can be co-gasified with seaweed in a biorefinery, leading to enhanced syngas yields [95,96].

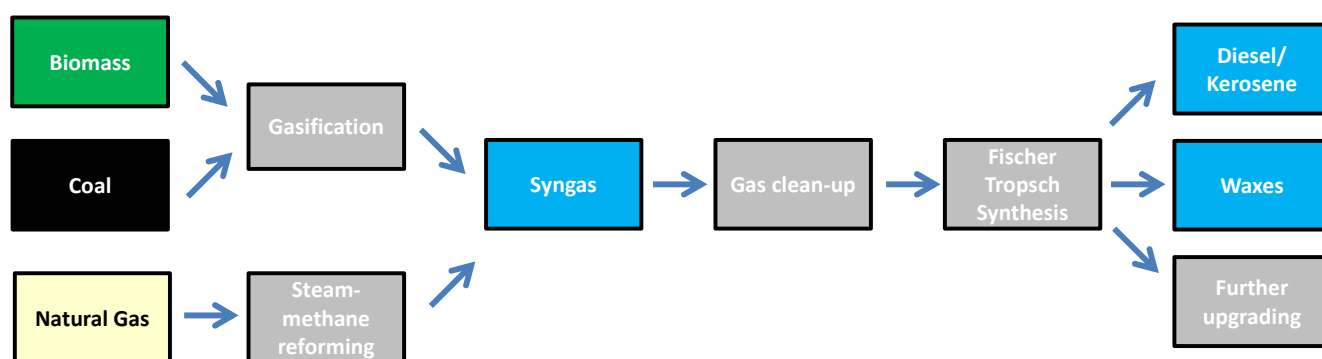
A recent review has concluded that there is little data available on the gasification of algae and in particular on the energy balance and the need for drying of algae prior to gasification [35]. If gasification

of macroalgae can be achieved using wet biomass it may be more economic and energetically attractive than traditional dry methods of gasification. The enthalpy change needed to take ambient temperature liquid water to a low-density supercritical state (400 °C and 250 bar) is similar to that required to vaporise liquid water at ambient temperature, but the advantage of the SCWG process is that much of the energy invested in reaching a supercritical state can be captured and used again, with the hot effluent from the gasification reactor being used to preheat the wet biomass feed stream [88]. Both gasification and anaerobic digestion have been suggested as promising methods for exploiting bioenergy from biomass in India [97]. A recent study analysed four methods of microalgal bioenergy production and concluded that supercritical gasification produced more net energy than that from anaerobic digestion [98]. However, following subsequent correction of errors in these calculations (acknowledged by the author in a private communication in 2014), it can be estimated that anaerobic digestion produces more net energy than supercritical gasification, the latter requiring higher energy input and hence giving a negative return on energy investment. 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 [99]. Despite the energy benefits from anaerobic digestion processes, gasification is a significantly more rapid process, which is a clear operational benefit, and if higher yields of combustible gas can be achieved through gasification then this may lead to a more favourable energy balance. Rowbotham *et al.* [70] have suggested that thermochemical processing methods, such as gasification and hydrothermal liquefaction, are more applicable and versatile treatment options than anaerobic digestion and fermentation, due to the technological difficulties associated with treatment and refining to liquid fuels of complex, heterogeneous, multi-component feedstocks, such as seaweed.

Fischer-Tropsch Synthesis

Syngas from gasification of biomass can be converted catalytically into hydrocarbons and water through Fischer-Tropsch Synthesis (FTS) [100], Figure 1. Additionally, other secondary products may form such as branched hydrocarbons, aromatics and oxygenates such as alcohols.

Figure 1. Stages involved in the overall Fischer-Tropsch Synthesis (FTS) process from feedstock to products.



FTS was originally developed in Germany, with the first commercial plant being constructed in 1936 [101], followed by large-scale developments in South Africa by Sasol which currently produces diesel using FTS. Shell currently operates the largest FTS plants in the world, with the Pearl GTL facility,

located in Qatar and jointly operated with Qatar petroleum being capable of producing 140,000 barrels of liquid hydrocarbons per day. The National Energy Technology Laboratory (NETL) [102] has stated that, “Fischer-Tropsch (FT) synthesis is a near-term solution for diesel fuel production; the technology has been in commercial use since the 1930s and the fuel produced can be used in today’s fuelling infrastructure”. The overall process of gasification through to FTS is known as Biomass-To-Liquids (BTL) [103].

FTS catalysis is usually carried out at pressures of 2–3 MPa and either temperatures of 210–260 °C (low temperature Fischer-Tropsch, LTFT) usually with cobalt-based catalysts or high temperatures of 310–340 °C (high temperature Fischer-Tropsch, HTFT) with iron-based catalysts [100]. Cobalt-based catalysts produce mainly linear hydrocarbons whereas iron-based catalysts tend to form alkenes and oxygenates [104]. Biomass-derived syngas H₂:CO ratio ranges are between 1.0–1.5 or 1.5–2.2 depending on whether the gasifying agent used is air or O₂ respectively [100]. The required H₂:CO ratio for FTS is around 2:1, thus the water-gas shift reaction is often employed to convert CO and H₂O into H₂ and CO₂, increasing the syngas ratio. This may be done prior to the FT reactor or *in situ* with iron-based catalysts. Other inert gases may be present in the reaction such as N₂ from air gasification, or if the FTS employs a recycle to improve conversion, low molecular weight hydrocarbons from FTS (methane, ethane) will behave as inerts on subsequent throughputs.

In FTS, CO is adsorbed dissociatively onto a metal surface, and is then hydrogenated by H₂ from the syngas, forming a C₁ intermediate which then grows in a similar fashion leading to hydrocarbon chains [105]. Overall the reaction is highly exothermic at $-165 \text{ kJ}\cdot\text{mol}^{-1}$ [106]. However, the mechanisms involved in FTS, are still widely debated after 90 years [107].

In addition to the liquid fraction, longer-chain waxes are also produced through FTS and these may be further upgraded to diesel through hydrocracking [108]. The synthetic diesel and jet fuel fractions produced from FTS may also require upgrading to meet current local fuel specifications through hydroprocessing as a final stage to the overall biomass to liquid transportation fuels process [105].

Depending on the biomass feed for the prior gasification step, the resulting syngas may contain a comparatively high concentrations of contaminants, including NH₃, HCN and H₂S, which require prior removal through a gas purification system down to pm-ppb levels since such compounds are well-established to poison the essential FTS catalysts [109]. This said, iron-based catalysts are less vulnerable than their cobalt counterparts to sulphur-containing contaminants [110] and so may be preferred for the processing of syngas derived from seaweed, where the concentrations of sulphur contaminates are likely to be high. Furthermore, irrespective of the nature of the FT catalyst employed, the bio-derived syngas will also contain tars, alkali and dust, which require removal prior to use in FTS [111].

3.1.5. Fatty Acid Ester-Derived Fuels via Trans-Esterification

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 [13,112,113]. Macroalgal biomass typically has lower lipid content, 0.3%–6% compared to microalgae which can have over 70%. Oil levels of 20%–50% are common for microalgae, but more typically reach only 10%–30% when grown under nutrient replete conditions [24,114–116].

A study of microalgal biomass has shown that when the lipid content is below 40% the anaerobic digestion of the entire biomass without lipid extraction for conversion to biodiesel via trans-esterification may be the optimal strategy for energy recovery [117]. However this study [117] contains errors and if lipid is digestible then energetically it is always better to digest algae [118].

Biodiesel has been produced from the macroalgae, *Chaetomorpha linum* [119] *Ulva lactuca* [120], *Enteromorpha (Ulva) compressa* [121], but oil yields are low at 11% of the total dry macroalgal biomass [120,121]. Macroalgae would, therefore, not appear to be a suitable feedstock for the production of biodiesel via trans-esterification.

3.2. Energy Extraction Methods for Wet Macroalgae

As noted above the high water content (80%–90%) of macroalgae impacts negatively on the energy balance. The HHV of the dry biomass of *Laminaria Saccharina* was calculated to be $12 \text{ MJ}\cdot\text{kg}^{-1}$ [122], if the moisture content of wet biomass is assumed to be 80% then 10.4 MJ are required to evaporate the moisture, equivalent to 87% of the total calorific value of the seaweed. These types of analysis have led to a focus on energy production from wet algae [123], and it has been suggested that only wet processes can produce net energy due to the high energy requirement to dry the algae [24,27].

3.2.1. Hydrothermal Liquefaction

Liquefaction is a low temperature high pressure process where biomass is converted into a stable liquid hydrocarbon fuel (bio-oil) in the presence of a catalyst and hydrogen [38,42]. During hydrothermal upgrading the biomass is converted to partially oxygenated hydrocarbons at high pressure in the presence of a catalyst in a wet environment [38,42]. In practice it would appear that the terms liquefaction, hydro-liquefaction and hydro-thermal liquefaction are synonymously used for processes where wet biomass is converted to bio-oil by temperature and pressure in the presence of a catalyst, with and without the presence of gaseous hydrogen. Hydrothermal liquefaction can be considered as pressurised aqueous pyrolysis [61], but produces bio-oil that is lower in oxygen and moisture content (therefore a more stable product) than from pyrolysis [124]. Reviews of thermal treatments for biofuel production have concluded that commercial interest in liquefaction is low due to the more complex feed systems and higher costs compared with those for pyrolysis and gasification [38,42,61]; but hydrothermal upgrading of algae is attracting much interest and has the advantage of the conversion taking place in a water-containing environment and drying of biomass after harvesting may not be required prior to hydrothermal liquefaction [125–127]. The ability of hydrothermal liquefaction to handle wet biomass makes it one of the most interesting methods of producing biofuel from algae [128]. Nevertheless, hydrothermal liquefaction of biomass with a moisture content above 90% is believed to have an unfavourable energy balance [129].

Bio-oil yields from experimental hydrothermal liquefaction of microalgae, as percentage mass of original dry microalgal biomass, have been reported as: up to 41% for *Spirulina* [60], between 24%–45% for *Scenedesmus* [129], 37% for *Dunaliella* [125], and up to 49% for *Desmodesmus* or 75% recovery of the energy in the microalgal biomass as bio-oil [130]. The yield of bio-oil from macroalgae hydrothermal liquefaction has been reported as up to 23% [15,24] with an energy recovery from the original macroalgal biomass of 63% for *Laminaria saccharina* [122] and 56% for *Enteromorpha*

prolifera [15]. However, hydrothermal liquefaction of *Laminaria saccharina* with high heating rates ($585\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) up to $350\text{ }^{\circ}\text{C}$ led to 79% yield [131]. Hydrothermal liquefaction of *Oedogonium* and *Cladophora*, freshwater macroalgae, gave 26% and 20%, respectively, bio-crude yield per dry mass, higher than marine macroalgae with *Derbesia* giving 20% yield, though this led to less bio-char than the freshwater macroalgae species [124].

Co-liquefaction of microalgae (*Spirulina platensis*) and macroalgae (*Enteromorpha prolifera*) at $340\text{ }^{\circ}\text{C}$ led to synergistic effects of conversion with 50% wt/wt being the optimal. The fatty acid content of *Spirulina* greatly enhanced the conversion of *Enteromorpha*, whereas inorganic salts present in the latter feed did not greatly hinder bio-oil production [132]. The overall effect was a greater amount of energy being recovered in the resulting bio-oil, though it contained less oxygen and more nitrogen than the separately produced micro and macroalgae bio-oils.

3.2.2. Bioethanol

First generation bioethanol, such as that produced from corn in the USA and sugarcane ethanol in Brazil, is now widely produced and used [133] and there is considerable interest in producing second-generation bioethanol from cellulosic biomass [134].

Cellulosic ethanol was expected to play a large role in meeting the goals of the U.S. Energy Independence and Security Act of 2007 for renewable biofuels [135]; but despite extensive research and the availability of low cost lignocellulosic biomass there is, as yet, no large-scale commercial production of fuel bioethanol from lignocellulosic materials [134,136]. One of the problems encountered with production of bioethanol from straw is that biodegradation of hemicelluloses and cellulose by cellulases can be inhibited by lignin, found in many terrestrial sources of second generation biofuel biomass [137]. Macroalgae do not normally contain significant quantities of lignin and therefore, hold out the prospect of the components of macroalgae being more readily converted to sugars, but seaweeds contain low amounts of polysaccharides composed of glucose. Ethanol will, therefore, need to be produced from other carbohydrate components of seaweeds, including sulphated polysaccharides, mannitol, alginate, agar and carrageenan [138]. However, some of the sugars produced from the breakdown of seaweed polysaccharides such as xylose and rhamnose are poorly utilised by yeast, such *Saccharomyces cerevisiae*. The lack of “tractable microorganisms” that can efficiently convert the monosaccharides derived from seaweed into ethanol is considered one of the major limitations of macroalgae as a bioethanol feedstock [139,140].

Hydrolysis of the seaweed biomass, normally by the use of acid or enzymes, is required to release the sugars in polysaccharides for fermentation [141]. Acid hydrolysis has been found to hydrolyse the polysaccharides of brown, green and red algae [142]. However, the methods of pre-treatment and saccharification prior to fermentation cannot only influence the amount sugar for ethanol production, but may also inhibit microbial fermentation with both acid and heat-treatments producing inhibitor-compounds [141]. Yoza and Masutani [143] found that, although acid saccharification released 49% of the total biomass as sugars in the hydrolysate, fermentation was “problematic”, but enzymatic saccharification only produced a maximum of 20% glucose based on the initial dry mass weight. Hydrothermal pre-treatment of *Ulva lactuca* was found to reduce ethanol yield despite the release of simple sugars, but mechanical pressing increased ethanol production to $0.14\text{ g}\cdot\text{g}^{-1}$ dry matter with yield

increase being attributed to the removal of fermentation inhibitors [49]. Another inhibitor of microbial fermentation could be higher metals/mineral content of macroalgae compared to that for terrestrial biomass which could be released to the fermentation liquid during pre-treatment and saccharification. These inhibitors could be removed by applying lime and activated charcoal treatments [144]. The need to for pre-treatment, saccharification and application of materials to remove fermentation inhibitors will add considerable cost to seaweed bioethanol production relative to that of more readily fermented substrates such as the simple sugars extracted from sugarcane.

Brown, green and red algae have all been fermented to ethanol, but brown algae are suggested as the principal feedstock for bioethanol production because they have high carbohydrate contents and can be readily mass-cultivated [141]. Laminarin and mannitol derived from *Laminaria hyperborean* have been found to undergo fermentation to give relatively high yields to ethanol in the presence of the yeast, *Pichia angophorae* [145]. The green alga, *Ulva lactuca*, dry biomass contains 58% carbohydrate, but only 6.1% C₆ sugars. Consequently, the ethanol production yield from the fermentation of untreated biomass was low 0.03 g·g⁻¹ dry matter [49]. Red algae have also been fermented, following acid hydrolysis to convert agar, the main component, to fermentable sugars, but rates of conversion to ethanol were low, yielding only 45% of the theoretical maximum [146]. Ethanol yields from the fermentation of seaweed are typically between 0.08 and 0.12 kg·kg⁻¹ dry seaweed varying with the alga and method of pre-treatment and saccharification [19]. Wargacki *et al.* [147] has found higher experimental ethanol yields of up to 0.281 g·g⁻¹ dry seaweed, 80% of the maximum theoretical conversion, while Aizawa *et al.* [148] suggested a potential commercial yield from seaweed 0.296 g ethanol g⁻¹ dry seaweed. However, a conversion to ethanol of 50% of the theoretical from seaweed is considered ambitious and has not been demonstrated at scale [19]. A recent study has concluded that the potential ethanol yield corresponded to approximately 90 litres tonne⁻¹ of dried macroalgae which is low compared with terrestrial fuel crops such as corn [143].

The energy balance for the fermentation and ethanol distillation of seaweed is thought to be similar to that for land crops, with energy inputs being approximately 70% of the calorific value of the ethanol produced [148]. The energy balance of corn ethanol production is probably marginal [149] and it has been suggested that currently only in Brazil is sugarcane-derived bioethanol a realistic fuel manufacturing process in energy terms [150] due to considerable quantities of bagasse which are burnt to produce heat to distil bioethanol and high content of fermentable sugars in sugarcane. The energy balance of seaweed-derived ethanol, like that from corn, may therefore also be marginal. Energy return on energy investment (EROI) of seaweed ethanol has been estimated as being comparable to corn ethanol at 1.78 [151]. Large seaweed ethanol production facilities have been proposed in both Denmark [152] and Japan [148], but the economic and energy feasibility of these schemes is unknown, and as yet there appears to be no large scale production of ethanol from macroalgae [152]. Horn *et al.* [153] in a study of brown seaweed concluded that a commercial industrial process will require higher ethanol yields and the “total” utilisation of all components of the seaweed biomass including the production of higher value non-fuel products.

Bioethanol can be readily used in current supply chains, with 86% of cars sold in Brazil in 2008 capable of using ethanol or a mixture of ethanol and fossil fuel petroleum [150]. However, there are disadvantages with bioethanol; “lower energy density than gasoline, corrosiveness, low flame luminosity, lower vapour pressure (making cold starts difficult), miscibility with water, and toxicity to

ecosystems” [134]. On the other hand, fermentation to biobutanol may be more readily integrated with existing petroleum supply chains.

3.2.3. Biobutanol Production from Seaweed

While seaweed cultivation for bioethanol and biogas is being explored in Asia, Europe and South America, it is biobutanol from macroalgae that is attracting research interest and investment in USA [154]. Butanol has been explored as a transportation fuel for around 100 years, and has been suggested as a biofuel with the potential, not only to augment, but even replace ethanol as a gasoline additive due to its, low vapour pressure and higher energy density [155]. Butanol production from biomass could also be more energy-efficient than ethanol as some bacteria used in butanol production digest not only starch and sugars, but also cellulose [152].

Some species of *Clostridium* are able to produce acetone, butanol and ethanol (ABE) by anaerobic fermentation from a wide variety of sugars, both hexoses (C₆) and pentoses (C₅), a process known as the ABE fermentation [116], but butanol is inhibitory to the fermentation limiting yield and productivity. The fermentation of *Ulva Lactuca* by *Clostridium* strains have produced butanol with a yield of 0.16 g butanol g⁻¹ C₅ and C₆ sugars, but the yield of butanol is lower than that of ethanol produced under comparable conditions [49]. *Ulva lactuca* solubilised by hot-water treatment followed by hydrolysis using commercial cellulases to produce sugars was used as feedstock for fermentation by *Clostridium* for the production of acetone, butanol and ethanol (ABE) with a yield of 0.35 g ABE g⁻¹ sugar [116]. Although these results demonstrate the potential of the seaweed, *Ulva lactuca*, as a substrate for ABE fermentation, ABE was proposed for the subsequent production of 1, 2 propanediol (propylene glycol) in a seaweed biorefinery replacing fossil fuel derived product rather than as a source of butanol as fuel. In a study using the naturally occurring macroalgae (*Ulva*) from Jamaica Bay, New York City it was found that butanol could be made on a pilot scale from algal sugars [155].

In a study of brown algae (*Saccharina*), although butanol fermentation of acid extracted soluble organic matter was demonstrated, yields were low at 0.12 g g⁻¹ extracted soluble solids [145]. The main fermentation substrates were found to be mannitol and glucose derived from laminarin, but abundant alginates were recalcitrant and did not undergo fermentation. In brown algae, such as *Laminaria hyperocea*, the largest organic fraction is alginate [153]. It has been concluded that significant improvements are still needed to make industrial-scale butanol from the fermentation of seaweed economically feasible [145].

3.2.4. Anaerobic Digestion of Macroalgae

Various groups assessing the suitability of seaweed anaerobic digestion (AD) from the 1970s through to 1990s generally found that seaweeds were mostly a suitable biomass for AD [156]. Indeed, during the 19th century, algal derived biogas was used to light an iodine production factory in Tiree [157,158], and more recently Tokyo Gas demonstrated that 20 m³ of methane can be produced from one tonne of seaweed which when blended with natural gas was used to power a 9.8 kW electrical generation plant [152]. It has been suggested that the use of biogas from seaweed could reduce GHG emissions by 42%–82% compared to the use of natural gas [123]. Moreover, the digestate (material remaining after the anaerobic digestion) contains both nitrogen- and phosphorus-containing compounds, which makes

it a possible seaweed-derived fertiliser or biological feedstock, and could add additional income streams to seaweed AD processes [25].

The bacteria involved in the production of methane by anaerobic digestion are sensitive to the chemical composition of the feedstock [159–161]. The proportions of carbohydrates, proteins and lipids affect the potential of algae as a substrate for anaerobic digestion [162] with lipids yielding higher volumes of biogas per gram of feed material than either carbohydrate or protein [118,163,164]. It has been suggested that the low lipid content of macroalgae make them “especially suitable” for biogas production using anaerobic fermentation [24,115]. The theoretical yield of biogas, calculated from the chemical composition of macroalgae ($C_cH_hO_oN_nS_s$) using the “Buswell equation” [165,166], can be high.

However, practical yields of biogas from the anaerobic digestion of macroalgae are considerably below the theoretical maximum. The destruction of organic volatile solids from microalgae was found to be only 60%–70% of that found in raw sewage [167], however the methane yield ($0.271 \text{ m}^3 \cdot \text{kg}^{-1}$) from *Ulva lactuca* was found to be similar to that from cattle manure and land-based energy crops, such as grass-clover [48,49]. Methane yields from the anaerobic digestion of macroalgae have been reported in the range of $0.14\text{--}0.40 \text{ m}^3 \text{ kg}^{-1}$ of volatile solids [24], but are typically $0.2 \text{ m}^3 \text{ CH}_4 \text{ g}^{-1}$ [47]. The hydrolysis of seaweed-derived polysaccharides, particularly alginates is considered the rate limiting step in the AD of seaweed [156]. Typical inocula for anaerobic digesters are from municipal sewage sludge and animal manure slurry, but inocula containing higher proportions of bacteria capable of fermenting marine phycocolloids have been shown to increase methane production [156]. The addition of bacteria from the rumen of Ronaldsay sheep, which had a diet almost entirely of seaweed, was found to increase the methane yield ($0.253 \text{ L CH}_4 \text{ g}^{-1} \text{ VS}$) and volatile solid utilisation (67%) from anaerobic digestion of *Laminaria hyperborean* [156].

AD methane yields from brown algae are generally higher than those from green algae [156]. The high sulphate concentration typical for green macroalgae can also lead to the formation of H_2S which results in inhibition of methane production; foul odours; sulphur dioxide emissions on combustion of the biogas; and a corrosive environment [24,168]. The emission of H_2S can be controlled by the addition of metal ions such as iron or by gas scrubbers, but both add to the cost of biogas production [24,168].

One of the advantages of growing macroalgae for biofuel is that they grow in seawater and do not compete for limited fresh water resources. Low salt concentrations can stimulate microbial growth, but high salt concentrations ($\geq 10 \text{ g} \cdot \text{L}^{-1}$) are known to inhibit anaerobic systems through an increase of osmotic pressure or dehydration of methanogenic microorganisms [169,170]. The toxicity of salt is predominantly determined by the sodium cation and other light metal ions, such as potassium, have also been found to be toxic to methanogens at high levels [171]. An optimal sodium concentration for mesophilic methanogens in waste treatment processes of 230 mg Na L^{-1} has been recommended [172]. Mesophilic methanogenic activity is halved at 14 g Na L^{-1} [172,173], the approximate level of sodium found in sea water [174]. However, in a study of *Ulva lactuca* it was found that washing of algae had no effect on methane yield [49]. Anaerobic digesters can be acclimatised to higher salt levels if they are continuously exposed to gradually increasing salt concentration rather than salt shock [170]. Adaptation of methanogens to high concentrations of sodium over prolonged periods of time can allow the anaerobic digestion of high salt concentration wet biomass, with the sodium concentration to halve methanogenic activity increasing to 37.4 g Na L^{-1} after acclimation [172]. It therefore appears possible to produce

biogas from macroalgae without the use of fresh water, but the high salt concentration could also be mitigated by mixing algal biomass with other types of biomass to “dilute” the salt [24].

Size reduction of macroalgae biomass, as with direct combustion, may be required prior to AD as the reduction in size of the algal fronds prior to anaerobic digestion has been shown to significantly increase the yield of methane from *Ulva lactuca* from 174 to 271 m³·kg⁻¹ [49] and from Baltic beach-cast seaweeds by up to 53% [175].

It has been suggested the cost of production of biogas from seaweed is high with estimates suggesting that it could be 7–15 times more expensive than natural gas [154]. A survey by Bruton *et al.* [37] found seaweed AD to be the closest process to commercialisation, but the cost of the raw material must be reduced by at least 75% over current levels to be economically viable. Roesijadi *et al.* [19] in an economic assessment of the production of gasoline from methane from seaweed AD found that it was not economic, but assumed a biogas yield of 0.17 m³·kg⁻¹ VS at the lower end of the literature methane yield. However, recent studies on energy return of the production of biogas from microalgae have shown it to be potential energetically viable with an EROI of over 3 [13,176,177]. Anaerobic digestion of seaweed has been proven to be technically feasible at scale and it has been suggested that it could be a cost-competitive with anaerobic digestion of terrestrial biomass and municipal solid waste [152].

4. Discussion

Apart from anaerobic digestion, which is considered to be economically feasible and has been operated at scale the production of biofuel from seaweed by other conversion technologies, particularly those that lead to liquid transportation fuels are at an early stage and there is a need for considerably more research [19].

Life Cycle Assessment and techno-economic models of seaweed are sparse in the published literature [47]. However, the cost of near-shore production of algal biomass has been estimated at between €336 and 669 tonne⁻¹ [178], and the economic feasibility of floating seaweed cultivation systems for biofuel is considered doubtful with current technology [24].

Current commercially viable exploitation of macroalgae and microalgal products is limited to products other than fuel, and the immediate future for the commercialisation of algae may be in combination with non-fuel products [8,141,179,180]. The cultivation of macroalgae simply for biofuels may not be currently profitable and the macroalgal industry must take advantage of markets for additional high-value products such as “nutraceuticals”, pigments and vitamins [8,21,27,141,181,182].

The term “biorefinery” has been used in the literature since the 1980s, and refers to the co-production of a spectrum of high value bio-based products (food, feed, nutraceuticals, pharmaceutical and chemicals) and energy (fuels, power, heat) from biomass [183–185]. The biorefinery concept is an “emerging research field” [141,186], and in December 2009, the U.S. Department of Energy [187] announced a \$100 million grant for three organisations to research algae biorefineries. Application of a biorefinery concept could increase the value of the seaweed biomass and the economics production of bioenergy from macroalgae [48].

Although biorefineries could allow the exploitation of the entire algal biomass, and improve the economics of biofuel production [188], they are likely to be energy intensive with increased energy inputs, process complexity and reduced energy outputs [184,186]. The extraction of alginates, laminaran

and fucoidan is estimated to lower the amount of fermentable compounds available in seaweed to produce bioenergy by half [37], but a biorefinery plant should operate sustainably with its energy demands met by biofuels produced [189].

Although high value algal products may allow the commercialisation of algae in the short term, the immense potential scale of algal fuel production could result in the creation of such large quantities of algal non-fuel materials that the market price is dramatically reduced. Bruton *et al.* [37] has suggested that the world market growth for phycocolloids is only a few percent per year and that any large additional supply could rapidly saturate the market. However, the lessons learned from high value, low tonnage non-fuel macroalgal-derived products, together with their potential for co-production with fuel, may lead to the more rapid commercial realisation of algal-derived biofuels [182].

5. Conclusions

This review suggests that macroalgal biomass has potential for the production of various biofuels, although it is evident that there are significant technological hurdles to be overcome before macroalgal biofuel is energetically and commercially viable. 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. However, currently anaerobic digestion is closest to industrial exploitation. Not only is it a relatively simple process from an engineering/infrastructure stance, 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 likely to play a leading role in combination with other methods, and could be the major method of biofuel production from macroalgae.

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Conflicts of Interest

The authors declare no conflict of interest.

References

1. Sheehan, J.; Dunahay, T.; Benemann, J.; Roessler, P. *A Look Back at the us Department of Energy's Aquatic Species Program—Biodiesel from Algae*; NREL/TP-580-24190; National Renewable Energy Laboratory (NREL): Golden, CO, USA, 1998; Volume 7.
2. Harvey, P.J.; Psycha, M.; Kokossis, A.; Abubakar, A.L.; Trivedi, V.; Swamy, R.; Cowan, A.K.; Schroeder, D.; Highfield, A.; Reinhardt, G.; *et al.* Glycerol production by halophytic microalgae: Strategy for producing industrial quantities in saline water. In Proceedings of the 20th European Biomass Conference and Exhibition, Milan, Italy, 18–22 June 2012; pp. 85–90.
3. Chisti, Y. Biodiesel from microalgae. *Biotechnol. Adv.* **2007**, *25*, 294–306.

4. Hughes, A. Scottish seaweed aquaculture; research, development and commercialisation. In Proceedings of the Seaweed for Biofuel: Towards a Sustainable Seaweed Supply Chain, Oban, UK, 21 May 2014.
5. Walker, D. Biofuels, facts, fantasy, and feasibility. *J. Appl. Phycol.* **2009**, *21*, 509–517.
6. Tredici, M.R. Photobiology of microalgae mass cultures: Understanding the tools for the next green revolution. *Biofuels* **2010**, *1*, 143–162.
7. Williams, P.J.L.B.; Laurens, L.M.L. Microalgae as biodiesel & biomass feedstocks: Review & analysis of the biochemistry, energetics & economics. *Energy Environ. Sci.* **2010**, *3*, 554–590.
8. Rajkumar, R.; Yaakob, Z.; Takriff, M.S. Potential of the micro and macro algae for biofuel production: A brief review. *BioResources* **2013**, *9*, 1606–1633.
9. Leu, S.; Boussiba, S. Advances in the production of high-value products by microalgae. *Ind. Biotechnol.* **2014**, *10*, 169–183.
10. Menetrez, M. An overview of algae biofuel production and potential environmental impact. *Environ. Sci. Technol.* **2012**, *46*, 7073–7085.
11. Service, R.F. Algae's second try. *Science* **2011**, *333*, 1238–1239.
12. Aresta, M.; Dibenedetto, A.; Barberio, G. Utilization of macro-algae for enhanced CO₂ fixation and biofuels production: Development of a computing software for an LCA study. *Fuel Process. Technol.* **2005**, *86*, 1679–1693.
13. Milledge, J.J.; Heaven, S. Methods of energy extraction from microalgal biomass: A review. *Rev. Environ. Sci. Biotechnol.* **2014**, *13*, 301–320.
14. Liu, X.; Saydah, B.; Eranki, P.; Colosi, L.M.; Greg Mitchell, B.; Rhodes, J.; Clarens, A.F. Pilot-scale data provide enhanced estimates of the life cycle energy and emissions profile of algae biofuels produced via hydrothermal liquefaction. *Bioresour. Technol.* **2013**, *148*, 163–171.
15. 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.
16. Lundquist, T.J.; Woertz, I.C.; Quinn, N.W.T.; Benemann, J.R. *A Realistic Technology and Engineering Assessment of Algae Biofuel Production*; Energy Biosciences Institution: Berkeley, CA, USA, 2010.
17. Smit, A. Medicinal and pharmaceutical uses of seaweed natural products: A review. *J. Appl. Phycol.* **2004**, *16*, 245–262.
18. Kelly, M.S.; Dworjanyn, S. *The Potential of Marine Biomass for Anaerobic Biogas Production a Feasibility Study with Recommendations for Further Research*; The Crown Estate on behalf of the Marine Estate: Scotland, UK, 2008.
19. Roesijadi, G.; Copping, A.E.; Huesemann, M.H.; Foster, J.; Benemann, J.R. *Techno-Economic Feasibility Analysis of Offshore Seaweed Farming for Bioenergy and Biobased Products*; PNNL-19944; U.S. Department of Energy: Washington, DC, USA, 2010.
20. Kraan, S. Mass-cultivation of carbohydrate rich macroalgae, a possible solution for sustainable biofuel production. *Mitig. Adapt. Strateg. Glob. Chang.* **2013**, *18*, 27–46.
21. Milledge, J.J. Microalgae—Commercial potential for fuel, food and feed. *Food Sci. Technol.* **2012**, *26*, 26–28.
22. Holdt, S.; Kraan, S. Bioactive compounds in seaweed: Functional food applications and legislation. *J. Appl. Phycol.* **2011**, *23*, 543–597.

23. Pereira, L. A review of the nutrient composition of selected edible seaweeds. In *Seaweed*; Pomin, V.H., Ed.; Nova Science Publishers: Hauppauge, NY, USA, 2011.
24. Murphy, F.; Devlin, G.; Deverell, R.; McDonnell, K. Biofuel production in Ireland—An approach to 2020 targets with a focus on algal biomass. *Energies* **2013**, *6*, 6391–6412.
25. Roesijadi, G.; Jones, S.B.; Snowden-Swan, L.J.; Zhu, Y. *Macroalgae as a Biomass Feedstock: A Preliminary Analysis*; U.S. Department of Energy: Washington, DC, USA, 2010.
26. Fei, X.; Bao, Y.; Lu, S. Seaweed cultivation: Traditional way and its reformation. *Chin. J. Ocean. Limnol.* **1999**, *17*, 193–199.
27. Horn, S.V. *Bioenergy from Brown Seaweeds*; Norwegian University of Science and Technology (NTNU): Trondheim, Norway, 2000.
28. Black, W.A.P. The preservation of seaweed by ensiling and bactericides. *J. Sci. Food Agric.* **1955**, *6*, 14–23.
29. Uchida, M.; Miyoshi, T. Algal fermentation—the seed for a new fermentation industry of foods and related products. *Jpn. Agric. Res. Q.* **2013**, *47*, 53–63.
30. Wout, R.; Greenwell, H.; Davies, D.; Theodorou, M. Methods of Ensiling Algae, Ensiled Algae and Uses of Ensiled Algae. WO2013045931-A1, 4 April 2013.
31. McLaren, J. *Sugarcane as a Feedstock for Biofuels: An Analytical White Paper*; National Corn Growers Association: Chesterfield, MO, USA, 2009.
32. *Eurostat Handbook for Annual Crop Statistics*; European Commission Eurostat: Luxembourg, 2014.
33. Valderrama, D.; Cai, J.; Hishamunda, N.; Ridler, N. *Social and Economic Dimensions of Carrageenan Seaweed Farming*; FAO Fisheries and Aquaculture Technical Paper 580; Food and Agriculture Organisation of the United Nations (FAO): Rome, Italy, 2014.
34. Fudholi, A.; Sopian, K.; Othman, M.Y.; Ruslan, M.H. Energy and exergy analyses of solar drying system of red seaweed. *Energy Build.* **2014**, *68*, 121–129.
35. Brennan, L.; Owende, P. Biofuels from microalgae—A review of technologies for production, processing, and extractions of biofuels and co-products. *Renew. Sustain. Energy Rev.* **2010**, *14*, 557–577.
36. Oswald, W.J. Large-scale algal culture systems (engineering aspects). In *Micro-Algal Biotechnology*; Borowitzka, M.A., Borowitzka, L.J., Eds.; Cambridge University Press: Cambridge, UK, 1988.
37. Bruton, T.; Lyons, H.; Lerat, Y.; Stanley, M.; Rasmussen, M.B. *A Review of the Potential of Marine Algae as a Source of Biofuel in Ireland*; Sustainable Energy Ireland: Dublin, Ireland, 2009.
38. Demirbas, A. Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy Convers. Manag.* **2001**, *42*, 1357–1378.
39. Yu, L.J.; Wang, S.; Jiang, X.M.; Wang, N.; Zhang, C.Q. Thermal analysis studies on combustion characteristics of seaweed. *J. Therm. Anal. Calorim.* **2008**, *93*, 611–617.
40. Wang, S.; Jiang, X.M.; Wang, Q.; Han, X.X.; Ji, H.S. Experiment and grey relational analysis of seaweed particle combustion in a fluidized bed. *Energy Convers. Manag.* **2013**, *66*, 115–120.
41. Ross, A.B.; Jones, J.M.; Kubacki, M.L.; Bridgeman, T. Classification of macroalgae as fuel and its thermochemical behaviour. *Bioresour. Technol.* **2008**, *99*, 6494–6504.
42. McKendry, P. Energy production from biomass (part 2): Conversion technologies. *Bioresour. Technol.* **2002**, *83*, 47–54.

43. Varfolomeev, S.D.; Wasserman, L.A. Microalgae as source of biofuel, food, fodder, and medicines. *Appl. Biochem. Microbiol.* **2011**, *47*, 789–807.
44. Yantovski, E.I. Solar energy conversion through seaweed photosynthesis and zero emissions power generation. *Surface Eng. Appl. Electrochem.* **2008**, *44*, 138–145.
45. Saidur, R.; Abdelaziz, E.A.; Demirbas, A.; Hossain, M.S.; Mekhilef, S. A review on biomass as a fuel for boilers. *Renew. Sustain. Energy Rev.* **2011**, *15*, 2262–2289.
46. Misra, M.K.; Ragland, K.W.; Baker, A.J. Wood ash composition as a function of furnace temperature. *Biomass Bioenergy* **1993**, *4*, 103–116.
47. Alvarado-Morales, M.; Boldrin, A.; Karakashev, D.B.; Holdt, S.L.; Angelidaki, I.; Astrup, T. Life cycle assessment of biofuel production from brown seaweed in nordic conditions. *Bioresour. Technol.* **2013**, *129*, 92–99.
48. Bruhn, A.; Dahl, J.; Nielsen, H.B.; Nikolaisen, L.; Rasmussen, M.B.; Markager, S.; Olesen, B.; Arias, C.; Jensen, P.D. Bioenergy potential of ulva lactuca: Biomass yield, methane production and combustion. *Bioresour. Technol.* **2011**, *102*, 2595–2604.
49. Nikolaison, L.; Dahl, J.; Bech, K.S.; Bruhn, A.; Rasmussen, M.B.; Bjerre, A.B.; Nielsen, H.B.; Ambus, P.; Rost, K.A.; Kadar, Z.; *et al.* Energy production fom macroalgae. In Proceedings of the 20th European Biomass Conference, Milan, Italy, 18–22 June 2012.
50. Adams, J.M.M.; Ross, A.B.; Anastasakis, K.; Hodgson, E.M.; Gallagher, J.A.; Jones, J.M.; Donnison, I.S. Seasonal variation in the chemical composition of the bioenergy feedstock laminaria digitata for thermochemical conversion. *Bioresour. Technol.* **2011**, *102*, 226–234.
51. Milledge, J.J.; Staple, A.; Harvey, P. Pyrolysis of Invasive Seaweed Species. In Proceedings of the British Phycological Society Annual Meeting, Galway, Ireland, 25–27 June 2014.
52. Salter, A.; Banks, C. Anaerobic digestion: Overall energy balances—parasitic inputs & beneficial outputs. In Proceedings of the Sustainable Organic Resources Partnership—Advances in Biological Processes for Organics and Energy Recycling, Birmingham, UK, 15 May 2008.
53. Belosevic, S. Modeling approaches to predict biomass co-firing with pulverized coal. *Open Thermodyn. J.* **2010**, *4*, 50–70.
54. Kadam, K.L. Environmental implications of power generation via coal-microalgae cofiring. *Energy* **2002**, *27*, 905–922.
55. Li, L.; Rowbotham, J.S.; Greenwell, C.H.; Dyer, P.W. An introduction to pyrolysis and catalytic pyrolysis: Versatile techniques for biomass conversion. In *New and Future Developments in Catalysis : Catalytic Biomass Conversion*; Suib, S.L., Ed.; Elsevier: Amsterdam, The Netherlands, 2013; pp. 173–208.
56. Ghasemi, Y.; Rasoul-Amini, S.; Naseri, A.T.; Montazeri-Najafabady, N.; Mobasher, M.A.; Dabbagh, F. Microalgae biofuel potentials (review). *Appl. Biochem. Microbiol.* **2012**, *48*, 126–144.
57. Peacocke, C.; Joseph, S. Notes on Terminology and Technology in Thermal Conversion. Available online: http://www.biochar-international.org/publications/IBI#Pyrolysis_guidelines (accessed on 15 April 2014).
58. Miao, X.L.; Wu, Q.Y.; Yang, C.Y. Fast pyrolysis of microalgae to produce renewable fuels. *J. Anal. Appl. Pyrolysis* **2004**, *71*, 855–863.

59. Song, L.; Hu, M.; Liu, D.; Zhang, D.; Jiang, C. Thermal cracking of enteromorpha prolifera with solvents to bio-oil. *Energy Convers. Manag.* **2014**, *77*, 7–12.
60. Jena, U.; Das, K.C. Comparative evaluation of thermochemical liquefaction and pyrolysis for bio-oil production from microalgae. *Energy Fuels* **2011**, *25*, 5472–5482.
61. Marcilla, A.; Catalá, L.; García-Quesada, J.C.; Valdés, F.J.; Hernández, M.R. A review of thermochemical conversion of microalgae. *Renew. Sustain. Energy Rev.* **2013**, *27*, 11–19.
62. Bholá, V.; Desikan, R.; Santosh, S.K.; Subburamu, K.; Sanniyasi, E.; Bux, F. Effects of parameters affecting biomass yield and thermal behaviour of chlorella vulgaris. *J. Biosci. Bioeng.* **2011**, *111*, 377–382.
63. Demirbas, A. Hydrogen from mosses and algae via pyrolysis and steam gasification. *Energy Sources Part A-Recovery Util. Environ. Eff.* **2010**, *32*, 172–179.
64. Miao, X.L.; Wu, Q.Y. High yield bio-oil production from fast pyrolysis by metabolic controlling of chlorella protothecoides. *J. Biotechnol.* **2004**, *110*, 85–93.
65. Ozkurt, I. Qualifying of safflower and algae for energy. *Energy Educ. Sci. Technol.-Part A* **2009**, *23*, 145–151.
66. Du, Z.Y.; Li, Y.C.; Wang, X.Q.; Wan, Y.Q.; Chen, Q.; Wang, C.G.; Lin, X.Y.; Liu, Y.H.; Chen, P.; Ruan, R. Microwave-assisted pyrolysis of microalgae for biofuel production. *Bioresour. Technol.* **2011**, *102*, 4890–4896.
67. Trinh, T.N.; Jensen, P.A.; Dam-Johansen, K.; Knudsen, N.O.; Sorensen, H.R.; Hvilsted, S. Comparison of lignin, macroalgae, wood, and straw fast pyrolysis. *Energy Fuels* **2013**, *27*, 1399–1409.
68. Yanik, J.; Stahl, R.; Troeger, N.; Sinag, A. Pyrolysis of algal biomass. *J. Anal. Appl. Pyrolysis* **2013**, *103*, 134–141.
69. Wang, S.; Wang, Q.; Jiang, X.M.; Han, X.X.; Ji, H.S. Compositional analysis of bio-oil derived from pyrolysis of seaweed. *Energy Convers. Manag.* **2013**, *68*, 273–280.
70. Rowbotham, J.S.; Dyer, P.W.; Greenwell, H.C.; Selby, D.; Theodorou, M.K. Copper(II)-mediated thermolysis of alginates: A model kinetic study on the influence of metal ions in the thermochemical processing of macroalgae. *Interface Focus* **2013**, *3*, doi: 10.1098/rsfs.2012.0046.
71. Stratford, J.P.; Hutchings, T.R.; de Leij, F.A.A.M. Intrinsic activation: The relationship between biomass inorganic content and porosity formation during pyrolysis. *Bioresour. Technol.* **2014**, *159*, 104–111.
72. Choi, J.; Choi, J.-W.; Suh, D.J.; Ha, J.-M.; Hwang, J.W.; Jung, H.W.; Lee, K.-Y.; Woo, H.-C. Production of brown algae pyrolysis oils for liquid biofuels depending on the chemical pretreatment methods. *Energy Convers. Manag.* **2014**, *86*, 371–378.
73. Bridgwater, A.V. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* **2012**, *38*, 68–94.
74. Peng, W.M.; Wu, Q.Y.; Tu, P.G. Effects of temperature and holding time on production of renewable fuels from pyrolysis of chlorella protothecoides. *J. Appl. Phycol.* **2000**, *12*, 147–152.
75. Rowbotham, J.S.; Dyer, P.W.; Greenwell, H.C.; Theodorou, M.K. Thermochemical processing of macroalgae: A late bloomer in the development of third-generation biofuels? *Biofuels* **2012**, *3*, 441–461.

76. Williams, P.T.; Besler, S. The influence of temperature and heating rate on the pyrolysis of biomass. *Renew. Energy* **1996**, *7*, 233–250.
77. Zhao, H.; Yan, H.X.; Liu, M.; Sun, B.B.; Zhang, Y.; Dong, S.S.; Qi, L.B.; Qin, S. Production of bio-oil from fast pyrolysis of macroalgae enteromorpha prolifera powder in a free-fall reactor. *Energy Sources Part A-Recovery Util. Environ. Eff.* **2013**, *35*, 859–867.
78. Lee, H.W.; Choi, S.J.; Park, S.H.; Jeon, J.-K.; Jung, S.-C.; Joo, S.H.; Park, Y.-K. Catalytic conversion of laminaria japonica over microporous zeolites. *Energy* **2014**, *66*, 2–6.
79. Maddi, B.; Viamajala, S.; Varanasi, S. Comparative study of pyrolysis of algal biomass from natural lake blooms with lignocellulosic biomass. *Bioresour. Technol.* **2011**, *102*, 11018–11026.
80. Anex, R.P.; Aden, A.; Kazi, F.K.; Fortman, J.; Swanson, R.M.; Wright, M.M.; Satrio, J.A.; Brown, R.C.; Daugaard, D.E.; Platon, A.; *et al.* Techno-economic comparison of biomass-to-transportation fuels via pyrolysis, gasification, and biochemical pathways. *Fuel* **2010**, *89*, S29–S35.
81. Babich, I.V.; van der Hulst, M.; Lefferts, L.; Moulijn, J.A.; O'Connor, P.; Seshan, K. Catalytic pyrolysis of microalgae to high-quality liquid bio-fuels. *Biomass Bioenergy* **2011**, *35*, 3199–3207.
82. Bird, K.T.; Benson, P.H. *Seaweed Cultivation for Renewable Resources*; Elsevier: Bergen, Norway, 1987.
83. Viger, M.; Hancock, R.D.; Miglietta, F.; Taylor, G. More plant growth but less plant defence? First global gene expression data for plants grown in soil amended with biochar. *GCB Bioenergy* **2014**, doi:10.1111/gcbb.12182.
84. McKendry, P. Energy production from biomass (part 3): Gasification technologies. *Bioresour. Technol.* **2002**, *83*, 55–63.
85. *Production of Bio-Methanol-Technology Brief*; International Renewable Energy Agency (IRENA): Abu Dhabi, UAE, 2013.
86. Ahmed, I.I.; Gupta, A.K. Pyrolysis and gasification of food waste: Syngas characteristics and char gasification kinetics. *Appl. Energy* **2010**, *87*, 101–108.
87. Hayashi, J.-I.; Kudo, S.; Kim, H.-S.; Norinaga, K.; Matsuoka, K.; Hosokai, S. Low-temperature gasification of biomass and lignite: Consideration of key thermochemical phenomena, rearrangement of reactions, and reactor configuration. *Energy Fuels* **2013**, *28*, 4–21.
88. Guan, Q.Q.; Savage, P.E.; Wei, C.H. Gasification of alga nannochloropsis sp in supercritical water. *J. Supercrit. Fluids* **2012**, *61*, 139–145.
89. Guan, Q.Q.; Wei, C.H.; Savage, P.E. Kinetic model for supercritical water gasification of algae. *Phys. Chem. Chem. Phys.* **2012**, *14*, 3140–3147.
90. Woolf, D.; Lehmann, J.; Fisher, E.M.; Angenent, L.T. Biofuels from pyrolysis in perspective: Trade-offs between energy yields and soil-carbon additions. *Environ. Sci. Technol.* **2014**, *48*, 6492–6499.
91. Cherad, R.; Onwudili, J.A.; Ekpo, U.; Williams, P.T.; Lea-Langton, A.R.; Carmargo-Valero, M.; Ross, A.B. Macroalgae supercritical water gasification combined with nutrient recycling for microalgae cultivation. *Environ. Prog. Sustain. Energy* **2013**, *32*, 902–909.
92. Onwudili, J.A.; Lea-Langton, A.R.; Ross, A.B.; Williams, P.T. Catalytic hydrothermal gasification of algae for hydrogen production: Composition of reaction products and potential for nutrient recycling. *Bioresour. Technol.* **2013**, *127*, 72–80.

93. Kwon, E.E.; Jeon, Y.J.; Yi, H. New candidate for biofuel feedstock beyond terrestrial biomass for thermo-chemical process (pyrolysis/gasification) enhanced by carbon dioxide (CO₂). *Bioresour. Technol.* **2012**, *123*, 673–677.
94. Ross, A.B.; Anastasakis, K.; Kubacki, M.; Jones, J.M. Investigation of the pyrolysis behaviour of brown algae before and after pre-treatment using PY-GC/MS and TGA. *J. Anal. Appl. Pyrolysis* **2009**, *85*, 3–10.
95. Kaewpanha, M.; Guan, G.; Hao, X.; Wang, Z.; Kasai, Y.; Kusakabe, K.; Abudula, A. Steam co-gasification of brown seaweed and land-based biomass. *Fuel Process. Technol.* **2014**, *120*, 106–112.
96. Rizkiana, J.; Guan, G.Q.; Widayatno, W.B.; Hao, X.G.; Huang, W.; Tsutsumi, A.; Abudula, A. Effect of biomass type on the performance of cogasification of low rank coal with biomass at relatively low temperatures. *Fuel* **2014**, *134*, 414–419.
97. Singh, J.; Gu, S. Biomass conversion to energy in India—A critique. *Renew. Sustain. Energy Rev.* **2010**, *14*, 1367–1378.
98. Ventura, J.-R.S.; Yang, B.; Lee, Y.-W.; Lee, K.; Jahng, D. Life cycle analyses of CO₂, energy, and cost for four different routes of microalgal bioenergy conversion. *Bioresour. Technol.* **2013**, *137*, 302–310.
99. Delrue, F.; Seiter, P.A.; Sahut, C.; Cournac, L.; Roubaud, A.; Peltier, G.; Froment, A.K. An economic, sustainability, and energetic model of biodiesel production from microalgae. *Bioresour. Technol.* **2012**, *111*, 191–200.
100. Dry, M.E. The fischer-tropsch process: 1950–2000. *Catal. Today* **2002**, *71*, 227–241.
101. De Klerk, A.; Furimsky, E. Fischer-tropsch synthesis. In *Catalysis in the Refining of Fischer-Tropsch Syncrude*; The Royal Society of Chemistry: Cambridge, UK, 2010; pp. 11–23.
102. *Affordable, Low-Carbon Diesel Fuel from Domestic Coal and Biomass*; DOE/NETL-2009/1349; National Energy Technology Laboratory NETL: Morgantown, WV, USA, 2009.
103. Van Steen, E.; Claeys, M. Fischer-tropsch catalysts for the biomass-to liquid process. *Chem. Eng. Technol.* **2008**, *31*, 655–666.
104. Jahangiri, H.; Bennett, J.; Mahjoubi, P.; Wilson, K.; Gu, S. A review of advanced catalyst development for fischer-tropsch synthesis of hydrocarbons from biomass derived syn-gas. *Catal. Sci. Technol.* **2014**, *4*, 2210–2229.
105. Triantafyllidis, K.; Lappas, A.; Stöcker, M. *The Role of Catalysis for the Sustainable Production of Bio-Fuels and Bio-Chemicals*; Elsevier Science: Amsterdam, The Netherlands, 2013.
106. Derouane, E.G.; Parmon, V.; Lemos, F.; Ribeiro, F.R. *Sustainable Strategies for the Upgrading of Natural Gas: Fundamentals, Challenges, and Opportunities*; Springer: Dordrecht, The Netherlands, 2005.
107. Lapidus, A.L. The mechanism of hydrocarbon synthesis from Co and H₂ on cobalt catalysts. *Solid Fuel Chem.* **2013**, *47*, 315–328.
108. Leckel, D. Hydrocracking of iron-catalyzed fischer-tropsch waxes. *Energy Fuels* **2005**, *19*, 1795–1803.
109. Hamelinck, C.N.; Faaij, A.P.C.; den Uil, H.; Boerrigter, H. Production of FT transportation fuels from biomass; technical options, process analysis and optimisation, and development potential. *Energy* **2004**, *29*, 1743–1771.

110. Maitlis, P.M.; de Klerk, A. *Greener Fischer-Tropsch Processes for Fuels and Feedstocks*; Wiley-VCH: Weinheim, Germany, 2013.
111. Tijmensen, M.J.A.; Faaij, A.P.C.; Hamelinck, C.N.; van Hardeveld, M.R.M. Exploration of the possibilities for production of fischer tropsch liquids and power via biomass gasification. *Biomass Bioenergy* **2002**, *23*, 129–152.
112. Huang, G.; Chen, F.; Wei, D.; Zhang, X.; Chen, G. Biodiesel production by microalgal biotechnology. *Appl. Energy* **2010**, *87*, 38–46.
113. Bahadar, A.; Bilal Khan, M. Progress in energy from microalgae: A review. *Renew. Sustain. Energy Rev.* **2013**, *27*, 128–148.
114. Lenstra, W.J.; Hal, J.W.V.; Reith, J.H. Economic aspects of open ocean seaweed cultivation. In Proceedings of the Alg'n Chem 2011, Algae, New Resources for Industry, Montpellier, France, 7–10 November 2011.
115. Streefland, M. *Report on Biofuel Production Processes from Micro, Macroalgae and Other Aquatic Biomass*; AquaFUELS: Brussels, Belgium, 2010.
116. 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.
117. Sialve, B.; Bernet, N.; Bernard, O. Anaerobic digestion of microalgae as a necessary step to make microalgal biodiesel sustainable. *Biotechnol. Adv.* **2009**, *27*, 409–416.
118. Heaven, S.; Milledge, J.; Zhang, Y. Comments 'on anaerobic digestion of microalgae as a necessary step to make microalgal biodiesel sustainable'. *Biotechnol. Adv.* **2011**, *29*, 164–167.
119. Aresta, M.; Dibenedetto, A.; Carone, M.; Colonna, T.; Fragale, C. Production of biodiesel from macroalgae by supercritical CO₂ extraction and thermochemical liquefaction. *Environ. Chem. Lett.* **2005**, *3*, 136–139.
120. Suganya, T.; Renganathan, S. Optimization and kinetic studies on algal oil extraction from marine macroalgae *Ulva lactuca*. *Bioresour. Technol.* **2012**, *107*, 319–326.
121. 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.
122. 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*, 4876–4883.
123. Florentinus, A.; Harmelinck, C.; Lint, S.D.; Iersel, S.V. *Worldwide Potential of Aquatic Biomass*; Ecofys: Utrecht, The Netherlands, 2008.
124. Neveux, N.; Yuen, A.K.L.; Jazrawi, C.; Magnusson, M.; Haynes, B.S.; Masters, A.F.; Montoya, A.; Paul, N.A.; Maschmeyer, T.; de Nys, R. Biocrude yield and productivity from the hydrothermal liquefaction of marine and freshwater green macroalgae. *Bioresour. Technol.* **2014**, *155*, 334–341.
125. Minowa, T.; Yokoyama, S.; Kishimoto, M.; Okakura, T. Oil production from algal cells of *Dunaliella-tertiolecta* by direct thermochemical liquefaction. *Fuel* **1995**, *74*, 1735–1738.
126. Sawayama, S.; Minowa, T.; Yokoyama, S.Y. Possibility of renewable energy production and CO₂ mitigation by thermochemical liquefaction of microalgae. *Biomass Bioenergy* **1999**, *17*, 33–39.

127. Brown, T.M.; Duan, P.; Savage, P.E. Hydrothermal liquefaction and gasification of *Nannochloropsis sp.* *Energy Fuels* **2010**, *24*, 3639–3646.
128. Torri, C.; Alba, L.G.; Samori, C.; Fabbri, D.; Brillman, D.W.F. Hydrothermal treatment (HTT) of microalgae: Detailed molecular characterization of HTT oil in view of htt mechanism elucidation. *Energy Fuels* **2012**, *26*, 658–671.
129. Vardon, D.R.; Sharma, B.K.; Blazina, G.V.; Rajagopalan, K.; Strathmann, T.J. Thermochemical conversion of raw and defatted algal biomass via hydrothermal liquefaction and slow pyrolysis. *Bioresour. Technol.* **2012**, *109*, 178–187.
130. Alba, L.G.; Torri, C.; Samori, C.; van der Spek, J.; Fabbri, D.; Kersten, S.R.A.; Brillman, D.W.F. Hydrothermal treatment of microalgae: Evaluation of the process as conversion method in an algae biorefinery concept. *Energy Fuels* **2012**, *26*, 642–657.
131. Bach, Q.-V.; Sillero, M.V.; Tran, K.-Q.; Skjermo, J. Fast hydrothermal liquefaction of a norwegian macro-alga: Screening tests. *Algal Res.* **2014**, doi:10.1016/j.algal.2014.05.009.
132. Jin, B.; Duan, P.; Xu, Y.; Wang, F.; Fan, Y. Co-liquefaction of micro- and macroalgae in subcritical water. *Bioresour. Technol.* **2013**, *149*, 103–110.
133. Yang, J.; Xu, M.; Zhang, X.Z.; Hu, Q.A.; Sommerfeld, M.; Chen, Y.S. Life-cycle analysis on biodiesel production from microalgae: Water footprint and nutrients balance. *Bioresour. Technol.* **2011**, *102*, 159–165.
134. Balat, M.; Balat, H.; Oz, C. Progress in bioethanol processing. *Prog. Energy Combust. Sci.* **2008**, *34*, 551–573.
135. U.S. Department of Energy (DOE). *National Algal Biofuels Technology Roadmap*; U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Biomass Program: Washington, DC, USA, 2010.
136. Puri, D.J.; Heaven, S.; Banks, C.J. Improving the performance of enzymes in hydrolysis of high solids paper pulp derived from MSW. *Biotechnol. Biofuels* **2013**, *6*, doi:10.1186/1754-6834-6-107.
137. Gressel, J. Transgenics are imperative for biofuel crops. *Plant Sci.* **2008**, *174*, 246–263.
138. Yanagisawa, M.; Kawai, S.; Murata, K. Strategies for the production of high concentrations of bioethanol from seaweeds: Production of high concentrations of bioethanol from seaweeds. *Bioengineered* **2013**, *4*, 224–235.
139. Golberg, A.; Vitkin, E.; Linshiz, G.; Khan, S.A.; Hillson, N.J.; Yakhini, Z.; Yarmush, M.L. Proposed design of distributed macroalgal biorefineries: Thermodynamics, bioconversion technology, and sustainability implications for developing economies. *Biofuels Bioprod. Biorefining* **2014**, *8*, 67–82.
140. Borines, M.G.; de Leon, R.L.; Cuello, J.L. Bioethanol production from the macroalgae *Sargassum spp.* *Bioresour. Technol.* **2013**, *138*, 22–29.
141. Jung, K.A.; Lim, S.R.; Kim, Y.; Park, J.M. Potentials of macroalgae as feedstocks for biorefinery. *Bioresour. Technol.* **2013**, *135*, 182–190.
142. Wei, N.; Quarterman, J.; Jin, Y.S. Marine macroalgae: An untapped resource for producing fuels and chemicals. *Trends Biotechnol.* **2013**, *31*, 70–77.
143. Yoza, B.A.; Masutani, E.M. The analysis of macroalgae biomass found around Hawaii for bioethanol production. *Environ. Technol.* **2013**, *34*, 1859–1867.

144. Meinita, M.; Hong, Y.-K.; Jeong, G.-T. Detoxification of acidic catalyzed hydrolysate of *Kappaphycus alvarezii* (cottonii). *Bioprocess Biosyst. Eng.* **2012**, *35*, 93–98.
145. 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.
146. Meinita, M.D.N.; Marhaeni, B.; Winanto, T.; Jeong, G.T.; Khan, M.N.A.; Hong, Y.K. Comparison of agarophytes (*Gelidium*, *Gracilaria*, and *Gracilariopsis*) as potential resources for bioethanol production. *J. Appl. Phycol.* **2013**, *25*, 1957–1961.
147. 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.; *et al.* An engineered microbial platform for direct biofuel production from brown macroalgae. *Science* **2012**, *335*, 308–313.
148. Aizawa, M.; Asaoka, K.; Atsumi, M.; Sakou, T. Seaweed Bioethanol Production in Japan—The Ocean Sunrise Project. In Proceedings of the OCEANS 2007, Vancouver, BC, Canada, 29 September–4 October 2007; pp. 1–5.
149. Beal, C.M. Algal Biofuels: Energy and Water. In *WEG Symposium*; University of Texas: Austin, TX, USA, 2011.
150. Walker, D.A. Biofuels—for better or worse? *Ann. Appl. Biol.* **2010**, *156*, 319–327.
151. Philippsen, A. *Energy Input, Carbon Intensity, and Cost for Ethanol Produced from Brown Seaweed*; University of Victoria: Victoria, BC, Canada, 2013.
152. Huesemann, M.; Roesjadi, G.; Benemann, J.; Metting, F.B. Biofuels from Microalgae and Seaweeds. In *Biomass to Biofuels*; Blackwell Publishing Ltd.: Oxford, UK, 2010; pp. 165–184.
153. Horn, S.J.; Aasen, I.M.; Ostgaard, K. Ethanol production from seaweed extract. *J. Ind. Microbiol. Biotechnol.* **2000**, *25*, 249–254.
154. Parliamentary Office of Science & Technology. *Biofuels from Algae*; Postnote: London, UK, 2011.
155. Potts, T.; Du, J.; Paul, M.; May, P.; Beitle, R.; Hestekin, J. The production of butanol from Jamaica bay macro algae. *Environ. Prog. Sustain. Energy* **2012**, *31*, 29–36.
156. Sutherland, A.; Varela, J. Comparison of various microbial inocula for the efficient anaerobic digestion of *Laminaria hyperborea*. *BMC Biotechnol.* **2014**, *14*, doi:10.1186/1472-6750-14-7.
157. Biomara. A Short History of Seaweed Exploitation in the Western British Isles. Available online: <http://www.biomara.org/understanding-seaweed/the-importance-of-seaweed-across-the-ages> (accessed on 27 January 2014).
158. Discover Tiree. Brown Gold. Available online: <http://www.isleoftiree.com/about-tiree/the-land/> (accessed on 27 January 2014).
159. Park, J.B.K.; Craggs, R.J.; Shilton, A.N. Wastewater treatment high rate algal ponds for biofuel production. *Bioresour. Technol.* **2011**, *102*, 35–42.
160. Samson, R.; LeDuy, A. Improved performance of anaerobic digestion of spirulina maxima algal biomass by addition of carbon-rich wastes. *Biotechnol. Lett.* **1983**, *5*, 677–682.
161. Gonzalez-Fernandez, C.; Sialve, B.; Bernet, N.; Steyer, J.P. Impact of microalgae characteristics on their conversion to biofuel. Part II: Focus on biomethane production. *Biofuels Bioprod. Biorefining* **2012**, *6*, 205–218.
162. Park, S.; Li, Y.B. Evaluation of methane production and macronutrient degradation in the anaerobic co-digestion of algae biomass residue and lipid waste. *Bioresour. Technol.* **2012**, *111*, 42–48.

163. Weiland, P. Biogas production: Current state and perspectives. *Appl. Microbiol. Biotechnol.* **2010**, *85*, 849–860.
164. Zamalloa, C.; Vulsteke, E.; Albrecht, J.; Verstraete, W. The techno-economic potential of renewable energy through the anaerobic digestion of microalgae. *Bioresour. Technol.* **2011**, *102*, 1149–1158.
165. Buswell, A.M.; Mueller, H.F. Mechanism of methane fermentation. *Ind. Eng. Chem.* **1952**, *44*, 550–552.
166. Symons, G.E.; Buswell, A.M. The methane fermentation of carbohydrates. *J. Am. Chem. Soc.* **1933**, *55*, 2028–2036.
167. Golueke, C.G.; Oswald, W.J.; Gotaas, H.B. Anaerobic digestion of algae. *Appl. Microbiol.* **1957**, *5*, 47–55.
168. Hilton, M.G.; Archer, D.B. Anaerobic digestion of a sulfate-rich molasses wastewater: Inhibition of hydrogen sulfide production. *Biotechnol. Bioeng.* **1988**, *31*, 885–888.
169. Hierholtzer, A.; Akunna, J.C. Modelling sodium inhibition on the anaerobic digestion process. *Water Sci. Technol.* **2012**, *66*, 1565–1573.
170. Lefebvre, O.; Moletta, R. Treatment of organic pollution in industrial saline wastewater: A literature review. *Water Res.* **2006**, *40*, 3671–3682.
171. Chen, Y.; Cheng, J.J.; Creamer, K.S. Inhibition of anaerobic digestion process: A review. *Bioresour. Technol.* **2008**, *99*, 4044–4064.
172. Chen, W.H.; Han, S.K.; Sung, S. Sodium inhibition of thermophilic methanogens. *J. Environ. Eng.-ASCE* **2003**, *129*, 506–512.
173. Ramakrishnan, B.; Kumaraswamy, S.; Mallick, K.; Adhya, T.K.; Rao, V.R.; Sethunathan, N. Effect of various anionic species on net methane production in flooded rice soils. *World J. Microbiol. Biotechnol.* **1998**, *14*, 743–749.
174. El-Dessouky, H.T.; Ettouney, H.M. *Fundamentals of Salt Water Desalination*; Elsevier: Amsterdam, The Netherlands, 2002.
175. Tedesco, S.; Barroso, T.M.; Olabi, A.G. Optimization of mechanical pre-treatment of *Laminariaceae spp.* Biomass-derived biogas. *Renew. Energy* **2014**, *62*, 527–534.
176. Ter Veld, F. Beyond the fossil fuel era: On the feasibility of sustainable electricity generation using biogas from microalgae. *Energy Fuels* **2012**, *26*, 3882–3890.
177. Milledge, J.J. Micro-algal biorefineries. In *Towards Establishing Value Chains for Bioenergy*; The African, Caribbean and Pacific Group of States (ACP) Science and Technology Programme: Swakopmund, Namibia, 2013.
178. Lenstra, W.J.; Reith, J.H.; Hal, J.W.V. Economic Perspectives of Seaweed. In Proceedings of the 4th International Algae Congress, Amsterdam, The Netherlands, 1–2 December 2010.
179. Milledge, J.J. Commercial application of microalgae other than as biofuels: A brief review. *Rev. Environ. Sci. Biotechnol.* **2011**, *10*, 31–41.
180. Milledge, J.J. Micro-Algal Process Flow-Sheet Energy Balance Optimisation: Initial Software Evaluation. In *Algal Biotechnology: Biofuels and Beyond*; University College (UCL): London, UK, 2012.

181. Milledge, J.J. The Challenge of Algal Fuel: Economic Processing of the Entire Algal Biomass. In *Condensed Matter—Materials Engineering Newsletter*; McMaster University: Hamilton, PA, USA, 2010; Volume 1, pp. 4–6.
182. Hannon, M.; Gimpel, J.; Tran, M.; Rasala, B.; Mayfield, S. Biofuels from algae: Challenges and potential. *Biofuels* **2010**, *1*, 763–784.
183. Taylor, G. Biofuels and the biorefinery concept. *Energy Policy* **2008**, *36*, 4406–4409.
184. Olguin, E.J. Dual purpose microalgae-bacteria-based systems that treat wastewater and produce biodiesel and chemical products within a biorefinery. *Biotechnol. Adv.* **2012**, *30*, 1031–1046.
185. Gonzalez-Delgado, A.D.; Kafarov, V. Microalgae based biorefinery: Issues to consider. A review. *CTF Cienc. Tecnol. Futuro* **2011**, *4*, 5–21.
186. Rawat, I.; Ranjith Kumar, R.; Mutanda, T.; Bux, F. Biodiesel from microalgae: A critical evaluation from laboratory to large scale production. *Appl. Energy* **2013**, *103*, 444–467.
187. Singh, U.; Ahluwalia, A. Microalgae: A promising tool for carbon sequestration. *Mitig. Adapt. Strateg. Glob. Chang.* **2013**, *18*, 73–95.
188. Pires, J.C.M.; Alvim-Ferraz, M.C.M.; Martins, F.G.; Simoes, M. Carbon dioxide capture from flue gases using microalgae: Engineering aspects and biorefinery concept. *Renew. Sustain. Energy Rev.* **2012**, *16*, 3043–3053.
189. Cherubini, F. The biorefinery concept: Using biomass instead of oil for producing energy and chemicals. *Energy Convers. Manag.* **2010**, *51*, 1412–1421.

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