2 Algae-based bioenergy options

2.1 Background

In recent years, biofuel production from algae has attracted the most attention among other possible products. This can be explained by the global concerns over depleting fossil fuel reserves and climate change. Furthermore, increasing energy access and energy security are seen as key actions for reducing poverty thus contributing to the Millennium Development Goals. Access to modern energy services such as electricity or liquid fuels is a basic requirement to improve living standards.

One of the steps taken to increase access and reduce fossil fuel dependency is the production of biofuels, especially because they are currently the only short-term alternative to fossil fuels for transportation, and so until the advent of electromobility. The so-called first generation biofuels are produced from agricultural feedstocks that can also be used as food or feed purposes. The possible competition between food and fuel makes it impossible to produce enough first generation biofuel to offset a large percentage of the total fuel consumption for transportation. As opposed to land-based biofuels produced from agricultural feedstocks, cultivation of algae for biofuel does not necessarily use agricultural land and requires only negligible amounts of freshwater (if any), and therefore competes less with agriculture than first generation biofuels. Combined with the promise of high productivity, direct combustion gas utilization, potential wastewater treatment, year-round production, biochemical content of algae and chemical conditions of their oil content can be influenced by changing cultivation conditions. Since they do not need herbicides and pesticides (Brennan and Owende 2010), algae appear to be a high potential feedstock for biofuel production that could potentially avoid the aforementioned problems. On the other hand, microalgae, as opposed to most plants, lack heavy supporting structures and anchorage organs which pose some technical limitations to their harvesting. The real advantage of microalgae over plants lies in their metabolic flexibility, which offers the possibility of modification of their biochemical pathways (e.g. towards protein, carbohydrate or oil synthesis) and cellular composition (Tredici 2010). Algae-based biofuels have an enormous market potential, can displace imports of fossil fuels from other countries (hence reduce a country's dependence), and is one of the new, sustainable technologies which can count on ever-increasing political and consumer support.

The reasons for investigating algae as a biofuel feedstock are strong but these reasons also apply to other products that can be produced from algae. There are many products in the agricultural, chemical or food industry that could be produced using more sustainable inputs and which can be produced locally with a lower impact on natural resources. Co-producing some of these products together with biofuels, can make the process economically viable, less dependent from imports and fossil fuels, locally self sufficient and expected to generate new jobs, with a positive effect on the overall sustainability (Mata, Martins et al. 2010).

A wave of renewed interest in algae cultivation has developed over the last few years. Scientific research, commercialization initiatives and media coverage have exploded since 2007. In most cases, the main driver of the interest in algae is its high potential as a renewable energy source, mainly algae-based biofuels (ABB) for the transport sector. In 2009 FAO published a report detailing various options for algae cultivation, multiple biofuels that can be produced and the environmental benefits and potential threats associated with ABB production. One of the main conclusions of this report is that the economic feasibility of producing a (single) low-price commodity like biofuels from algae is not realistic, at least in the short term.

This chapter summarizes some of the technology key findings of the aforementioned report and gives a brief overview of how algae can be cultivated and which biofuels can be produced. The following chapter investigates which other products can be produced from algae, and tries to asses the viability of co-production with bioenergy.

2.2 Cultivation systems for algae

Although not specific to biofuel production from algae, it is important to understand the basics of algae cultivation systems. Systems which use artificial light demand, per definition, more energy in lighting than what is gained as algal energy feedstock, hence only systems using natural light are considered in this document.

Seaweed has historically been harvested from natural populations or collected after washing up on shore. To a much lesser extent, a few microalgae have also been harvested from natural lakes by indigenous populations. Given that these practices are unlikely to sustain strong growth, only the cultivation of algae in man-made systems will be considered in this report. The main cultivation options are described in detail in (FAO 2009a) and the main types are briefly presented below, since these have a significant different impact on the economics associated, the selection of the species, the technology requirements, etc.

A production system is geared towards a high yield per hectare because it reduces the relative costs for land, construction materials and some operation costs. It is not uncommon for published yield estimates to be too high, sometimes higher than theoretically possible⁴. These overestimations lead to unrealistic expectations. Realistic estimates for productivity are in the order of magnitude of 40-80 tons of dry matter per year per hectare, depending on the technology used and the location of production (Wijffels, Barbosa et al. 2010). This is still substantially higher than almost all agricultural crops. Surpassing yields of 80 tons per year per hectare will likely require genetically improved strains or other technologies able to counteract photosaturation and photoinibition (Tredici 2010).

2.2.1 Open cultivation systems

The main large-scale algae cultivation system is the so-called raceway pond. These are simple closed-loop channels in which the water is kept in motion by a paddle wheel. The channel is usually 20-30 cm deep and made of concrete or compacted earth, often lined with white plastic. It is designed for optimal light capture and low construction costs. The main land requirement is that of flat land.

Process control in such an open system is difficult since these are unstable ecosystems, temperature is dependent on the weather and, depending on climatic conditions, large amounts of water cyclically evaporate or are added by rainfall. Furthermore, the open character of the system makes it possible for naturally occurring algae or algae predators to infiltrate the system and compete with the algae species intended to be cultivated. Therefore a monoculture can only be maintained under extreme conditions, like high salinity (e.g. *Dunaliella*), high pH (e.g. *Spirulina*) or high nitrogen (e.g. *Chlorella*) water. These conditions generally limit optimal growth and operate at a low algae concentration, making harvesting more difficult.

In conclusion, there is an important trade-off between a low price for the cultivation system and its production potential.

⁴ It is important to point out that, conversely to what is sometimes stated, microalgal cultures are not superior to higher plants in terms of photosynthetic efficiency and productivity, as explained in Tredici (2010).

2.2.2 Closed cultivation systems

Many of the problems of open systems can be mitigated by building a closed system which is less influenced by the environment. Many configurations exist but all of them rely on the use of transparent plastic containers (usually tubes) through which the culture medium flows and in which the algae are exposed to light⁵. Such a system is clearly more expensive⁶ and therefore capital intensive if produced on a large scale, but allows a wider number of species to be cultivated under ad-hoc conditions, normally with a higher concentration and productivity. On the other hand, these systems suffer from high energy expenditures for mixing and cooling than open ponds and are also technically more difficult to build and maintain.

Closed systems allow for the cultivation of algal species that cannot be grown in open ponds.

2.2.3 Sea-based cultivation systems

Whereas the previously described cultivation systems are almost exclusively used for microalgae, algae cultivation in the sea is the domain of seaweed. Seaweed cultivation, although very labour intensive near shore in shallow water and often at small-scale, is common practice in parts of Asia. To make an impact as bioenergy feedstock, seaweed should be produced in floating cultivation systems spanning hundreds of hectares. Most seaweeds require a substrate to hook to; which in practice means that the cultivation system must contain a network of ropes. The amount of construction material could be drastically reduced when free-floating seaweed (like some *Sargassum* species) is cultivated as just a structure to contain the colony would then be needed. Sea-based systems are less well developed than land based systems, although some R&D initiatives have been undertaken and are still ongoing. The system for seaweed cultivation in China has not changed much since it was invented in the 1950s, although options for modernization have been identified (Tseng 2004). Some countries, such as

⁵ They can also be oriented to maximize light capture hence productivity per square meter of reactor, or to dilute light to maximize algae photosynthetic efficiency.

⁶ In general, PBRs are much more expensive to build than ponds, but simple low-cost systems can also be designed. Tredici et al. have recently patented a panel reactor made of a disposable polyethylene film that costs approximately \notin 5 per square meter (Tredici 2010).

Chile, are important seaweed producers, but rely completely on the harvesting of natural populations (Vásquez 2008).

2.3 Algae-based bioenergy products

There are a variety of ways to produce biofuel with algae. Figure 1 provides an overview of the options, which are explained in detail in FAO (2009a). In this section only the requirements of the algal biomass needed to produce various biofuels are briefly discussed in order to facilitate the selection of co-production options further in the report.



Figure 1: Overview of algae-to-energy options

2.3.1 Biodiesel

Biodiesel production from algal oils has received most attention since algae can contain potentially over 80% total lipids, (while rapeseed plants, for instance, contain about 6% lipids). Under normal growth conditions the lipid concentration is lower (<40%) and high oil content is always associated with very low yields. The various lipids production can be stimulated under stress conditions, e.g. insufficient nitrogen

availability. Under such conditions, biomass production is not optimal though, reducing the non-lipid part of the biomass that can be further used as a source for co-products.

2.3.2 Hydrocarbons

One genus of algae, *Botryococcus*, does not produce the above-mentioned lipids, but longer chain hydrocarbons, which are not suitable for biodiesel production. Instead, they can be converted in a process similar to the production of conventional fuels from fossil oil. *Botryococcus* is a freshwater species but can also grow in saline water and it can produce certain carotenoids (Banerjee, Sharma et al. 2002). Its drawback is the relatively slow growth speed.

2.3.3 Ethanol

Ethanol is commonly produced from starch-containing feedstocks; some algae have been reported to contain over 50% of starch. Algal cell walls consist of polysaccharides which can be used as a feedstock in a process similar to cellulosic ethanol production, with the added advantage that algae rarely contain lignin and their polysaccharides, are generally more easily broken down than woody biomass. Co-products can potentially be derived from the non-carbohydrate part of the algal biomass.

2.3.4 Biogas

Anaerobic digestion converts organic material into biogas that contains about 60%-70% biomethane, while the rest is mainly CO₂, which can be fed back to the algae. A main advantage is that this process can use wet biomass, reducing the need for drying. Another advantage is that the nutrients contained in the digested biomass can be recovered from the liquid and solid phase.

Biogas as the main product is not economically viable⁷, but this process can be applied to any left-over biomass after extraction of a co-product.

⁷ Biogas production, as well as other conversion processes, is not viable to date because of the current high cost of the feedstock, although it is currently one of the cheapest biofuel that can be produced from biomass

2.3.5 Thermochemical treatment

The biological treatment of algal organic material has a non-biological counterpart, with the advantage that no live organisms are involved and therefore more varied and extreme process conditions can be used. The biomass undergoes a chemical conversion under high temperature and pressure conditions. Depending on the water content and how extreme these conditions are, the biomass carbon ends up in a raw gaseous, liquid or solid phase which can be upgraded for usage as a biofuel.

The energy input of this type of treatment is clearly higher compared to biogas production.

2.3.6 Hydrogen

Some algae can be manipulated into producing hydrogen gas. Currently the yield of this process is low and since energy is lost by the cells to form hydrogen, not much biomass is produced and therefore there is little potential for co-production.

2.3.7 Bioelectricity

Algal biomass can also be co-combusted in a power plant. For this, the biomass needs to be dried, which implies a significant amount of energy. This process is thus only interesting if the biomass is required to be dried in order to extract a certain co-product as a first step before being used as a biofuel.

3 Algae-based non-energy options

The number of products that can be made from algae is virtually unlimited, due to the large variety of species (possibly in the millions) whose composition can be influenced by changing the cultivation conditions. With only a few commercial algae-based products available, this resource is largely untapped. This is due to a range of reasons: poor marketing (Edwards 2008), the economic and bureaucratic barrier of getting new products approved by regulating authorities (especially for food) (Reith 2004), insufficient experience with algae production, and the commercial barrier due to lack of investments in large-scale production facilities.

The bulk of commercial products from algae are derived from seaweed, produced for food and alginates and partially harvested from natural populations, rather than cultivated. Commercial products from microalgae are largely limited to a few easily cultured species with proven market demand and market value, often as health food or feed in aquaculture. Table 1 shows the 7000 tons dry weight of total commercial microalgae production in 2004, adapted from Pulz and Gross (2004) in Brennan and Owende (2010). The total seaweed production in 2007 was 16 million tons fresh weight (FAO 2009b). The amount of commercially produced algae products is small if compared to the amount of known algal products, and more products are being discovered every day. A good example of this is shown in the annual reviews entitled "Marine natural products" by *Faulkner* and later by *Blunt et al.* Between (2000 and 2008): 7218 new marine products come from algae (sponges are a very rich source as well). Well-known products and products from freshwater and brackish water algae are not included either.

Both commercial and yet-to-be-commercialized algal products can be interesting to coproduce with bioenergy.

| Mianalaa | Annual | Duoduoon | Application and | Duico |
|-------------------|-----------------|--------------------|-------------------|---------------|
| Microalga | Annual | Producer | Application and | Price |
| | production | country | product | |
| Spirulina | 3000 tons dry | China, India, | Human nutrition | 36 €/kg |
| | weight | USA, | Animal nutrition | |
| | | Myianmar, Japan | Cosmetics | |
| | | | Phycobiliproteins | 11 €/mg |
| Chlorella | 2000 tons dry | Taiwan, | Human nutrition | 36 €/kg |
| | weight | Germany, Japan | Cosmetics | |
| | | | Aquaculture | 50 €/L |
| Dunaliella salina | 1200 tons dry | Australia, Israel, | Human nutrition | |
| | weight | USA, Japan | Cosmetics | |
| | | | β-carotene | 215-2150 €/kg |
| Aphanizomenon | 500 tons dry | USA | Human nutrition | |
| flos-aquae | weight | | | |
| Haematococcus | 300 tons dry | USA, India, | Aquaculture | 50 €/L |
| pluvialis | weight | Israel | Astaxanthin | 7150 €/kg |
| Crypthecodinium | 240 tons DHA | USA | DHA oil | 43 €/g |
| cohnii | oil | | | |
| Shizochytrium | 10 tons DHA oil | USA | DHA oil | 43 €/g |

Table 1: Commercially produced microalgae; amounts, locations, applications and market value (2004) (Brennan and Owende 2010)

Depending on the microalgae species, other compounds can also be extracted with several applications for many industrial sectors (biofuels, cosmetics, pharmaceuticals, nutrition and food additives, aquaculture, and pollution prevention): oil, fats, polyunsaturated fatty acids, natural dyes, pigments, antioxidants, sugar, high-value bioactive compounds, and other fine chemicals and biomass. (Mata, Martins et al. 2010).

3.1 Algae-based products for human consumption

Algae use as food has been cited in Chinese literature as early as 2500 years ago (Tseng 2004). Several parts of Asia are well known for consuming algae (mostly seaweed) directly and some indigenous people in Africa, South America and Mexico consume small quantities of naturally occurring algae mostly because of the vitamins and nutrients they provide (Edwards 2008).

Much less known to the general public is the variety of algae-derived ingredients that is used in food processing. Mostly as subordinate ingredients such as emulsifiers, thickeners, emollients (Edwards 2008), fats, polyunsaturated fatty acids, oil, natural dyes, sugars, pigments, antioxidants, bioactive compounds (Mata, Martins et al. 2010).

Microalgae for human nutrition are nowadays marketed in different forms such as tablets, capsules and liquids. They can also be incorporated into pastas, snack foods, candy bars or gums, and beverages, noodles, wine, beverages, breakfast cereals, nutrition bars, cookies (Lee 1997; Spolaore, Joannis-Cassan et al. 2006).

3.1.1 Staple food

Most algae cannot be used directly as a human food because the cell walls are not digestible. However, mechanical solutions, strain selection or bioengineering could overcome this problem. Digestible cell walls would potentially create the tipping point that enables algae to serve the world as food (Edwards 2008). Best known for large-scale consumption are the selected species of seaweed that are eaten in Asia (Moore 2001).

The cultivation and harvesting of this seaweed is a labor intensive process. The seaweed is dried and consumed completely, leaving no option for co-production.

Proteins are of major importance in human nutrition and the lack of them is one of the biggest factors in malnutrition. Some algae contain up to 60% protein. A well-known alga that is currently cultivated for its protein content is the cyanobacterium species *Athrospira*, better known as *Spirulina*. Consumption of *Spirulina* by the Aztecs during the sixteenth century in Mexico and by the Kanembo tribe at Lake Chad has been reported (Vonshak 1990).

Table 2 gives a comparison of nutritional values of some food products compared to *Spirulina* (dry matter) two decades ago in South India.

| Food item | Protein content per 100 g (g) | Cost per 100 g of protein (Rs) | Comparative ratio of cost of protein with Spirulina | Comparative ratio of cost of lysine with Spirulina | Comparative ratio cost of cystine with Spirulina | Comparative ratio cost of tryptophan with Spirulina |
|------------------|--|---|---|--|---|---|
| Spirulina | 66 | 1.38 | 1 | 1 | 1 | 1 |
| Egg | 13.2 | 11.20 | 8.23 | 5.10 | 5.11 | 3.82 |
| Milk (100 ml) | 3.3 | 15.15 | 10.97 | 6.19 | 11.98 | 6.62 |
| Cluster beans | 3.2 | 31.25 | 22.64 | 14.67 | 26.13 | 15.09 |
| Eggplant | 1.4 | 57.14 | 41.41 | 44.45 | 78.52 | 19.48 |
| Carrot | 0.9 | 88.88 | 64.41 | 10.10 | 28.90 | 14.13 |
| Potato | 1.6 | 62.50 | 45.28 | 26.56 | 95.97 | 7.55 |
| Onion | 1.20 | 66.66 | 48.30 | 46.30 | 96.66 | 13.88 |
| Mutton | 18.50 | 16.21 | 11.75 | 6.31 | 26.45 | 1.68 |
| Notes: | es: Only the cost of protein from consumed foods other than staple food is compared here. The costs per unit of vitamin A, nicotinic acid, riboflawin, thiamin, vitamin B12 and iron are | | | | | |

costs per unit of vitamin A, nicotinic acid, riboflawin, thiamin, vitamin B12 and iron are cheaper in Spirulina than from other sources. The protein content of Spirulina is based on a dry weight whereas the protein content of other food sources is reported on a wet weight basis.

Table 2: Spirulina protein content compared with other staple foods in
(vegetarian) South India, 1991 (Babu and Rajasekaran 1991)

The reason why *Spirulina* is the most cultivated microalga (see Table 1), besides its protein content, is that it is easy to cultivate as a monoculture. This is because it is one of the few species that grows at a high pH and is bigger than single cell algae⁸ and easier to harvest. Following a resolution entitled "*Use of Spirulina to combat hunger and malnutrition and help achieve sustainable development*" by five developing countries at the UN General Assembly, the FAO published a comprehensive report on this microalga (Habib 2008). With reference to human consumption, it reports

⁸ Spirulina is a prokaryote which can form multicellular groups.

numerous cases of beneficial health effects, although it also warns that some species may produce toxins of the microcystin group.

Spirulina is reported to contain not only around 60% raw protein, but also vitamins, minerals and many biologically active substances. Its cell wall consists of polysaccharides, has a digestibility of 86 percent, and can be easily absorbed by the human body (Becker 1994). In general, amounts for *Spirulina* consumption are around 15 grams per day, which is only a small part of the daily protein intake for adults.

As mentioned above, co-production for bioenergy purposes is not an option if the complete *Spirulina* cell mass is used as food. There are two main extracts from *Spirulina*: phycobiliproteins (a blue food dye) and a tasteless, odourless yellow-white protein extract that can have several food applications. The biomass remaining after extraction could be used for bioenergy or other products.

Spirulina is the main example of small-scale microalgae cultivation in various parts of the developing world. It also has applications in feed for livestock and aquaculture and as fertilizer, which will be reported on in the relevant sections of this chapter.

Other algae species are known to have high protein content as well (see Table 3), of a quality comparable with conventional protein sources. Despite its high protein content algae have not gained significant importance as food or food substitute yet. Strict approval regulations for new foodstuffs are a barrier, but also the lack of texture and consistency of the dried biomass, its dark green colour and its slight fishy smell are undesirable characteristics for the food industry (Becker 2007).

| Alga | Protein | Carbohydrates | Lipids |
|---------------------------|---------|---------------|--------|
| Anabaena cylindrical | 43-56 | 25-30 | 4-7 |
| Aphanizomenon flos-aquae | 62 | 23 | 3 |
| Chlamydomonas rheinhardii | 48 | 17 | 21 |
| Chlorella pyrenoidosa | 57 | 26 | 2 |
| Chlorella vulgaris | 51-58 | 12-17 | 14-22 |
| Dunaliella salina | 57 | 32 | 6 |
| Euglena gracilis | 39-61 | 14-18 | 14-20 |
| Porphyridium cruentum | 28-39 | 40-57 | 9-14 |
| Scenedesmus obliquus | 50-56 | 10-17 | 12-14 |
| Spirogyra sp. | 6-20 | 33-64 | 11-21 |
| Arthrospira maxima | 60-71 | 13-16 | 6-7 |
| Spirulina platensis | 46-63 | 8-14 | 4-9 |
| Synechococcus sp. | 63 | 15 | 11 |

Table 3: General composition of different algae (% of dry matter) (Becker 2007)

3.1.2 Health foods and pharmaceuticals

In addition to food, algae provide a wide variety of medicines, vitamins, vaccines, nutraceuticals and other nutrients that may be unavailable or too expensive to produce using plants or animals. Health food products currently dominate the microalgae market (Pulz and Gross 2004). A wide variety of algae and algal products have shown medical or nutritional applications. In Japan alone the 1996 consumption of health food from microalgae amounted to 2400 tons (Lee 1997).

Many of the algal applications in this section are highly technical or scientific. Since detailed analyses of all medical or biological effects are outside of the scope of this review, they are only given to illustrate the large variety of options and to refer the interested reader to more specialized literature.

Pigments

Microalgae contain a multitude of pigments associated with light incidence. Besides chlorophyll (the primary photosynthetic compound) the most relevant are phycobiliproteins (they improve the efficiency of light energy utilization) and carotenoids (they protect them against solar radiation and related effects). Carotenoids from microalgae have already many applications in the market: β -Carotene from *Dunaliella* in health food as a vitamin A precursor; Lutein, zeaxantin and canthaxantin for chicken skin coloration, or for pharmaceutical purposes and Astaxanthin from Haematococcus in aquaculture for providing the natural red colour of certain fish like salmon. Also the phycobiliproteins phycocyanin and phycoerythrin (that are unique to algae) are already being used for food and cosmetics applications (Pulz and Gross 2004).

The antioxidant functionality of carotenoids is of major importance for human consumption. Anti-oxidants function as free radical scavengers, which gives them an anti-cancer effect. Astaxanthin is known to be the most potent natural anti-oxidant. β -carotene is currently used in health foods as a vitamin A precursor and because of its anti-oxidant effect.

Many pigments from algae can also be used as natural food colorants, for instance in orange juice, chewing gum, ice sorbets, candies, soft drinks, dairy products and wasabi (Spolaore, Joannis-Cassan et al. 2006).

Polyunsaturated fatty acids (PUFAs)

PUFAs are important nutrients that must be supplied by external sources as they cannot be produced by the organism itself. Well-known PUFAs include n–3 fatty acids (commonly known as ω –3 fatty acids or omega-3 fatty acids) the most well-known source of PUFAs is fish oil. However, fish do not produce PUFAs but accumulate them by eating algae (or other algae-eating organisms). Algae are the true source of these essential nutrients. PUFA production from algae has been developed only in the last decade and has the advantages of lacking unpleasant fish odor, reduced risk of chemical contamination and better purification potential (Pulz and Gross 2004). PUFAs are known to play an important role in reducing cardiovascular diseases, obesity, in cellular and tissue metabolism, including the regulation of membrane's fluidity, electron and oxygen transport, as well as thermal adaptation ability (Cardozo, Guaratini et al. 2007).

| PUFA | Structure | Potential application | Microorganism producer |
|-----------------------------|---------------------------|---|--|
| γ-Linolenic acid (GLA) | 18:3 ω6, 9, 12 | Infant formulas for full-term infants | Arthrospira |
| | | Nutritional supplements | |
| Arachidonic acid (AA) | 20:4 ω6, 9, 12, 15 | Infant formulas for full- term/preterm infants | Porphyridium |
| | | Nutritional supplements | |
| Eicosapentaenoic acid (EPA) | 20:5 ω3, 6, 9, 12, 15 | Nutritional supplements Aquaculture | Nannochloropsis, Phaeodactylum, Nitzchia |
| Docosahexaenoic acid (DHA) | 20:6 w3, 6, 9, 12, 15, 18 | Infant formulas for full- term/preterm infants | Crypthecodinium, Schizochytrium |
| | | Nutritional supplements | |
| | | Aquaculture | |

Table 4: The four most important PUFAs sourced from algae (Spolaore, Joannis-Cassan et al. 2006)

Some of the PUFAs are worth a particular attention:

- DHA is an omega-3 fatty acid present e.g. in the grey matter of the brain and in the retina, and is a major component of heart tissue. It has been shown to be important for cardiovascular health in adults and for brain and eye development in infants. DHA is found in a limited selection of foods such as fatty fish and organic meat and naturally present in breast milk, although absent in cow's milk. Since 1990, its inclusion in infant formula for pre-term and full term infants has been recommended by a number of health and nutrition organizations (Spolaore, Joannis-Cassan et al. 2006).
- EPA is normally esterified (by cyclo-oxygenase and lipo-oxygenase activities) to form complex lipid molecules and plays an important role in higher animals and humans as the precursor of a group of eicosanoids, hormone-like substances such as prostaglandins, thromboxanes and leukotrienes that are crucial in regulating developmental and regulatory physiology (Cardozo, Guaratini et al. 2007)

Other bioactive algal products

In *Chlorella* species, the most important compound from a medical point of view is β -1,3-glucan, an active immunostimulator, a free radical scavenger and a blood lipid reducer. Efficacy of this compound against gastric ulcers, wounds and constipation, preventive action against atherosclerosis and hypercholesterolemia, and antitumor action have also been reported (Spolaore, Joannis-Cassan et al. 2006).

Microalgae also represent a valuable source of almost all essential vitamins (e.g., A, B1, B2, B6, B12, C, E, nicotinate, biotin, folic acid and pantothenic acid) (Richmond 2004).

Furthermore, sulfated polysaccharides of microalgae can be used in anti-adhesive therapies against bacterial infections both in cold- and warm-blooded animals (Banerjee, Sharma et al. 2002).

The development of the cultivation of the alga *Caloglossa leprieurii* (Mont.) J. Ag., to produce an antihelmintic (a drug that expels parasitic worms) is needed (Tseng 2004).

3.1.3 Ingredients for processed foods

The most economically-valuable algae products are the macroalgal polysaccharides, like agar, alginates and carrageenans, especially due to their rheological gelling or thickening properties. An increase in research and development activities on microalgae, transgenic microalgae, protoplast fusion, or macroalgal cell cultures as biotechnological sources has been observed in the last years (Pulz and Gross 2004).

As previously mentioned, many pigments from algae can also be used as natural food colorants (Spolaore, Joannis-Cassan et al. 2006).

Agar

Agar is made from seaweed and is used in a wide range of applications: in food products (such as frozen foods, bakery icings, meringues, dessert gels, candies and fruit juices), industry uses (like paper sizing/coating, adhesives, textile printing/dyeing, castings, impressions), in biological culture media, in molecular biology (more specifically agarose, used for separation methods) and in the medical/pharmaceutical field (to produce bulking agents, laxatives, suppositories, capsules, tablets and anticoagulants) (Cardozo, Guaratini et al. 2007). When used in the EU, it is listed in the ingredients as E406.

Carrageenan

Carrageenan is a water soluble group of polysaccharides that are more widely used than agar as emulsifiers and stabilizers in numerous (especially milk-based) foods. κ - and ι -carrageenans are especially used in chocolate milk, ice cream, evaporated milk, puddings, jellies, jams, salad dressings, dessert gels, meat products and pet foods, due to their thickening and suspension properties. Several potential pharmaceutical uses of carragenans (like antitumor, antiviral, anticoagulant and immunomodulation activities) (Cardozo, Guaratini et al. 2007) have also been explored. When used in the EU, it is listed in the ingredients as E407.

Alginate

Alginate (or alginic acid) is produced by brown seaweed and is used in the textile industry for sizing cotton yarn. Its gelling capabilities make it of considerable technological importance. It is widely used in the food and pharmaceutical industries due to its chelating ability and its capability to form a highly viscous solution (Cardozo, Guaratini et al. 2007) When used in the EU, it is listed in the ingredients as E400 to E405, depending on the form of alginate.

3.2 Algae for livestock consumption

A biodiesel anecdote tells that, in the past, soy was cultivated for animal feed purposes due to its rich protein content. The oil was considered a waste product and discarded. Nowadays, the use of oil as a biodiesel feedstock is the main soybean product in many countries, while animal feed has become the by-product. Potentially, the opposite may occur for algae: biodiesel is currently the main focus for ABB, but the use of biomass as feedstock for animals after oil extraction also has an enormous market potential⁹. Most algae have a natural high protein content while a high oil content is mostly achieved

⁹ To have an idea of the scale: all livestock in US consume about 300 million tons of protein/year Mayfield, S. (2008). Micro-algae as a platform for the production of therapeutic proteins and biofuels (presentation). Bundes-Algen-Stammtisch, 9-10 Oct 2008, Hamburg, Germany, Department of Cell Biology and The Skaggs Institute for Chemical Biology, The Scripps Research Institute.

though manipulation of cultivation conditions. If recent soy meal prices are taken as a reference, the value of algae after oil extraction would be at least \notin 230/t (Steiner 2008).

The use of micro-algae as animal feed is relatively recent and predominantly aimed at poultry, mainly because it improves the color of the skin, shanks and egg yolks. Multiple nutritional and toxicological evaluations demonstrated the suitability of algae biomass as a valuable feed supplement or substitute for conventional protein sources (soybean meal, fish meal, rice bran, etc.) (Becker 2007).

Besides the use of algae as a protein source for livestock, many of the health benefits mentioned in section 3.1 also apply to animals (i.e. improved immune response, improved fertility, better weight control, healthier skin and a lustrous coat (Pulz and Gross 2004)) thus improving the product for subsequent human consumption of meat and milk. Adding algae to the diet of cows resulted in a lower natural breakdown of unsaturated fatty acids and a higher concentration of these beneficial compounds in meat and milk. Another important example is the feeding of poultry with algae rich in omega-3 fatty acids, which flows through the food chain, placing this cholesterol-lowering compound in eggs.

The use of algae in food for cats, dogs, aquarium fish, ornamental birds, horses, cows and breeding bulls has also been reported (Spolaore, Joannis-Cassan et al. 2006).

3.3 Algae for fish and shellfish consumption

Microalgae are essential during the processes of hatchery and nursery of bivalves, shrimp, and some finfish cultures. Microalgae are also used to produce zooplankton, typically rotifers, which are fed to the freshly hatched carnivorous fish (Benemann and Oswald 1996).

In 1999, the use of microalgae in aquaculture was reported to be divided as 62% for mollusks, 21% for shrimps, and 16% for fish. Like for humans and livestock, protein and PUFAs are of main importance. Algae are used fresh in fish cultivation, which is a big difference compared with other uses of microalgae. As production techniques advance, the trend is to avoid using live algae. The small scale of fish-feed algae cultivation is difficult, expensive and problematic to store. Alternatives have been developed, like preserved, microencapsulated and frozen algae, as well as a concentrated algae paste (Spolaore, Joannis-Cassan et al. 2006).

Wild salmon and trout acquire their characteristic red (muscle) color by eating algae with red pigments. Cultured species lack this color, resulting in a lower market value. This can be corrected by adding astaxanthin to fish feed. Astaxanthin is mostly produced synthetically, but there is a growing market for algae-based astaxanthin from *Haematococcos pluvialis*.

Abalone cultivation is a booming industry in Chile, requiring an estimated 100 tons of fresh seaweed for the production of each ton of abalone. The current harvesting of natural populations cannot support this, so the switch to cultivation has to be made. (Vásquez 2008)

Smith et al (2010) looked at ABB production from an ecologist point of view and mentioned herbivorous zooplankton (tiny microalgae-eating animals) as a major threat of invasion of the cultivation system, especially for open systems, which can have a strong negative effect on productivity. An example of a natural system is given: the introduction of zooplankton caused a more than 100 times decrease in algae concentration. The main option for controlling zooplankton is co-cultivating their predator: zooplankton-eating fish. This approach offers co-production during the cultivation phase rather than the processing phase.

3.4 Algae based non-food options

3.4.1 Chemical industry

The chemical industry is currently highly dependant on fossil oil, from which chemicals and transportation fuels are commonly co-produced. The chemical industry shows some important similarities to the combustion fuel industry, such as the low price of the fossil based feedstock and the primary interest into hydrocarbon parts of primary feedstock. Due to the specific processes in the chemical industry, it is currently generally not possible to use bio-based feedstocks in existing processes because of their higher cost. Novel bio-based processes require significant R&D and will initially focus on cheaper feedstocks than algae¹⁰.

¹⁰ Many developments exist yet, including large quantities of bio-based chemical already produced (capacity for 2009 is estimated to be over 5 Million tons). In some cases algae may already be competitive in specific applications like polyols and, possibly, 3GT, lactate acid, succinic acid and ascorbic acid (vitamin C)

Co-production of chemical products with bioenergy does not seem to have much potential yet at this stage. A more expectable pathway is the initial establishment of a biofuels' market, after which some of the algal bio-oil will be diverted into the chemical industry (Jensen 1993)

There are a few exceptions, mainly where big chemical companies like DuPont and DOW consider algae to produce some of the important small platform chemicals for their industry, like ethanol and butanol. Other projects, such as producing bio-plastics from algae (Cereplast) and paints (Algicoat), are in a very preliminary R&D stage.

3.4.2 Cosmetics

The use of some microalgal species, especially *Arthrospira* and *Chlorella*, is well established in the skin care market and some cosmeticians have even invested in their own microalgal production system (LVMH, Paris, France and Daniel Jouvance, Carnac, France). Their extracts are found in e.g. anti-aging cream, refreshing or regenerating care products, emollient and as an anti-irritant in peelers and also in sun protection and hair care products. Some of these products' properties based on algal extracts include: repairing the signs of early skin aging, exerting a skin tightening effect, preventing stria formation and stimulation of collagen synthesis in skin (Spolaore, Joannis-Cassan et al. 2006). In what lipid-based cosmetics (like creams or lotions) are concerned, ethanol or supercritical CO₂-extracts are gaining commercial importance and other lipid classes from microalgae, like glyco- and phospholipids, should not be neglected in future developments (Muller-Feuga, Le Guédes et al. 2003; Pulz and Gross 2004).

Due to the awareness that sun exposure is the main cause for of skin cancer and photoaging process, the consumption of sunscreen products has increased significantly in the last decades. The use of mycosporine-like amino acids as a highly efficient natural UV blocker in sunscreen is becoming commercially attractive (Cardozo, Guaratini et al. 2007)

3.4.3 Fertilizer

Historically, seaweed has been used as a fertilizer worldwide in coastal regions, mainly for its mineral content and to increase the water-binding capacity of the soil. Microalgal species that fix nitrogen are important, especially in rice cultivation. Both macro- and microalgae can contain compounds that promote germination, leaf or stem growth, flowering or can be used as a biological protection agent against plant diseases (Pulz and Gross 2004).

After the extraction of oil or carbohydrates from both seaweed and microalgae, most of the nutrients are still present in the left-over biomass. One potential market for this nutrient-rich biomass is as biofertilizer. Market volume is large while the market value is low. In many cases it might be more economic to extract these nutrients for reuse in algae cultivation.

Whether left-over biomass is used as fertilizer or algaculture nutrient source, anaerobic digestion is a valuable option. With this technology, the biomass doesn't need to be dried, but can be directly fed into the anaerobic digester where a large part of the remaining organic carbon is converted into biogas, while the nutrients are further concentrated in the liquid and solid output, so separated from the cell biomass, and easily concentrated.

Another option with significant sustainability benefits is the production of organic fertilizer. When applied in agriculture, the nutrients are released slowly which both benefits plant growth and reduces the microbial production of GHG emissions (Mulbry, Kondrad et al. 2008). More importantly, the production of chemical fertilizer is energy intensive with relative high greenhouse gases emissions. Given the expected increasing demand in fertilizers in the coming decades, the production of algae-based fertilizer shows potential to reduce the use of chemical fertilizer and hence alleviate their associated negative environmental impacts.

3.4.4 Fibres for paper

Most plant cell walls consist of cellulose, but in algae cell coverings are very diverse. Some algae species have intracellular walls, or scaly cell walls made of deposits of calcium carbonate or silica, but most algae derive structural strength from continuous sulphated polysaccharides in marine algae; other possibilities being cellulose, carrageenan, alginate and chitin (Okuda 2002).

Cellulose-containing algae can potentially be used as a renewable feedstock for paper production as the strong green colour of algae is more difficult to bleach than wood fibres but, although algae are generally known for their low cellulose and hemicellulose content, there are a few examples of research into the use of algae as a non-wood fibre source. Ververis *et al.* (2007) used a mix of algae taken from a municipal waste water treatment as 10% of the pulp mix, resulting in a significant increase in the mechanical

paper strength and a decrease in paper brightness were reported, as well as a 45% lower material cost, which resulted in a 0.9-4.5% reduction in the final paper price. Hon-Nami *et al.* (1997) used a *Tetraselmis* strain as a 5-15% pulp additive, and found anti-print through, smoothness and tolerance for deterioration.

Using *Rhizoclonium* from brackish water in Taiwan containing 38-44% holocellulose, high pulp yields were found at short cooking times with a low chemical charge. The best result of pure algae-paper approached standard paper quality, showing lower bursting, tearing and folding strengths. Mixing with softwood pulp improved the paper to Kraft quality (Chao, Su et al. 1999; Chao, Su et al. 2000; 2005). This alga is filamentous (forms long threads) and is therefore much easier and cheaper to harvest than unicellular algae. Another benefit is the salt tolerance of *Rhizoclonium*, ranging from 1.0 to 3.3 % salt, with an optimum at 2.0% salt (seawater averages 3.4% salt). At this optimum, most naturally occurring freshwater algae will not be able to grow. *Chaetomorpha linum* and *C. melagonium* have similar cellulose contents (Chao, Su et al. 1999), while *Vaucheria* species can contain about 90% cellulose in their cell wall (Parker, Fogg et al. 1963) in (Okuda 2002).

Biologically different from algae and seaweed, but similar in cultivation and processing are certain aquatic plants. These may also have high productivities and may be grown on waste streams, and since they are closer to land plants, have high fibre contents.

Joedodibroto (1983) has investigated several aquatic plants (as shown in

Table 5) and concluded that all three weeds produced moderate quality paper pulp. Water hyacinth gave good folding and tearing resistance, but the processing of material from this plant was rather difficult. Other investigators reported that paper from 75% water hyacinth pulp and 25% bamboo pulp gave a high strength and also good greaseproof properties to the paper (Goswami and Saikia 1994).

| | Cellulose | Lignin | Ash |
|---------------------|-----------|--------|-----|
| Stem water hyacinth | 58% | 9% | 22% |
| Leaf water hyacinth | 49% | 24% | 15% |
| Torpedo grass | 62% | 21% | 7% |
| Giant bulrush | 62% | 26 | 11% |

Table 5: Cellulose content of aquatic plants (Joedodibroto, Widyanto et al. 1983)

There is some promising research on the utilisation of aquatic biomass for paper pulp, a development that deserves future attention, from economical, renewable and quality points of view. However this concept has not moved beyond the research stage yet and it is unclear when it will be commercialised.