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ORIGINAL ARTICLE

Mass-cultivation of carbohydrate rich macroalgae, a possible solution for sustainable biofuel production

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Abstract Global demand for bio-fuels continues unabated. Rising concerns over environmental pollution and global warming have encouraged the movement to alternate fuels, the world ethanol market is projected to reach 86 billion litres this year. Bioethanol is currently produced from land-based crops such as corn and sugar cane. A continued use of these crops drives the food versus fuel debate. An alternate feed-stock which is abundant and carbohydrate-rich is necessary. The production of such a crop should be sustainable, and, reduce competition with production of food, feed, and industrial crops, and not be dependent on agricultural inputs (pesticides, fertilizer, farmable land, water). Marine biomass could meet these challenges, being an abundant and carbon neutral renewable resource with potential to reduce green house gas (GHG) emissions and the man-made impact on climate change. Here we examine the current cultivation technologies for marine biomass and the environmental and economic aspects of using brown seaweeds for bio-ethanol production.

Keywords Biofuel · Bioethanol · CO_2 uptake · Fermentation · Large-scale cultivation · Macroalgae · Seaweed

1 Introduction

Our global economic development mainly has been driven by the availability of cheap fossil fuel resources, such as oil and gas. The world has become strongly dependent on these fossil fuels for its transport needs (Annon 2006a). However, the current rate of consumption should result in the depletion of oil by the middle of this century (Peak Oil 2009). More importantly, burning these fossil fuels over the last 100 years has led to an increased atmospheric CO_2 concentration, currently around the 350–380 ppm and predicted to rise to 450 ppm by 2020 if no action is taken. Moreover, the general consensus is that fossil oil usage has been responsible for another global impact, i.e., global warming and the effects on climate through green house gas emission (GHG) (Global Warming 2009). In

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addition to fossil oil, also coal, gas, cement factories, ruminant digestion, etc., contribute much to GHG production. It has become urgent to identify alternatives to oil and to manage the effects of releasing carbon by-products into the atmosphere (Copenhagen Climate Conference 2009).

To meet the sustainability goals set out in the Kyoto protocol, a clean, secure and affordable supply of transportation fuels is needed. Biofuels such as bioethanol or butanol derived from fermentation of carbohydrates of plant biomass (i.e. corn, sugar-cane and cellulosic plant-materials) can provide a very significant contribution in the short to medium term (Annon 2006a).

Alternative fuel sources are emerging in the form of renewable options (solar, wind, wave and biofuels). The renewable options are part of the answer but in their current form will only supply a fraction of the energy requirement. The solution lies in the exploitation of nature's energy cycle, photosynthesis and the resulting plant biomass. Society has to make a transition from a hydrocarbon to a carbohydrate economy. Plants in general are efficient solar energy converters, and can create large amounts of biomass in a short-term; however, marine biomass is often an overlooked source, and potentially represents a significant source of renewable energy. The average photosynthetic efficiency of aquatic biomass is higher (up to 5%; Torzillo et al. 1986; Doucha et al. 2005; Huntley and Redalje 2007) than that of terrestrial biomass (1.8–2.2%; FAO 1997).

One of the main issues of biomass utilisation is that the amount of biomass required in order to make significant progress in renewable fuel production and an impact in CO_2 reduction will be governed by supply. Consequently, there is now serious discussion of the use of biomass supplies originating from an aquatic environment either cultivated or wild harvested.

Macroalgae are fast growing marine and freshwater plants that can grow to considerable size (up to tens of meters in length in the case of Pacific kelp species), although Atlantic species would be smaller at ~3 m length (Lüning 1990). Growth rates of marine macroalgae far exceed those of terrestrial biomass. The large brown algae of kelp forests found on rocky shores inhabit an environment of vigorous water movement and turbulent diffusion. This allows very high levels of nutrient uptake, photosynthesis and growth. Highest productivity of kelp forests is found along the North American Pacific coast, which out-performs that of the most productive terrestrial systems (Velimirov et al. 1977). *Laminaria*-dominated communities of the European coasts have an annual productivity of approximately 2 kg carbon per m^2, which is still higher than, for example, temperate tree plantations or grasslands with a productivity of generally less than 1 kg carbon per m^2 (Thomas 2002). Production figures have been reported in the range of 3.3–11.3 kg dry weight m^{-2} yr^{-1} for non-cultured and up to 13.1 kg dry weight m^{-2} over 7 month for cultured brown algae compared with 6.1–9.5 kg fresh weight m^{-2} yr^{-1} for sugar cane, a most productive land plant. In addition marine biomass does not require fertilisation as currents and water exchange provide a continuous flow of a base level of nitrates and phosphates and large scale cultures may be useful in alleviating increased nitrogen levels in inshore waters. Due to the absence of lignin and a low content of cellulose, brown macroalgae may be easily convertible in biological processes compared to land plants.

Seaweeds are already farmed on a massive scale in Asia and substantial quantities are also harvested from natural populations. Recent research has shown the potential for large scale culture of macroalgae in Atlantic waters (Canada: Chopin et al. 2008a; France: Kaas 2006; Germany: Buck and Buchholz 2004; Ireland: Kraan et al. 2000; Isle of Man, UK: Kain et al. 1990; Spain: Peteiro and Freire 2009). The challenges now lie in further developing cost-effective methodologies to grow, harvest, transport and process large quantities of macroalgae.

The uses of seaweeds at present include human foods, phycolloids, fertilizers, cosmetics, and the extraction of other industrial gums and chemicals (Kelly and Dworjanyn 2008; Notoya 2010). The residues from such processing also represent a renewable source of energy. While much of the bio-diesel industry has been focussing on microalgae, some preliminary research into genetic engineering of seaweeds for increased oil production has been emerging (Qin et al. 2005).

The different thermochemical options for macroalgae utilization include direct combustion, gasification, pyrolysis and liquefaction. These conversion routes of macroalgae have received very little attention. Initial studies of combustion and pyrolysis characteristics have been undertaken (Ross et al. 2008) and it is clear that the mineral content, especially the alkali chlorides, are potentially problematic. Consequently, viable utilisation options could include: pre-treatment or pre-processing for added value products and utilisation of the residue for energy; seaweed blended with other fuels to minimise the impact of the inherent minerals; or wet conversion methods, such as liquefaction anaerobic digestion/ fermentation. A large body of research on fermentation of seaweeds into methane exists starting in the early 1980s and is extensively reviewed in Kelly and Dworjanyn (2008).

The road transport sector in the European Union (EU) is the main consumer of oil based products (47% in 2006; Annon 2008a) It accounts for more than 30 % of the total energy consumption in the EU and is 98% dependent on fossil fuels with a high share of imports and thus extremely vulnerable to oil market disturbance (Annon 2006a). The growing transport sector is considered to be one of the main reasons for the EU failing to meet the Kyoto targets. It is expected that 90% of the increase of CO2 emissions between 1990 and 2010 will be attributable to transport. Transportation fuels are thus promising targets for a reduction in GHG-emissions. The aim of replacing 10 % of transport fuels by 2020 with biofuels is motivated not only by improving the CO_2-balance, but also reducing the dependency on imported oil products and securing the energy supply (Annon 2006b). By 2030, the EU aims to cover as much as one quarter of its road transport fuel needs by clean and CO_2-efficient biofuels.

This significantly decreases the EU fossil fuel import dependence. Biofuels have to be produced using sustainable and innovative technologies which create opportunities for (aquatic) biomass providers, biofuel producers and the automotive industry (Annon 2008a).

The only commercially available biofuels today are first generation biofuels, mainly bioethanol and biodiesel, produced from e.g. sugar cane and corn, and rapeseed, respectively. However, continued use of these crops will drive the food versus fuels debate even more as demand for ethanol increases. Not only does the large-scale production of corn and sugar cane damage the environment by the use of pesticides, it uses two other valuable resources: arable land and enormous quantities of water. For instance, the production of corn in the USA used over 3 trillion litres of water a year in 2007 (Chiu et al. 2009).

Nevertheless, the global demand for bio-fuels continues unabated. Driven by high oil prices, concerns over environmental pollution and global warming, and the movement to alternate fuels, the world ethanol market is projected to reach 100 billion litres per annum by the year 2012 (F.O. Licht 2009). Global demand is currently 86 billion litres (GRFA 2010). Stringent legislation on emission standards and governmental intervention by way of subsidies and tax incentives are expected to foster significant market growth in the medium to long term. Increased demand and the competition with food production has called for the development of second generation biofuels, based on utilization of lignocellulosic biomass, such as wood and agricultural waste. Second generation biofuels do not compete with food as a feedstock, but they compete for land and fresh water resources.

Therefore the challenge is to find a feedstock which is abundant and carbohydrate-rich. This crop must be sustainable, use no agricultural inputs (pesticides, fertiliser, land, water), and must not be part of the human or animal food chain. Such a feedstock and an alternative to terrestrial biomass are marine macroalgae or seaweeds. Macroalgae and aquatic biomass are emerging as one of the most promising potential sources for biofuels production. The cultivation, transformation and final use of aquatic biomass are attracting the interest of the scientific community, the industry and an increasing number of stakeholders at an international level. This is first of all related to the ability to further improve the sustainability of the production of biofuels. One of the most critical aspects of biofuel sustainability stands in the way in which biofuels raw materials are produced, especially with respect to their CO_2 balance and to the competition with food agriculture areas that they create. Macroalgae and aquatic biomass can represent major progress in this sense: higher carbohydrate levels and biomass yields, their widespread availability, the absence of a competition with food or agricultural surfaces, the high quality of the by-products, their use as a means to capture CO_2 and their suitability for integrating in wastewater treatments to reduce pollution make them one of the most attractive renewable sources for a sustainable energy strategy.

2 Suitable species and production

Several species of macroalgae accumulate high levels of carbohydrates, which are suitable as substrate for microbial conversion processes, e.g. for production of bioethanol, biobutanol as biofuels or other desirable chemicals with an attractive high product value (Table 1). Certain red algal species such as *Gelidium* J.V. Lamouroux have been used for paper production of which the waste products from processing have been converted into bioethanol (Yung-Bum et al. 2010). Also green algae species such as the *Ulva* sp Linnaeus with high levels of the polysaccharide Ulvan (Lahaye and Ray 1996; Lahaye 1998) have been used in ethanol and methane production (Morand et al. 1991; Adams et al. 2009). This paper mainly focuses on brown macroalgae and in particular kelp as in general these species contain 50–60% carbohydrates of the dryweight and cultivation techniques have been firmly established for the last 50 years. Moreover, kelp is cultivated in large quantities up to 15.5 million wet tonnes in the Far East (FAO 2010). Another suitable brown alga is *Sargassum* C.

Table 1 Possible fermentation products, yield per tonne seaweed and value (adjusted from Reith et al. 2005)

Product	Market value ($/tonne)	Production yield (kg/tonne seaweed)	Value ($/tonne seaweed)
Ethanol	331	255	84
Acetic acid	728	247	179
Butyraldehyde	948	123	117
Adipinic acid	1,433	370	530
Butanol	904	123	111
Lactic acid	300	486	146
Succinic acid	772	429	331
Propylene glycol	1,279	133	170
Glycerol	1,279	247	315
Citric acid	1,808	429	775
Proprionic acid	904	227	205
2–3 Butanediol	1,984	163	323

Agardh. The floating fronds of the *Sargassum* spp. are convenient, as they could be harvested just by separating their holdfasts from the culture system, which is very easy compared with the *Laminaria* spp. Most species of *Sargassum* are grown in regions that have comparatively warm currents and can produce 2–5.5 kg/m^2 (Notoya 2010). Large communities are built on coastal areas, thus allowing the growth of useful fish and shellfishes as well as maintenance and preservation of marine resources (Notoya 2010). Therefore, artificial propagation and culture of *Sargassum* spp. is effective for the increase and preservation of marine fish and shellfish resources. Over the last decade *Sargassum* has firmly established itself the North Atlantic as an invasive species and could perhaps be harvested or cultivated for the production of marine biomass (Kraan 2008; Notoya 2010).

Five Atlantic kelp species are suitable to fulfill a similar role, i.e., *Saccorhiza polyschides* (Lightfoot) Batters; *Alaria esculenta* (L.) Greville; *Laminaria hyperborea* (Gunnerus) Foslie; *Laminaria digitata* (Hudson) J.V. Lamouroux; and S*accharina latissima* (Linnaeus) C.E. Lane, C. Mayes, Druehl & G.W. Saunders (Werner and Kraan 2004). They differ in various aspects, such as morphology, ecophysiology and longevity. *Laminaria digitata* and *Laminaria hyperborea* are the only species that form extended monospecific kelp beds. The vertical distribution of these five species on the shore depends on factors such as light penetration, tolerance to desiccation, interspecific competitiveness and adaptation to rigorous wave impact (Werner and Kraan 2004). Kelp inhabits the continuously submersed sublittoral zone with the upper sublittoral occasionally emerging at extreme low water levels. The lower limit for algal growth in the sublittoral is naturally determined by light levels. In coastal waters rich in particles, the depth limit for kelp growth may be 10–15 m below mean low water, whereas in clearer waters of the open Atlantic coasts kelps are found down to 30–40 m of depth (Lüning 1990).

The biomass productivity of macroalgae ranges converted to carbon is about 1 to 3.4 kg carbon m^{-2} year^{-1} (Mann 1982; Gao and McKinley 1994; Mohammed and Fredriksen 2004). Seaweed communities of the North Atlantic coasts have an annual productivity of approximately 2 kg C per m^2, which is far higher than, for example, temperate tree plantations or grasslands with a productivity of generally less than 1 kg C m^{-2}, year^{-1} (Mann 1982; Chapman 1987; Thomas 2002; Lüning and Pang 2003; Mohammed and Fredriksen 2004), and 2.8 times higher than for sugar cane (Gao and McKinley 1994). Macroalgae can be cultivated in the open sea (Zhang et al. 2008; Bartsch et al. 2008; Kelly and Dworjanyn 2008). Ocean farming of seaweed does not depend on fresh water and does not occupy land areas (Yarish and Pereira 2008). Sustainable utilization of algal biomass—a largely unexplored feed stock resource can be a complement to terrestrial biomass for the future global energy and carbon security and thereby also strengthen the maritime economies.

Ocean farming of seaweed has the potential to produce in the order of 40 tonne dry weight biomass per hectare per annum (Table 2). An area of 2,500 km2, the size of Co. Waterford in Ireland or similar to the size of the country of Luxembourg, would be able to provide 10 million tonne dry biomass, representing 5.6–5.8 million tonne carbohydrates. With current 90% enzymatic conversion into ethanol (McCaughren 2008) this would yield close to 2 billion litres of bioethanol. This is about 2–3 % of the world's global bioethanol production (F.O. Licht 2009); however, it would cover about 50% of the EU's ethanol demand (Annon 2008b). For comparison reasons, if the size of the country Luxembourg as an area is projected on the North Sea and on the Celtic sea surface area, it shows a marginal uptake of available space (Fig. 1.). On the other hand these large-scale farms might perhaps cause other problems such as localised nutrient depletion or emission of volatile short-lived organo-iodines and molecular iodine from kelp which are believed be main vectors of the iodine biogeochemical cycle as well as to have a significant impact on atmospheric

Table 2 Production of some kelp species in the wild and cultivated dry weight per hectare per year

Species	Kelp forest Tonne dry Per hectare y^{-1}	Wet Kg m^{-1} of rope	Tonne dry of cultivated kelp hectare y^{-1}	Reference
Kelp species	33–113			Gao and McKineley, 1994
Saccharina latissima		3.75	20	Buck and Buchholz, 2004
		3–28		Druehl et al. 1988
Alaria esculenta		7–45	1.5–2	Kain, J.M. & Dawes, C. P. (1987).
				Kraan and Guiry 2001
Laminaria digitata		3–15		Arzel (1998), Werner & Kraan, 2004
Macrocystis pyrifera			38–62	Chynoweth, 2002
Saccharina japonica			15–60	Tseng, 1987
			54–115	Chynoweth, 2002
			131	Brinkhuis et al. 1987

chemistry (Leblanc et al. 2006). Furthermore disease, predation and epiphytes may play a negative role and affect production in large-scale farms (Roesijadi et al. 2008). It is therefore suggested not to operate such large farms but rather work with smaller units of 1–10 km^2 for example within existing wind farms (Reith et al. 2005). With respect to nutrients, the surface oceans contain almost 2×10^{15} metric tonne of nitrogen in a form usable by seaweed; the potential removal by offshore seaweed farms envisioned here is negligible in the world oceans. Localized nitrogen removal may be more significant; siting offshore seaweed farms in areas of active upwelling should minimize potential declines in nitrogen availability to the marine food web (Roesijadi et al. 2008). Current cultivation in China and Japan where over 15 million tonnes of kelp are cultivated has not created nutrient depletion (Critchley et al. 2006; FAO 2010). Nevertheless, the two 2,500 km^2 large-scale farms described above would be able to produce all bio-ethanol currently used in the EU. Besides bioethanol, algal biomass can be used for sustainable production of a great variety of other products, including plastics, protein and other valuable chemicals such as pigments (Table 3). The use of algal biomass has the potential to not only replace fossil resources, and thereby mitigate climate change, but also aid in the recycling potential of nitrates and phosphates in near and inshore waters.

Global food production depends upon availability of phosphate rock, a non-renewable fertilizer ore that is in diminishing global supply, much of which presently comes from countries such as Togo or Moracco (FAO 2004; von Horn and Sartorius 2009). Most agricultural practices remove nutrients faster than they are replenished by natural processes of soil formation; consequently potassium, nitrogen, phosphorus and micronutrient fertilizers are purchased and applied by most farmers. Nitrogen fertilizer is manufactured from atmospheric nitrogen, potassium fertilizer is derived from geological potash deposits, and phosphorus from phosphorite. Thus, ensurability of food production is dependent upon the secure availability of fertilizer products upon which high crop yields depend. Phosphorite is a non-renewable fertilizer ore that is in diminishing global supply and for which there is no substitute. (FAO 2004). With a growing world population and increased pressure on food production, it is estimated that by 2030 about half the world reserves of phosphate will have been used for agricultural purposes. Furthermore the projected increase

Fig. 1 Size of two 2,500 km^2 seaweed farms depicted in the Celtic and North Sea (indictaed by black arrow) both equaling the size of country Luxembourg

of agri-fuel crops such as rapeseed and corn will increase the use of phosphate rock even more (von Horn and Sartorius 2009). Over the last 5 years phosphate rock has increased from \$30–40/tonne to \$430 in 2009 and diammonium phosphate to over \$1,000/tonne. Currently run-off from land washes many nutrients (N and P) into the rivers (causing algae blooms) and ultimately into our inshore waters where it continuous to be deposited into the deep ocean. Phosphate recycling from wastewater will be self sufficient at costs of about 100\$/t. Especially for European countries without phosphate reserves even slightly higher prices might be acceptable to reduce the dependence on phosphate imports (von Horn and Sartorius 2009). Large-scale seaweed cultivation in inshore and near shore seas could prevent the loss of phosphates and nitrates from run-off as these macroalgae have a high uptake rate of these nutrients (Chopin et al. 2008a; Kelly and Dworjanyn 2008). After harvesting, N and P can be recovered and re-used and thus help the recycling of these important nutrients.

Table 3 Other high-value by-products from ethanol production of macroalgae (Reith et al. 2005; Wijffels 2009)

Product	Market value ($/tonne)	Content (% of dry weight)	Value ($/tonne dw)
Alginates	6,000	23	1,380
Mannitol	6,000	12	720
Fucoidan	12,000	5	600
Iodine	14,500	0.45	65.25
Potash	60	9.5	5.7
Phosphorus	1,000	0.3	3
Protein Human	5,000	12	600
Protein Feed	750	12	90
Lipids Human	2,000	3	60
Lipids Feed	500	3	15
C-removed	15	33	4.95
N-removed	2,000	3	60

3 Status of the cultivation of brown macroalgae

Among marine macroalgae, species of the brown algal order Laminariales (so-called kelp species) are among the fastest growing plants in the world. These large algae prefer and thrive in temperate waters, which in the case of Europe stretches from northern Portugal to Northern Norway. In the Americas in the northern hemisphere kelp grows from Mexico to Alaska and in the southern hemisphere from Peru down to the tip of Chile (Guiry and Guiry 2009). The annual production of macroalgae is 15.5 million t wet weight and represents the largest aquaculture production on a global basis and 93 % of the worldwide commercial harvest of seaweeds in 2008 (FAO 2010). Seaweed cultivation in Europe is still in its infancy with a few commercial attempts, notably in France, Germany and Ireland (Buck and Buchholz 2004; Kraan and Guiry 2006; Kaas 2006). Total production of these farms combined is less than 50 tonne wet weight and all is used in the food or feed industry.

The main cultivated species in order of importance are: *Saccharina japonica* (J.E. Areschoug) C.E. Lane, C. Mayes, Druehl and G.W. Saunders, previously called *Laminaria japonica, Undaria pinnatifida* (Harvey) Suringar, *Porphyra yezoensis* Ueda, *P. Tenera* Kjellman, *Kappaphycus alvarezii* (Doty) Doty ex P.C. Silva and *Gracilaria* spp. Greville (Critchley et al. 2006). There are two main approaches to cultivate seaweeds; one is based on the sexual reproduction of the various species and the other on the ability of some species to propagate vegetatively (Bartsch et al. 2008; Hernández-González et al. 2007; Titlyanov et al. 2006). New approaches using micro-propagation proved to be efficient but still require improvement (Reddy et al. 2008). During the last 20 years various trials and experiments have been carried out on species interesting for their hydrocolloid content like *Gelidium sesquipedale* (Clemente) Thuret, their value as edible seaweeds (*Undaria pinnatifida*, *Alaria esculenta*, *Palmaria palmata* (Linnaeus) Kuntze (Kraan and Guiry 2006), or their ability to extract nutrients from effluent (*Ulva* spp. Linnaeus) while having a potential value like *Gracilaria* spp. (Buschmann et al. 2001). The integration of seaweeds for the treatment of shellfish and finfish aquaculture effluents or urban sewage is of global interest (Chopin et al. 2004; Carmona et al. 2006). Not only can they remove large amounts of inorganic nutrients but they have also the capacity to accumulate heavy metals and other contaminants. Knowing that shellfish and finfish aquaculture represents a yearly production of about 30 million tonnes and produces large quantities of ammonia, integrated systems including shellfish and/or finfish and macroalgae have been tested with success in order to remove this excess of nitrogen in land based systems as well as in open sea cultures (Neori et al. 2000; Schuenhoff et al. 2003; Chopin et al. 2008a; Troell et al. 2009).

Among North Atlantic kelp species *Saccharina latissima* (previously known as *Laminaria saccharina*) is the fastest-growing macroalgal species. This species is similar to *S. japonica* of which 4 million tonne fresh weight is harvested annually from aquaculture in northern China, and almost 0.3 million tonne fresh weight additionally in Korea with Japan trailing at close to 50,000 tonnes (Ohno and Largo 2006; Wu and Pang 2006; FAO 2010). Other relevant brown algal species for cultivation as a possible energy crop in the Northern Hemisphere are *Alaria* spp. *Laminaria* spp, *Macrocystis pyrifera* and *Nereocystis luetkeana* (K.Mertens) Postels & Ruprecht. In the Southern Hemisphere candidate species might perhaps be *Ecklonia* sp. (Hornemann), *Lessonia* sp. (Bory de Saint-Vincent) and *Durvillaea* sp. (Bory de Saint-Vincent).

Kelp as a rule contains approximately 60 % carbohydrates of the dry weight. Laminaran (a glucose polymer) and mannitol are energy storage compounds, resembling starch in land plants, while alginates are structural compounds and correspond to cellulose and lignin in land plants. The seasonal variations in algal carbohydrate composition are considerable (Honya et al. 1993; ISC 2009). The content of storage carbohydrates has a maximum in autumn. During the winter season, with nutrients in excess, the stored carbohydrates are utilized as energy source for protein synthesis reproduction and growth. Growth conditions and harvesting time may therefore strongly affect the quality of the seaweed biomass as substrate for microbial production processes.

4 Cultivation systems

Over the last couple 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 (Critchly et al. 2006). During the late 1970s and early 1980s several U.S. designed kelp farming systems have been tested. However, the development of open ocean seaweed farming systems and its off-shore challenges was premature in the 1970s and failed. For an extensive review see Roesijadi et al. (2008). Modifications of long-line systems have been tested at small scale in Europe (Kelly and Dworjanyn 2008) amongst them a novel ring system from Germany (Buck and Buchholz 2004). These cultivation systems show that there is potential to develop large-scale ocean cultivation of seaweeds. However, existing cultivation and harvesting technology is labour intensive and needs to be optimised to reduce costs and energy demand (Roesijadi et al. 2008; Troell et al. 2009).

A major bottle-neck in mass cultivation of kelp biomass in the sea is the production of juvenile sporophytes on ropes from zoospores via female and male gametophytes (Pérez et al. 1984, 1992; Kaas 2006; Bartsch et al. 2008). In China and Japan *Laminaria* cultivation from zoospores relies exclusively on naturally occurring sori restricted to a certain part of the year, so that hatchery facilities are not in use throughout the whole year. However, previous work in France on the free-living stage of the gametophytes (Pérez et al. 1984, 1992) and recent developments in China in mass culture of filamentous gametophytes with establishment of vegetative gametophyte stocks in the range of kilograms of fresh weight has changed this concept. (e.g. Kaas 2006; Xu et al. 2008; Zhang et al. 2008). Using the so called free-living technique to keep male and female or mixed cultures free floating as stock cultures allows seeding of long-lines virtually any time of the year, although successful growth at sea is still dependant on physical and environmental conditions, such as nutrients, light and temperature (Bartsch et al. 2008).

5 Processing and fermentation of macroalgal biomass

The water content in macroalgae is higher than in terrestrial biomass (80–85 %), making seaweeds more suited for microbial conversion than for direct combustion or thermo-chemical conversion processes, which is an alternative for land-based biomass (Horn et al. 2000a; Ross et al. 2008). Seaweed carbohydrates may be used as substrates for microbial production of a wide range of fuels and chemicals. For a cost-efficient production the seaweed biorefinery concept should be applied (Fig. 2). It can produce several products, e.g. by using different processes of conversion of the different substrates in the most efficient way, and by co-production of compounds with higher prices than fuels. Target products, such as energy carriers like ethanol and butanol or other materials like itaconic acid for the biofuel and plastics industry, represent important industrial products that can replace or substitute products that currently are produced from oil sources. Ethanol production from hexose sugars such as glucose, sucrose, laminarin etc. derived from e.g. corn stover or sugar cane, is a well-known process. However, hexose-based poly-saccharides constitute only about 30–40% of the carbohydrates in kelp. The remaining fraction is composed of C-5 sugars that until now have not been applied as substrates for industrial microbial production processes. However, recent breakthroughs have been made in C5 sugar fermentation technology allowing up to 90% of the available

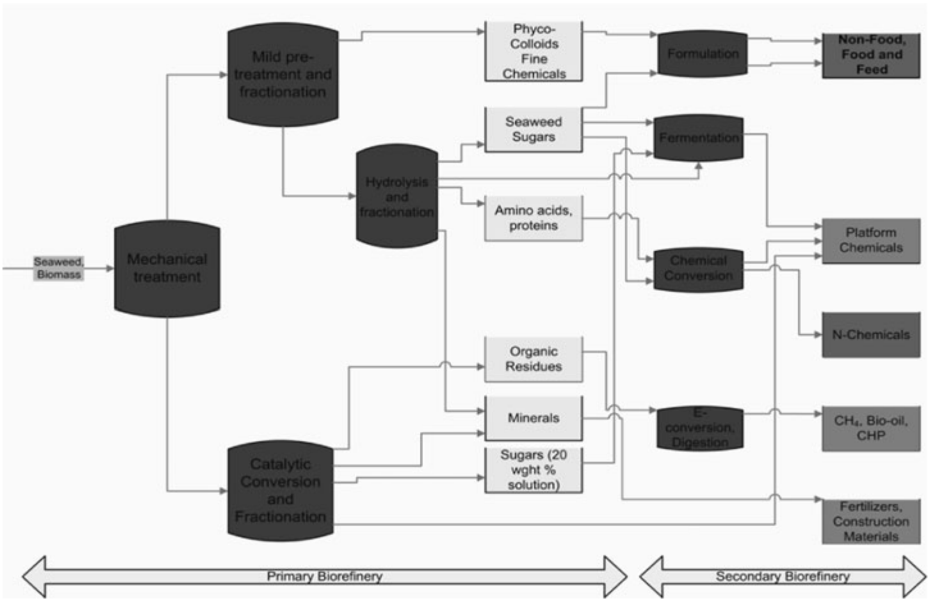

Fig. 2 A schematic representation of the seaweed biorefinery concept (Reith et al. 2009 with permission)

carbohydrates to be fermented (McCaughren 2008; Trevors J CEO of AER Ltd 162 Clontarf Road, Dublin 3, Ireland, pers. Comm.).

6 Pre-treatment of the seaweed biomass and hydrolysis of the polysaccharides of brown seaweed biomass

Fresh harvested brown seaweed contains about 15–20 % carbohydrates of the total wet weight, which equals about 200 g carbohydrates per kg wet weight, which is an appropriate substrate concentration for microbial conversion processes (Horn et al. 2000a). Lack of lignin in seaweeds implies that the harsh pre-treatment applied for release of fermentable sugars from lignocellulosic biomass is not required. Laminaran and mannitol can easily be extracted by water (Horn et al. 2000b). Alginates (consisting of polymer blocks of Uronic and guluronic acid) are present in the macroalgae biomass at 30–40% (Honya et al. 1993; McHugh 2003). Sodium alginate can be removed from the initial extraction solution by adding a calcium salt. This causes calcium alginate to form with a fibrous texture; it does not dissolve in water and can be separated from it. The separated calcium alginate is suspended in water and acid is added to convert it into alginic acid. This fibrous alginic acid is easily separated, placed in a planetary type mixer with alcohol, and sodium carbonate is gradually added to the paste until all the alginic acid is converted to sodium alginate. The paste of sodium alginate is sometimes extruded into pellets that are then dried and milled (McHugh 2003) . Due to the high viscosity, dilution with large amounts of water is required. The process is operating at alginate concentrations in the order of ~2 %. Such a dilution cannot be applied to processes aimed at use of alginate as fermentation substrate. Preferably, no water should be added, as it will increase the downstream processing costs (McHugh 2003).

Bioethanol production from cellulosic materials can be achieved by running simultaneously enzymatic hydrolysis and fermentation. For the wet seaweed biomass hydrolysis is not as easy due to the alginates which are harder to release from the biomass causing enzymatic degradation of un-treated biomass and hydrolysis will be the rate-limiting step if combined with fermentation. Hydrolysis should therefore be a part of the biomass pre-treatment. This hydrolysis can be carried out mechanically through grinding and emulsifying equipment, chemically using acid or alkali, or enzymatic. Researchers at the Biochemistry Department of The National University of Ireland, Galway, in conjunction with AER Ltd in Ireland, have developed an enzyme cocktail with key enzymes isolated from a marine fungus that is able to degrade 90 % of the polysaccharides of *L. digitata*, leaving only some insoluble fibre and salts (Tuohy, M. Department of Biochemistry, National University of Ireland, Galway, pers. Comm.). Moreover, several alginate lyases have been isolated from marine bacteria that can degrade alginates (Doubet and Quatrano 1982; Wang et al. 2006). The Norwegian institute SINTEF-MK has established large-scale processes for production of microbial alginate lyases (Aasen et al. 1992; Dyrset et al. 1994) using the technology which has been available since the early 1980s (Doubet and Quatrano 1982). Several methods for partial or complete degradation of alginate as an integrated part of the mechanical pre-treatment of the biomass are known. Chemical hydrolysis should follow existing technologies , e.g. by modification and adaptation of methods used for acid and alkali pre-treatment of wood biomass (e.g. Klinke et al. 2001; Ballesteros et al. 2002) and by combination of acid- or alkali with steam treatment. Other studies with macroalgae demonstrated the need for pre-treatment at 65°C, pH 2 for 1 h prior to fermentation (Horn et al. 2000a; 2000b, Percival and McDowell 1967). This in contrast with Adams et al. (2009) who found that these pre-treatments are not required for the fermentations with *Saccharina* *latissima* conducted, with higher ethanol yields being achieved in untreated fermentations than in those with altered pH or temperature pre-reatments. This result was seen in fresh and defrosted macroalgae samples using *Saccharomyces cerevisiae* and 1 unit of the enzyme laminarinase per kg of defrosted macroalgae.

Other existing technologies make use of a brown-rot fungus and are based on the dihydroxybenzene driven Fenton reaction (Contreras et al. 2007), which produce hydroxyl radicals and other oxidants that partially depolymerise carbohydrates and oxidize phenols and other fermentation inhibitors. Nevertheless, the easiest and environmental friendliest way of pre-treatment of algal biomass is through a combination of mechanical and enzymatic hydrolysis (Doubet and Quatrano 1982).

7 Ethanol and butanol from brown seaweeds

Ethanol production from fermentation is the most obvious one as it has a direct application in the replacement of fossil fuels. However other products such as butanol and itaconic acid can be produced as well which can substitute and/or replace similar products produced from fossil resources. There are many microorganisms in the marine environment that can degrade and utilize algal carbohydrates as a carbon source for energy. Often these microorganisms are associated with the seaweeds being present on the blade surface or in tissue as many kelp species produce exo-polysaccharides as mucus layer or shed entire skin. This would imply that these organisms possess the necessary enzymes for cleavage of the algal polysaccharides. However, compounds such as ethanol and butanol are produced by anaerobic fermentation that require the presence of specific metabolic pathways generating these compounds as end products, e.g. yeast for ethanol production and *Clostridia* for butanol production. Limited information is available on the efficiency of these processes with seaweed carbohydrates (Horn et al. 2000a; 2000b), although several breakthroughs have recently been made in respect of ethanol production from brown seaweeds (McCaughren 2008; Adams et al. 2009).

7.1 Ethanol

The potential of ethanol production from seaweeds can be calculated and is based on the following assumptions: a carbohydrate content of 60 % of dry weight and a 90 % conversion ratio to ethanol. Through fermentation 1 g of sugar can yield 0.4 g ethanol. This will yield 0.22 kg or 0.27 l ethanol from 1 kg dry weight seaweed biomass, corresponding to approximately 0.05 l ethanol per kg wet weight.

Several companies and institutes can produce ethanol through carbohydrate fermentation including alginates using a marine fungus; however, no studies on production of ethanol from alginate or its monomers, mannuronic acid and guluronic acid have been published as this information is often confidential and is not published in the public domain. Bacteria can metabolize uronic acids to pyruvate and glyceraldehyde-3-P, which may then be fermented to ethanol by the glycolytic pathway (van Maris et al. 2006). In anaerobic fermentation processes, as ethanol and butanol production, oxygen is not available for removal of excess hydrogen generated. This implies that the conversion reaction from substrate to product must be red-ox balanced. Ethanol-production from hexose sugars is red-ox balanced, while production from pentoses or mannitol generates excess hydrogen. In many bacteria but not in yeast the enzyme transhydrogenase solves this problem. Yeasts can avoid the problem by receiving a small, controlled supply of oxygen. However, oxygen leads to complete oxidation of the substrate to CO_2 and water, and reduced ethanol yields. Another strategy is introduction of transhydrogenase into strains that lack this enzyme, through genetic engineering (Fortman et al. 2008; Lee et al. 2008).

7.2 Butanol

Butanol is an alternative to ethanol with a higher energy content (butanol 29.2 MJ/l, ethanol 19.6 MJ/l), compared to gasoline (32 MJ/l). It can be used to supplement both gasoline and diesel fuels and can be handled by existing infrastructures (Fortman et al. 2008). Butanol is an important industrial chemical and is currently produced via petrochemical processes. In the last century butanol was produced through bacterial fermentation of starch rich compounds using *Clostridia* strains (Zverlov et al. 2006), which can use hexose as well as pentose sugers.

8 Current situation

Recently an exponential growth of research, technological development and demonstration initiatives has kick-started the exploration of aquatic biomass as alternative source for the biofuel industry, e.g., projects in the UK, Ireland, Norway and Denmark. Scientific research has been initiated on the production of various species and families of algae including micro-algae, macroalgae, plankton, and other aquatic biomass in fresh water, e.g., duckweed, in order to transform them into biofuels using very different technology pathways ranging from the esterification of fats and oils (biodiesel) to Fischer-Troops (BTL), anaerobic digestion (biogas) or ethanol production. Industrial pilots are also being developed and built and some companies already claim to be able to provide large-scale production in the short term. However, such initiatives are not coordinated neither at a European level, nor at a national level. The enthusiasm expressed by the scientific community, the industry and also by political representatives has created the conditions for further development but also the risk of confusion and overlapping R&D areas. Additionally, a disconnection between lab and field results was one of the most important issues underlined by US Department of Science (DOE) scientists on their report in 1998, after a 20 year study on algae at US National Renewable Energy Laboratory (Chynoweth et al. 1981, 1987; Chynoweth 2002; Roesijadi et al. 2008). The development of open ocean seaweed farming systems was premature in the 1970s. The Marine Biomass Program did not gather sufficient experience to overcome offshore challenges of open ocean forces and balance them with the engineering needed to successfully site a seaweed farm. The Marine Biomass Program moved towards nearshore systems to gain needed experience. The current situation has changed with pertinent experience gained through oil and gas exploration, oceanographic and atmospheric surveillance of ocean conditions and weather prediction, and major improvements in tensile strength and weight of materials that can be used at sea (Roesijadi et al. 2008).

9 The seaweed biorefinery concept

The replacement of fossil-fuel based products and energy by bio-based products and bioenergy is an important route for the reduction of CO_2 emissions. The development of biorefinery concepts in order to enable the manufacturing of bio-based products is essential part for successful implementation. At the same time, the targets set for bio-based products and bioenergy increase the demand for biomass as feedstock. Several initiatives in Europe aim to further develop the bio-refinery concepts for a still unexploited and large volume of biomass, seaweed from the Atlantic area. Some currently running large scale projects are: BioMara (EU Programme for Cross Border Territorial Cooperation INTERREG IVA; Supergen II (EPSRC, UK: Potential of Marine Biomass for Energy, Fuels and Chemicals); Biorefinery and Biofuel Competency Centre, Enterprise Ireland; EOS LT Seaweed Bio-refinery project, SenterNovem, The Netherlands; and recent initiatives undertaken by SINTEF Norway to start large scale seaweed cultivation projects for biofuels. Due to the different biochemical composition of seaweed compared with land plants, seaweed offers a vast potential of new chemical components. Bio-refinery of seaweed has a large potential both in quantity as in quality for the production of a wide variety of unique chemical components and bio-energy.

Previous studies (Reith et al. 2005) have shown that growing seaweed can be made economically viable if the production processes of bio-based products, biofuels and bio-energy are combined. Growing seaweeds with the current technologies available for energy purposes only is not attractive on the short term, from an economic point of view. Certain products from the seaweed industry have long been used for the production of phycocolloids such as alginates, carrageenans or agars (McHugh 2003). These polymers are either located in cell walls or within the cells serving as storage materials. Characteristic for seaweed is the abundance of sulphated polyssacharides in the cell walls. From the cell walls of green seaweeds the polysaccharide ulvan can be produced (Lahaye and Robic 2007). This type of component consists of varying proportions of repeating sequences of rhamnose, glucuronic acid, iduronic acid, xylose and sulphate. Possible applications of these components (after modification) are as pharmaceuticals, gelling agents and other chemicals (Lahaye and Robic 2007). Ulvans (and its derivates) are hydrocolloids and components not found in terrestrial plants. Using seaweed as feedstock will add new classes of components for several traditional and novel applications.

Before a successful commercial implementation of a bio-refinery based on seaweed processing can be realized a number of questions and uncertainties need to be resolved. In respect of cultivation and harvesting aspects of seaweed in Europe and also the subsequent processing of the harvested seaweed into bio-based products and bio-energy. Another very important issue is Marine licensing. In most European countries an aquaculture license and or foreshore license has to be obtained from the Government to obtain adequate ocean surface in order to be able to grow the required biomass. Currently obtaining an aquaculture license is a huge stumbling block e.g., see Regulation (EC) No 889/2008 laying down detailed rules for the implementation of Council Regulation (EC) No 834/2007, as regards to organic aquaculture of animals and seaweed.

10 CO2 removal

A by-product from combustion is CO_2, which traditionally is seen as a waste product and as an aggravating factor in the projected global climate change. Reduction of CO_2 emissions is therefore a high political priority implemented in national and international policy through e.g. the Kyoto Protocol, which identifies the amount of CO_2 reduction on a national level. Reduction in the CO_2 emissions can be achieved by switching the energy production from fossil fuels to renewable energy or by pumping the CO_2 in underground storage. As the CO_2 released from combusted bioethanol was previously removed from the atmosphere by the plant into organic carbon, the return of this gas is considered 'carbon neutral'. Carbon is taken up by cultivated seaweed biomass and can be calculated based on their carbon content (Muraoke 2004). Muraoke (2004) estimated that the total amount of carbon-based biomass of cultured seaweeds in Japan was 32,000 tonnes of carbon a year based on 560,000 wet tonnes of cultivated seaweed a year. This figure is equivalent to about 1.2 % of the total amount of annual carbon absorption by marine plant beds in Japan which has been estimated at 2.7 million tonnes of carbon. On the other hand, the global production of cultivated seaweeds was about 14 million tonnes in 2008 (Bartsch et al. 2008). Using this figure and data on carbon content, the estimate of global production by seaweed cultivation in carbon would be about 887,855 tonnes (Bartsch et al. 2008; Muraoke 2004). In respect of direct CO_2 uptake a Korean study demonstrated that 8–10 tonne CO_2 per hectare per year is taken up which is comparable with temperate woodlands (Chung et al. 2010). Cultivated seaweed can be an important instrument for carbon fixation (Notoya 2010).

11 Other environmental and social benefits

The primary production of kelp per unit area is amongst the highest known in aquatic ecosystems (Birkett et al. 1988). Kelp primary production results in the production of new biomass, detrital material shed from the blade tip, mucus and other dissolved inorganic material and spores (Kelly 2005). The holdfast, stipe and fronds of kelp plants present available substratum for colonisation by marine flora and invertebrates. The holdfasts tend to host strongly associated communities of epiphytes and marine invertebrates. Kelp contributes directly and indirectly to the food resource of suspension and deposit feeding invertebrates that in turn serve as prey to more mobile invertebrates such as polychaetes, cnidaria and larger decapods (Steneck et al. 2004). The rich fauna of mobile invertebrates in kelp beds makes this an important habitat in the diet of fish species. Kelp forests provide a foraging habitat for birds due to the associated and diverse invertebrate and fish communities present. Some invertebrate and fish species exhibit egg attachment and nest-building, respectively, in kelp habitats while others such as juvenile gadoids and salmon utilise kelp habitats as important nursery and refuge grounds. A number of studies have indicated the importance of kelp forests as habitat for spawning and reproduction in fish species (Gordon 1983; Schultze et al. 1990; Notoya 2010). The importance of kelp habitat as a nursery area for the development of juvenile fishes has been widely recognized (Carr 1983; Shaffer 2003; Lorentsen et al. 2004; Notoya 2010). The effective extension of the substratum into the water column increases shelter, or refugia, available to fishes while also providing habitat for the prey species used as a forage base by reef fishes (Kelly 2005).

Seaweed farms in the sea function in a similar way and create high biodiversity areas as the kelp farmed will attract other animals such as fish, invertebrates and benthos. These animals on their turn attract birds and seals. These kelp farms also create good habitats for fish to spawn and shelter for juvenile fish and could act as nursery areas, and may thereby enhance locally the recruitment of fish stocks under pressure such as gadoid species. Sjøtun and Lorentsen (2003) recently demonstrated the importance of *Laminaria hyperborea* forests as important habitats for juvenile gadoids, which highlights the importance of the habitat for particular species. Development of future large-scale ocean farming of seaweeds will contribute to the growth of maritime sectors and can be a viable alternative for fisherman as existing infrastructure can be applied. It further might enhance employment opportunities in local rural coastal areas in the form of seed hatcheries, seeding units and processing units, and create employment opportunities that otherwise would not exist.

12 Eutrophication and bioremediation

Inputs of nutrients from biodegradable organic matter and inputs deriving from fertiliser run-off together with effluent from finfish and shellfish rearing in near-shore waters and land based activities impact the quality of coastal inshore waters and are a cause of eutrophication (EPA 2003). In estuaries and shallow coastal embayments, eutrophication can be in the form of vast green algal mats, known as 'green tides' (Fletcher 1996). Aesthetically unpleasant, noxious-smelling agglomerations of algae can influence local fisheries and tourism industries and can persist for years and may pervasively and fundamentally alter ecosystems (Valiela et al. 1997).

Kelp farms (inshore and nearshore) are able to act as bio-filters and are able to remove nitrates and phosphates from the surrounding eutrophic inshore waters. This allows for increased production of farmed seaweed as demonstrated by Chopin et al. (2001, 2008a, b). Eutrophic waters are high in ammonia and phosphorous which can be stripped from the water by seaweed at rates varying from 60% up to 90% of the nutrient input (Neori et al. 2000). Moreover, primary production in coastal waters is about 10 times higher than that of phytoplankton on an area basis. These data indicate that macroalgae have a greater potential to remove nutrients compared to phytoplankton in inshore waters (Kelly and Dworjanyn 2008). Production of macroalgae from near-shore sea cultivation can be harvested for the bioethanol or biobutanol market while producing value added by-products in the process. Together with the removal of nitrates and phosphates from inshore waters macroalgae cultivation has both economic and environmental incentives. Open ocean seaweed farming has, in principle, inherent advantages over terrestrial biofuels production systems, where the availability resources—land, nutrients, water—are much more limited for such large-scale biomass production.

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