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Review

Biofuel Production in Ireland—An Approach to 2020 Targets with a Focus on Algal Biomass

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Abstract: Under the Biofuels Obligation Scheme in Ireland, the biofuels penetration rate target for 2013 was set at 6% by volume from a previous 4% from 2010. In 2012 the fuel blend reached 3%, with approximately 70 million L of biodiesel and 56 million L of ethanol blended with diesel and gasoline, respectively. Up to and including April 2013, the current blend rate in Ireland for biodiesel was 2.3% and for bioethanol was 3.7% which equates to approximately 37.5 million L of biofuel for the first four months of 2013. The target of 10% by 2020 remains, which equates to approximately 420 million L yr^{-1}. Achieving the biofuels target would require 345 ktoe by 2020 (14,400 TJ). Utilizing the indigenous biofuels in Ireland such as tallow, used cooking oil and oil seed rape leaves a shortfall of approximately 12,000 TJ or 350 million L (achieving only 17% of the 10% target) that must be either be imported or met by other renewables. Other solutions seem to suggest that microalgae (for biodiesel) and macroalgae (for bioethanol) could meet this shortfall for indigenous Irish production. This paper aims to review the characteristics of algae for biofuel production based on oil yields, cultivation, harvesting, processing and finally in terms of the European Union (EU) biofuels sustainability criteria, where, up to 2017, a 35% greenhouse gas (GHG) emissions reduction is required compared to fossil fuels. From 2017 onwards, a 50% GHG reduction is required for existing installations and from 2018, a 60% reduction for new installations is required.

Keywords: biodiesel; bioethanol; microalgae; macroalgae; indigenous production; Ireland

1. Introduction

The cultivation of algal biomass for the production of third generation biofuels has received increasing attention in recent years as they can be produced in the marine environment and on non-arable lands, thus bypassing the food *versus* fuel debate. There are two types of algae: seaweeds (macroalgae) and phytoplanktons (microalgae).

Algae have been receiving attention as a potential biofuel feedstock as they have a number of advantages over traditional biofuel crops:

- Production yields of algae per unit area are significantly higher than those for terrestrial biomass [1,2].
- The chemical composition of algae makes it suitable for conversion into biofuels [3–6]. In general, microalgae are potential sources of bio-oils whilst macroalgae are potential sources of carbohydrates for fermentation or thermo-chemical based conversions [7].
- Microalgae can be cultivated in brackish water on non-arable land, and therefore may not incur land use change, minimizing associated environmental impacts [6]. Utilizing marine biomass, which can be grown in a variety of marine environments including fresh water and salt water, avoids the problem of land use change from arable to bioenergy crops [1,8]. Utilizing the marine environment ensures a large cultivation area, limiting competition with other land uses and resources [3].
- Microalgae production can utilize the carbon dioxide component of flue gas, reducing the carbon emissions from power plants [2]. Marine macroalgae have a high rate of carbon dioxide fixation from the atmosphere and water at 8–10 t ha^{-1} yr^{-1}, comparable to temperate woodlands [3,4]. As such, they have a high potential for carbon dioxide remediation.

The main steps in algae production; cultivation, harvesting and conversion to biofuel, are discussed separately for microalgae and macroalgae since there are intrinsic differences between them in all aspects of the process.

2. European Union (EU) Sustainability Criteria

The increased use of biomass for biofuel production has led to concerns regarding the sustainability of this practice. Concerns surround the methods of cultivating and producing biofuels, particularly in regard to actual greenhouse gas (GHG) emissions reductions in comparison with fossil fuels, and in relation to land use change due to increased demand for arable land for biomass production. In order to ensure the sustainability of biofuel used to achieve the targets in the EU, the European Commission proposed a set of sustainability criteria in the Directive 2009/28/EC on the promotion of the use of energy from renewable sources. The sustainability criteria consist of the following main points:

- The directive lays out certain GHG emissions reductions to be achieved from the use of biofuels. In the case of biofuels and produced by installations that were in operation on 23 January 2008,

GHG emissions savings must be at least 35% from 2013. This figure rises to 50% in 2017, and further to 60% in 2018 for biofuels produced in installations in which production started on or after January 2017.

- The raw materials sourced for biofuel production, from within the EU or from third countries, should not be obtained from land with high biodiversity value, land with a high carbon stock, or land that was peatland in 2008 [9].

These criteria, while undoubtedly positive for the sustainable production of biofuels, may restrict growth of the biofuel production industry in Ireland as biofuels must meet these minimum criteria.

3. Microalgae

Microalgae are microscopic algae that typically range from unicells to colonies and filaments of up to a few hundred cells. Microalgae include prokaryotes (cyanobacteria and blue-green algae) and eukaryotes (green algae, diatoms, red algae and others) [10]. There are thousands of microalgae species, only some of which have been studied for biofuel production.

Microalgae are particularly suited to biofuel production due to their high photosynthetic growth rates, high lipid content, low land usage and high carbon dioxide absorption [11]. Algae absorb freely available sunlight and can utilize waste streams to provide essential nutrients for cultivation. Algae can convert waste CO_2 from power plant exhaust gas to organic biomass which can then be converted to energy [12]. Moreover, municipal wastewater streams can be harvest to provide additional nutrients [13].

Microalgae are already reported to produce 15–300 times more oil for biodiesel production than traditional crops on an area basis (Table 1). Furthermore compared with conventional crop plants which are usually harvested once or twice a year, microalgae have a very short harvesting cycle (1–10 days depending on the process), allowing multiple or continuous harvests with significantly increased yields [2].

Table 1. Comparison of crop-dependent biodiesel production efficiencies from plant oils [2]. TAG: Triacylglycerols.

Plant source	Biodiesel ($L\ ha^{-1}\ yr^{-1}$)	Area required to produce global oil demand (hectares × 10^6)	Area required as percent global land mass	Area as percent global arable land
Cotton	325	15,002	100.7	756.9
Soybean	446	10,932	73.4	551.6
Mustard seed	572	8,524	57.2	430.1
Sunflower	952	5,121	34.4	258.4
Rapeseed/canola	1,190	4,097	27.5	206.7
Jatropha	1,892	2,577	17.3	130
Oil palm	5,950	819	5.5	41.3
Microalgae ($10\ g\ m^{-2}\ day^{-1}$ at 30% TAG)	12,000	406	2.7	20.5
Microalgae ($50\ g\ m^{-2}\ day^{-1}$ at 50% TAG)	98,500	49	0.3	2.5

3.1. Cultivation and Harvest

There are two main methods for cultivating microalgae; raceway pond systems and photobioreactors. A typical raceway pond comprises a closed loop oval channel, approximately 0.25–0.4 m deep, open to the air, and mixed with a paddle wheel to circulate the water and prevent sedimentation. Ponds are kept shallow as optical absorption and self-shading by the algal cells limits light penetration through the algal broth [14]. In photobioreactors, the culture medium is enclosed in a transparent array of tubes or plates and the micro-algal broth is circulated from a central reservoir. Productivity is higher in the controlled, contained environment of a photobioreactor, but capital and operating expenses are also substantially higher than for open systems [6]. Auxiliary energy demand may also be higher [14].

Algae typically have a high water content and downstream harvesting and processing requires its removal [15]. In existing algal aquaculture the most common harvesting processes are flocculation, microscreening and centrifugation. Most importantly, cost-effective and energy-efficient harvesting methods are required to make the entire biofuels production process economical [2].

Cell disruption is an important step in recovering intracellular products from micro-algae, and so properties of the cell wall play an important role in the extraction process. Some of the commonly used methods for cell disruption include mechanical disruption, such as bead-beating, ultrasound and steam extraction [16] and non-mechanical disruption, including application of organic solvents and addition of inorganic acids and alkali for pre-treatment processing [17]. For extraction of oils and other microalgal products, chemical solvents can be chosen in one or two-step extraction approaches [2]. The residue remaining after oil extraction contains starch and proteins and can be further processed to produce ethanol, animal feed, or used as a feedstock for anaerobic fermentation [18].

3.2. Processing

The optimal usage is highly dependent on the microalgal composition, for example species with high lipid content will preferably be used for biodiesel production, while algae high in carbohydrates are more suitable for bioethanol. Combinations are also possible, in which for instance the lipid fraction is used for biodiesel, while the remaining biomass is fermented for biogas production. Biorefinery-type processes may be the most economical method of producing algal biofuels as several commercial products can be obtained from the algal biomass. Lipids can be extracted for biodiesel production, while other products can be fermented to produce ethanol and biogas. It is also possible to produce protein-rich feed for both animal and human consumption [19]. Bulk markets for the co-products are potentially available [20]. The common biochemical and thermochemical processes are outlined in Figure 1.

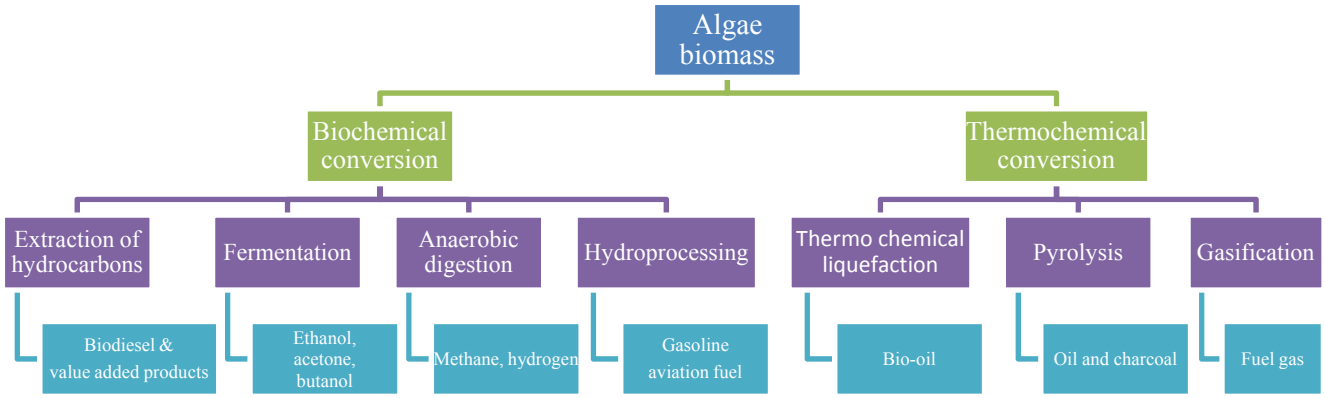
3.3. Biochemical Processing

3.3.1. Transesterification

The transesterification process involves reaction of an alcohol with triglycerides, in the presence of a catalyst, forming fatty acid alkyl esters. The transesterification process can be acid or base catalyzed, and involves enzymatic conversion. In acid-catalyzed reactions, HCl, H_2SO_4 or H_3PO_4 is used for

transesterification, while in base catalysis strong bases like KOH or NaOH are commonly used. Base catalysis has several advantages over the acid-catalyzed reaction as it is conducted at low temperature and pressure, and it has also a high conversion rate. Despite these advantages, the process is energy intensive, and there are problems associated with removal and treatment of alkaline catalyst from the final product. These problems could be solved by the use of biocatalysts, such as lipases, but large-scale demonstration has not been reported [17].

Figure 1. Potential algal biofuel conversion processes, adapted from [21].



3.3.2. Fermentation

Microalgae are also a suitable feedstock for bioethanol production. Besides their high lipid content, some microalgae also contain carbohydrates (generally not cellulose) that can be utilized as a carbon source or substrate for fermentation. Certain algae accumulate starch in stress conditions, and this can be exploited for ethanol production by fermentation. Ethanol can be produced either from algal biomass or from algal cake. The processes for producing bioethanol from microalgae are very similar to establishing first-generation technologies that use corn- and sugarcane-derived feed stocks [2]. Despite these possibilities, research on the fermentation of microalgae biomass to bioethanol is still limited in the literature [19].

3.3.3. Anaerobic Digestion

Anaerobic digestion is a potential option for conversion of algal residue to energy. The anaerobic digestion of algae can achieve methane yields of about 250 $m^3\ t^{-1}$ of algae. The three main bottlenecks to digest microalgae are; low biodegradability of microalgae depending on both the biochemical composition and the nature of the cell wall, high cellular protein content results in ammonia release which can lead to potential toxicity, and the presence of sodium for marine species can also affect the digester performance [22].

3.3.4. Hydroprocessing

In recent years, hydroprocessing technology has been used to convert lipid feedstocks into distillate fuels [20]. The two main products consist of a liquid distillate fuel with similar properties to petroleum diesel, and propane in the gas phase stream. With the various hydroprocessing technologies

utilised by refineries to catalytically remove impurities or reduce molecular weight, algal oils can be processed into a kerosene-like fuel very similar to petroleum-derived jet fuels [23]. This fuel is being considered as a jet fuel for several reasons; the cold weather properties are superior, the propane byproduct is preferable over glycerol byproduct, the heating content is greater, and the cetane number is greater [24]. The main advantage of hydroprocessing is that it requires infrastructure which is widely available in all refinery units [25].

3.4. Thermochemical Processing

3.4.1. Hydrothermal Liquefaction

An alternate approach that requires no feedstock drying and no use of organic solvents is hydrothermal liquefaction. This approach converts the microalgae, with high moisture content, in water at temperatures of 250–350 °C and high pressure (5–20 MPa) [26], and has been investigated for various strains (*Botryococcus braunii*, *Spirulina platensis*, *Chlorella vulgaris*, *Nannochloropsis sp.* or *Desmodesmus sp*., among others) [27–29]. This process is particularly suited for high moisture feedstocks, overcoming one of the key barriers for other processing techniques [30]. Under these conditions, the biomacromolecules in the microalgae break down to form a liquid energy carrier called "bio-oil" or "biocrude", next to gaseous, aqueous and solid by-products [27,31]. The biocrude produced, with an energy value close to that of fossil petroleum [30] is not directly suited as transportation fuel, but it is expected to be a suitable renewable feedstock for co-refining in existing fossil-based refineries [31]. Maximum biocrude yields in the vicinity of 50%–60% have been reported, and the use of several homogeneous and heterogeneous catalysts has explored [28,32], though in a very early stage of development.

3.4.2. Gasification

Gasification is a thermochemical process that, in the near absence of oxygen, converts organic material into a combustible gas called synthesis gas (syngas) [22]. Gasification of microalgae can result in production of clean H_2 with yields ranging from 5% to 56% and CO with yields ranging from 9% to 52% [33]. Methane can be considered to be a co-product and is only produced in small amounts of approximately 2%–25% [33]. However, the production of clean methane-rich gas can be achieved in the catalyzed supercritical water gasification process where approximately 60%–70% of the heating value from the microalgal biomass can be recovered as methane. The hydrocarbon products of gasification can be further processed to produce methanol. At 1000 °C, the methanol production is approximately 64% (*w*/*w*) based on the biomass weight [34]. However, methanol production is an energy intensive process, due to the use of the centrifuge process during harvesting, with the ratio of energy produced to energy required of 1.1 [35]. The biomass gasification also produces unwanted products in small quantities such as water, ash and tar, which cause various problems with the main product yield. The tar produced can range from 0.1% to 20% depending on the gasifier agent and type of reactor, either an updraft or a downdraft reactor [33].

3.4.3. Pyrolysis

Pyrolysis is accomplished at moderate to high temperatures (400–600 °C) and atmospheric pressure and requires drying of the feedstock. Slow pyrolysis is the heating of biomass at slow heating rates (5–80 °C min^{-1}) and longer residence times (5–30 min), compared to high heating rate (1000 °C min^{-1}) and short residence times (10–20 s) in case of fast pyrolysis [30]. Bio-oil yields of 17.5% and 23.7% were reported from the fast pyrolysis of *C. protothecoides* [36] and *M. aeruginosa* [37]. The bio-oil yield from the slow pyrolysis of *C. protothecoides* was temperature dependent and was 5.7%–55.3% [30].

Pyrolysis was found to produce less energy than it consumed, mainly due to the high energy penalty of the drying process of the wet microalgae, which contained around 80% of moisture. Despite the advantage of processing the whole microalgal biomass, this high energy cost is a significant hindrance that may prevent the complete development of this technology [31].

3.5. Properties

Besides high productivities and yields, fuel properties are important in the selection of the most adequate species for biofuel production. Table 2 gives some important fuel properties of two micralagal biodiesel samples.

Table 2. Algae biodiesel properties [38].

Parameter	Algae 1	Algae 2	Unit
Free-fatty acids	0.45	1.75	% weight
Cloud point	−5.2	3.9	°C
Cold filter plugging point	−7	2	°C
Free Glycerin	0.009	0.014	mass%
Total Glycerin	0.091	0.102	mass%
Monoglycerides	0.265	0.292	mass%
Diglycerides	0.078	0.070	mass%
Triglycerides	0.020	0.019	mass%
Water & sediment	<0.005	<0.005	% volume
Acid number	0.022	0.003	mg KOH/g
Visual inspection	1	1	Haze
Relative density at 60 F	0.8780	0.8780	N/A
Oxidative stability (110 °C)	8.5	11	h
Flash point (closed cup)	>160	>160	°C
Moisture	0.037	0.026	mass%
Cold soak filtration	85	84	s
Sulfur	5.1	0.6	ppm
Calcium	<0.1	0.7	ppm (μg/g)
Magnesium	0.3	1.1	ppm (μg/g)
Phosphorus	<0.1	<0.1	mass%
Carbon residue	0.007	0.042	mass%
Sulfated ash	<0.005	<0.005	mass%
Kinematic viscosity at 40 °C	4.519	4.624	mm^2/s
Copper corrosion (3 h at 50 °C)	1a	1a	N/A

3.6. Commercial Biofuel—Worldwide Production

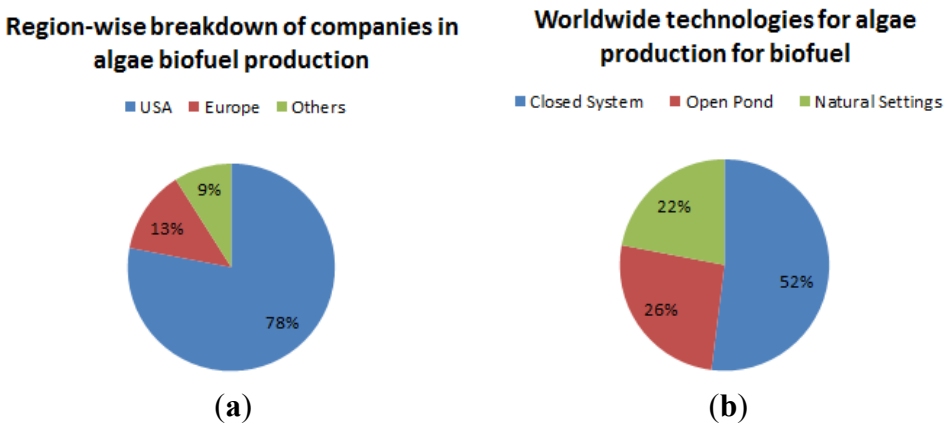
Table 3 gives a breakdown of algal biofuel processing capacity due to come online until 2017. Algenol's first commercial plant, a 250,000 L plant based on algae fermentation is due to come online in 2016 in Mexico, significantly increasing the overall capacity. Solazyme are producing renewable oils based on hydroprocessing technology. In France, 15,000 L of capacity were due to come online in 2012 with another 27,000 L due to come online in Brazil in 2013.

Table 3. Projected algae biofuel capacity worldwide (million L) [39].

Technology	2011	2012	2013	2014	2015	2016	2017
Fermentation	0.38	0.38	0.38	0.38	0.38	945.38	945.38
Hydroprocessing	0.57	61.88	162.69	166.47	166.47	166.47	166.47
Transesterification	1.87	2.06	14.42	14.42	14.42	14.42	14.42
Other	0.38	0.76	0.76	1.66	1.66	1.66	1.66
Total	3.20	65.08	178.25	182.94	182.94	1127.94	1127.94

Figure 2 shows two pie charts representing the percentage distribution of algal biofuel producing companies around the world in different regions, and the percentage distribution of various algae production technologies being used by these companies [6]. These figures indicate that the majority of companies involved in algal biofuel development are based in the USA, with fewer European companies involved. The figures also show that closed systems (photobioreactors) are receiving more attention for cultivation than open pond or natural systems.

Figure 2. (**a**) Regions and (**b**) technologies in algae biofuel production, adapted from [6].



3.7. Resource Potential—Ireland

Assessing the potential availability and location of algal biomass is difficult due to uncertainty over the amount of land that is available and affordable in locations such as coastal areas, where the climate, water and nutrients may be sufficient to support the commercial cultivation of algae. Further research and development is required into the production of algal biofuels, as such any contribution to Irelands 2020 targets is likely to be minimal. Bruton [12] has estimated that approximately 79 TJ could come from microalgae resources by 2020 (approximately 2.3 million L).

The University of Limerick in Ireland is coordinating the EU-funded project "Direct Ethanol from MicroAlgae" (DEMA) [40]. The DEMA Consortium, composed of nine partners from both academia and industry from six EU countries, is aiming to develop, demonstrate and licence an economically competitive technology for the direct production of bioethanol from microalgae with low-cost scalable photobioreactors by 2016. The project is focusing on a strain of the cyanobacterium, *Synechocystis sp.*, which will be metabolically engineered to directly transform carbon dioxide, water and sunlight into bioethanol at a concentration level of >1%–2% (*v*/*v*). Subsequently, the bioethanol will be continuously extracted from the culture media via a membrane technology process exploiting existing EU expertise and technology. Initial proof-of-concept results from life cycle assessments and economic balances suggest the feasibility of using microalgae to produce bioethanol for less than 0.40/L.

4. Macroalgae

Macroalgae are multicellular, macroscopic algae, which are abundant in coastal environments, primarily in nearshore coastal waters with suitable substrate for attachment. Such algae also occur as floating forms in the open ocean [41]. Macroalgae have relatively high photon conversion efficiency and can therefore rapidly synthesize biomass through assimilating abundant resources in nature such as sunlight, carbon dioxide, and inorganic nutrients [1]. The fast growing macroalgae are capable of yielding more biomass (*ca.* 2 kg C m^{-2} yr^{-1}) [4], than fast growing terrestrial crops such as sugarcane [42]. Macroalgae can grow to a considerable size (up to tens of meters in length in the case of Pacific kelp species) [43], although Atlantic species are smaller at approximately 4 m in length [42].

Macroalgae traditionally have not been considered as feedstocks for bioenergy production, but have been used in food, in medicine, or as fertilizer and in the processing of phycolloids and chemicals [8]. Research and development for a marine bioenergy and biofuel industry is still in its infancy in Ireland [44], however, macroalgae are already farmed on a large scale in Asia and to a lesser extent in Europe, primarily in France, and on a research scale in Scotland [8].

Macroalgae are suitable for biofuel production, however they do not generally contain triglycerides and are therefore being considered for the natural sugars and other carbohydrates they contain, making them suitable for biogas and ethanol production rather than biodiesel. Macroalgae has a negative lower heating value and high moisture content (*ca.* 80%–85%) as such the most appropriate method of processing for energy is fermentation by anaerobic digestion, to create biogas or ethanol [19].

Table 4 outlines the carbohydrate composition for some species of macroalgae. Based on the presence or lack of phytopigments other than chlorophyll, marine macroalgae are classified into three major classes: brown algae (Phaeophyceae), red algae (Rhodophyceae), and green algae (Chlorophyceae) [1]. Cell wall components of algae are the major sources of carbohydrates. Green algae mostly contain cellulose and hemicellulose; red algae contain cellulose and polysaccharides like agar and carrageenan; and brown algae contain cellulose and alginic acids.

There are approximately 1800 species of brown algae, and most are marine algae. Brown algae are generally the largest of the algae species, and are more often found in colder waters. The majority of algae biomass worldwide comes from a relatively small number of species in the orders Laminariales and Fucales [45]. The subtidal large brown kelps of the order Laminariales have been identified as

having the greatest potential for bioconversion to energy [46]. Among green macroalgae, *Ulva* is the most important prospect from an energy perspective [12].

Table 4. Seaweed composition and sugars released by hydrolysis (% *w*/*w* dry biomass) for a variety of species [1].

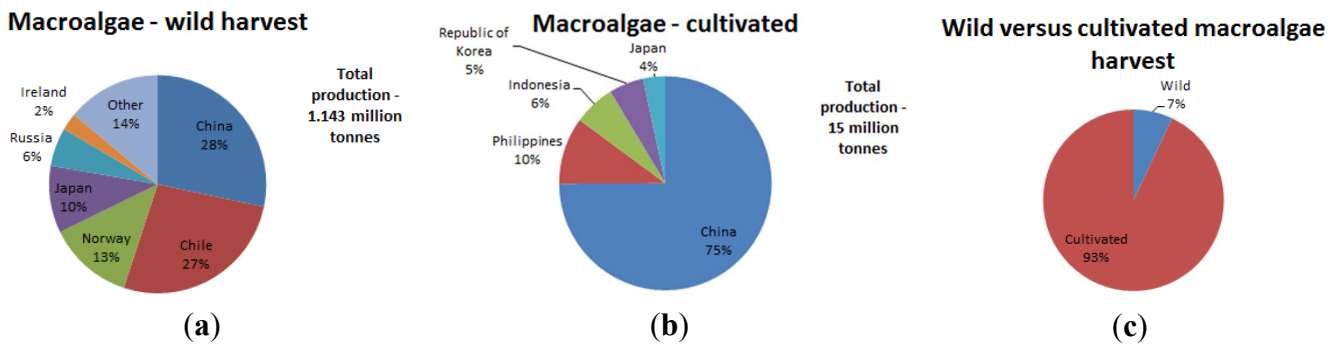
Seaweed	Class	Carbohydrate composition	Total carbohydrates (%)	Lipid (%)	Protein (%)	Ash (%)	Sugars released by hydrolysis	Sugar composition
Gelidium amansii	Red	Agar, Carrageenan, Cellulose	75.2–83.6	0.6–1.1	12.2–18.5	3.3–5.7	34.6–67.5	Glucose. Galactose
Laminaria japonica	Brown	Laminarin, Mannitol, Alginate, Fucoidan, Cellulose	51.9–59.5	1.5–1.8	8.1–14.8	30.9–31.5	9.6–37.6	Glucose, Mannitol
Sargassum fulvellum			39.6	1.4	13	46	9.6	
Ulva lactuca	Green	Starch, Cellulose	54.3	6.2	20.6	18.9	19.4	Glucose
Ulva pertusa			65.2	2.6	7.0	25.2	59.6	

4.1. Cultivation and Harvest

There are essentially two ways of obtaining marine macroalgae; harvesting natural stocks or cultivation. Seaweed exploitation in Europe is currently restricted to manual and mechanized harvesting of natural stocks. The majority of Asian seaweed resources are cultivated [12]. Figure 3 gives a breakdown of wild harvest *versus* cultivated macroalgae along with the major countries involved.

Macroalgae for biofuel purposes are mainly harvested from the wild. Cultivation of seaweed does occur, mainly in Asian countries, but this is usually for higher value purposes such as food, or hydrocolooid (*i.e.*, agar-agar and alginate) production. Traditionally harvest is being done by hand, but this is now largely replaced by mechanical harvesting using trawler systems [47]. *Laminaria digitata* and *Laminaria hyperborea* are both harvested mechanically by boat in France and Norway. *Ascophyllum nodosum*, is harvested by boat in Norway. In France and Ireland, *Ascophyllum nodosum* is harvested manually. All the other species are harvested manually, either on foot or by diving [48].

Figure 3. Breakdown of macroalgae (**a**) wild harvest by region; (**b**) cultivated harvest by region; and (**c**) wild *versus* cultivated in 2011 [49].



(**a**) (**b**) (**c**)

Macroalgae cultivation is currently in its infancy in Europe. Commercial aquaculture of seaweed is found in France (Brittany, six farms) Spain (Galicia, two farms) and on an experimental basis in Ireland, Asturias (Spain), Norway and the United Kingdom. The main cultivated species are *Saccharina latissima* and *Undaria pinnatifida*. In Ireland, *Palmaria palmata* farming is being experimented with on the west coast but the results seem limited.

In order to generate significant volumes of biomass for any biofuel industry, cultivation will be required in the long-term. Cultivation can occur, subject to appropriate licences, either at nearshore locations, or offshore. Over the last number of decades different cultivation systems for seaweeds have been developed and improved ranging from intertidal fixed and floating bottom farms for *Eucheuma*/*Kappaphycus* and *Gracilaria* (e.g., Philippines, Vietnam and Thailand) to elaborate floating net structures for *Porphyra* and long-line systems for kelp in China, Korea and Japan [50]. Modifications of long-line systems have been tested at small scale in Europe [8] amongst them a novel ring system from Germany [51]. These cultivation systems show that there is potential to develop large-scale ocean cultivation of seaweeds. However, existing cultivation and harvesting technology is labor intensive and needs to be optimized to reduce costs and energy demand [41,52].

Several designs and pilot systems have been developed for floating cultivation systems (farms) in open sea, some with surface areas up to 4000 hectares but no full-scale systems have been put in operation so far and their economic feasibility remains doubtful [3]. There is the possibility that cultivated macroalgae may be deployed through integration with existing aquaculture enterprises or in conjunction with new offshore wind farms [3]. Wind farms offer an ideal opportunity as the area is already closed for shipping, it would allow multifunctional use of area and offshore constructions, and joint operation and maintenance could occur involving synergy and cost benefits.

4.2. Processing

After cultivation and harvesting, the macroalgal biomass must be pre-treated for most biofuel applications. The first step of pre-treatment is to remove foreign objects and debris such as stones, sand, snails, or other litter that may be caught in the biomass either manually or by washing [12]. In many cases, chopping or milling is then required to increase the surface area/volume ratio [41]. Finally, the biomass should be dewatered to 20%–30% to increase shelf life and reduce transportation costs in situations where it must be stored for long periods or transported over long distances before further processing [1].

The principal energy process considered for seaweed is fermentation, either anaerobic digestion (AD), to create biogas, or ethanol fermentation. Other thermochemical options for macroalgae utilization include direct combustion, gasification, pyrolysis and liquefaction.

4.2.1. Fermentation

Hydrolysis of seaweeds converts the storage carbohydrate into simple fermentable sugars, which can be easily used to produce ethanol by some natural microorganisms [1]. Major sugars from brown seaweeds include glucan (laminarin or cellulose), mannitol, and alginates. However, natural microorganisms cannot utilize these various sugars concurrently, because they lack the ability to use alginate, and thus ethanol production from brown seaweed cannot reach its maximum level [1].

A recent breakthrough by Wargacki *et al.* [53] in the efficient use of brown seaweed biomass arose from an engineered *E. coli* platform capable of alginate degradation and metabolism. Here, ethanol was produced through co-fermentation of glucose, mannitol, and alginate from brown seaweed. This breakthrough allows a theoretical ethanol outcome of 80% conversion. As such 0.281 L of ethanol could be obtained per kg of dry seaweed.

4.2.2. Anaerobic Digestion

Macroalgae with low lipid content are especially suitable for biogas production using anaerobic fermentation. However, macroalgal biomass has some drawbacks over other types of biomass. For marine species, the high saline content may inhibit growth or productivity of the anaerobic microorganisms in the fermenter. This can be mitigated by mixing algal biomass with other types of biomass to "dilute" the saline concentration. Another problem, typical for green macroalgae, is the formation of H_2S due to the high sulphate concentration in these species. This can be solved by using iron-based chemicals to bind H_2S, as has been applied in wastewater treatment systems [47]. Seaweeds have methane yields ranging from 0.14 m^3 kg^{-1} to 0.40 m^3 kg^{-1} volatile solids [41].

4.2.3. Hydrothermal Liquefaction

Hydrothermal liquefaction is a promising method of processing algae which takes advantage of the high moisture content of algae though reaching supercritical state [47], as discussed for microalgae above. Recently, a study on the hydrothermal liquefaction of the green seaweed *Enteromorpha prolifera* was made by Zhou *et al.* [54], which showed maximum yield of bio-crude of 23 wt% with an energy density of 29.89 MJ/kg.

Anastasakis and Ross [55] investigated the influence of reaction conditions on the liquefaction behavior of a typical brown seaweed commonly found around the British Isles, *Laminaria saccharina*. *L. saccharina* has high carbohydrate content and contains large amounts of mannitol and laminarin. The bio-crude yields ranged from 3.8 wt% to 19.3 wt%.

4.2.4. Pyrolysis

The conditions of pyrolysis are described previously for microalgae. The application of pyrolysis to macrolagae has been studied, however it suffers a number of serious problems which affects its viability; it requires relatively dry material and so is only viable when high-value products are formed [55], there are high costs associated with bulk handling and transport and there is difficulty in separating the complex mixtures of chemicals [8].

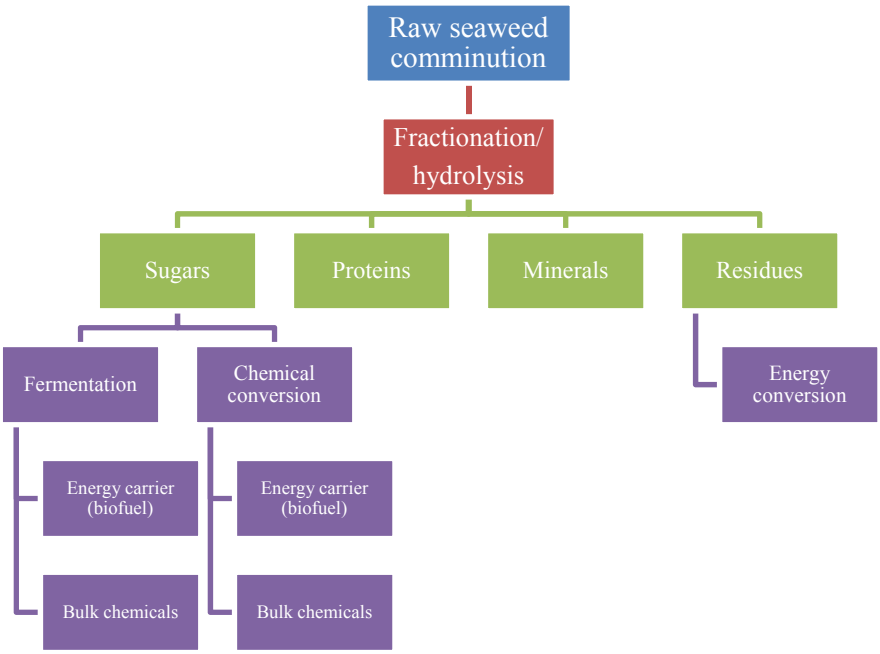
4.2.5. Transesterification

Transesterification is not a commonly investigated method for processing macroalgae due to their low lipid content, however transesterification has been used to produce biodiesel from the green macroalgae *Enteromorpha compressa* [56]. It was found that, by carrying out a base transesterification through optimum conditions of 1% NaOH, 9:1 methanol-oil ratio, 600 rpm and 60 °C temperature for 70 min, the maximum biodiesel yield of 90.6% of the oil used in the reaction was achieved [56].

4.3. Biorefinery Concept

Macroalgae contain a range of polysaccharides, proteins, minerals [3], and some species produce higher value compounds such as alginates, fucoidan, and mannitol [47]. As such, macroalgae is a suitable feedstock for biorefinery for co-production of chemicals and fuels to attain optimum valorization, as shown in Figure 4. Similar to how crude oil is refined in both fuel and fine chemicals; the value of algae is greatly increased if the parts of the biomass that cannot be converted into fuels are utilized for food, feed, chemicals, cosmetics, biomaterials or even pharmaceutical applications [57].

Figure 4. Macroalgae biorefinery concept, adapted from [3].



4.4. Properties

Table 5 displays some important fuel properties of macroalgal biodiesel in relation to the American Society for Testing and Materials (ASTM) fuel Standards.

4.5. Commercial Biofuel from Macroalgae

Biofuel from macroalgae is in its infancy. Statoil has entered into a partnership with Seaweed Energy Solutions AS (SES) and Bio Architecture Lab (BAL), to develop a macroalgae-to-ethanol system in Norway. The aim of the partnerships is to develop a 10,000 ha seaweed farm off the coast of Norway which will produce 200,000 t of ethanol (2% of EU's ethanol marked) [58]. SES is developing the technology for large scale cultivation and harvesting technology [59], while BAL is responsible for developing the technology and process to convert the macroalgae into ethanol [60].

Table 5. Physicochemical characterization of algal biodiesel compared with American Society for Testing and Materials (ASTM) Standards (ASTM D 6751-06) [56].

Properties	Units	Algal biodiesel	ASTM limits
Flash point	°C	166	>160 min
Kinematic viscosity at 40 °C	$mm^2 s^{-1}$	4.35	1.9–6.0
Water and sediment	vol.%	0.005	0.050 max
Density at 15 °C	$kg m^{-3}$	878.47	n/a
Cetane number	-	58.5	47 min
Cloud point	°C	3	n/a
Acid value	$mg KOH g^{-1}$	0.43	0.8
Free glycerine	mass%	0.0034	0.020
Total glycerin	mass%	0.123	0.240
Sulfated ash	mass%	0.0024	0.020
Pour point	°C	−2	n/a
Carbon residue	mass%	0.01	0.050
Sulfur	mass%	0.00056	0.05
Copper strip corrosion	-	1	No. 3 max
Distillation temperature	°C	346	360
Phosphorous	mass%	0.0004	0.001

4.6. Macroalgae in Ireland

Ireland is one of the largest producers of macroalgae in Europe, producing 29,500 t, 13% of the European total (226,500 t. Approximately 30,000 t of algae is processed in Ireland annually [61]. Location of macroalgae processing capacity in Irland is shown in Figure 5. Currently the majority of seaweed collection in Ireland is for human consumption and for hydrocolloid production, with 29,000 t harvested in 2006 for Arramara Teo, a state owned company [19]. The *Ascophyllum nodosum* species dominates the industry, accounting for approximately 25,000 t or 95% of domestic production. *Ascophyllum nodosum* is processed at two factories on the west coast (Donegal & Galway) and is used to produce fertilizers, horticultural products and animal feed, as shown in Figures 5 and 6. A significant quantity of national production is sold as raw material for further industrial processing. Numerous other species are harvested and used for commercial purposes in Ireland including; *Fucus serratus*, *Chondrus crispus*, *Laminaria digitata*, *Fucus vesiculosus* and *Saccharina latissima*. Ireland has been importing significant quantities of *Lithothamnion corallioides* from Iceland for processing into agricultural and nutritional products. Aquaculture of macroalgae is still largely experimental in Ireland and has not contributed significantly to domestic production of algae, experimental cultivation of *Asparagopsis armata*, *Alaria esculenta*, *Palmaria palmata*, *Laminaria digitata* and *Porphyra* has been achieved over the last 20 years [61].

Ireland has considerable macroalgal resources, with an estimation of three million t of standing kelp stock, however this estimation is highly uncertain [19]. Barriers exist to the further exploitation of marine biomass, in particular any potential effects on marine biodiversity [19].

Figure 5. Irish macroalgae industry 2010 [61].

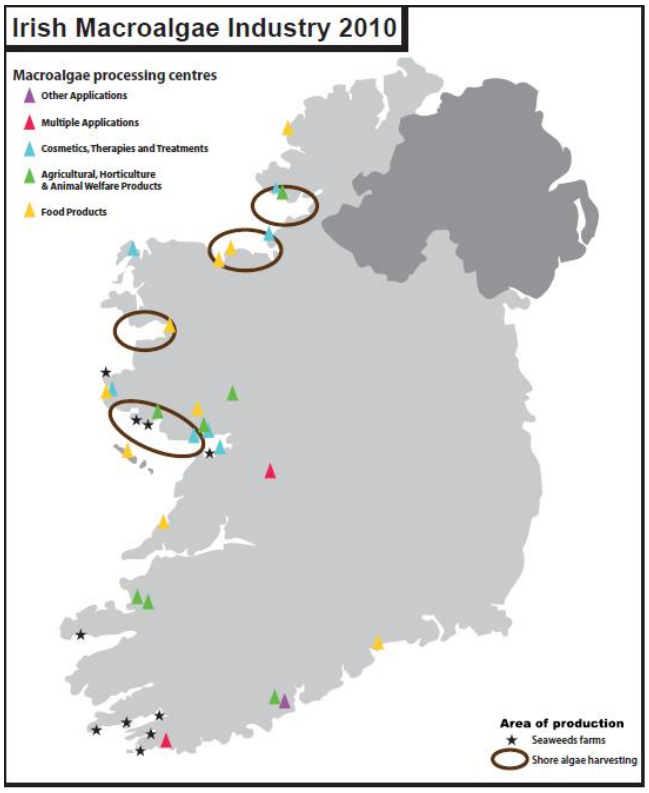
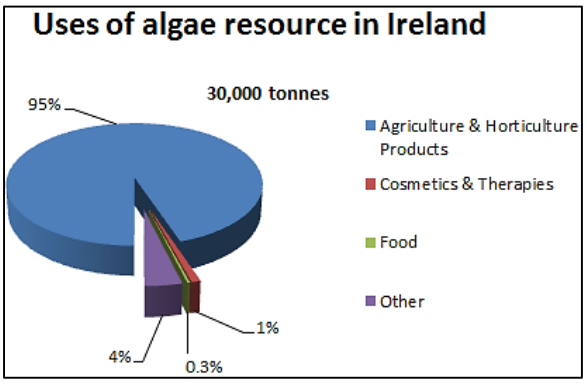


Figure 6. Uses of macroalgae in Ireland [61].



Recently, the potential of algae for bio-energy production and strong interest in developing integrated multi-trophic aquaculture systems has given a new dimension to algae aquaculture [61].

The BioMara project was a joint UK and Irish project that aimed to demonstrate the feasibility and viability of producing third generation biofuels from marine biomass [62]. BioMara was a partnership between six scientific institutes in the EU Interreg IVA cross-border collaboration area (the Border region of Ireland and Northern Ireland, and Western Scotland). Dundalk Institute of Technology and Sligo Institute of Technology were the two Irish partners involved. As part of the project five potential seaweed species common in Irish waters, *Saccorhiza polyschides*, *Ulva sp.*, *Laminaria digitata*, *Fucus serratus* and *Saccharina latissima*, were co-digested individually with bovine slurry [63]. The combination of *S. latissima* with slurry produced the maximum methane yield (335 mL g volatile solids^{-1}) followed by *S. polyschides* with (255 mL g volatile solids^{-1}). The methane and CO_2

percentages ranged between 50%–72% and 10%–45%, respectively. The results of the study established that the seaweed species investigated are promising feedstocks for the production of biogas and methane for energy production. However, their use on a large-scale will require further development to increase yields and reduce production costs [63].

Sanderson [8] estimated the costs of setting up a one hectare seaweed farm in the UK. The study was based on a detailed breakdown of the costs per 40 m longline (surface barrelfloats, headline, anchor rope, stainless steel swivels, thimbles for splicing, shackles and mooring blocks) of £2382.49, depreciated over five years, together with approximations of other annual costs. It was estimated that the one hectare plot would need to yield 130 t wet weight, worth £500/t to break even [64]. However, the study notes that the estimated costs are potentially over estimates, and could be considerably lower given economies of scale. For example, there is the opportunity to avail of technology transfer from countries where macroalgae are cultivated on a very large scale, as in areas in Asia. Reducing labor costs in the UK could be achieved by further mechanization of the culture methods and would be vital in improving the economic viability of the system [8].

In Ireland, the Mabfuel project at the Daithi O'Mhurchu Marine Research Station [65] is just reaching its conclusion after three years of investigating the feasibility of using algae as a feedstock for producing bio-fuels in Ireland and Turkey. The Mabfuel project aimed to develop optimal methods to extract oil from algal biomass and to develop intensive large-scale culture methods for micro-algal species for indoor and outdoor facilities. The project was run in conjunction with seven partners, including two Turkish universities as well as Green Biofuels Ireland, which operates a biofuel plant at New Ross, Ireland. A business plan is being prepared with the aim of becoming Ireland's first commercial scale producer of algae for biofuels.

Energetic Algae ("EnAlgae") [66], is a multi-year project (2009–2015) aiming to investigate the potential of reducing GHG emissions in the North West Europe (NWE) region by producing microalgae and macroalgae for biofuel. The project brings together 19 partners and 14 observers across 7 EU Member States and has received funding from the European Regional Development Fund through Interreg IVB [67]. The National University of Ireland Galway (NUIG) is involved in work package one of the project, the objective of which is to maximise the transnational value of pilot scale algal culture facilities across NWE. NUIG has developed a large-scale hatchery which is used to grow kelps, including *Saccharina latissima* ("Sugar kelp") and *Alaria esculenta* ("Atlantic wakame"). The aim of this facility is to standardise and increase the production of a hectare site at sea. It is hoped that by monitoring of the environmental conditions of the site, considerable insights may be gained into macroalgal yield is influenced by surrounding habitat.

University College Dublin (UCD), is involved in work packages two and three of the project which aim to "identify political, economic, social and technological opportunities which promote the adoption of algal biomass within NEW" and "to combine information across the algal bioenergy delivery chain into a comprehensive and user friendly ICT tool which will facilitate decision making, identify gaps in current knowledge and capability, and provide a roadmap by which stakeholders can focus future actions in the region" [68]. UCD is working to develop materials and methods for the sustainable conversion of biomass to bioenergy, and ways is which this energy can be stored. UCD studies on artificial photosynthesis, the production of H_2 and hydrocarbon from water and CO_2 [69], will assist the EnAlgae project.

Further research and development is required into the production of algal biofuels, as such any contribution to Ireland's 2020 targets is likely to be minimal. Bruton [19] has that up to 447 TJ (approximately 21 million L) of energy may be generated from macroalgae by 2020.

5. Life Cycle Assessment (LCA) of Micro and Macroalgae Systems

From 2013 to 2017, biofuels must achieve a minimum 35% reduction in GHG emissions *versus* fossil fuels.

5.1. Microalgae

Slade and Bauen [14] reviewed reported energy balances and associated GHG emissions from a number of studies of microalgae production systems. They found that the net energy ratio (the sum of the energy used for cultivation, harvesting and drying, divided by the energy content of the dry biomass) is less than one for 75% of the open pond studies reported. In these systems there are high energy requirements associated with pumping, fertilizer production, and drying and de-watering. However, the net energy ratios of all photobioreactor studies reported are all greater than one, with the majority of energy requirements associated with cultivation and harvesting. The results show that while positive energy balances are possible, algae production systems will need to be optimized and technical advances will be required to make these systems viable.

The associated carbon dioxide emissions associated with the algae production systems were estimated by multiplying the external energy inputs reported in the studies by the default emissions factors described in the EU renewable energy directive [14]. The production of algae biomass by the open pond method is comparable in terms of CO_2 emissions to the production of rape methyl ester biodisesel (45 g CO_2 eq. MJ^{-1}), while production in photobioreactors produces emissions higher than conventional fossil diesel (84 g CO_2 eq. MJ^{-1}) [14].

5.2. Macroalgae

Alvarado-Morales *et al.* [70] analyzed the energy requirements and environmental impacts of two macroalgae-based biofuel scenarios in Scandinavia. The two scenarios analyzed were biogas production (Scenario 1), and bioethanol with biogas production (Scenario 2), from the brown seaweed (*Laminaria digitata*). The production of seaweed was identified to be the most energy intensive step, mainly due to the energy required in the land based growth of juveniles and the grow-out phase. The net energy consumption was 2.26 and 3.04 GJ/t of dry macroalgae for Scenarios 1 and 2, respectively. The energy produced from Scenario 1 was approximately 555 kW h (2 GJ) of electricity per tonne of dried macroalgae, resulting in a negative energy balance for the system. For Scenario 2, the energy produced amounted to 2.01 GJ/75 kg of produced ethanol and 359 kW h (1.29 GJ) of electricity per tonne of dry macroalgae. This corresponds to a total energy production of 3.30 GJ/t of dry macroalgae, therefore resulting in a slight positive energy return. In terms of GHG emissions, Scenario 1 has lower emissions compared to Scenario 2, where the increase in emissions can be attributed to energy consumption for bioethanol production downstream and the purification process [70]. The study highlights the need for development of seaweed production, bioethanol distillation, and

management of digestate in order to improve the environmental performance of macraolgae biofuel production.

6. Conclusions

While the algae industry is relatively well developed for food, feed and nutraceutical applications, along with high value products, algae for biofuel is in its infancy. The industry still requires considerable research and development in order to develop economically viable algae biofuel production. The high biomass productivity of both micro and macroalgae, along with favorable biomass compositions, make them ideal feedstocks for conversion into a range of biofuels. Microalgae is more typically suited to biodiesel production due to its high lipid content, while the high levels of natural sugars in macroalgae makes it more suitable for fermentation to produce ethanol. The technology for production and conversion of microalgae to biofuels has not reached any appreciable commercial scale, with only one or two algae biofuel plants coming online in recent years. Macroalgal biofuel is limited to a research and demonstration scale.

It is predicted that microalgal biofuel capacity will reach 1128 million L by 2017. The majority of companies involved in algae production are based in the USA, this could influence trade flows. The costs for aquatic biomass production for energy applications are currently too high to compete with bio energy applications from biomass produced on land. However, there is potential to improve the value of algae if the parts of the biomass that cannot be converted into fuels are utilized for food, feed, chemicals, cosmetics, biomaterials or even pharmaceutical applications.

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Conflicts of Interest

The authors declare no conflicts of interest.

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