A perspective on algal biogas

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SUMMARY

Algae are suggested as a biomass source with significant growth rates, which may be cultivated in the ocean (seaweed) or on marginal land (microalgae). Biogas is suggested as a beneficial route to sustainable energy; however the scientific literature on algal biogas is relatively sparse. This report comprises a review of the literature and provides a state of the art in algal biogas and is aimed at an audience of academics and energy policy makers. It was produced by IEA Bioenergy Task 37 which addresses the challenges related to the economic and environmental sustainability of biogas production and utilisation.

IEA Bioenergy

A perspective on algal biogas

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Executive Summary

There is a lot of scientific literature available on liquid biofuel production from microalgae; less literature is available on biogas from microalgae. Prior to 2010 few academic papers dealt with biofuel production from seaweed; however since 2010 a significant number of papers have been published in the scientific press. This publication has an ambition of synthesising the literature, and providing a perspective, on production of biogas from algae.

The rationale for producing biogas from algae is driven by the food-fuel debate and indirect land use change (ILUC). The ethics in using our finite resources of arable land (0.2 ha of arable land per head of population on a worldwide basis) for energy and not for food is dubious. Algae take bioenergy off agriculture land and onto our seas and oceans. Seaweed can be used to clean nutrient enriched water (associated with salmon farms for example) while microalgae may capture CO_2 from power plants.

There are numerous species of seaweed that may be segregated or distinguished in a number of ways; for example colour. The genetic difference between green seaweed *Ulva lactuca* and the brown seaweed *Fucus* is larger than that between *U. lactuca* and an oak tree. *U. lactuca* contains a lot of sulphur and typically has a carbon to nitrogen (C:N) ratio of less than 10, making mono-digestion extremely difficult. This is not the case for brown seaweeds such as *laminaria*; typically the C:N ratio and the corresponding specific biomethane yield increases from winter to summer and achieves a maximum C:N ratio of over 20 in late summer. Seaweed may be collected as a residue (such as the algae bloom associated with the green seaweed *U. lactuca*); may be cast on beaches (such as *Fucus* sp. and *Ascophylum nodosum*) or may be cultivated in aquaculture systems (such as growing *Laminaria* sp. in association with salmon farms). A sustainable significant biofuel industry would probably require the scale associated with aquaculture. The economics of a seaweed biofuel industry are dubious as certain seaweeds are used for food and have high economic value. The authors believe that biogas from cast seaweed will have applications in the short term, however the quantities of seaweed required to match a significant portion of renewable energy are very large and it is as yet unknown as to how this can be achieved in a sustainable manner.

There are also numerous species of microalgae. Cultivation may take place in open ponds (which are open to contamination) or in closed photobioreactors (which are more expensive in terms of energy input and financial investment and operation). The C:N ratio tends to be lower than for seaweed, but the composition varies greatly from species to species and depends on the growing conditions and the availability of nutrients. For biodiesel production the ambition is to maximise lipid production for esterification. Lipids also yield high levels of biogas but microalgae with excess levels of lipids are not amenable to stable anaerobic digestion. The big advantage of anaerobically digesting microalgae is that neither a pure culture is needed, nor a specific compound (e.g. lipids for biodiesel) needs to be produced. Both these advantages can significantly reduce the costs of producing microalgae biomass. Microalgae may be used to capture CO_2 produced by power plants. The microalgae may be digested to produce biogas; this however releases the CO_2 when combusted. Therefore the benefit of capturing the CO_2 from fossil fuel power plants is more in extending the work done by the original fossil fuel rather than sequestering the CO_2. The scale of raceway ponds or photobioreactors for significant carbon capture is very large. The energy input in mixing, harvesting and conversion of microalgae to biogas is very significant and may be of a scale that more energy is used in the process than generated in the biogas. A microalgal biogas industry is far from commercialisation. Innovation is required in optimising

microalgae systems. Ideally they should be cultivated, capturing the CO_2 from renewable energy such as biogas facilities thereby reducing the need for biogas upgrading and thus improving the net energy return. Currently, the microalgae industry is focussed on high value products to offset high production costs. A more economic approach to producing biogas from microalgae is a cascade usage in a biorefinery concept: a high value product will yield the most significant revenue whereas the biomass residue would be transformed into biogas.

The authors consider that a viable seaweed or microalgae biofuel or biogas industry is a number of years away from providing significant quantities of renewable energy and much research is required in optimising prospective algal biogas systems.

IEA Bioenergy Task 37 addresses the challenges related to the economic and environmental sustainability of biogas production and utilisation. IEA Bioenergy is one of 40 currently active Implementing Agreements within the International Energy Agency and has the aim of improving cooperation and information exchange between countries that have national programmes in bioenergy research, development and deployment. IEA Bioenergy's vision is to achieve a substantial bioenergy contribution to future global energy demands by accelerating the production and use of environmentally sound, socially accepted and cost-competitive bioenergy on a sustainable basis, thus ensuring increased security of supply whilst reducing greenhouse gas emissions from energy use.

1 Introduction

1.1 Macroalgae or Seaweed
1.1.1 Types of Seaweeds

There are of the order of 10,000 species of seaweed. Jard et al. (2013) segregates seaweeds into three broad types: brown, red and green seaweeds.

- Brown seaweeds include for: *Saccharina latissima; Himanthalia elongate; Laminaria digitata; Fucus serratus; Ascophylum nodosum; Undaria pinnatifida; Saccorhiza polyschides; Sargassum muticum.*
- Red seaweeds include *Gracilaria verrucosa, Palmaria palmate* and *Asparagopsis armata.*
- Green seaweeds include *Codium tomentosum* and *Ulva lactuca.*

Hughes et al. (2013) stress the need to differentiate between macroalgae of intertidal zones (between high and low water of tides) and sub-tidal zones (submerged most of the time). The species are different, as are the methods of harvest. Seaweeds from the intertidal zone would be considered cast seaweed and are traditionally hand harvested. Hughes et al. (2013) caution the optimism of over estimating the resource of cast seaweed; it is a fraction of the sub-tidal seaweed. It is also typically found in a spread of separated remote coastal areas with poor transport infrastructure (Burrows et al., 2011). This has major implications for a viable, sustainable, macroalgae biofuel industry.

Figure 1 indicates cast seaweeds, collected from the shore in West Cork, Ireland in 2013; five of these are brown and one green. Despite the collective description of seaweed there are more genetic differences between *Fucus* (Figure 1 c) and *Ulva* (Figure 1f) than between *Ulva* and an oak (Cabioch and Le Toquin, 2006). Kelp is a common name used for species of *Laminaria. Saccharina latissima* is also known as sugar kelp.

1.1.2 Harvest of seaweed

Seaweed has long been harvested. Brown seaweeds dominate the harvest with twice the volume of red seaweeds. Green seaweeds are less valuable and are not harvested in significant quantities (Werner et al., 2004). In 2000 the harvest on a worldwide basis of seaweed was ca. 11,350,000 wet tonnes (1,219,028 wet tonnes wild and 10,130,448 wet tonnes from aquaculture). An estimate for total production of seaweed in 2010 was 19 million tonnes (FAO, 2010). The latest estimates (FAO, 2014) for 2013 indicate that globally 26 million tonnes (wet weight) of farmed aquatic plants (predominately seaweed) were produced. There has been an increase of 129 % in seaweed harvested in 13 years. The seaweed harvest may be compared with the fish harvest. In 2012, 158 Mt of fish were harvested; aquaculture contributed 66 Mt of this (FAO, 2014).

China harvested 13.5 Mt of seaweed in 2013 (FAO, 2014). In a European context, Norway and France have the biggest harvests; Norway harvests 120,000 tons of *Laminaria* annually; France 50,000 to 70,000 tons per annum (Jard et al., 2013). Traditionally in Ireland, cast seaweed (including for *Laminaria* spp., *Fucus* spp. and *Ascophyllum* spp.) was collected and used primarily as a fertiliser, but also for cattle fodder, human consumption and medical applications (Werner et al., 2004). Approximately 30,000 tons of *A.nodosom* is harvested each year in Ireland at a cost of € 330/t (Burton et al., 2009).

Figure 1: Cast seaweeds collected from the shore (a) *Himanthalia elongate* (b) *Laminaria digitata* (c) *Fucus serratus* (d) *Saccharina latissima* (e) *Ascophylum nodosum* (f) *Ulva lactuca* (Photos from Eoin Allen and Muhammad Rizwan Tabassum, Environmental Research Institute, University College Cork, Ireland)
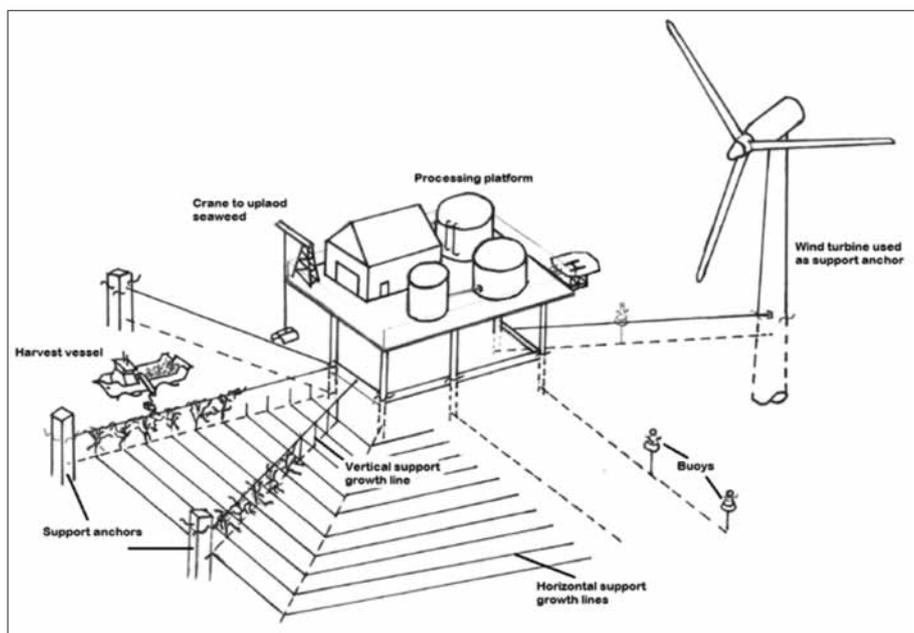
Figure 2: Conceptual design of seaweed farm unit associated with wind turbine adapted from (Leese, 1976) and (Chynoweth, 2002)

1.1.3 Potential resource of sub-tidal seaweed

The resource of sub-tidal seaweed is far higher than the resource of cast seaweed. A 2008 report suggested that the island of Orkney (UK) has a kelp forest of 1 million tons covering 22,000 hectares along 800 km of coastline (Christiansen, 2008). This equates to 44.5 t of kelp per hectare. It further suggested that there are approximately 100,000 hectares of kelp forests in UK waters which could be commercially harvested. Kelp (or *Laminaria*) is typically found at depths of 8 to 30m in the north Atlantic. Kelps are considered optimal for bioconversion to energy (Chynoweth et al., 1987).

1.1.4 Seaweed associated with aquaculture

An industry whereby seaweed could be harvested may be visualised in Figure 2. Harvest would consist of

mechanised stripping of seaweed from suspended ropes. This aquaculture system is suggested as more likely than cast seaweeds for a financially viable biofuel industry (Hughes et al., 2013). In assessing the carbon balance of macroalgae biofuel from aquaculture, there is potential to include for carbon sequestration associated with the growth of seaweed (Werner et al., 2004). In assessing the environmental sustainability there is scope to consider the role of seaweed farms in removing nutrients from eutrophic waterways. The industry of seaweed aquaculture could be very beneficial in tandem with large fish farms (such as salmon farms of the west coast of Ireland, Norway and Scotland). The industry may also benefit if associated with renewable energy installations such as off shore wind farms and tidal turbines.

1.2 Microalgae
1.2.1 Classification of microalgae

In contrast to macroalgae, microalgae are microscopically small. Figure 3 shows pure cultures of *Chlorella* sp. and *Scenedesmus* sp. Many microalgae species exist as solitary cells, but the formation of colonies, consisting of several to many cells, is also common (Graham et al., 2009). The specialization of cells within colonies is highly variable, which is also the case for cell shapes
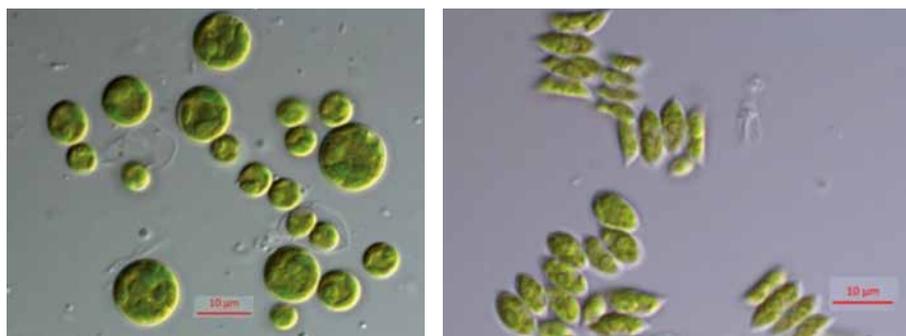
Figure 3: Pure culture of *Chlorella* sp., left and *Scenedesmus* sp., right (both - green algae; © Markus Gruber, IFA Tulln - University of Natural Resources and Life Sciences, Vienna)
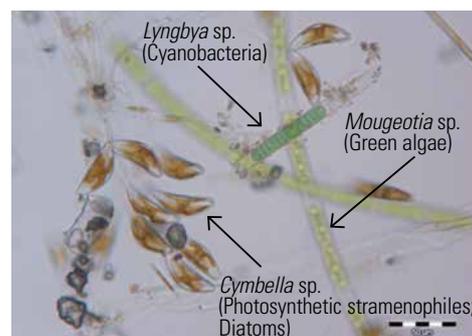
Figure 4: Mixed sample containing representatives of three major algal groups.

Table 1: Summary of major algal groups and their storage products (adapted from Graham et al., 2009)

	Group	Photosynthetic and protective pigments	Storage products
Prokaryotes	Cyanobacteria	Chlorophyll a, phycobilins, ß-carotene, xanthophylls	Cyanophycin granules, cyanophytan starch (glycan)
Eukaryotes	Glaucophytes	Chlorophyll a, phycobilins, ß-carotene, xanthophylls	Starch
	Chlorarachniophytes	Chlorophyll a and b, ß-carotene, other carotenes, xanthophylls	Carbohydrate
	Euglenoids	Chlorophyll a and b, ß-carotene, other carotenes, xanthophylls	Paramylon
	Cryptomonads	Chlorophyll a and c, α- and ß-carotene, xanthophylls	Starch
	Haptophytes	Chlorophyll a and c, ß-carotene, xanthophylls	Chrysolaminarin
	Dinoflagellates	Chlorophyll a and c, ß-carotene, xanthophylls	Starch
	Photosynthetic stramenofiles	Chlorophyll a and c (chlorophyll a alone in some, ß-carotene, xanthophylls)	Chrysolaminarin, lipids
	Red algae	Chlorophyll a, phycoilins, α- and ß-carotene, xanthophylls	Floridean starch
	Green algae	Chlorophyll a and b, ß-carotene, lutein, other carotenes, xanthophylls	Plant-like starch

of microalgae. There are plenty of different cell shapes (filamentous, flagellate or simple spherical shapes), which are commonly used for differentiation of cells (Figure 4). Depending on the level of cellular organization and abundance of protective pigments, microalgae can be divided into several major groups, as outlined in Table 1.

1.2.2 Microalgae biomass production

Microalgae can occur in highly diverse habitats and grow under strongly varying environmental conditions. Successful cultivation of microalgae requires knowledge about the algal ecology in order to set up accurate growth conditions. Benemann (2013) estimated amounts of microalgae dry matter production worldwide to be around 15,000 t/year (Table 2). Microalgae biomass is harvested from natural waters as well as cultures in artificial ponds or photobioreactors (PBRs). It is subsequently separated and spray- or sun-dried.

1.3 Why generate biogas from algae?
1.3.1 Perception of biofuels and the impact on policy

The perception of biofuels, in particular first generation biofuels, has suffered greatly over the last decade. In the early 2000s biofuels were mooted as the panacea for renewable energy in transport. In particular the market for ethanol from maize in the USA, ethanol from sugar cane in Brazil, rape seed biodiesel and grain ethanol in continental Europe, was flourishing. The turning point came in 2008 when there was a significant

Table 2: Estimation of the worldwide microalgal biomass production (adapted from Benemann, 2013)

Algae	Production (t dry matter/year)
Spirulina	10,000
Chlorella	4,000
Dunaliella	1,000
Haematococcus	200

jump in the cost of crops which were used to make bio-fuel; this led to food riots in some developing countries. This started the food-fuel debate which was reflected in new policy and legislation. For example in Europe the 2003 Biofuels Directive (2003) (2003/30/EC) stated that 5.75% of the transport fuel market (by energy content) should be biofuel by 2010. However, as a consequence of the food-fuel debate the Renewable Energy Directive (2009/28/EC) (RED, 2009) placed more emphasis on renewable energy rather than biofuels by stating that 10% of energy in transport should be renewable by 2020. This facilitated a change in approach, for example through use of Electric Vehicles.

In June 2014, EU energy ministers agreed to limit the share of biofuels from cereal and other starch rich crops, sugar and oil crops to 7% (European Commission 2014). This poses a very difficult challenge to the transport fuel sector due to the unavailability of sufficient commercially available second (or third) generation biofuel systems to deliver 3% of energy in transport within the EU. On the 24th February 2015, a press release from the Environment Committee of the European Parliament concluded that "advanced biofuels sourced from seaweed or certain types of waste should account for at least 1.25% of energy consumption in transport by 2020" (European Parliament News, 2015).

1.3.2 Second generation biofuels

Second generation biofuels are based on inedible parts of plants, including straw, wood and waste streams (EASAC, 2013). However, for woody lignocellulosic substrates, second generation biofuel technologies may be as (or more) energy intensive than first generation biofuels. Lignocellulosic material may require a pre-treatment stage (such as steam explosion) prior to the biofuel production technology stage. Thus the energy required in the second generation biofuel process may be greater than for the first generation process. The benefit of the second generation process is that the energy in production (or collection) of the substrate (as opposed to the energy required to make the biofuel) may be low when compared to energy production in food crops (ploughing, fertilising, harvesting). Lignocellulosic substrate such as straw may be cheap (maybe only transport costs) and may ultimately result in a cheaper biofuel (than first generation food based biofuel) if the capital cost of the more complex production process is offset by the cheap substrate. The primary issue with second generation biofuel processes is that they may not be commercially available by 2020, either due to cost or technology.

1.3.3 Third generation algal biofuels

Third generation biofuels do not require agricultural land for production. Typically third-generation biofuels tend to be based on algae, which are supposed to have lower area requirements compared to terrestrial crops, such as corn, canola (rape seed) or switch grass (Clarens et al., 2010). According to Oncel (2013) microalgae show higher productivity per hectare, compared to crop plants. In literature there is a very wide range of yields, which is partly due to the fact that calculations are based on laboratory or pilot-scale data. Box 1 attempts to put a perspective on achievable yields.

Box 1
Relative yields of microalgae compared to land based crops

According to Chaumont (1993) data on microalgal productivity varies between $10 – 50$ g m^{-2} d^{-1} with an average rate of 20 g m^{-2} d^{-1}. Becker (1994) presents selected data on yields of different algae, grown under outdoor conditions, ranging between $7 – 60$ g m^{-2} d^{-1} of dry matter. This shows that productivity can vary highly, depending on species and cultivation. A recent publication (Moody et al., 2014), modelling algae biomass and lipid production, underlined the strong influence of the climate on microalgae productivity. A growth model was used to determine the current near-term lipid productivity potential of microalgae around the world and a maximum biomass yield of $13 – 15$ g m^{-2} d^{-1} was assumed (Moody et al., 2014). The high variability of the available data in the scientific press makes it somewhat difficult to accurately compare the productivities per unit area between different algal species.

Compared to land plants, for example maize, where the whole plant is used for biomethane production, algae might be more productive under optimal conditions. Maize can reach a yield of between $5 – 13$ g m^{-2} d^{-1} (dry matter; whole plant) (Döhler et al., 2013). If a growing season of 6 months is assumed this equates to $9 – 23$ t TS ha^{-1} a^{-1}. Microalgae can yield up to $45 – 60$ t VS ha^{-1} a^{-1} based on year round growth under favourable conditions (Benemann, 2013).

The assumption that microalgae can devote more of their energy into trapping and converting light energy and CO_2 into biomass, because they do not generate elaborate support and reproductive structures (Darzins et al., 2010), has to be cautioned. According to Walker (2009) the photosynthetic efficiency of microalgae and C3 plants does not vary and is around 4.5% of solar energy.

1.3.4 Sustainability of biofuels

The Renewable Energy Directive (2009/28/EC) (RED, 2009) states that biofuels must achieve at least a 60% reduction of greenhouse gas emissions compared to the fossil fuel displaced on a whole life cycle basis, by 2018. As of 2015, (European Parliament News, 2013) indirect land use change (ILUC) must be considered in assessing sustainability of the biofuel system.

In the recent past a lot of attention was given to production of biodiesel from microalgae. Although the potential oil yield obtained from microalgae can be much higher than from other sources of biodiesel (see Table 3), large scale production of algae based biofuels is not yet economically viable and as such will struggle to displace petroleum-based fuels in the near term (Van Iersel and Flammini, 2010). The European Academies Science Advisory Council (EASAC, 2013) produced a report in 2013 entitled *"The current status of biofuels in the European Union, their environmental impacts and future prospects"*. Microalgae are discussed in terms of total solids content. In open ponds microalgae generate concentrations of 0.5 g of dry mass per litre or 0.05% total solids (TS) content. In closed PBRs biomass concentrations of 5–10 g dry mass per litre (0.5 to 1% TS) may be achieved. The energy balance associated with removing the water from the microalgae solids to allow esterification to be undertaken is significant; 2.5 GJ of energy is required to evaporate a tonne of water. Stephenson et al., (2010) suggest that the energy consumption for microalgal biomass production for biodiesel amounts to six times the energy produced in the microalgae biodiesel (EASAC, 2013).

The total solids content within continuously mixed anaerobic digesters is typically less than 12 %. This is significantly less arduous to achieve than the requirement for biodiesel. This suggests that there is a strong potential for biogas based on microalgae to have a superior energy balance than microalgae biodiesel. A further advantage of biogas production from microalgae is that pure cultures are not needed if algae are digested in a biogas plant. Algal biodiesel systems on the other hand require microalgae rich in lipids. Thus, less effort is required to grow microalgae for biogas systems as opposed to biodiesel systems. A further option for a bioenergy pathway is the production of high-value products from microalgae in combination with conversion of the residual biomass to biogas.

1.3.5 Objectives

Both microalgae and macroalgae are mooted as third generation transport biofuels of the future. At present (2015) however there is minimal commercial production of algal biofuels. Pathways for sustainable algal bioenergy are not well documented (or agreed) in scientific publications. Jard et al., (2013) argue that biogas production from seaweed is close to commercialization as even complex carbohydrates can be transformed into biogas. A perspective of the authors (of this IEA report) is that biogas production from microalgae should be less arduous than biodiesel production from microalgae as there is no specific requirement for composition or pure culture; typically biomass resulting from "contamination" in open ponds is suitable for anaerobic digestion.

The report sets out to synthesize the scientific literature on biogas production from algae and to provide a perspective on production routes to sustainable algal biogas.

Table 3: Comparison of some sources of biodiesel (Chisti, 2007)

Crop	Oil yield (L/ha)	Land area needed (M ha)[a]	Percent of existing US cropping area[a]
Corn	172	1540	846
Soybean	446	594	326
Canola	1190	223	122
Jatropha	1892	140	77
Coconut	2689	99	54
Oil palm	5950	45	24
Microalgae [b]	136,900	2	1.1
Microalgae [c]	58,700	4.5	2.5

[a] For meeting 50 % of all transport fuel needs of the United States
[b] 70 % oil (by wt) in biomass
[c] 30 % oil (by wt) in biomass

2 Biogas from seaweed

2.1 Characteristics of seaweeds

Seaweeds are characterised as having no lignin, low cellulose and lipid content (Morand et al., 1991; Jard et al., 2013). Brown seaweeds (such as *Ascophylum nodosum*) can be rich in polyphenols which are difficult to degrade under anaerobic conditions and can inhibit anaerobic digestion (Ragan and Glombitza, 1986).

Seaweeds reproduce in a number of ways; sexual reproduction can take place through joining together of male and female gametes. Often the seaweed grows and divides into many small pieces (Werner et al., 2004).

Brown seaweeds are used to produce alginates. Alginates are used as thickeners, gelling agents and stabilizers for frozen food and cosmetics (Jard et al., 2013). Red seaweeds are used for anti-fouling, antibiotic and anti-malarial applications (Werner et al., 2004).

Seaweeds are excellent indicators of pollution (Werner et al., 2004). Algae blooms of *U. lactuca* are an indicator of eutrophication through excess nitrogen in estuarine waterways (Allen et al., 2013a) associated with non-point source pollution (run off of slurries) and point source pollution (sewage outfalls). However growing and harvesting of macroalgae removes nutrients from water and therefore can be used to reduce eutrophication (Hughes et al., 2013).

U. lactuca can have a sulphur content of up to 5%. This leads to significant levels of hydrogen sulphide (H_2S) in anaerobic digestion. In long shallow coastal estuaries suffering from eutrophication and associated algae blooms, the "rotten egg" smell of H_2S is apparent at low tide when the bloom is deposited on the bay (Allen et al., 2013a).

2.2 Protein and carbon to nitrogen (C:N) ratios

Optimum levels of a substrate's C:N ratio for anaerobic digestion are in the range 20:1 to 30:1. Digestion of nitrogenous substrates (C:N ratio less than 15) can lead to problematic digestion caused by excess levels of ammonia (Allen et al., 2013b). Protein (primary source of nitrogen) concentrations are low in brown seaweeds, whilst high in red and green seaweeds (Jard et al., 2013). This can lead to situations whereby *U. lactuca* may have a C:N ratio less than 10 (Allen et al., 2013a) whilst *Saccharina latissima* can have a C:N ratio of 22 (Jard et al., 2013).

Jard et al. (2013) describe a seasonal variation in protein content. S. latissima had a maximum value of protein in May (150 g/kg TS) and a minimum (at half the protein content) in summer (73 g/kg TS). Higher protein content leads to increased N and lower C:N ratios. Thus, as the summer progresses from May to August (in the northern hemisphere) the C:N ratio rises. This in turn can lead to higher biomethane potential assay results. Values of 204 L CH_4/kg VS were recorded in May digesting S. latissima, rising to 256 L CH_4/kg VS in August (Jard et al., 2013).

Bruhn et al. (2011) cultivated *U. lactuca* in ponds. The C:N ratio of *U. lactuca* was found to vary from of 7.9 to 24.4. Incoming irradiance was suggested as the controlling factor in the C:N ratio. With more light, seaweed accumulates more carbon (and carbohydrates) which leads to an increase in the C:N ratio.

Bruhn et al. (2011) found that nitrogen starved *U. lactuca* produced more biomethane than nitrogen replete *U. lactuca*. The critical value of N of 2.17% of TS for maximum growth was recorded (Bruhn et al., 2011) while a subsistence value of 0.71% of TS as N was noted by Pedersen and Borum (1996).

2.3 Categorisation of seaweed
2.3.1 Proximate analysis

Proximate analysis assesses the dry or total solids content, the volatile solids content and the ash content of the substrate. The total solids may be defined as the mass of material remaining after heating the substrate to 105°C for 1 hour expressed as a percentage of the mass of the starting wet material. The volatile solids content may be defined as the mass of solids lost during ignition at 550°C for 2 hours in a covered crucible expressed as a percentage of total solids (APHA, 2005).

Jard et al. (2013) found a TS content in brown

seaweeds ranging from 8.5 to 18.5% (*Saccorhiza polyschides* and *Saccharina latissima* respectively), in red seaweeds from 8.3 to 16% (*Asparagopsis armata* and *Palmaria palmate* respectively) and 10.1% in *Ulva*. Fresh *U. lactuca* had a TS content between 9.6% (Msuya and Neori, 2008) and 20.4% (Lamare and Wing, 2001).

In assessing a wide range of brown, red and green seaweeds Jard et al. (2013) found a significant range for VS in different seaweeds collected in France. For brown seaweeds the values ranged from 44.6% to 63% of total solids (*Saccorhiza polyschides* and *Himanthalia elongate* respectively) and for red seaweeds, from 51.6% to 73.8% (*Asparagopsis armata* and *Palmaria palmate* respectively). *U. lactuca* had the highest volatile solid content of 82.1%.

However, other authors showed lower values for VS/TS ratio of *Ulva*. Bruhn et al. (2013) reported a VS content of 57% for *U. lactuca* in Denmark. Allen et al. (2013a) found a VS content of 58% for *U. lactuca* collected in June 2011 from an estuary in West Cork. It is suggested by Jard et al. (2013) that as the summer proceeds, the seaweed would accumulate more carbon, the C:N ratio would increase and the *Ulva* would have a higher VS content. However this is contradicted by Briand and Morand (1997) who found a different trend in

the variation in the volatile solids of *U. lactuca*; a June harvest resulted in an 83 % ratio of VS/TS whilst an August harvest yielded 65%. As the season progressed the biodegradability decreased.

2.3.2 Ultimate analysis

Ultimate analysis assesses the portion of carbon, hydrogen and nitrogen in a dry solid sample of the substrate. This allows generation of a stoichiometric equation of the total solids content of the substrate. For example Allen et al. (2013a) found that fresh *Ulva* had 25% carbon, 3.7% hydrogen, 27.5% oxygen and 3.3% nitrogen. The proportions yielded a stoichiometric equation of the *Ulva* sp. as $C_9H_{16}O_7N$. Application of the Buswell equation allows a theoretical biogas production potential to be determined. Using the stoichiometric equation for *Ulva* sp. collected by Allen et al. (2013a), a theoretical maximum methane production of 431 L CH_4/kg VS at 51.5% methane content is found.

Allen et al. (2015) collected seaweeds from the coast of West Cork in 2013. The C:N ratio for most of the samples were in excess of 15 with many in excess of 20. The optimum range for anaerobic digestion is 20:1 to 30:1. Volatile solids ranged from a low of 8% of wet weight to 19% of wet weight.

Table 4: Characteristics of raw seaweeds collected in Cork in 2013 (adapted from Allen et al., 2015)

Substrate	TS % of wet wt	VS % of wet wt	Ash % of TS	C % of TS	H % of TS	N % of TS	O % of TS	C:N ratio
A. nodosum	23.2	19.4	16.1	40.4	5.3	1.6	36.6	26.0
H. elongate	12.65	8.10	36.0	30.8	4.1	1.4	27.7	21.4
L. digitata	14.20	10.34	27.2	34.2	4.8	1.5	32.3	22.3
F. spiralis	19.72	13.92	29.4	36.1	4.7	2.1	27.7	17.3
F. serratus	20.07	14.74	26.6	37.1	4.8	2.4	29.1	15.5
F. vesiculosus	21.18	16.11	24.0	26.8	3.2	1.5	44.5	17.6
S. polyschides	15.25	13.11	14.0	36.1	5.0	1.6	44.3	23.2
S. latissima	15.49	10.09	34.9	29.1	3.8	1.2	31.0	24.0
A. esculenta	18.72	11.91	36.4	29.3	4.2	1.9	28.2	15.5
U. lactuca	18.03	10.88	39.7	30.0	4.4	3.5	22.4	8.5

Table 5: Specific Methane Yields obtained from Ulva

Ulva lactuca	Pre-treatment	SMY (L CH$_4$/kg VS)	Country	Reference
No pre-treatment				
Fresh		183	Ireland	Allen et al., 2013a
Fresh		174	Denmark	Bruhn et al., 2011
Fresh		128	France	Peu et al., 2011
Unwashed				
Unwashed	Wilted	165	Ireland	Allen et al., 2013a
Unwashed	Macerated	271	Denmark	Bruhn et al., 2011
Washed not dried				
Washed	Chopped	171	Denmark	Bruhn et al., 2011
Washed	Milled	191	Ireland	Vanegas and Bartlett, 2013
Washed	Macerated	200	Denmark	Bruhn et al., 2011
Washed	Wilted	221	Ireland	Allen et al., 2013a
Dried with size reduction				
Washed and dried	Chopped	241	France	Jard et al., 2013
Washed and dried	Macerated	250	Ireland	Allen et al., 2013a

2.4 Biomethane potential from seaweed
2.4.1 BMP results from mono–digestion of Ulva lactuca (green seaweed)

Allen et al. (2013a) collected *U. lactuca* from West Cork, Ireland and assessed the biomethane potential (Box 2) of fresh *Ulva* as 183 L CH$_4$/kg VS. The Buswell equation suggests 431 L CH$_4$/kg VS. Thus the biodegradibility index (BI) (see Box 2) is 42% indicating that a lot of energy remains in the digested material and less than half has been released as biomethane. *Ulva* typically has a low C:N ratio; all the samples sourced from West Cork had a C:N ratio of less than 10. Table 5 outlines results from BMP assays on *U. lactuca*. The values from fresh *Ulva* from Ireland and Denmark are very similar. Bruhn et al. (2011) collected *U. lactuca* from Seden Beach (Odense Fjord), Denmark. The ratio of VS/TS for these seaweeds were very similar (57% and 58%). Untreated fresh *Ulva* collected in Ireland generated 183 L CH$_4$/kg VS while the *Ulva* from Denmark generated 174 L CH$_4$/kg VS. This would suggest that similar results can be obtained from *Ulva* in Northern Europe. However pre-treatments can vary the BMP result significantly. With reference to Table 5, relationships may be established.

- Wilting is suggested as a cheap method to increase the TS content and as such the methane production per unit volume. However wilting is difficult in temperate oceanic climates with significant summer precipitation (such as Ireland). Wilting however appears of little benefit compared with maceration.
- Washing may be carried out to reduce the concentration of salts which may be inhibitory to the

Box 2
Biomethane Potential (BMP) test or assay

The biomethane potential test or assay is a batch test whereby a sample of substrate is usually introduced to a small digestion vessel (2L or less in volume) with an inoculum. The vessel is heated to the mesophilic temperature range and mixed. Gas production is monitored over time along with composition. The result of the test is recorded in L CH$_4$/kg VS which is termed the specific methane yield (SMY). The methodology of the test can vary. The ratio of substrate to inoculum is defined by the ratio of VS in both. For example Angelidaki et al. (2009) suggest a minimum ratio of 2:1 (VS$_{inoculum}$:VS$_{substrate}$). The test continues until gas production is exhausted. If the ratio of inoculum to substrate is sufficient this may take 30 days or less. Typically the test is carried out in triplicate to allow assessment of the range of values and statistical accuracy of the result to be given. Another three vessels contain only inoculum allowing assessment of the SMY of the inoculum. This is deducted from the vessel with inoculum and substrate to yield the SMY of the substrate only.

The biodegradibility index (BI) is defined as the ratio of the SMY recorded in the BMP assay to the theoretical maximum that may be achieved according to the Buswell equation (Allen et al., 2015).

methanogenic bacteria. However washing does not appear beneficial in terms of increasing the specific methane yield (SMY).

- Drying seems to be of great benefit. This raises the SMY to 241 – 250 L CH$_4$/kg VS. It is also beneficial as it increases the methane production per volume of substrate from ca. 20m³/t to 100 m³/t (Allen et al., 2013a; Bruhn et al., 2011)

2.4.2 BMP results from mono-digestion of brown seaweeds

The BMP results from the literature are summarised in Table 6. The results are varied and reflect the fact that the seaweed was collected from different countries, at different times of year, with differing day length and light radiation, with different levels of nitrogen in the water, etc. The methodology of assessing the BMP may also differ; employing different inoculum, different inoculum to substrate ratio, different reactor volumes. However, it can be stated that brown seaweeds (excluding *F. serratus*) tend to generate between 150 and 350 L CH$_4$/kg VS.

Table 6: Specific Methane Yields obtained from brown and red seaweeds

Seaweed	BMP Yield L CH$_4$/kg VS	Country	Reference
Brown Seaweeds			
H. elongate	261	West Cork, Ireland	Allen et al., 2015
	202	Brittany, France	Jard et al., 2013
L. digitata	218	West Cork, Ireland	Allen et al., 2015
	246	Sligo, Ireland	Vanegas and Bartlett, 2013
F. serratus	96	West Cork, Ireland	Allen et al., 2015
S. latissima	342	West Cork, Ireland	Allen et al., 2015
	335	Sligo, Ireland	Vanegas and Bartlett, 2013
	223	Trondheim, Norway	Vivekanand et al., 2011
	220	Norway	Østgaard et al., 1993
	209	Brittany, France	Jard et al., 2013
A. nodosum	166	West Cork, Ireland	Allen et al., 2015
U. pinnatifida	242	Brittany, France	Jard et al., 2013
S. polyschides	255	Sligo, Ireland	Vanegas and Bartlett, 2013
	216	Brittany, France	Jard et al., 2013
S. muticum	130	Brittany, France	
Red Seaweeds			
P. palmata	279	Brittany, France	Jard et al., 2013
G. verrucosa	144	Brittany, France	Jard et al., 2013

2.5 Storage of seaweed prior to digestion

2.5.1 Annual variation in specific biomethane yield in brown seaweed

Adams et al. (2011) found a peak in specific methane yield in July (northern hemisphere). From Figure 5 it may be noted that June to November would be a good time to harvest seaweed (mean yield in excess of 235 L/kg VS) while December to May yielded mean yields less than 220 L/kg VS. This may lead to a necessity to ensile seaweed to allow a year round supply of biogas.

2.5.2 Ensiling of seaweeds

Harvesting of seaweeds can be conducted at optimal times throughout the year to allow for maximum biomass yield and high methane potential. However, biogas production at large scale is usually a continuous process which needs year-around supply of high-quality feedstock. Thus, seasonal harvest would require preservation of seaweed biomass. One possibility to preserve seaweeds is to remove moisture by drying. This is an energy-intensive process since the TS content of most seaweeds at harvest is below 20%.

Another method for wet preservation and storage of seaweed can be the preservation by ensiling. Ensiling is widely practiced throughout the world to preserve agricultural crops such as maize or grass (Wilkinson et al., 2003). The principle of silage preservation is based on the conversion of water-soluble carbohydrates to organic acids, mainly lactic acid, by lactic-acid producing bacteria under anaerobic conditions. Accumulation of organic acids results in a reduction of the pH-value of ensiled biomass and inhibits the growth of
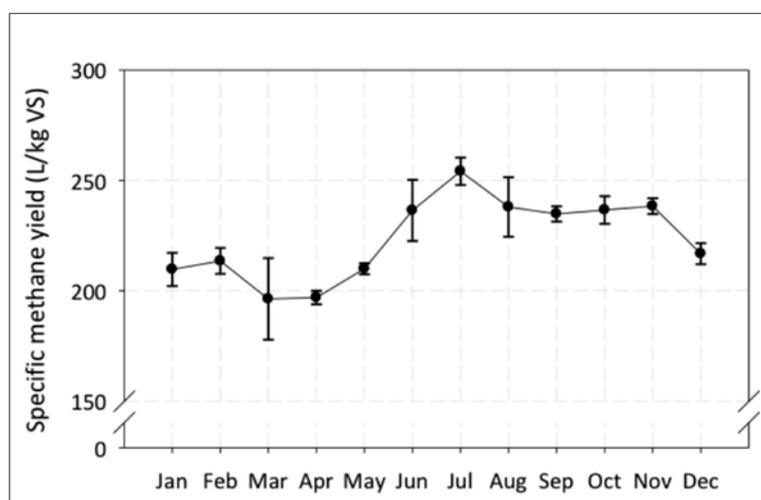
Figure 5: Annual variation in methane potential of L.digitata in the UK in 2008 (adapted from Adams et al., 2011)

undesired microorganism such as clostridia, yeasts and moulds in the absence of oxygen (McDonald et al., 1991). This prevents decomposition of organic compounds. Silage preservation is commonly used for forage production but has also been shown to be an appropriate method for storage of feedstock for biogas production (Herrmann et al., 2011). It was found that products of silage fermentation increase the specific methane yield and can compensate for storage losses (Herrmann et al., 2011).

Ensiling of seaweed has received little attention so far. Black (1955) investigated ensiling of *L. cloustoni*, *L. digitata*, *L. saccharina* and *A. nodosum* for animal feed and chemical processing purposes. It was concluded that these macroalgae support lactic acid fermentation and can be ensiled without inoculation (Black, 1955). However, pH-values of the seaweed silages did not decline below 4.8 in this study. High concentrations of carbohydrates in seaweeds are advantageous and can

provide sufficient substrate to ensure a proper ensiling process. On the other hand, TS content in seaweed bio-mass is low, thus, a significant decline in pH and a high rate of lactic acid production is necessary for efficient inhibition of undesirable bacteria (McDonald et al., 1991). Furthermore, TS contents below 25% will result in excessive formation of silage effluent (McDonald et al., 1991). Since effluent contains easy digestible components such as soluble carbohydrates, organic acids and alcohols, it is essential to collect and utilise the liquor in order to avoid large losses in biomethane potential.

2.6 Continuous digestion of seaweed with other substrates
2.6.1 Seaweed digestion in Solrød Kommune, Denmark

There is not a lot of data available on long term digestion of seaweed. There are very few commercial applications of such a technology. In Solrød Kommune a biogas plant has been constructed and in 2014 was in commissioning (Solrød Kommune, 2014). The drivers for the facility included removal of foul odours from cast seaweed on the beaches, a better marine environment, reductions in nitrogen load to the sea and reductions in CO_2 associated with energy production.

The feedstocks include cast seaweed (from 20 km of beach); organic waste from a gelling agent production factory (CPKelco); food processing waste from Chr. Hansen A/C and liquid pig manure (Table 7). CPKelco produces pectin (gelling agent produced from citrus fruits) and carrageenan (gelling agent extracted from red edible seaweed). Chr. Hansen A/S is a producer of food cultures, probioti and enzymes.

Table 7: Feedstocks and methane production from biogas facility at Solrød Kommune (adapted from Solrød Kommune, 2014)

Feedstock	Substrate		Methane production		Specific methane yield
Liquid pig manure	53,200 t/a	26.6%	570,000 m³/a	9.5%	10.7 m³/t
Biomass from CPKelco	79,400 t/a	39.7%	4,590,000 m³/a	76.5%	57.8 m³/t
Biomass from Chr. Hansen	60,000 t/a	30%	810,000 m³/a	13.5%	13.5 m³/t
Seaweed	7,400 t/a	3.7%	30,000 m³/a	0.5%	4 m³/t
Total	200,000 t/a	100%	6,000,000 m³/a	100%	30 m³/t

A significant challenge for the seaweed is sand removal as the seaweed is cast. A two stage process is used: sieving at the beach collection followed by washing at the biogas plant. The specific methane yield for seaweed is very low; from section 2.4.1 *Ulva* generates 20m³ of methane per tonne wet weight. It is stated that the BMPs were taken in January which is not optimal (see Figure 5). No data is given on the species of seaweed, nor the dry or volatile solids content (Solrød Kommune, 2014).

The facility cost 85 million DKK ($11.9M) excluding the CHP plant, produces 23 GWh of electricity, 28 GWh of energy for district heating, and generates an annual return from gas sales of 23 million DKK ($3.22M). It is expected that 14 people will be involved in the operation of the plant and transport of the feedstocks and digestates. The saving to the municipality in greenhouse gas emissions will be of the order of 40,000 t of CO_2 per annum.

2.6.2 Difficulties in long term digestion of seaweed

Biogas production from seaweed is innovative, challenging and does not have a lot of empirical data to learn from. High concentrations of sulphur, sodium chloride and heavy metals can lead to potential inhibition (Nkemka and Murto, 2010). Sodium chloride is a process inhibitor at high levels but is still required in small concentrations (Suwannoppadol et al., 2012). Sodium ions are required at levels between 100 and 350 mg/L for healthy anaerobic digestion microbial community metabolism. However at levels of 3,500 mg/L to 5,500 mg/L a medium inhibitory effect to methane-producing microorganisms is caused, while a strong inhibitory effect occurs above 8,000 mg/L. Acclimatisation of inoculum to a high sodium concentration over a long period, such as 12 months to 24 months, can significantly increase the tolerance and reduce the lag phase time during AD. Alternatively, direct use of inoculum sourced from marine environments may be a cost-effective approach to reduce the sodium inhibition (Chen et al., 2008). It was reported that when ammonia levels are low that tolerance for salts can be higher (Hierholtzer and Akunna, 2012).

Inhibition of the digestion process can also occur when the C:N ratio is lower than 15. This can lead to increased levels of ammonia in the reactor, which can eventually lead to failure (Allen et al., 2013b).

2.6.3 Co-digestion of green seaweed with slurry

U. lactuca is a problematic seaweed both in that it reduces the amenity of the shore and that it is problematic for anaerobic digestion having a particularly low C:N ratio and a high sulphur content. Co-digestion with cattle manure can overcome some of these problems (Sarker at al., 2012). Allen et al. (2014) co-digested both fresh and dried *Ulva* with cattle slurry in long term continuous digestion at laboratory 5L scale reactors. Three reactors co-digested *Ulva* with slurry at 25%, 50% and 75% of the VS in the feedstock. The optimum mix was 25% fresh *Ulva* and 75% dairy slurry which reached 93% of the biomethane potential (170 L CH_4/kg VS) at an organic loading rate (OLR) of 2.5 kg VS/m³/d with a FOS/TAC (alkalinity ratio) of 0.3 (stable) and total ammoniacal nitrogen levels (TAN) of 3000 mg/l. The worst mix was 75% fresh *Ulva* and 25% dairy slurry which could only operate at an OLR of 1 kg VS/m³/d with a FOS/TAC of 0.45 (unstable).

2.7 Gross energy yields in seaweed biomethane

2.7.1 Gross energy yields per hectare of seaweed biomethane systems

There is little agreement or established data on the yields of seaweed per hectare per annum. This obviously varies by species, by geographical location, by nutrient levels, by method of cultivation, on whether the seaweed is cast or cultivated. Christiansen (2008) suggests that a one hectare farm could yield 130 wet tonnes of kelp per annum. Kelly and Dworjanyn (2002) suggest 15 t TS ha⁻¹yr⁻¹ for brown algae in temperate water. Bruhn et al. (2011) undertook laboratory based tank results which suggested yields of *U. lactuca* of 45 t TS ha⁻¹yr⁻¹ at latitudes of 56°N (Denmark). These yields may be compared with grass silage yields of 10 to 15 t TS ha⁻¹yr⁻¹ (Smyth et al., 2009). Table 8 provides an estimation of the gross energy yields per hectare for a number of seaweeds and energy crops. The yields of

seaweed vary greatly depending on variety and method of cultivation. Existing methods of growing seaweed on ropes with separation to allow boat travel between lines for harvest leads to relatively low potential yields. This may be noted in the first entry in Table 8 where the yield of laminaria is 5 t TS/ha/year. Larger yields are predicated on systems that allow maximum growth per unit of water area. For example the European Commission funded research project AT-SEA is investigating advanced textiles for seaweed cultivation. These textiles will be seeded in-house and taken to the site where seaweed will grow. A test facility is in place in Galway Bay, Ireland. It is expected that yields of 20 kg/m^2 may be achieved. This equates to 200 t wet weight (ww) per hectare per annum or approximately 30 t TS ha^{-1}yr^{-1}(assuming 15% TS; see Table 4). This is not yet proven. Furthermore it is expected that only 60–70% of a hectare would actually be covered by textiles. This would reduce the yield to ca. 130 t ww or 19.5 t TS ha^{-1}yr^{-1}.

2.7.2 Comparison of biofuel systems on a gross energy yield per hectare basis

Maize is the dominant crop used for biomethane production (Murphy et al., 2011). The yield per hectare is remarkable, particularly in warm continental summers. Fodder beet also has a high yield though it is used less than maize. Grass would be an optimal crop for biomethane production in oceanic temperate climates, such as Ireland (Smyth et al., 2009).

There is a wide range of data on potential yields of biomethane from seaweeds, but taking conservative values the energy yield per hectare from seaweeds could be of a similar order to that from grass. Obviously seaweed is not available for digestion in continental climates situated remotely from the sea. However, seaweed has large potential as a biogas crop in temperate oceanic climates in coastal areas, where it could be co-digested with grasses and slurries. The exact length of coastline depends on the length of grid to evaluate the length, however according to Wikipedia, the UK has

Table 8: Potential gross energy production per hectare per annum based on a variety of species of seaweed (Allen et al., 2015; Smyth et al., 2009; Murphy et al., 2011)

Substrate	Yield (harvest)		Bio-methane yield	Biomethane yield	Gross Energy
	t TS ha^{-1} yr^{-1} (*t VS ha^{-1} yr^{-1})	t ww ha^{-1} yr^{-1}	m^3 CH$_4$ t^{-1}ww	m^3 ha^{-1} yr^{-1}	GJ ha^{-1} yr^{-1}
L. digitata	5.0[a]	35.2	22.5	792	28
S. polyschides	22.5[b]	147.5	34.5	5090	181
S. latissima	30.0[c]	297.3	34.5	10,260	365
A. esculenta	36.0[d]	302.2	26.9	8130	289
U. lactuca	45.0[e]	249.6	20.9	5216	186
L. hyperborean	30.0 – 90.0[f]			6,630 – 19,890	239 – 716
L. japonica	31.0[c] – 80.0[g]			8,060 – 20,800	290 – 749
M. pyrifera	34.0[d] – 50.0[h]			13,260 – 19,500	477 – 702
Biomethane from crops					
Fodder beet	16			6,624	250
Maize	19.5			5,748	217
Grass	12.5			4,303	163
Rye	2.1			732	28

[a] BIM. Business plan for the establishment of a seaweed hatchery and grow-out farm. Part 2. Bord Iascaigh Mhara; 2013.

[b] SEAI. A review of the potential of marine algae as a source of biofuel in Ireland. 2009.

[c] Sanderson JC, Dring MJ, Davidson K, Kelly MS. Culture, yield and bioremediation potential of Palmaria palmata (Linnaeus) Weber & Mohr and *Saccharina latissima* (Linnaeus) C.E. Lane, C. Mayes, Druehl & G.W. Saunders adjacent to fish farm cages in northwest Scotland. Aquaculture 2012; 354-355:128-35.

[d] Kain J, Dawes CP. Useful European seaweeds: past hopes and present cultivation. Hydrobiologia 1987;151-152(1):173-81.

[e] Bruhn A, Dahl J, Nielsen HB, Nikolaisen L, Rasmussen MB, Markager S, et al. Bioenergy potential of *Ulva lactuca*: biomass yield, methane production and combustion. Bioresour Technol 2011; 102(3): 2595-604.

[f] Norderhaug KM, Christie H. Secondary production in a *Laminaria hyperborea* kelp forest and variation according to wave exposure. Estuar Coast Shelf Sci 2011; 95(1): 135-44.

[g] Yokoyama S, Jonouchi K, Imou K. Energy production from Marine biomass: fuel cell power generation driven by methane produced from seaweed. Int J Appl S. C Eng Technol 2010.

[h] Brinkhuis BH, Levine HG, Schlenk CG, Tobin S. Laminaria cultivation in the Far East and North America. In: Bird KT, Benson PH, editors. Seaweed cultivation for renewable resources. Amsterdam: Elsevier; 1987. p. 107-46.

a coastline of 19,700 km, South Korea 12,500 km, France 7,300 km and Ireland 6,400 km.

Table 9 provides a comparison of the gross energy yield from first generation liquid biofuel systems. Data tends to be site specific. It is difficult to be precise. The data expressed in Table 9 are typical values in the middle of ranges. It can be stated that seaweed biomethane has the potential to surpass the best yields of first generation biofuels with the advantage of not requiring agricultural land. This is noteworthy when considering that 0.2 ha of arable land per person was available on the planet in 2011 (Murphy & Thamsiriroj, 2011).

2.7.3 Perspective on net energy yields in macroalgae biomethane

The net energy per hectare of seaweed biomethane is unknown. Typically macroalgae can be categorised into three cases:
1. *U. lactuca*: a residue which is detrimental to coastal estuaries and may require removal to ensure the amenity of a bay.
2. Cast seaweed: seaweed collected from the shore
3. Aquaculture: harvesting of seaweed.

The energy necessary for "crop" production will increase from case 1 to case 3. If *Ulva* needs to be removed from a bay, the energy in transport may be neglected as the *Ulva* must be removed, whether it is digested or not. This is comparable to digestion of food waste. Cast seaweed is not "sowed". The only energy in production is harvesting and transporting. Aquaculture will likely require the highest energy in production. It is grown, harvested and transported. It is unlikely that it has the same level of energy in production as crops on land. Fertiliser, herbicides and lime should not be used for cultivation. Typically the seaweed will draw nitrogen from polluted waters (such as in close proximity to salmon farms) and act as enhancers of the environment.

2.7.4 Yield of seaweed to satisfy 1.25% renewable energy in transport in EU

As per section 1.3.1 a press release from the Environment Committee of the European Parliament concluded that "advanced biofuels sourced from seaweed or certain types of waste should account for at least 1.25% of energy consumption in transport by 2020". Jacob et al. (2015b) suggest, through preliminary calculations, this would require 168 Mt of seaweed per annum (producing 34 m^3 CH$_4$/t ww); this is in excess of the present world harvest of 26 Mt. Considering a density of 55 t ww per hectare this would require an area of 2.96 M ha or 35% of the land area of Ireland. This indicates the scale of production that would be necessary for transport fuel production that relies on seaweed.

2.8 Alternative uses of seaweed

The opportunity cost of using seaweed for energy must be considered. The present world harvest of seaweed of 26 Mt has a market. Several countries including China, Japan and the Republic of Korea eat seaweed. *Laminaria* (kombu), *Undaria* (wakame) and *Porphyra* (Nori) are sold at $2,800/dry tonne, US$ 6,900/dry tonne and US$ 16,800/dry tonne respectively (Jacob et al., 2015b).

Seaweeds are also used to produce hydrocolloids and gelling agents in the food processing and cosmetics industry. An example of this is outlined in section 2.6.1 where CPKelco produces carrageenan a gelling agent extracted from red edible seaweed. Other applications of seaweeds include bio-catalysis and bio-plastics (Jacob et al., 2015b). It is most likely that the optimal seaweed biofuel industry is associated with a biorefinery where products are extracted from seaweeds with biogas for energy as a by-product.

Table 9: Estimated gross energy production from first generation biofuel data from (Thamsiriroj and Murphy, 2009; Murphy and Power, 2008)

Substrate	Crop yield per hectare	Biofuel yield		Gross Energy
	t/ha/a	L/t	L/ha/a	GJ/ha/a
Ethanol				
Wheat	8.4	375	3,150	66.5
Fodder beet	55	100	5,500	117
Biodiesel				
Palm Oil			5,000	160
Rape seed oil			1,320	42
Sun flower			800	26

Figure 6: Relevant abiotic (filled spheres) and biotic (empty spheres) parameters for microalgae cultivation

3 Biogas from microalgae

3.1 Cultivation of microalgae

For sufficient growth photoautotrophic microalgae, like higher plants and macroalgae, need appropriate amounts of light, water, carbon and a variety of mineral nutrients. Essential elements such as nitrogen, iron, phosphate and silicate are required in large quantities. A lack of these nutrients leads to a cessation in growth. To ensure optimal growth, the cultivation media should contain nutrient levels comparable or above the C:N:P ratio of the algae themselves. As summarized by Falkowski (2000) values between $C_{103-137}$: N_{15-20}: P_1 occur in plankton and seawater. Principally, growth media should satisfy this nutrient composition, although nutrient amounts vary, depending on the species cultivated (Becker, 1994). Culture media applied in large scale cultivation are the same as in the laboratory, with modifications to meet the purpose of cultivation (Borowitzka, 2005). BG11 medium (Rodolfi et al., 2009) adapted after Rippka et al. (1979) was used in pilot scale, Mann and Meyers medium and modified Ukeles medium were applied by Sánchez Mirón et al. (1999). Since synthetic cultivation media are expensive, large scale production of microalgae is also carried out with seawater (Moazami et al., 2012), artificial seawater enriched with F/2 growth medium nutrients (Zhang & Richmond, 2003) or wastewater (Olguín et al., 2003). Figure 6 outlines parameters, which have to be considered and adjusted according to the needs of the specific algae species to allow optimal growth.
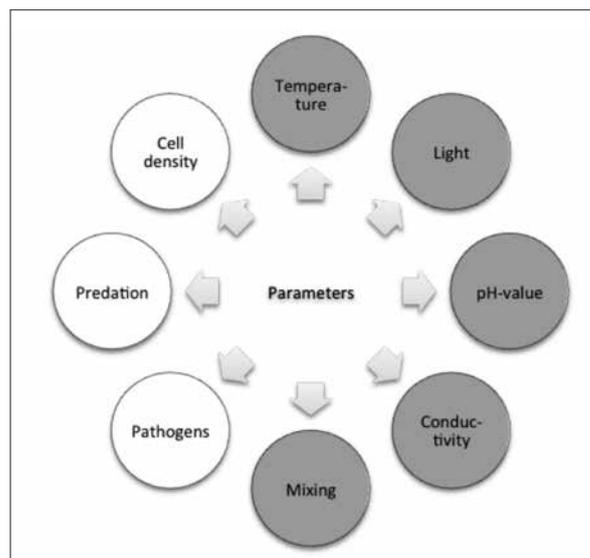
3.2 Cultivation systems

The most efficient way to produce microalgae biomass economically and environmentally has yet to be defined. There are several approaches for producing microalgae biomass, which strongly differ from each other in terms of construction, efficiency and economy.

Principally microalgae mass cultivation systems can be divided into outdoor and indoor systems; outdoor systems are more economic because of the utilization of sunlight. Another differentiation can be made between open and closed cultivation systems (Table 10) and between the application of immobilized (benthic) and free floating (pelagic) species.

Biomass productivity by area differs widely across the various cultivation systems (Pulz, 2001): open systems achieve a productivity rate of 10 – 25 g m^{-2} d^{-1}, closed systems 35 – 40 g m^{-2} d^{-1} and thin-film systems 80-100 g m^{-2} d^{-1}.

Figure 7: Solar drying of microalgae on the shore of Lake Kossorom (Abdulqader et al., 2000)

Box 3

Naturally occurring mass development of microalgae, such as *Arthrospira platensis* in Lake Kossorom (Chad) and its harvest and application as food is probably the cheapest option to produce microalgae biomass. As estimated by Abdulqader et al. (2000), around 40 t of dried *Arthrospira platensis* are harvested from this lake per year. The geographic location is an important factor when using only sunlight for algae cultivation; light intensity decreases with distance from the equator.

Table 10: Advantages and disadvantages of common cultivation systems (adapted from Pulz and Gross, 2004)

Cultivation system	Advantages	Disadvantages
Open	• Cheap • Good gas exchange with the atmosphere (release of O_2 is possible) • Easy to operate • Easy to scale up	• High risk of contamination (not as significant for biogas systems) • High evaporation losses • Large area required • Light limitation if thick layers are used
Closed	• Good control of cultivation parameters • Reduced contamination risk • Less CO_2 losses • Reproducible cultivation conditions	• Expensive • Scale up is difficult

3.2.1 Open cultivation systems

According to Pulz (2001) open cultivation systems can be divided into open vessels, natural water, inclined surface devices and raceway ponds (see Figure 8). Open systems have several drawbacks, such as, insufficient monitoring and control options for parameters such as pH, temperature, mixing and light availability. Sparged CO_2 has a very short residence time, resulting in high losses and poor solubility. Furthermore seasonal variations contribute to reduced reproducibility of data. Other disadvantages include, high water losses due to evaporation; major risk of contamination by predators and other fast growing heterotrophs, which can lead to poor productivity or even a total loss of the desired production strain (Brennan & Owende, 2010; Kumar et al., 2010; Pulz, 2001; Wang et al., 2008; Ugwu et al., 2008). In spite of all these negative aspects, the advantages of open systems can still outweigh disadvantages. The large benefit of open cultivation systems is their

cheap and simple maintenance (Becker, 1994). Since this is also the case for construction of raceway ponds, upscaling is easy (Christenson and Sims, 2011). Therefore they are more often applied in large scale approaches (Table 10).

3.2.2 Closed cultivation systems (photobioreactors)

Among the closed systems several types of PBRs exist (examples shown in Figure 9). The following configurations were tested for microalgal mass cultures; tubular reactors, laminar (or flat panel) reactors, hanging plastic sleeves and fermenter-like tank reactors (Pulz 2001). The latter are often artificially illuminated, while the others are, in the majority of cases, operated without artificial illumination. Although closed systems are more complex, they offer better control of crucial parameters and at the same time contamination is less likely (Carvalho et al., 2006). The main challenges in any PBR system are: light availability; CO_2 introduc-

Figure 8: Open cultivation systems for cultivation of microalgae; left: Race way ponds at pilot-scale (© Elad Zohar, Erber Future Business GmbH); right: cascade system (= thin film system) (© Jiri Kopecky, Institute of Microbiology, Trebon)
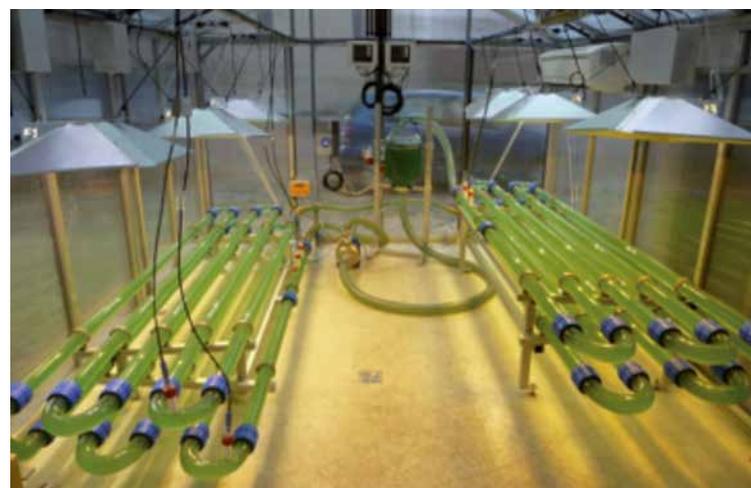
Figure 9: Closed pilot-scale cultivation systems for cultivation of microalgae, left: sleeve-bag photobioreactor (© Markus Gruber, IFA Tulln – University of Natural Resources and Life Sciences, Vienna) and right: tubular photobioreactor (© Katharina Meixner, IFA Tulln – University of Natural Resources and Life Sciences, Vienna)

tion; O_2 removal and sufficient mixing. Despite all the advantages, closed systems are much more expensive than open pond systems, if ground area is cheaply available.

3.3 Harvest of microalgae

A lot of harvesting techniques were developed in the last decades, but only a few of them were found to be effective at reasonable operational costs. The process of separating microalgae floating in a cultivation medium creates several difficulties. First of all, the concentration of cells in the culture medium is mostly quite low. Secondly, their size is often below 30µm. Thirdly, the density of cells is only slightly greater than water (Bekker, 1994). This means that a lot of energy is needed to concentrate the algae biomass in order to separate it from the medium.

Golueke et al. (1957) argued that alum flocculation is an essential step for economical harvesting of algae. According to Becker (1994) choosing the proper harvesting technique is crucial for further processing of the algae biomass and strongly depends on the species used (see Box 4).

According to Christenson & Sims (2011) current harvesting methods include chemical, mechanical, electrical and biological harvesting methods (Table 11). In the case of attached algae cultivation, mechanical harvesting, like scraping (Higgins & Kendall, 2012) or vacuuming (Craggs et al., 1996) can be applied. In these cases, algal biomass is already very dense and further concentration is most likely not necessary.

3.4 Chemical composition of microalgae
3.4.1 Typical composition of microalgae

The chemical composition of algal cells can vary over a wide range, as with any higher plant. Proportions of different constituents are influenced by several environmental factors. Among the most important factors are temperature, illumination, pH-value, mineral nutrients, and CO_2 supply (Becker, 1994). The components analyzed by most studies are carbohydrates, lipids and proteins (Table 12). The amount of proteins, carbohydrates and lipids ranged between 6–71, 4–64 and 1.9–40% of total solids (TS) within the studies compa-

Box 4
Questions to consider, when harvesting algae biomass
(Becker, 1994)
- What type of algae should be used: unicellular-coccoid, unicellular with spines or filamentous?
- Should the harvest be continuous or discontinuous?
- Is pre-concentration necessary?
- What is the required percentage of dry matter in the concentrate?
- What are the investment costs?
- What is the energy demand per cubic meter of algae suspension?

Table 11: Overview of different harvesting methods (Christenson & Sims, 2011) and dry solids output concentration (Milledge and Heaven, 2013). n.a. = not available.

Method	Process	Comments	Dry solids output concentration (%)
Chemical based	Precipitation / flocculation	– Addition of electrolytes or synthetic polymers to neutralize negative surface charge – The use of metal salts for coagulation and flocculation is cautioned due to potential inhibition of the specific methanogenic activity of methanogenic and acetogenic microbes	3 – 8
Mechanical based	Centrifugation	– Centrifugal forces are utilized to separate based on density differences – Probably the most rapid and reliable method of recovering suspended algae – Easy to operate – High investment and operating costs	10 – 22
	Filtration	– Often used for filamentous strains – For small, suspended algae tangential flow filtration is considered to be more feasible – high costs and power requirements	2 – 27
	Sedimentation	– Low costs – Low reliability because of fluctuating density of algal cells – Slow	0.5 – 3
	Dissolved Air flotation	– Air is released under high pressure and forms tiny bubbles in the water column, which adhere to the suspended matter causing the suspended matter to float – Has been proven in large scale – The additional use of flocculants might be problematic for further processing of the algae	n.a.
Electrical based	Separation based on electrophoresis	– No chemicals needed – High power requirements and electrode costs	n.a.
Biological based	Autoflocculation	– High pH and the consumption of dissolved CO_2 lead to co-precipitation of algal cells together with calcium phosphate	n.a.
	Bioflocculation	– Flocculation caused by secretion of polymers	n.a.
	Microbial flocculation	– Addition of flocculating microbes	n.a.

red by Becker (1994). The high variation makes comparison difficult, but generally the composition of algae biomass can be expected to be within the ranges given in Table 12.

3.4.2 Manipulation of microalgae composition

The composition of algal biomass can be manipulated by adapting growth media. This adaptation is due to the phenomenon of nutrient accumulation, when microalgae are cultivated in a nutrient deprived media.

The influence of nutrient levels in the growth media on the algal biomass composition was shown by Illman et al. (2000), where the highest lipid content (63%) was found in *C. emersonii*, grown in low nitrogen medium (Table 13). The highest calorific value of 29 kJ/g occurred in a nitrogen deprived media.

3.5 Production of biomethane from microalgae

Microalgae may be considered an advantageous substrate for anaerobic digestion due to high biomass productivity, low ash content and the reduced competition for arable land. The choice of optimal algal strains can lead to faster conversion of biomass to methane.

Table 12: Chemical composition of different microalgae expressed as a percentage of dry matter (Becker, 1994)

Strain	Protein	Carbohydrates	Lipids	Nucleic acid
Scenedesmus obliquus	50 – 56	10 – 17	12 – 14	3 – 6
Scenedesmus quadricauda	47	–	1.9	–
Scenedesmus dimorphus	8 – 18	21 – 52	16 – 40	–
Chlamydomonas rheinhardii	48	17	21	–
Chlorella vulgaris	51 – 58	12 – 17	14 – 22	4 – 5
Chlorella pyrenoidosa	57	26	2	–
Spirogyra sp.	6 – 20	33 – 64	11 – 21	–
Dunaliella bioculata	49	4	8	–
Dunaliella salina	57	32	6	–
Euglena gracilis	39 – 61	14 – 18	14 – 20	–
Prymnesium parvum	28 – 45	25 – 33	22 – 38	1 – 2
Tetraselmis maculata	52	15	3	–
Porphyridium cruentum	28 – 39	40 – 57	9 – 14	–
Spirulina platensis	46 – 63	8 – 14	4 – 9	2 – 5
Spirulina maxima	60 – 71	13 – 16	6 – 7	3 – 4.5
Synechoccus sp.	63	15	11	5
Anabaena cylindrica	43 – 56	25 – 30	4 – 7	–

Table 13: Cell contents of Chlorella strains grown on Watanabe and low–nitrogen media (Illman et al. 2000)

Species	Growth conditions	Protein (%)			Carbohydrate (%)			Lipid (%)			Calorific value (KJ/g)		
C. vulgaris	control	29	±	2.5	51	±	2	18	±	2.1	18	±	0.7
	Low-N	7	±	1.6	55	±	3.2	40	±	2.1	23	±	2.1
C. emersonii	control	32	±	2.9	41	±	2.5	29	±	2.5	21	±	0.7
	Low-N	28	±	3.8	11	±	2.2	63	±	1	29	±	0.7
C. protothecoides	control	38	±	3	52	±	2.3	11	±	3.2	19	±	1.6
	Low-N	36	±	3	41	±	3	23	±	1.2	24	±	2
C. sorokiniana	control	45	±	2.9	38	±	2.2	20	±	1.6	21	±	0.7
	Low-N	42	±	1.6	32	±	2.5	22	±	2.6	20	±	1.6
C. minutissima	control	24	±	3.1	42	±	3.2	31	±	3.2	21	±	1.2
	Low-N	9	±	2	14	±	2.1	57	±	2.5	21	±	1

Some strains possess no cell walls; some strains have protein-based cell walls without cellulose or hemicellulose. These attributes make them more easily degradable (Mussgnug et al., 2010).

Besides easy degradability, other features, like productivity or sensitivity to contamination, have to be considered. If the species of choice possesses rigid cell walls, resistant to anaerobic digestion, the application of a suitable pre-treatment is necessary (see 3.5.3).

3.5.1. Biomethane potential of microalgae

Measured specific biogas yields of microalgae vary between 287 and 611 L/kg VS and specific methane yields between 100 to 450 L/kg VS (Table 14). The reason for these broad ranges is that anaerobic digestion performance is very much strain specific, which might be explained by the different cell composition as well as the different cell wall characteristics of the strains.

After anaerobic digestion, intact cells of *Scenedesmus* sp. were detected in samples stored in the dark (Mussgnug et al., 2010; Golueke et al., 1957). This can be explained by the fact that *Scenedesmus* sp. is able to grow mixotrophically (Girard et al., 2014). The variation in biomethane yields may also be explained by the influence of the differing biomethane potential (BMP) test methodologies.

Some practical recommendations can be found for digesting microalgae. According to Heerenklage et al. (2010) and Golueke et al. (1957) thermophilic digestion of microalgae leads to higher biogas yields than meso-

Table 14: Methane and biogas production from different microalgae species measured by BMP tests (adapted after Mussgnug et al. (2010); Sialve et al. (2009) and Heerenklage et al. (2010))

Species	Temp. [°C]	Biogas prod. [L/kg VS]	CH$_4$ prod. [L/kg VS]	CH$_4$ content [%]	Literature
Arthrospira platensis		481 ± 14	293	61	Mussgnug et al., 2010
Chlamydomonas reinhardtii		587 ± 9	387	66	Mussgnug et al., 2010
Chlorella kessleri		335 ± 8	218	65	Mussgnug et al., 2010
Chlorella vulgaris	28 – 31		310 – 350	68 – 75	Sanchez and Travieso, 1993
Dunaliella salina		505 ± 25	323	64	Mussgnug et al., 2010
Dunaliela	35		420		Chen, 1987
Euglena gracilis		485 ± 3	325	67	Mussgnug et al., 2010
Nanochloropsis spp.	38	388	312	80.5	Schmack, 2008
Scenedesmus obliquuus		287 ± 10	178	62	Mussgnug et al., 2010
Spirulina	35		320 – 310		Chen, 1987
	38	556	424	76.3	Schmack, 2008
Spirulina maxima	35		190 – 340		Samson and LeDuy, 1983
Mixed algae sludge *(Clorella-Scenedesmus)*	35 – 50		170 – 320	62 – 64	Golueke et al., 1957
	50	500	Not specified		Golueke et al., 1957
	35	405	Not specified		Oswald et al., 1960
	45	611	Not specified		Golueke et al., 1959
	35		100 – 140		Yen et al., 2007
Green algae	38	420	310	73.9	Schmack, 2008

philic digestion. Zamalloa et al. (2012) noted that thermophilic digestion of *Scenedesmus obliquus* resulted in a biogas production 1.3 times that of mesophilic digestion. Drying of microalgae reduces biogas yields and is therefore not recommended. A decrease of 20% was reported by Mussgnug et al. (2010) and a comparable decrease of 16% was shown by degradation tests of *Tretraselmis* sp.

3.5.2 Theoretical biogas yields from microalgae

High lipid contents in the biomass can be advantageous because the theoretical biogas yield from lipids is generally higher (1390 L/kg VS) than proteins (800 L/kg VS) or carbohydrates (746 L/kg VS) (VDI 4630 2006). Microalgal biomass is of different composition to other biomass, therefore these yields must be adapted in order to prevent overestimation of the overall process feasibility. A recent publication recalculated theoretical methane yields for microalgal biomass giving 1014, 446 and 415 L/kg VS for lipids, proteins and carbohydrates (Heaven et al., 2011). Excess lipid and/or protein contents are not desirable as they can lead to accumulation of ammonia and long chain fatty acids (LCFAs), which are important inhibitors of anaerobic microorganisms (Chen et al., 2008).

3.5.3 Pre-treatment of microalgae

Some microalgae contain very thick cell walls, which can make anaerobic digestion quite challenging. The thickness of the relatively stable cell wall of *Chlorella pyrenoidosa* is for example 0.1 to 0.3 μm (Northcote et al., 1958). If a specific strain is considered suitable for biogas production due to high productivity, a pre-treatment step may allow higher biogas production

rates and yields. Table 15 gives an overview of different pre-treatment methods to improve anaerobic degradability of sludge. These methods are also applicable for microalgae. Schwede et al. (2013) showed that thermal pre-treatment of *Nannochloropsis salina*, prior to anaerobic digestion, significantly increased the methane yield. It could also be shown that the type of storage of the microalgae can have a significant effect on the methane yield (Gruber-Brunhumer et al., 2015).

In activated and primary sludge treatment, different technologies have been successfully applied to pre-treat biomass to increase the methane yield (Carrère et al., 2010). These pre-treatments could be used for microalgae to enhance their anaerobic digestion. Alzate et al. (2012) tested the anaerobic digestion of three microalgae mixtures. Pre-treatments included thermal, ultrasound, and biological treatment. Biological pre-treatments showed negligible enhancement of CH_4 productivity (Alzate et al., 2012). The highest CH_4 increase (46–62%) was achieved by thermal hydrolysis. The optimum temperature of this pre-treatment depended on the microalgae species (Alzate et al., 2012). The ultrasound pre-treatment increased the CH_4 productivity up to 24% at 10,000 kJ/kg TS; no further increase in productivity was noted at higher energy input (Alzate et al., 2012). In Figure 10 the effect of ultrasound pre-treatment on cells of *Chlorella vulgaris* can be seen.

It should be cautioned that parasitic demands of 10 MJ/kg TS is probably more than 50% of the energy in the starting substrate and as such will be significantly more than 50% of the energy in the biogas produced. This has major implications for the net energy in microalgae biogas and the sustainability of the bioenergy system.
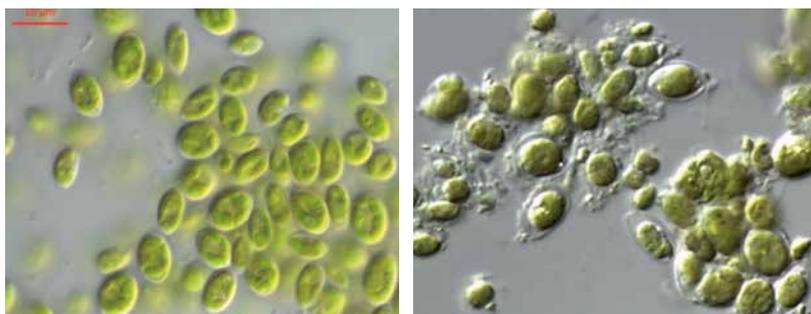

Figure 10: *Chlorella vulgaris* before (left) and after (right) ultrasound pre-treatment
(© Markus Gruber, IFA Tulln –University of Natural Resources and Life Sciences, Vienna)

Table 15: Overview of pre-treatment methods to improve sludge anaerobic degradability, (adapted after Carrère et al., 2010)

Pre-treatment method	Options
Thermal hydrolysis (>100°C)	– Different temperatures
Mechanical treatment	– Ultrasound
	– Lysis-centrifuge
	– Liquid shear (collision plate, high pressure homogenizer)
	– Grinding
Chemical pre-treatment	– Oxidation
	– Alkali treatments
Biological pre-treatments	– Enzymes
	– Predators

with microalgae biomass. The highest methane yield was 310 L/kg VS. Sialve et al. (2009) showed that the methane yield strongly depends on the species and culture conditions. As before, the effect of experimental conditions on results must be considered. The proportion of methane in the biogas is in a similar range (68 to 74%) for the majority of the studies, regardless of species and operating conditions; this indicates a good quality of conversion of the algal organic matter into methane (Sialve et al., 2009).

The influence of low temperature thermal (50–57°C) and freeze-thaw on algal digestion were studied by Kinnunen et al. (2014); they showed that both pre-treatments promoted protein hydrolysis and increased methane yields by 32–50% when digested at 20°C, compared to digestion of untreated microalgal biomass. The application of high pressure treatment by a French press or enzymatic treatment also increased methane yields compared to untreated *C. vulgaris* as shown by Heerenklage et al. (2010).

Semi-continuous digestion of *Scendedesmus* sp., grown in an open raceway pond was carried out by Tran et al. (2014). A specific methane yield of 130 to 140 L CH_4/kg VS added was achieved. The accompanying low VS destruction of 30% was attributed to the recalcitrant nature of the specific microalgal species and insufficient short retention times. A remedy would be longer retention times and/or application of pre-treatment methods (Tran et al., 2014).

3.5.4. Continuous microalgae digestion

According to Murphy and Thamsiriroj (2013) the optimal reactor design and configuration is a function of the feedstock characteristics. For fermentations with 2 – 12% TS continuously stirred tank reactors (CSTRs) are commonly used (e.g. Figure 11). The solids concentration of microalgae, harvested by mechanical harvesting methods (Table 11), is in the range 0.5 – 27% (Christenson & Sims, 2011), which makes it suitable for digestion with a CSTR. Hydraulic and solid retention time (HRT and SRT) are key parameters in anaerobic processes (Sialve et al., 2009) and should be high enough to allow the active microbial population, especially methanogens, to remain in the reactor. Insufficient HRT would limit hydrolysis.

Table 16 highlights studies, which investigated methane production in continuous systems operated

Figure 11: Continuous biogas fermentation at laboratory scale

Table 16: Methane and biogas production from different microalgae species measured by continuous fermentation trials (adapted after Sialve et al., 2009)

Species	Temp. [°C]	HRT [d]	OLR [g VS/L*d]	CH$_4$ prod. [L/kg VS]	Biogas prod. [L/kg VS]	CH$_4$ content [%]	Literature
Tretraselmis (fresh)	35	14	2	310	419 – 431	72 – 74	Asinari Di San Marzano et al., 1982
Tretraselmis (dry)	35	14	2	260	351 – 361	72 – 74	
Tretraselmis (dry) + NaCl 35 g/L	35	14	2	250	338 – 347	72 – 74	
Spirulina maxima	35	33	0.97	260	361 – 382	68 – 72	Samson and LeDuy, 1982

3.6. Synergies of microalgae production and biogas plants

3.6.1 Digestate as a nutrient source for algae cultivation

Digestate produced during fermentation processes contains high amounts of nutrients (Fuchs & Drosg, 2013) which could be utilized for microalgae cultivation (Franchino et al., 2013). Different microalgae strains (*Neochloris oleoabundans*, *C. vulgaris* and *Scenedesmus obliquus*) were cultivated on digestate obtained from a pilot anaerobic digester treating a mixture of cattle slurry and raw cheese whey. *C. vulgaris* cultivated in an 1:10 dilution showed the best performance and all three strains almost completely removed different nitrogen forms and phosphate within 11 days (Franchino et al., 2013).

Utilization of anaerobically digested microalgae effluent as a nutrient source for algae cultivation forming a closed nutrient loop system is another approach (Erkelens et al., 2014). Erkelens et al. (2014) showed that growth of *Tetraselmis* sp. on microalgae digestate is possible, but not as effective as in F/2 media, which was used for comparison.

The specific composition of digestate might be a challenge for microalgae cultivation. Excess concentrations of nutrients can have a negative effect on algal growth. For example, high ammonia concentrations of more than 1 g/L, which can occur in digestate, can inhibit photosynthesis (Abeliovich and Azov, 1976). Strong coloration of digestate can adversely affect growth efficiency of the algae due to reduced transparency. Turbidity of the growth medium has a negative influence on growth rates (Wang et al., 2010).

3.6.2. Biogas as carbon source

Biogas plants produce different types of CO_2-rich exhaust fumes, which could be utilized for algae cultivation. One source could be combined heat and power (CHP) units, other options are the usage of off-gas obtained by upgrading of biogas or untreated biogas. Usually the CO_2 content of most flue gases is between 3 and 15% (IPCC, 2005). Exhaust fumes originating from agricultural biogas plants have a relatively high CO_2 content of ca. 12% (Pfeifer and Obernberger, 2006).

These gases have been shown to be suitable as carbon source for microalgae cultivation (Travieso et al., 1993). Several projects aiming to cultivate microalgae by application of CO_2 from flue gas were presented by Van Iersel and Flammini (2010).

According to Doucha et al. (2005) about 50% of flue gas decarbonization can be attained in their outdoor open thin-layer photo-bioreactor and the production costs of algal biomass could be 15% lower with the help of flue gas utilization. NO_X and CO gases had no negative influence on the growth of *Chlorella* sp.

3.6.3. Microalgae as a means of upgrading biogas

Carbon dioxide biofixation using microalgae via efficient photosynthesis (Eq. 1) offers an alternative approach to upgrade biogas (Ho et al., 2011; Zhao and Su, 2014).

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 \quad \text{(Eq. 1)}$$
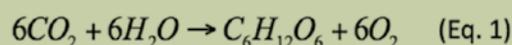
A lot of previous studies have reported carbon dioxide biofixation of flue gas, produced from coal-fired power plants, by high-growth rate microalgae (Cheng et al., 2013; Pires et al., 2012; Stephenson et al., 2010; Zhao and Su, 2014). Only a few studies have focused on carbon dioxide biofixation of biogas (Prajapati et al., 2013). Mann et al. (2009) used microalgae to directly upgrade biogas and found that the carbon dioxide content in biogas can be greatly reduced (by up to 97%) using *Chlorella* sp., but the photosynthetic oxygen (approximately 20%) made the gas mixture potentially explosive. This gas mixture needs high energy input and expensive processes to remove oxygen from gaseous transport fuels (Chaemchuen et al., 2013; Rykkebosch et al., 2011). Similar studies by others reinforced the oxygen content as in the range of 10 to 24% (Converti et al., 2009; Kao et al., 2012a).

Direct biogas upgrading by microalgae can be restricted by photosynthetic oxygen production. Xia et al. (2015) suggested an indirect biogas upgrading system which employs microalgae in a two-stage process, comprising carbon dioxide capture by carbonate solution and carbonate regeneration by microalgae cultivation, as shown in Figure 12 (Xia et al., 2015). In the first stage, carbon dioxide can be efficiently captured by a carbonate solution under alkaline conditions whereby bicarbonate is formed. In the second stage, bicarbonate is used as a carbon source for microalgae cultivation. Conversion of bicarbonate to carbon dioxide yields hydroxide and increases pH, leading to carbonate production (Chi et al., 2011). Therefore, carbonate can be regenerated from bicarbonate after carbon dioxide biofixation by

microalgae. The microalgae strains used in this system would need to be resistant to high pH. Microalgal strains grown in saline lakes, such as *Arthrospira*, *Synechococcus* and *Dunaliella*, can be used in halophilic and alkaliphilic systems. For instance, *Arthrospira platensis* and *Arthrospira maxima* can be cultivated with sodium concentration of 0.2–1.2 M Na$^+$ (or 4,600–27,600 mg Na$^+$/L or 11,700–70,200 mg NaCl/L) and pH of 8.0–9.5.

The mixture of microalgae and bacteria also has the potential to upgrade biogas. Bahr et al. (2014) reported that a mixed culture of microalgae and hydrogen sulphide oxidising bacteria could allow simultaneous capture of carbon dioxide by microalgae, whilst consuming photosynthetic oxygen by hydrogen sulphide oxidising bacteria (Bahr et al., 2014). Some further issues may need to be solved to commercialise such a process. Firstly, the oxygen content in upgraded biogas could be increased due to variation in hydrogen sulphide content in the biogas and the variation in the population of microalgae and hydrogen sulphide oxidising bacteria. This may necessitate a further oxygen separation process. Secondly, high methane or hydrogen content in biogas can inhibit microbial growth (Kao et al., 2012b).

3.7 Applications of microalgae
3.7.1 Microalgae as a means of capturing CO$_2$

Jacob et al. (2015a) investigated CO$_2$ capture from coal combustion using three cultivation systems, tubular PBR, a flat plate PBR and a raceway pond. Assumptions were made that the PBRs could capture 80% of the CO$_2$ while the raceway pond could capture 50% of CO$_2$. The model was based on a 1GW$_e$ power plant burning a bituminous coal (energy value of 24GJ/t) producing 6.77 million tonnes of CO$_2$ per annum by producing 2.69 million tonnes of volatile solid microalgae per annum in the PBRs.

This would require 34,000 ha of flat plate PBR (Jacob et al., 2015a). The gross energy in biogas from the microalgae was estimated to be 35% of the primary energy in the coal. However questions were raised about the energy input to microalgae cultivation. The tubular
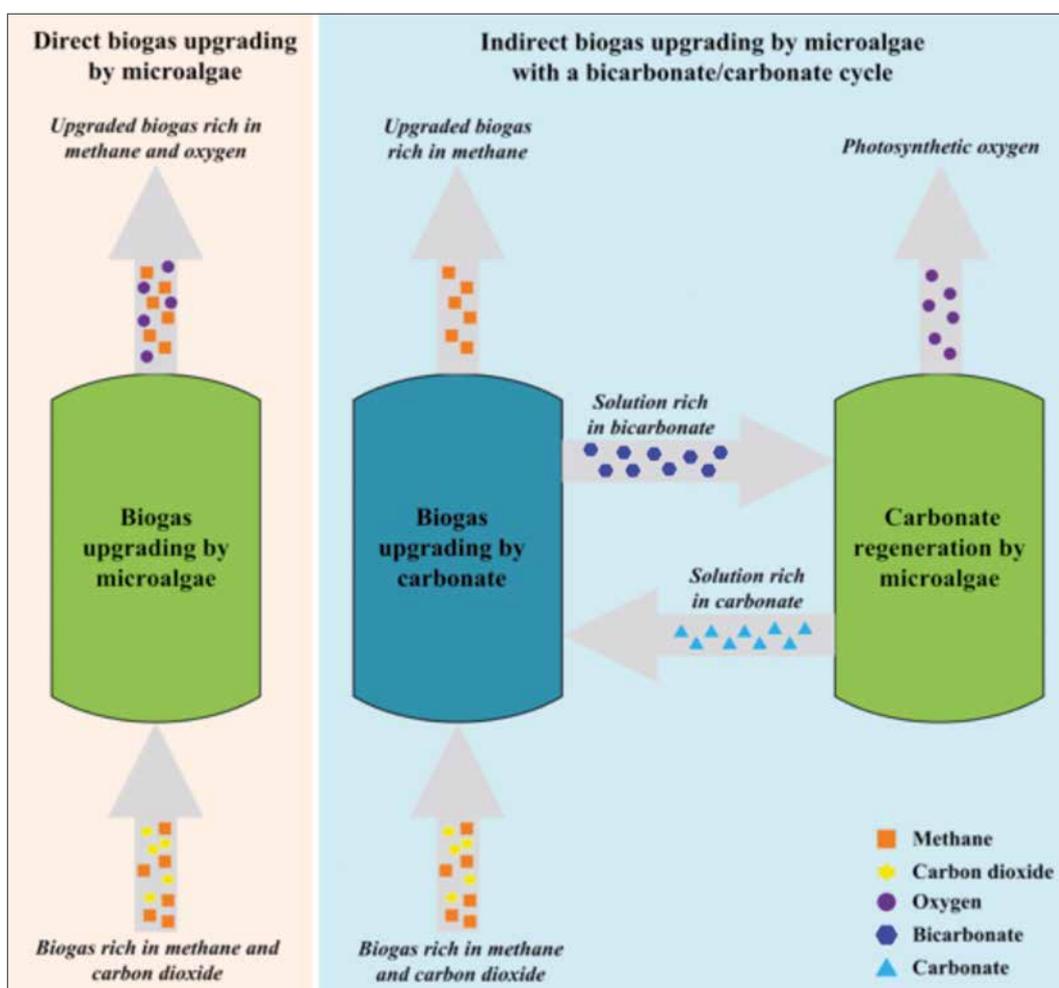
Figure 12: Biogas upgrading by microalgae (adapted from (Xia et al., 2015))

PBR has a very poor ratio of energy input to energy output (Jacob et al., 2015a). The system with the best energy input to energy output ratio was the raceway pond but this only captured 50% of CO_2.

3.7.2 An alternative – cascading usage of microalgal biomass: the microalgal biorefinery

In the last decade more attention has been paid to conversion of microalgal biomass to biofuels (Chisti, 2007). This option is not yet economically feasible and according to Hingsamer et al. (2012) is expected to be unprofitable in the short to medium term. A more economic approach for producing biogas from microalgae

is a cascade usage in a biorefinery concept: a high value product will yield the most significant revenue whereas the biomass residue will be transformed into biogas.

IEA Bioenergy Task 42 (IEA, 2014) defines a biorefinery as a sustainable processing of biomass into a spectrum of bio-based products (food, animal feed, chemicals, and materials) and bioenergy (biofuels, power and/ or heat). There are various pathways for utilizing algae biomass or algae derived components in combination with energy production.

Considering the enormous biodiversity of microalgae and recent developments in genetic and metabolic engineering, algae are suggested to represent one of the

most promising sources for new products and applications (Harun et al., 2010). Microalgae are the basis for a wide variety of products (Figure 13). When whole algal biomass is used as a source of protein or as health food, residual biomass will not be available for biorefinery purposes. Microalgae residual biomass will be available as a source of biofuel, for example after extraction of certain valuable compounds such as pigments or enzymes, or after application of microalgae for therapeutic agents. An overview of the current usage of microalgae for deriving different products is given in Table 17.
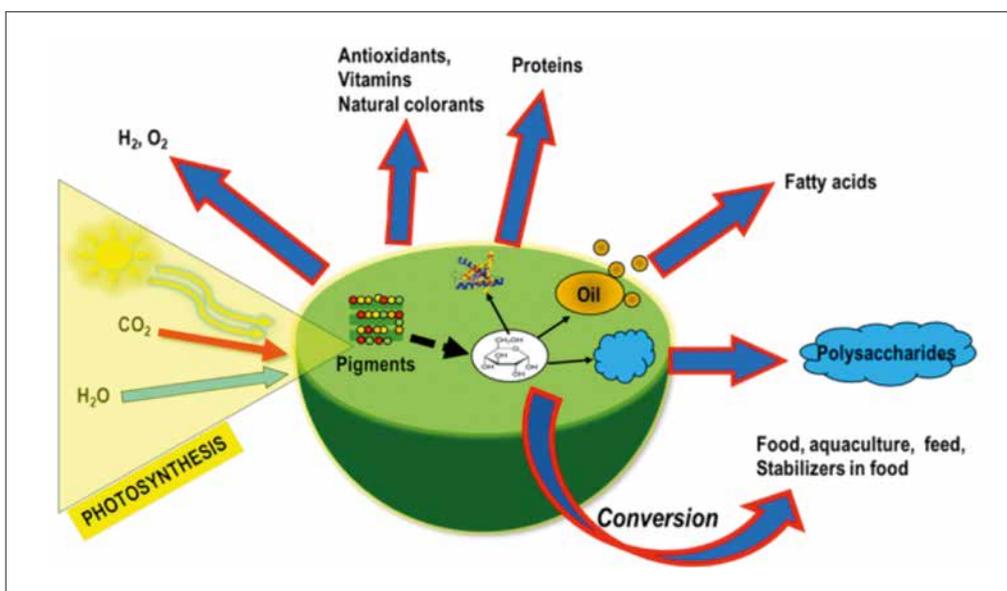

Figure 13: Overview of possible products from microalgae (© Markus Gruber, IFA Tulln –University of Natural Resources and Life Sciences, Vienna)

Table 17: Microalgae species with high relevance for biotechnological applications (adapted after Pulz & Gross 2004)

Microalgae	Main producers	Application and product	Price
Spirulina sp.	China, India, USA, Myanmar, Japan	Human nutrition Animal nutrition Cosmetics	36 €/kg
		Phycobiliproteins	11 €/mg
Chlorella sp.	Taiwan, Germany, Japan	Human nutrition Cosmetics	36 €/kg
		Aquaculture	50 €/L
Dunaliella salina	Australia, Israel, USA, Japan	Human nutrition Cosmetics ß-carotene	215 – 2150 €/kg
Aphanizomenon flos-aquae	USA	Human nutrition	–
Haematococcus pluvialis	USA, India, Israel	Aquaculture	50 €/L
		Astaxanthin	7150 €/kg
Crypthecodinium cohnii	USA	DHA oil	43 €/g
Shizochytrium	USA	DHA oil	43 €/g

4 Conclusions and Recommendations

Technology Readiness Level (TRL) is a parameter that describes the technology maturity of a process or system; TRL values range from 1 (very basic research) to 9 (technology ready for commercialization). TRL is an apt concept when discussing algal biofuels. In February 2015 the Environment Committee of the European Parliament stated that "Advanced biofuels sourced from seaweeds or certain kinds of wastes should account for at least 1.25 per cent of energy consumption in transport by 2020" (European Parliament News, 2015). This statement would suggest that seaweed biofuel is at a high TRL (8 or 9). Indeed Jard et al. (2013) argue that biogas production from seaweed is close to commercialization. Coupling this with the EU Alternative Fuel Infrastructure Directive which requires compressed natural gas dispensing stations at a minimum spacing of 150 km across the EU by 2020 would suggest that upgraded biogas from seaweed, injected into the gas grid is a third generation biofuel heavily supported by the EU with an ambition of significant scale in the next 5 years.

However there are very few seaweed digesters at commercial scale. There are a myriad of seaweed species and numerous potential pathways to produce energy from seaweed. Long-term anaerobic digestion may be problematic due to sand deposition in digesters and due to salinity. The environmental consequence of providing transport fuel from seaweed to the EU (at around 1.25%) has yet to be assessed. Preliminary calculations would set this number at close to 168 Mt of seaweed per annum (Jacob et al., 2015b) which is significantly in advance of the present world harvest of 26 Mt. It is unlikely that cast seaweed will be harvested to satisfy this demand; in the short term the impact could be intolerable and legal authorization for the harvest would very likely not be granted. The more likely scenario is new cultivation, more than likely associated with salmon farms. It is not yet known which species would

be best suited. Numerous parameters (such as the method of cultivation, the species of seaweed, the yields of seaweed per hectare, the time of harvest, the method of harvesting, the suitability of seaweed to ensiling, the gross and net energy yields in biogas, the carbon balance, the cost of the harvested seaweed, the cost of the produced biofuel) have not been assessed. In reality it could not be said that the system is at a TRL greater than 5. Much research is required. A definite pathway needs to be agreed for seaweed biofuels.

For microalgae the TRL may be even lower than for seaweed. A very big issue is the source of the biomass. Where is it produced? A recent paper by Jacob et al., (2015a) suggests that 34,000 ha of flat plate PBR would be required to capture 80% of the emissions of a 1 GW_e coal fired power station. If this were digested it could produce 35% of the primary energy in the coal, however the energy input in pumping the microalgae in the PBR could be higher than the energy output in the form of biogas. Other issues with microalgae include the length of the growing season, the lack of light (and growth) by night . Optimal temperatures are of the order of 27°C. This will not be attainable in temperate oceanic climates and may limit the technology to tropical or Mediterranean climates. Raceway ponds would appear to be the most likely cultivation pathway from an energy perspective (Jacob et al., 2015a). Contamination may be of issue for microalgal biodiesel but this would not be a problem for microalgal biogas. Contamination of the microalgae species with higher trophic lifeforms and other species of microalgae is not a problem for anaerobic digestion. The energy balance of biogas systems may also be better than biodiesel systems as biogas can be made from wet sources (removing the need for drying) and lipids do not need to be extracted as for biodiesel. However numerous questions need to be answered before deciding on an optimal microalgal biogas system. It is likely that innovative integrated systems will be required to optimise algal biogas systems. This may include coupling bioenergy systems with microalgae production in scrubbing the CO_2 from combustion systems. It may involve use of microalgae to upgrade biogas (indirecty with a bicarbonate/carbonate cycle), to use anaerobic digestate as growth media and co-digesting the microal-

gae produced with slurries and agri-food wastes. Numerous options need to be evaluated to reach optimal algal biofuel pathways, including:

• The particular species of algae
• The cultivation or harvesting techniques
• Pre-treatments for algae
• Configuration of biodigester system
• Composition of produced biogas (hydrogen or methane)
• Choice of co-substrates
• Integration of technology with other technologies.

It can be said that the TRL for microalgal biogas is below 4. Energy and carbon balances are not known. The cost of produced biogas is not known. It may well be that biorefineries are required to allow financially sustainable biofuel systems. The undoubted benefit of algal biofuels is the high energy yields per unit of area of sea (not land), the separation of bioenergy from agricultural land and the lack of indirect land use change effects.

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Glossary of terms

Alkalinity ratio

The Alkalinity ratio is a titration measurement with sulphuric acid and determines the ratio of the intermediate alkalinity (IA) caused by organic acids over the partial alkalinity (PA) caused by the bicarbonates. In the English literature it is called the IA/PA ratio, however, also other terms such as VFA/bicarbonate, VFA/ALK or Ripley ratio are in use. In German literature the parameter is called a FOS/TAC.

BMP

Tests for measuring the biochemical methane potential (or bio-methane potential) are mainly used to determine the possible methane yield of a feedstock. These tests also provide information on the anaerobic degradability of a feedstock, including the degradation rate. In addition, a first rough evaluation of the presence of inhibitory components can be made.

CSTR

Continuously stirred tank reactor. This is a type of digester which is regularly stirred and the substrate as well as the microbe concentration should be the same throughout the entire reactor. The design concept of a CSTR is different to that of, for example, a plug flow reactor.

HRT

The hydraulic retention time (HRT) is the average time during which the feedstock remains in the biogas digester. As in practice, the large majority of existing plants are CSTR reactors and do not show special retention systems for microbial biomass, the retention time of the microbes in the system can be assumed equal to the HRT.

Mesophilic

A mesophilic biogas process normally takes place between 36-43°C.

OLR

The organic loading rate (OLR) is given in kg VS m^{-3} d^{-1} or kg COD m^{-3} d^{-1} and stands for the amount of organic material which is fed daily to the biogas plant. The critical issue with this parameter is that with increased OLR the possibility of acidification by organic overload increases.

Thermophilic

A thermophilic biogas process normally takes place between 50-65°C.

TS

For estimation of the water content of a feedstock, total solids (TS) are determined; this parameter is also called dry matter (DM). Analysis involves drying the sample to constant weight in a drying chamber at 103 to 105°C.

VS

In order to determine the amount of organic material in a sample the volatile solids (VS) are determined, this parameter is also called organic dry matter (ODM). In general, this determination is carried out together with the TS determination described above. The sample is dried to constant weight in a drying chamber at 103 to 105°C. Then the sample is ignited to constant weight in a muffle furnace at 550°C. The VS is calculated by subtracting the ash from the total solids.

Task 37 – Energy from Biogas

IEA Bioenergy

IEA Bioenergy aims to accelerate the use of environmentally sustainable and cost competitive bioenergy that will contribute to future low-carbon energy demands. This report is the result of work carried out by IEA Bioenergy Task 37: Energy from Biogas.

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