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Anaerobic Digestion and Gasification of Seaweed

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Abstract The potential of algal biomass as a source of liquid and gaseous biofuels is a highly topical theme, with over 70 years of sometimes intensive research, and considerable financial investment. A wide range of unit operations can be combined to produce algal biofuel, but as yet there is no successful commercial system producing such biofuel. This suggests that there are major technical and engineering difficulties to be resolved before economically viable algal biofuel production can be achieved.

Both gasification and anaerobic digestion have been suggested as promising methods for exploiting bioenergy from biomass and 2 major projects have been funded in the UK on the gasification and anaerobic digestion of seaweed, MacroBioCrude and SeaGas.

This chapter discusses the use of gasification and anaerobic digestion of seaweed for the production of biofuel.

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1. Introduction

Global utilisation of macroalgae is a multi-billion dollar industry (Smit 2004; Milledge and Harvey 2016b) with world production of seaweed increasing, between 1970 and 2010 from < 2 million to 19 million tonnes fresh weight (Yeong et al. 2014). The volume of seaweed commercially produced has increased by 8% per annum in the last decade with seaweed production reported at 27 million tonnes in 2014 (FAO 2016), and the commercial seaweed market is projected to grow to US$ 17.6 billion in 2021(Research and Markets 2016). The current uses of seaweeds include human foods, fertilisers, phycocolloids and cosmetic ingredients (Kraan 2013), with Asia being the main market (Kelly and Dworjanyn 2008; Roesijadi et al. 2010a), and the macroalgal non-fuel industry being currently 100 times bigger globally in wet tonnage terms than the microalgal industry (Ross et al. 2008; Lundquist et al. 2010; Chen et al. 2015b). However, seaweed is still considered an under-utilised resource worldwide (Marquez et al. 2014).

Algae, unlike terrestrial crops, 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 (Milledge and Heaven 2014; Chen et al. 2015b). The potential biomass yield of algae per unit area is also often higher than that of terrestrial plants with, for example, brown seaweeds grown 'under cultured conditions' having yields of ~13.1 kg dry weight (dw) m^{-2} yr^{-1}compared to ~10 kg dw m^{-2} yr^{-1} from sugarcane (Leu and Boussiba 2014; Rajkumar et al. 2014). This high potential biomass yield and growth systems that do not compete for land or freshwater with agricultural crops has led to research interest in the use of algae as a source of biofuel (Chen et al. 2015a; Kerrison et al. 2015), but much of the research on algal biofuels has been focused on micro rather

than macroalgae (Figure 1). Nevertheless despite their obvious potential and considerable research, there are no economically-viable commercial-scale quantities of fuel from either micro or macroalgae (Milledge and Harvey 2016b).

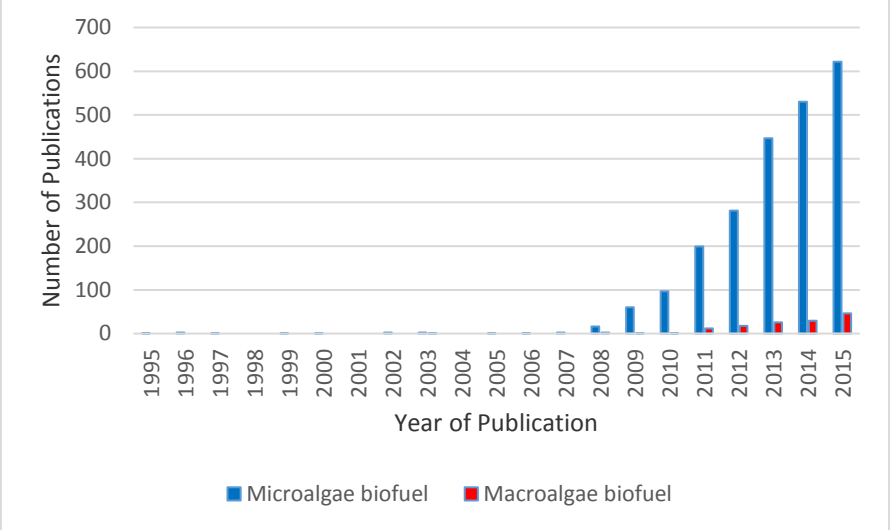

Figure 1 Number of publications per year in Web of Science for the search terms microalgae biofuel and macroalgae biofuel

The process operations used for algal-derived fuel production can be grouped into 4 main areas:

i. cultivation (including seedling 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. This chapter focuses on the methods of energy extraction from

macroalgae and in particular anaerobic digestion and gasification of macroalgae.

2. Method of Converting Seaweed to Biofuels

The methods of extraction of energy from macroalgae can be categorised according to whether an initial drying step is required or not. This leads to two distinct groups of processes (Milledge and Heaven 2014; Milledge and Harvey 2016b):

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 (AD)

A summary of the potential methods of energy extraction is given in Table 1, detailing the primary energy products and two major process parameters, the need for drying prior to processing and the potential to utilise the entire organic biomass feedstock, both of which have significant impacts on the overall energy balance of macroalgal biofuel.

Table 1 Methods of energy extraction from macroalgal biomass

	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

2.1. Seaweed as a feedstock

The composition of a biomass feedstock will influence the processing methods to produce biofuel. The water content of macroalgae (80-90%) is generally higher than that of many terrestrial crops (sugarcane ~75%, grain maize 14-31%) (McLaren 2009; Zhou et al. 2010; European Commission 2014; Rajkumar et al. 2014), and thus may be better suited to wet processing methods. The elemental analysis and Higher Heating Value (HHV) for a number of seaweeds is presented in Table 2. The HHV of seaweed is generally lower than terrestrial energy crops (17–20 kJ g^{-1} dw) due to their high ash content (Ross et al. 2008). Sulphur content of seaweed is generally higher than terrestrial plants with the sulphated polysaccharides of seaweeds also being chemically very different from those of land plants with those in brown seaweed being mainly sulphated fucans (fucoidans), with other sulphated polysaccharides containing galactose, xylose, glucose and other simple sugars also being found (Berteau and Mulloy 2003; Rodriguez-Jasso et al. 2014). The growth in a marine environment also results in the salt (sodium chloride) content of seaweed being higher than terrestrial plants with salt being 15% of dried weight of unwashed *Sargassum muticum* (Milledge and Harvey 2016a). The higher moisture, ash, salt and sulphur content of seaweed has considerable implications for the energy extraction from seaweed.

Table 2 Compositional and Higher Heating Value (HHV) data for some species of seaweed being considered as potential biofuels

	Ash	**Carbon**	**Hydrogen**	**Oxygen**	**Nitrogen**	**Sulphur**	**HHV**
	% dw	% dw	% dw	% dw	% dw	% dw	MJ kg^{-1} dw
Ascophyllum nodosum[1]	21.1	37.3	5.2	31.0	3.0	2.5	15.6
Chorda filum[2]	11.61	39.14	4.69	37.23	1.42	1.62	15.6
Enteromorpha prolif-era[3]	30.1	28.75	5.22	32.28	3.65	0	12.2*
Fucus serratus[2]	23.36	33.5	4.78	34.44	2.39	1.31	16.7
Fucus vesiculosus[2]	22.82	32.88	4.77	35.63	2.53	2.44	15.0
Laminaria digitata[2]	25.75	31.59	4.85	34.16	0.9	2.44	17.6
Laminaria hyperborea[2]	17.97	34.97	5.31	35.09	1.12	2.06	16.5
Laminaria saccharin4[3]	24.2	31.3	3.7	36.3	2.4	0.7	11.1*
Macrocyctis pyrifera[2]	38.35	27.3	4.08	34.8	2.03	1.89	16.0

[1] (Milledge and Harvey 2016b) [2] (Ross et al. 2008) [3] (Zhou et al. 2010) [4] (Anastasakis and Ross 2011) * Calculated using version of the DuLong equation (IFRF. International Flame Research Foundation 2004; Heaven et al. 2011)

2.2. Dewatering and drying 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 Energy Return on Investment (EROI). The energy to heat water from 20 to 100°C and evaporate it at atmospheric pressure requires an energy input of approximately 2.6 MJ kg^{-1} or over 700 kWh m^{-3} (Milledge and Heaven 2014). The removal of water from the algal biomass by evaporation can, therefore, be very energy intensive, and 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 (Valderrama et al. 2014).

Sun-drying is the main method of drying seaweed, (Aresta et al. 2005; Fudholi et al. 2014; Valderrama et al. 2014). 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 (Valderrama et al. 2014). Despite these limitations, solar methods are the least expensive drying option (Brennan and Owende 2010), but large areas are required as only around 100 g of dry matter can be produced from each square metre of sun-drier surface (Oswald 1988).

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 (Bruton et al. 2009). The energy to dry a seaweed with a moisture content of 88% has been calculated to be 0.7 MJ kg^{-1}, higher than the Lower Heating Value (LHV) of dry seaweed (Bruton et al. 2009).

The dewatering (the removal of water by mechanical methods from the algal biomass, such as pressing and centrifugation) generally uses less energy than evaporation to remove water and may be a useful step prior to drying to reduce overall energy input. However, screw-pressing brown

seaweed has been found to be infective unless the seaweed is pre-treated with hydrochloric acid (Gallagher et al. 2017) adding cost to mechanical dewatering. Reducing the moisture content of the seaweed is also beneficial as it prevents the growth of spoilage-causing microorganisms and slows down detrimental enzymatic reactions (Valderrama et al. 2014), but 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 (Bruton et al. 2009). The reduction of seaweed biomass moisture content to 20–30% not only increases 'shelf-life', but also reduces transportation costs (Bruton et al. 2009; Gallagher et al. 2017).

2.3. Direct Combustion

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 (Demirbas 2001). Macroalgal combustion does not appear to have been greatly explored (Yu et al. 2008; Wang et al. 2013). However, the high energy required to dry seaweed, the relatively low thermal values and high ash and sulphur of content, that can cause fouling and corrosion of boiler and unacceptable emissions, could preclude direct combustion as an economic method of exploiting seaweed (Yu et al. 2008; Wang et al. 2013; Milledge et al. 2014; Smith and Ross 2016).

2.4. Biodiesel

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 (Huang et al. 2010; Bahadar and Bilal Khan 2013; Milledge and Heaven 2014). Macroalgal biomass typically has lower lipid content, 0.3-6% compared to microalgae which can have over 70% (Streefland 2010; Lenstra et al. 2011; Murphy et al. 2013; van der Wal et al. 2013). Macroalgae would, therefore, not appear to be a suitable feedstock for the production of biodiesel via trans-esterification.

2.5. Bioethanol

First generation bioethanol, such as that produced from corn in the USA and sugarcane ethanol in Brazil, is now widely produced and used, and currently is the liquid biofuel with the highest production volume (> 90 GL) (Yang et al. 2011; Rosillo-Calle 2016). 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 (Walker 2010). 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 (Jung et al. 2013). Although polysaccharides are the predominant component of macroalgae making up to 76% of the total dry weight, and typically ~50% (Tiwari and Troy 2015), the polysaccharide composition of brown seaweed is different to that of terrestrial plants with the major polysaccharides of brown algae being Laminarin, Mannitol, Alginate and Fucoidan (Jung et al. 2013). These algal polysaccharides have been found to be difficult to ferment using conventional bioethanol technology and require considerable pre-treatment for the production of bioethanol (Yanagisawa et al. 2013; Kawai and Murata 2016). Wargacki et al. (2012) have concluded that the full potential of ethanol production from macroalgae cannot currently be realised because of the inability of industrial microbes to metabolise alginate polysaccharides. Research is currently being undertaken to increase bioethanol yield by using organisms that produce alginate lyases, such as *Vibrio splendidus* and engineered *Escherichia coli* to produce ethanol from alginate by expressing the requisite metabolic, transporter, and lyase genes from *V. splendidus* (Wargacki et al. 2012; Badur et al. 2015). Using organisms engineered with alginate lyases yields of ~80% of the maximum theoretical yield from macroalgae have been achieved (Wargacki et al. 2012).

Large seaweed ethanol production facilities have been proposed in both Denmark (Huesemann et al. 2010) and Japan, “Ocean Sunrise Project” (Aizawa et al. 2007), 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 (Huesemann et al. 2010). Horn et al.

(2000) concluded that a commercial industrial seaweed bioethanol process will require higher ethanol yields to be viable, and research is being carried on selection and genetic modification of microorganisms to increase bioethanol yield that may permit future commercial production of ethanol from seaweed.

2.6. Biobutanol

While seaweed cultivation for bioethanol is being explored in Asia, Europe and South America it is biobutanol from macroalgae that is attracting research interest and investment in the USA (Parliamentary Office of Science & Technology 2011). 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 (Potts et al. 2012). Although biobutanol has been produced on a pilot scale from algal sugars (Potts et al. 2012), it has been concluded that significant improvements in yield and process costs are still needed to make industrial-scale butanol from the fermentation of seaweed economically feasible (Huesemann et al. 2012).

2.7. Hydrothermal Processing

Hydrothermal processing is a high pressure process where 'wet' biomass is converted into primarily a stable liquid hydrocarbon fuel (bio-oil) in the presence of a catalyst (Demirbas 2001; McKendry 2002a; Smith and Ross 2016). The ability of hydrothermal liquefaction to handle wet biomass makes it one of the most interesting methods of producing biofuel from algae (Torri et al. 2012), and hydrothermal treatment of algae has attracted research interest (Minowa et al. 1995; Sawayama et al. 1999; Brown et al. 2010; Smith and Ross 2016). Hydrothermal liquefaction of biomass with a moisture content above 90% is believed to have an unfavourable energy balance (Vardon et al. 2012), and 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 (Demirbas

2001; McKendry 2002a; Marcilla et al. 2013; Lee et al. 2016). The production of biofuel from seaweed via hydrothermal treatment, thus will require considerable more research to reduce process costs.

3. Gasification and Anaerobic digestion

Both gasification and anaerobic digestion (AD) have been suggested as promising methods for exploiting bioenergy from biomass (Singh and Gu 2010), and 2 major projects have been funded in the UK on the gasification and anaerobic digestion of seaweed, MacroBioCrude and SeaGas. A recent study that analysed four methods of microalgal bioenergy production found that anaerobic digestion produces more net energy than supercritical gasification, the latter requiring higher energy input and having a negative return on energy investment (Ventura et al. 2013; Milledge and Heaven 2014). 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 (Delrue et al. 2012). 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.

3.1. Gasification

Gasification is the conversion of organic matter by partial oxidation at high temperature (800-1000 °C) mainly into a combustible gas mixture (syngas) (Demirbas 2001; McKendry 2002a; McKendry 2002b; Saidur et al. 2011). 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 O_2 or H_2O 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 (Ahmed and Gupta 2010). Syngas can be produced

from biomass with and without the presence of a catalyst, however non-catalytic processes require a higher temperature than catalytic processes (Suganya et al. 2016). Nickel compounds, olivine and dolomite have typically been employed as cracking catalysts to enhance gasification.

The syngas has a calorific value of 4-6 MJ m^{-3} (McKendry 2002a), and is a mixture of hydrogen (30-40%), carbon monoxide (20-30%) methane (10-15%), ethylene (1%), nitrogen, carbon dioxide and water vapour (Demirbas 2001; Saidur et al. 2011). The gas can be burnt to produce heat or converted to electricity and heat in combined gas turbine systems (Demirbas 2001; McKendry 2002a). Syngas from gasification of biomass can be converted catalytically into hydrocarbons and water through the Fischer-Tropsch process, a catalytic chemical reaction in which carbon monoxide (CO) and hydrogen (H_2) in the syngas are converted into hydrocarbons of various molecular weight (Dry 2002). The condition of the Fischer-Tropsch process are usually chosen to maximize the formation of higher molecular weight hydrocarbon liquid drop-in fuels which can used in current combustion engines and infrastructure. The syngas produced from gasification can also be used to produce methanol and hydrogen as a fuel for transport and other uses (McKendry 2002a; Saidur et al. 2011), but the cost of methanol produced from methane from biomass has been estimated at 1.5 – 4 times higher than from fossil fuel gas (International Renewable Energy Agency IRENA 2013).

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 (Hayashi et al. 2013), with the net energy return, including energy inputs, for pyrolysis operation of dry land agricultural biomass waste ranging from 42–53% (Anex et al. 2010).

Conventional biomass gasification processes require dry feedstock (Guan et al. 2012a; Smith and Ross 2016), and the energy required for drying may make it unviable energetically, but integration of drying and gasification processes could reduce overall energy input (Aziz et al. 2014), and the use of solar drying could allow gasification to be net energy positive (Aresta et al. 2005). Supercritical water gasification (SCWG) is an alternative gasification technology for the conversion of high moisture biomass and hydrothermal gasification is seen as a potential processing method

for wet carbohydrate-rich biomass, such as macroalgae (Suutari et al. 2015). It is suggested that SCWG processes can be net energy positive in well-engineered systems (Guan et al. 2012b), but the presence of water can alter the composition of the gases produced (Woolf et al. 2014). Catalytic supercritical water gasification of *Ulva lactuca* has produced a methane-rich gas (Nikolaison et al. 2012). 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 (Cherad et al. 2013). Upon addition of NaOH in the SCWG of the macroalgae, S*accharina,* there was a three-fold increase in H_2 production, along with an increase in methane, decrease in C_2-C_4 yields and the elimination of CO and CO_2 from the syngas (Onwudili et al. 2013). The origins of these observations are believed to be due to the removal of CO_2 through reactions that form Na_2CO_3, 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/Al_2O_3) catalysts was found to double the H_2 and CH_4 yields from SCWG of *S. latissima* compared to the uncatalysed reaction with an increase of the gasification efficiency from 58% to 92% (Cherad et al. 2013). CO and C_2-C_4 yields correspondingly decreased whilst CO_2 yield increased. However, subsequent reuse of the regenerated catalyst led to a decrease in the yields of H_2 and CH_4, although, after reuse of the catalyst three times the H_2 and CH_4 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 CO_2 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% (Kwon et al. 2012).

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% (Ross et al. 2009) which can lead to high char levels, but conversely alkaline species can catalytically aid the steam gasification of macroalgae to H_2 at temperatures above 700 °C (Kaewpanha et al. 2014). Higher syngas yields from steam gasification of macroalgae are possible due to their high con-

tent of inorganic elements compared to land based biomass such as Japanese Cedar and Apple branches, however the latter materials can be co-gasified with seaweed in a biorefinery, leading to enhanced syngas yields (Kaewpanha et al. 2014; Rizkiana et al. 2014).

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 (Brennan and Owende 2010). 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 (Guan et al. 2012a). However, supercritical water macroalgae gasification still faces a variety of engineering and scale-up issues and considerable further research and development is required. Both gasification and anaerobic digestion have been suggested as promising methods for exploiting bioenergy from biomass in India (Singh and Gu 2010), but 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.* (Rowbotham et al. 2013) 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. (Aziz et al. 2014), However, Smith and Ross (2016) reported that the high chlorine, ash and alkali content, low calorific value and high moisture content make macroalgae not only unattractive option for combustion, but also gasification without extensive pre-treatment, and as a consequence, the majority of research into utilising macroalgae as a biofuel has focused on the production of biogas by anaerobic digestion.

3.2. Anaerobic Digestion

Anaerobic Digestion (AD) consists of a series actions by different groups of bacteria that convert organic compounds to methane, carbon dioxide, and bacterial cells. The biogas produced from the AD of seaweed typically contains methane 50-70%, carbon dioxide 30-45%, hydrogen <2% and hydrogen sulphide <3.5% (Peu et al. 2011; Vanegas and Bartlett 2013; Tiwari and Troy 2015). AD consists of 4 stages (Weiland 2010; Ali Shah et al. 2014; Monlau et al. 2014; McKennedy and Sherlock 2015) (Figure 2):

a) Hydrolysis: carbohydrates and proteins, fats are decomposed into monosaccharides, disaccharides, amino acids, and fatty acids

b) Acidogenesis: acidifying bacteria convert hydrolysis products, to short-chain organic acids

c) Acetogenesis: Acetogenic bacteria produce acetic acid, H_2 and CO_2 from fermentation products (Dark fermentation is the fermentative conversion of organic substrate to hydrogen). The Acetogens fall into two main groups:

i. Hydrogen producing acetogens breakdown volatile fatty acids to CO_2 and H_2 (Butyrate: $CH_3CH_2CH_2COOH + 4H_2O \rightarrow CH_3COOH + 2CO_2 + 6H_2$

ii. Homoacetogens: $4H_2 + 2CO \rightarrow CH_3COOH + 2H_2O$

d) Methanogenesis: end of the degradation chain, two groups of methanogenic bacteria produce methane from acetate or hydrogen and carbon dioxide

i. Acetoclastic methanogenesis ($CH_3COOH \rightarrow CH_4 + CO_2$)

ii. Autotrophic or Hydrogenotrophic methanogenesis ($4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$)

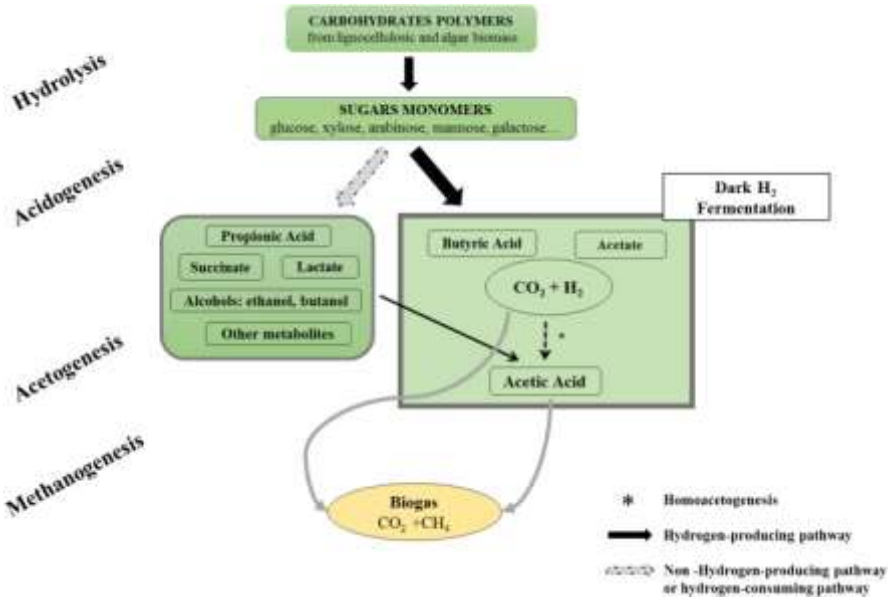

Figure 2 . Scheme of carbohydrate polymers degradation through anaerobic digestion (Monlau et al. 2014)

Anaerobic digestion is generally the process of choice for biomass with a high water content such as seaweed (Aresta et al. 2005; Barbot et al. 2016), and various groups assessing the suitability of seaweed for anaerobic digestion (AD) from the 1970s through to 1990s generally found that seaweeds were mostly a suitable biomass for AD (Sutherland and Varela 2014). Seaweed derived biogas was used industrially in 19th century, and more recently Tokyo Gas demonstrated that 20 m^3 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 (Huesemann et al. 2010); currently biofuel from seaweed AD is perhaps the closest to industrial exploitation (Lewis et al. 2011; Milledge et al. 2014). 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.

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 (Florentinus et al. 2008). 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 (Roesijadi et al. 2010b).

The bacteria involved in the production of methane by anaerobic digestion are sensitive to the chemical composition of the feedstock (Samson and LeDuy 1983; Park et al. 2011; Gonzalez-Fernandez et al. 2012). The proportions of carbohydrates, proteins and lipids affect the potential of algae as a substrate for anaerobic digestion (Park and Li 2012) with lipids yielding higher volumes of biogas per gram of feed material than either carbohydrate or protein (Weiland 2010; Heaven et al. 2011; Zamalloa et al. 2011). It has been suggested that the low lipid content of macroalgae (Table 3) make them ‘especially suitable’ for biogas production using anaerobic fermentation (Streefland 2010; Murphy et al. 2013). The theoretical yield of biogas, calculated from the chemical composition of macroalgae ($C_cH_hO_oN_nS_s$) using the "Buswell equation" (Symons and Buswell 1933; Buswell and Mueller 1952), can be high.

Table 3 Lipid, protein and carbohydrate composition of various macroalgae % dw (Monlau et al. 2014)

% Composition (dw)	Lipids	Proteins	Carbohydrates
Green algae			
Codium fragile	1.8	10.9	32.3
Enteromorpha linza	1.8	31.6	37.4
Ulva Lactuca	6.2	20.6	54.3
Red algae			
Gelidium amansii	0–3.1	15.6–16.3	61–67.3
Porphyra tenera	4.4	38.7	35.9
Gracilaria verrucosa	3.2	15.6	33.5
Brown algae			
Laminaria Japonica	1.8–2.4	9.4–14.8	51.9–59.7
Hizikia fusiforme	0.4–1.5	5.9–13.9	28.6–59
Saccharina japonica	0.5	19.9	44.5
Sargassum fulvellum	1.6	10.6	66
Ecklonia stolonifera	2.4	13.6	48.6
Unduria pinnatifida	1.8–2.0	15.9–18.3	40.1–52
Sargassum fulvelum	1.4	13	39.6

However, practical yields of biogas from the anaerobic digestion of macroalgae are considerably below the theoretical maximum at typically

≤50% of the calculated maximum yield (Passos et al. 2015; Milledge and Harvey 2016a). The destruction of organic volatile solids from microalgae was found to be only 60-70% of that found in raw sewage (Golueke et al. 1957; Passos et al. 2015), however the methane yield (0.271 m^3 kg^{-1}) from *Ulva lactuca* was found to be similar to that from cattle manure and land-based energy crops, such as grass-clover (Bruhn et al. 2011; Nikolaison et al. 2012). Methane yields from the anaerobic digestion of macroalgae have been reported in the range of 0.14-0.40 m^3 kg^{-1} of volatile solids (Murphy et al. 2013), but are typically 0.2 m^3 CH_4 kg^{-1} (Alvarado-Morales et al. 2013). There is considerable conjecture about the reasons for the relatively low practical methane yields from seaweed compared to their theoretical values (Milledge et al. 2014; Sutherland and Varela 2014; Ward et al. 2014; Soto et al. 2015; Tabassum et al. 2016). Potential causes of the recalcitrance of seaweed in AD are: a) seaweed structure and cell wall structure, b) seaweed polysaccharides, c) polyphenols, d) organic sulphur compounds, e) other antimicrobial and toxins, f) C:N ratio and g) heavy metals (McKennedy and Sherlock 2015; Barbot et al. 2016). The Consortium for Algal Biofuel Commercialization (CAB-Comm), established to conduct research to enable commercial viability of alternative liquid fuels produced from algal biomass, found in a sensitivity analysis that increasing CH_4 yield from anaerobic digestion from seaweed was the most important factor in improving process energy balance and reducing greenhouse gas emissions, and thus further research on the factors reducing practical methane yields is vital (Mayfield 2015).

The hydrolysis of seaweed-derived polysaccharides, particularly alginates is considered the rate limiting step in the AD of seaweed (Moen et al. 1997; Sutherland and Varela 2014). 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 (Sutherland and Varela 2014). 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 l CH_4 g^{-1} VS) and volatile solid utilisation (67%) from anaerobic digestion of *Laminaria hyperborean* (Sutherland and Varela 2014).

Brown seaweed can contains high levels of phenolics with levels up to 14% dw being reported (Holdt and Kraan 2011) with *Sargassum muticum* containing 0.7-6% (Gorham and Lewey 1984; Connan et al. 2006; Tanniou et al. 2014) and *Ascophyllum nodosum* 0.2-5% (Tabassum et al. 2016). Polyphenols are suggested as one of the elements in low yields of methane from brown seaweeds (Hierholtzer et al. 2013; Ward et al. 2014; Barbot et al. 2016; Pérez et al. 2016; Tabassum et al. 2016). Tabassum et al. (2016) found that methane yield decreased with seasonal increases in phenolic content of *Ascophyllum nodosum*, and Moen et al. (1997) found that methane yield from *Ascophyllum nodosum* increased when polyphenols were fixed with low concentrations of formaldehyde. Hierholtzer et al. (2013) found that there was a significant effect from the presence phloroglucinol and phlorotannins extracted from *L. digitata* (2-200 mg L^{-1}) on the methane production from the AD of sodium acetate. Gallic acid at concentration of 10 mg L^{-1} has been shown to inhibit biogas production from starch by up to 75% (Mousa and Forster 1999). However, recent research at the University of Greenwich has found no significant effect of lower Gallic acid concentrations of 7% of volatile solids (0.18 mg L^{-1}), more typical of seaweed, on methane yields from 3 substrates. López et al. (2011) has suggested that mixtures of phenolics can act either synergistically of antagonistically, and with phenolic concentration also appearing to have an effect on methane yield there is a need for considerable more research on the effect of concentration of individual phenolics and mixtures of phenolics on methane yield from compounds typically found in seaweed.

AD methane yields from brown algae are generally higher than those from green algae (Sutherland and Varela 2014). 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 (Hilton and Archer 1988; Murphy et al. 2013). Biogas from AD of *Ulva* contained up to 3.5% H_2S, making it unsuitable for energy recovery without treatment (Peu et al. 2011). 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 (Hilton and Archer 1988; Murphy et al. 2013). The upgrading of biogas is beyond the scope of this

chapter, but upgrading of biogas typically uses ~11 % of the energy content in the biogas (Berglund and Borjesson 2006), and has been extensively reviewed by Petersson and Wellinger (2009), Ryckebosch et al. (2011) and Bauer et al. (2013).

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 (≥10 g l^{-1}) are known to inhibit anaerobic systems through an increase of osmotic pressure or dehydration of methanogenic microorganisms (Lefebvre and Moletta 2006; Hierholtzer and Akunna 2012). 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 (Chen et al. 2008). An optimal sodium concentration for mesophilic methanogens in waste treatment processes of 230 mg Na L^{-1} has been recommended (Chen et al. 2003). Mesophilic methanogenic activity is halved at 14 g Na L^{-1} (Ramakrishnan et al. 1998; Chen et al. 2003), the approximate level of sodium found in sea water (El-Dessouky and Ettouney 2002). Adams et al. (2015) found that washing *Laminaria digitate* with freshwater tended to increase methane yields due to the loss of salt, despite >50% of laminarin being lost during washing. However, in a study of *Ulva lactuca* it was found that washing of algae had no effect on methane yield. (Nikolaison et al. 2012). Anaerobic digesters can be acclimatised to higher salt levels if they are continuously exposed to gradually increasing salt concentration rather than salt shock (Lefebvre and Moletta 2006; Roberts et al. 2016). 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 (Chen et al. 2003). 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 (Murphy et al. 2013).

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 m^3 kg^{-1} (Nikolaison et al. 2012) and from Baltic beach-cast seaweeds by up to 53% (Tedesco et al. 2014).

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 (Parliamentary Office of Science & Technology 2011). A survey by Bruton *et al.* (Bruton et al. 2009) 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. (2010a) 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 m^3 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 (ter Veld 2012; Milledge and Heaven 2017). 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 (Huesemann et al. 2010).

4. Conclusions

The production of biofuel from seaweed is economically, energetically and technically challenging at scale. 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 commercial exploited. Processes that exploit the entire algal biomass such AD or gasification appear to offer the best chances of success. 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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