The Macroalgae-Based Biorefinery

A comprehensive review and a prospective study of future macroalgae-based biorefinery systems

Abstract - In this thesis the macroalgae-based biorefinery is studied from an environmental and economic perspective. Macroalgae (or seaweed) could function as an interesting third-generation feedstock for the production of biofuels and chemical products. There is no need for arable land or freshwater during cultivation, in contrast to first-generation biofuels. Macroalgae is currently mainly cultivated for food production. The production of macroalgae-based biofuels alone is not economical feasible. Therefore, the biorefinery concept will be studied. By combining both fuels with higher-value compounds, the system could become profitable. The first part of the thesis consists of a review of macroalgae genera, cultivation methods, products, production methods and the design of the systems. In the second part of the thesis, the biorefinery concept is tested on the basis of three case-studies. In these cases, different species and scenarios will be studied from an environmental and economic perspective and a sensitivity analysis will be performed. In case-study 1 the brown seaweed *Saccharina latissima* is cultivated in order to produce alginate, biogas and compost in a biorefinery. In case-study 2 *Ulva lactuca* (green seaweed) is cultivated for the production of ulvan, biogas and compost. In case-study 3 *Ulva lactuca* is collected and will be subject to ABE fermentation (the production of acetone, butanol and ethanol).

Both the life-cycle analysis (LCA) and the economic analysis are founded on many assumptions, which increased the degree of uncertainty for the results. The LCA for the impact categories global warming potential, non-renewable and renewable energy use does not show positive results for the case-studies. Especially case-study 1 performed poor, which is mainly caused by the energy-intensive alginate extraction process . Case-study 3 performed much better, but the separation of the products caused the impact categories to remain high. The economic analysis resulted in very positive values for case-study 1. Case-study 2 and 3 did not perform well. The sensitivity analysis showed that the impact of the assumed yield for the alginate and ulvan has a large influence on the economic feasibility of the system.

There is a need for further research in order to design case-studies with more accurate results. The lack of pilot plant data and well-founded calculations made the environmental and economic analysis complicated to perform. The use of macroalgae for the production of chemicals and fuels could be very relevant in the future. Before this will happen there are many remaining barriers to take, mainly with regard to the cultivation and conversion of the biomass.

Student	Agnes Boonstra
Student number	F111246/ 3915743
Supervisor	dr. John A. Posada Duque
Second reader	dr. ir. Andrea Ramirez
Study program	Msc. Energy Science – System Analysis
Faculty	Faculty of Geosciences – University of Utrecht
ECTS	30
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Abbreviations

α	Annuity factor
ABE fermentation	Acetone-butanol-ethanol fermentation
B	Annual benefits
BMP	Biochemical methane potential
C	Annual costs
d.w.	Dry weight
DAFMT	Dry-and ash-free metric tonne
GHG	Green house gas
GWP	Global warming potential
Ha	Hectare
HTL	Hydrothermal liquefaction
I	Investment costs
kg	Kilograms
K_m	Substrate concentration at which reaction rate is half of V_{max}
kWh	Kilowatt hour
L	Life time
l	Liter
LCA	Life cycle inventory
LCI	Life cycle analysis
MJ	Mega joule
MTG	Methanol-to-gasoline
NPV	Net present value
NREU	Non-renewable energy use
O&M	Operation and maintenance costs
PBP	Pay-back period
r	Discount rate
REU	Renewable energy use
V_{max}	Maximum reaction rate
VS	Volatile solids

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1. Introduction

In this thesis, the concept of a biorefinery with macroalgae (seaweed) as a feedstock is studied. The use of macroalgae for the production of fuels and chemicals could be an interesting alternative to the feedstocks currently used for the production of these compounds. First, the available literature is analyzed, thereafter the macroalgae-based biorefinery concept is studied on the basis of several case-studies from an environmental- and economic perspective followed by a sensitivity analysis. This will give more insights in the future possibilities to utilize macroalgae for the production of biofuels and chemicals.

1.1 Projections for future energy use

The last couple of decades, both society and the scientific community became convinced of the fact that there is a need for alternatives for fossil resources. This point of view is based on several reasons. Firstly, many countries want to be less dependent on the import of energy, because of political instability. Energy security is often an important reason for countries to invest in renewable energy (Wu, Wang, Liu, & Huo, 2007). Secondly, the CO_2 concentration in the atmosphere increased largely due to anthropogenic sources like fuel combustion, which has caused global climate change (Kraan, 2010). Additionally, the demand both for energy and chemicals is projected to increase, due to population growth and an increased standard of living, particularly in Asia. This is illustrated in Figure 1 (EIA, 2012), where it can be seen that the projected energy consumption in non-OECD Asia will be the main cause for the increase of energy use. When this growth in demand will be met only by fossil resources, the consequences of climate change would increase even more (Hardy, 2002).

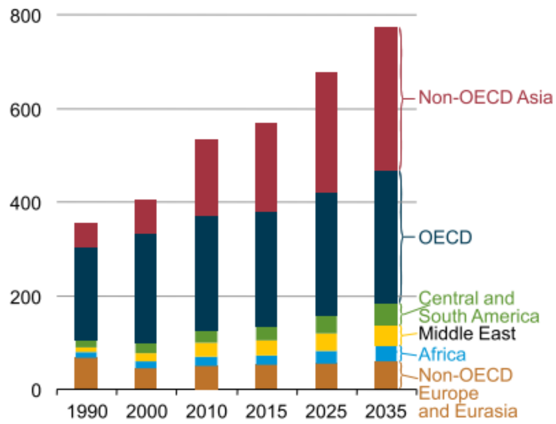


Figure 1 World energy consumption by region, 1990-1935 (quadrillion Btu). Source: IEA (2012), **Figure 68**

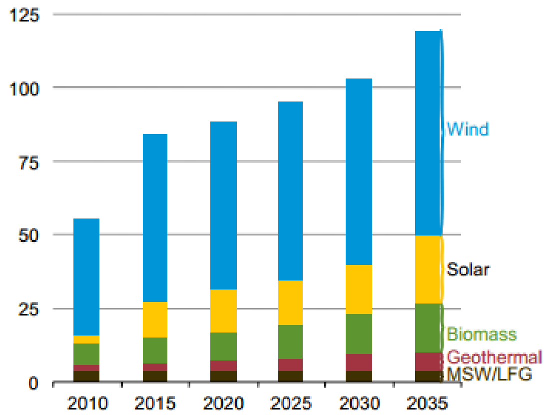


Figure 2 Nonhydropower renewable energy generation capacity by energy source, including end use capacity, 2010-2035 (gigawatts). Source: IEA (2012), **Figure 100**

1.2 Biofuels

One of the alternatives to fossil energy is the use of biofuels. Biofuels are gaseous or liquid fuels produced from land-or sea-based biomass. While it is currently not the most important renewable resource, the share of biofuels in the total amount of renewable energy is projected to increase in the coming years (see Figure 2; EIA, 2012).

Biofuels are classified in generations. The first generation biofuels are produced from food crops, and are therefore under a lot of controversy (Nigam & Singh, 2011). They are competing with food crops for land and fresh-water and furthermore they can affect food prices, which will mainly have a negative impact on vulnerable countries (Brennan & Owende, 2010). In the US for example, the bioethanol production increased around 25% between 2000 and 2008 and 30% of the cultivated corn is used for ethanol production (Jones &

Mayfield, 2012). This development had distinct effects on the corn price, 20-25% of the increase of the corn price in the US in this period was to be attributed to the biofuel production (Zilberman, Hochman, Rajagopal, Sexton, & Timilsina, 2012).

Second generation biofuels are produced from lignocellulosic biomass; since this type of biomass is not used for food production we can speak of dedicated energy crops (Taylor, 2008). This feedstock is harder to convert into biofuels, but will also compete less with the production of food. Third-generation biofuels are produced from algae. An important advantage of this feedstock, is that algae have a much higher photosynthetic efficiency[1] than terrestrial biomass (up to 8% compared with ±2%). This causes the seaweed to capture more CO_2 and have a higher biomass production rate than terrestrial biomass (Aresta, Dibenedetto, & Barberio, 2005; Jung, Lim, Kim, & Park, 2013; Kraan, 2010). The production of macroalgae biomass is not necessarily competing for land and fresh-water with common food crops, because many species can be cultivated in seawater or at land that is normally not in use for agricultural purposes. In some cases they can compete with food prices though, since certain species of macroalgae are cultivated for human consumption (FAO, 2003).

1.3 Bio-based products

The shift from a fossil-based economy towards a bio-based economy is not only related to energy production. Agriculture will function as a central component of the bio-based economy, by providing feedstocks for the production of fuels, chemicals and materials (Hardy, 2002). To this respect is often referred to the 5 F-cascade, which offers a priority list for the use of biomass (Royal Belgian Academy Council of Applied Science, 2011):

1. Food and feed
2. Fine and bulk chemicals and pharmaceuticals
3. Fibre and biomaterials
4. Fuels and energy
5. Fertilisers and soil conditioners

In 2002, only 10% of the chemicals was bio-based, while there is a potential for the production of a much larger share of the chemicals from biomass (Hardy, 2002). In the study by the Royal Belgian Academy Council of Applied Science (2011) attention is paid to different scenarios for 2050. When respectively 16, 40 or 83% of the chemicals would be replaced by biobased chemicals, 1 million to 38,2 million ha European arable land should be dedicated to this production. By applying enzymatic fermentation or chemical processes, biomass can be converted into a whole range of chemicals; including acids, alcohols and amino acids (Royal Belgian Academy Council of Applied Science, 2011). Fibers and other materials are already often produced from biomaterials. For example in the textile and paper industry biomass is an essential feedstock for production. Lastly, the production of compost or fertilizers could be an interesting way to process the residues from the production of other compounds (Royal Belgian Academy Council of Applied Science, 2011). Thus both energy-requirements and the demand for important materials and chemicals can be met by making use of biomass. Algae could function as an important future feedstock for the production of chemicals and fuels.

1.4 Micro- and macroalgae

Algae grow in aquatic environments, which can be both fresh-and salt water. Algae occur in a large variety of sizes and are mostly eukaryotic organisms (Singh, Nigam, & Murphy, 2011). The different types of algae can be very different from each other. Within algae, a distinction can be made between microalgae and macroalgae. Microalgae are single-cell organisms growing in fresh- or marine waters. Macroalgae (or seaweed) are fast growing marine -and freshwater plants. Microalgae are rich in fatty acids (a precursor for biodiesel production), while macroalgae contain mainly carbohydrates (suitable for production of fermentation products) and less

[1] Photosynthetic efficiency is defined as mol oxygen generated per mol of incident photons absorbed by the

lipids. Much of the research on third generation biofuels has been focused on microalgae (Hughes et al. 2012). However, the use of macroalgae has some important advantages over microalgae. The cultivation of macroalgae is not competing for land, neither with fresh water. Seaweed has been cultivated and harvested for centuries; therefore there is much knowledge on the nutrition, biology and cultivation methods of some of the microalgae.

Still, the cultivation of seaweed is relatively expensive, and the market prices for seaweed as a food product are much higher than for biofuels (Bruton et al. 2009). Furthermore, the conversion from macroalgae to biofuels delivers additional technical issues, since the feedstock contains carbohydrates not present in terrestrial biomass. This gives problems in the fermentation step and new micro-organisms need to be found that are able to convert these carbohydrates (Kraan, 2010). This indicates that there are some important barriers to overcome, before macroalgae can be a viable resource for the production of fuels. The potential resource base of macroalgae is very large, which means that it could offer an important alternative to the terrestrial energy crops (Roesijadi, Copping, & Huesemann, 2008). Furthermore, the macroalgae lack the structural compound lignin, which is a complicating factor in the conversion of terrestrial biomass. Also cellulose is almost absent in macroalgae (Kelly & Dworjanyn, 2008).

1.5 The biorefinery approach

Besides the production of biofuels, the production of chemicals and materials from renewable feedstocks is also a crucial part of the biobased economy. The production of these additional products could potentially make the whole cultivation and processing steps of macroalgae economically feasible and environmentally benificial. To this respect it is important to introduce the biorefinery concept. A biorefinery is:

"*A facility that integrates biomass conversion processes and equipment to produce fuel, power, and value-added chemicals from biomass analogous to today's petroleum refineries, which produce multiple fuels and products from crude petroleum"* (Taylor, 2008; referred in Subhadra, 2010, p. 5893).

In the definition the analogy with an oil refinery is mentioned, but the differences are important to keep in mind. For example, the distribution of the feedstock is scattered instead of concentrated, which will have large impacts on the supply chain (Kafarov, 2011). There are many interesting ideas for the design of a macro-algae based biorefinery. The literature dealing with the production of fuels and products from macroalgae dates back from the seventies. Mainly in the US, seaweed was considered as a very interesting feedstock for the production of fuels, a development catalyzed by the Oil Crisis. When the oil prices decreased again, also the interest in seaweed diminished. The biorefinery concept has been an important focus of the algae research of the last years. It offers a great opportunity to make the production and cultivation of algae economical feasible, by the production of co-products with a higher market value than biofuels. The products that serve a smaller niche market (so-called low-volume high-value products) can compensate for the costs of biofuel production that serve a bigger market. Macroalgae could be a very interesting feedstock for a biorefinery, since they are fast-growing and versatile in their applications (Jung et al., 2013). Currently macroalgae are mainly cultivated for food applications, but there are other possible products, like medicines, natural colours and biopolymers (Kerton, Liu, Omari, & Hawboldt, 2013). The sugars from macroalgae could also be converted into platform chemicals (Reith, Deurwaarder, & Hemmes, 2005).

1.6 The knowledge gap

The macroalgae-based biorefinery is an important topic for recent research articles. However, there is still much research to be done. The Tables in Appendix A give an overview of some of the available studies on the production of chemicals and fuels from macroalgae. Different types of studies are available; firstly, some of the studies address the general aspects of the macroalgae-based biorefineries (Kerton et al., 2013; Wei, Quarterman, & Jin, 2013; Roesijadi, 2008). Often, these descriptions are very broad, and only the general concept is introduced. In other articles, a case-study is constructed which is used to analyze the economic and environmental performance of a biorefinery (Goh & Lee, 2010; Golberg, 2012). Furthermore, many studies are conducted by non-academic institutes (Bruton et al., 2009; Reith et al., 2005). These reports are useful, since they offer a complete overview of the cultivation and processing of macroalgae for biorefineries. The more specific studies focused on one species or conversion technology can offer in depth-information which is needed to analyze the system (Vauchel et al., 2009; Yaich et al., 2011). Lastly, some articles study multi-product systems from specific species, which can be very useful for the analysis of the biorefinery approach (Kumar, Gupta, Kumar, Sahoo, & Kuhad, 2013; van der Wal et al., 2013). This type of articles can form the basis for specific configurations of the macroalgae-based biorefinery.

In Appendix A, the different studies are briefly indicated. Although it seems that many parts of the macroalgae biorefinery system are already studied, some crucial components are missing. For example, it is often indistinct on which basis the authors select the species they want to study. In other cases, species selection criteria are proposed, but it is not always clear if and how authors use these criteria. Further, in some articles an economic analysis is done, which is important to determine the feasibility of a biorefinery. There are still many assumptions that are applied by the authors, because the macroalgae-based biorefinery is in a concept-phase. This causes large uncertainties in the different analyses. Environmental analyses are even scarcer, while this is very important for the research to alternative feedstocks for the production of compounds and fuels. Thus, there is a substantial knowledge gap present related to the technical, environmental and economic analyses of the macroalgae-based biorefinery.

1.7 The research question

In order to gain a better understanding of a macroalgae-based biorefinery, the following research question will be answered in this thesis:

What are the technical, environmental and economic potentials for macroalgae-based biorefineries?

In order to answer the research question, the following questions will be addressed:

1. What are suitable species for a macroalgae biorefinery and how can these species be cultivated, harvested and processed?
2. What are the available methods for the production of biofuels and valuable co-products from macroalgae?
3. What are the most suitable configurations of technologies and products for a macroalgae-based biorefinery?
4. How does the previously selected concept of a macroalgae-base biorefinery perform from an environmental perspective?
5. How does the previously selected concept of a macroalgae-base biorefinery perform from an economic perspective?

First, the available literature will be reviewed in Chapter 2. In this review the characteristics of macroalgae compared to microalgae will be treated and the several fuels and other products that can be produced from macroalgae will be described. The characteristics of the main cultivated genera worldwide will be discussed. Subsequently, the production of single-products from macroalgae will be analyzed from a techno-economic and environmental perspective. Thereafter, the biorefinery concept will be studied more extensively and the knowledge gap will be discussed further. The issues related to the design of a macroalgae-based biorefinery will be discussed.

The methods in Chapter 3 are related to the construction of the case-studies. Here, two macroalgae genera will be selected, and these specific biorefinery systems will be analyzed from an economic and environmental perspective. The methods will describe how the genera are selected, how the products will be selected and how the comparative analyses will be done. The methods for the sensitivity analysis are also described in this Section.

In Chapter 4, the case-studies are analyzed and compared with each other. The results and discussion related to the macroalgae-based biorefinery case-studies selected in the previous sections are provided in Chapter 5, and finally the discussion and conclusions are presented in Chapter 6.

2. Literature review

2.1 Micro-and macroalgae

Algae are often associated with their high photosynthetic efficiency and high productivity. They make use of CO_2, water and light to generate biomass, like plants do. Algae do not need arable land for cultivation and fresh-water supply is not essential (FAO, 2009). Structurally they are very different from land-based crops. Algae almost lack lignin and cellulose (Jones & Mayfield, 2012), which is advantageous for bioconversion. Besides these similarities, micro-and macroalgae are very different from each other, for both their physical and chemical properties.

A very important and directly visible difference is size of the algae. Seaweeds are “macroscopic multicellular algae that have defined tissues containing specialized cells” (Singh, Nigam, & Murphy, 2011; p. 26) and can grow up to 70 meters in length, whereas microalgae are only 5-100 µm in diameter (Brennan, Mostaert, Murphy, & Owende, 2012). Macroalgae contain a thallus[2] and sometimes a stem and foot, while microalgae are most often single-cell organisms (Oilgae, 2010). These physical properties have direct implications for the modes of cultivation and harvesting. Macroalgae are most-often cultivated in seawater. Harvesting is easy because of the big size; a downside is that a large volume needs to be transported and treated (FAO, 2009, 2010). Microalgae are mostly cultivated in land-based systems, like photo-bioreactors or raceway ponds (FAO, 2009). An important advantage is that in this way the growing conditions are more easily controlled. Due to the smaller size, microalgae can be more challenging to harvest. Methods that are most commonly used are filtration, sedimentation or centrifugation (Garofalo, 2011). While effective, the harvesting and dewatering steps for microalgae can account for 20-30% of the total costs (Garofalo, 2011; referring to Uduman et al., 2010 and Pienkos et al., 2009).

Besides these physical differences, the two types of algae differ largely in composition as well. This will also influence the type of products that can be produced from them. Macroalgae are most often characterized by a high content of carbohydrates (Oilgae, 2010). These can potentially be hydrolyzed into sugars which can be fermented into bioethanol and other fermentation products by micro-organisms. In Section 2.4.2, more attention will be paid to the many different types of carbohydrates present in macroalgae, since these are very different from the carbohydrates present in terrestrial plants. Macroalgae are mainly cultivated for the production of food. Other applications for macroalgae are in the hydrocolloid industry and as a fertilizer (Schlarb, 2011). Lipids are a main component of many types of microalgae. The oil extracted from the organisms can be applied in the production of biodiesel (Olguín, 2012). Besides this, microalgae contain more high-value compounds than macroalgae. Examples are several nutraceuticals, pigments and the application as fish feed (Schlarb, 2011). This is one of the reasons why research on third-generation biofuels and chemicals is mainly focused on microalgae so far. However, because of the fast-growing nature, the large body of knowledge and the versatility of seaweed, macroalgae are very interesting to study for the production of biofuels and compounds as well.

2.2 Global macroalgae cultivation

Macroalgae can be divided in three classes, chlorophytes (green algae), rhodophytes (red algae) and phaeophytes (brown algae) (Roesijadi et al., 2008). Among these groups, large differences occur in biology and composition. The groups contain many genera and therefore within groups there are also important differences. The main connecting factor for the genera within a group is the type of pigments that are present in algae, which has impacts on the light requirement (Rote, Hays, & Benemann, 2012). Each of the groups will capture their own part of the photosyntetically active radiation, which will be at wavelengths between 400 and 700 nm (Florentinus, Hamelinck, de Lint, & van Iersel, 2008).

[2] The equivalent of leaves for seaweed (Oilgae, 2010)

There is a large global market of seaweed cultivation, where the red and brown species are especially important. Some of the seaweed production is originating from wild stocks, but nowadays most of the seaweed is cultivated (Jung et al., 2013). Table 1 gives an overview of the seaweed cultivation, with the nine main cultivated species in quantity in 2010 (FAO, 2013). Also the total value of these species is reported, which shows substantial differences in quantity and value in some cases. In the data underlying FAO's statistical program Fishstat (FAO, 2013) microalgae were also included. Furthermore, there were some poorly specified categories as 'brown seaweeds'. This shows the statistical problems that can occur with seaweed cultivation, not all of the cultivation activity is documented properly.

Table 1. Most important globally cultivated species (FAO, 2013)

Species/ Genus	Name in FishstatJ	Group of macroalgae	Number of countries producing in 2010 reported in FishstatJ	Quantity 2010 (ktonnes)	Value 2010 (million US$)	Average value per kg (US$/kg)
Saccharina /Laminaria japonica	Japanese kelp	Brown	4	5147	301	0,06
Eucheuma	(Spiny) Eucheuma	Red	12	3748	1143	0,31
Kappaphycus alvarezii	Elkhorn sea moss	Red	6	1875	265	0,14
Gracilaria	(Warty) Gracilaria	Red	9	1717	540	0,31
Porphyra	Bright green nori, laver, nori nei	Red	3	1648	1163	0,71
Undaria pinnatifida	Wakame	Brown	4	1537	667	0,43
Sargassum	Fusifrom Sargassum	Brown	1	78	36	0,46
Ulva	Green laver	Green	1	4	4	0,81
Caulerpa	Caulerpa	Green	1	4	3	0,59
Total				**15759**	**4122**	**0,26**
Total in FishstatJ				**19006**	**5651**	**0,30**

Table 1 shows that a big share of production comes from *Saccharina japonica* (earlier named *Laminaria japonica*, see for example Kraan (2010)), but this species is only cultivated in four countries at a large scale (with China as the main producer). *Eucheuma* on the other hand, is a genus which is cultivated in much more different countries, often on smaller scales. The reported values show large differences between the genera. *Saccharina* has a very low value per kg, while *Ulva spp*. stands out with the highest value of this list. This value will also be dependent on the other high-value products that can be produced. Currently 83-90% of the value from the seaweed industry comes from food production. The remaining part of the value is generated by the hydrocolloid industry, which includes alginate, agar and carrageenan (Wei et al., 2013, referring to Huesemann, Kuo, Urquhart, Gill, & Roesijadi, 2012 and Reith et al., 2005). As mentioned before, the brown and red seaweeds are cultivated in much larger quantities than the green species. This is illustrated in Figure 3. In the last couple of years, the production of red seaweed increased, and the production of brown seaweeds decreased slightly to stabilize. The total amount of cultivated seaweed is still increasing. More attention is paid to the characteristics and products of the genera presented in Table 1.

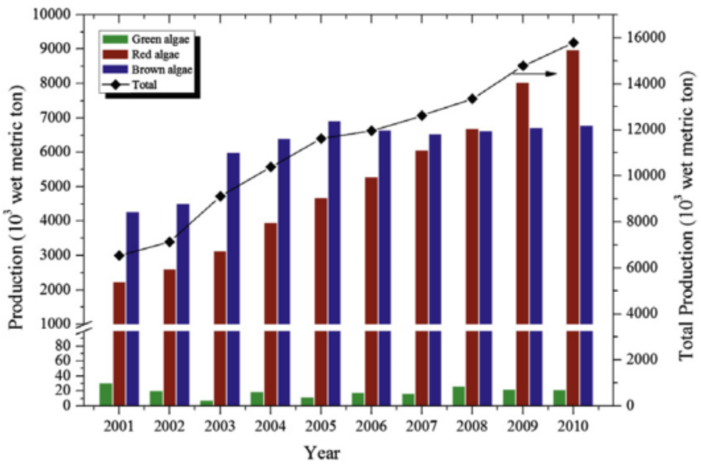


Figure 3. The production of green, red and brown algae from 2001-2010 (Jung et al., 2013; referred to FAO, 2012)

2.3 Cultivation methods

In this Chapter, an overview of the different cultivation techniques is supplied. First, the relatively small-scale methods will be treated, divided into extensive and intensive techniques. After this, larger-scale cultivation concepts are discussed. Often these methods are not in use yet or were tried out on a pilot base only.

Seaweed cultivation is a complicated practice, since the growth of the species is dependent on many factors. Very important are the hydrological and hydro-chemical circumstances at the cultivation site. This includes the right nutrient balance and temperature range of the seawater, enough solar irradiation and moderate currents and waves (Titlyanov & Titlyanova, 2010). These factors are different for various species, also because of the specific biology and growth cycle. This makes that there are many cultivation methods to distinguish. Some of the genera are more suitable for cultivation on a small scale, since there is a lot of manual work in the process. There are also potentially applicable concepts for large-scale cultivation, some of which are not tested under real conditions yet. Besides cultivation, another option is to exploit natural stocks of seaweed, which often leads to irreparable effects to the ecosystem (Titlyanov & Titlyanova, 2010). This is a less common practice than it used to be, but about 10% of the demand is met by natural stocks (FAO, 2003). There are some examples of good and sustainable management of the natural stocks (Ugarte & Sharp, 2001). Titlyanov and Titlyanova make the legitimate distinction between extensive and intensive cultivation. They define:

"*Extensively cultivated seaweeds are grown in natural water areas using only naturally available light, heat, water motion energy, and nutrients"* (p. 228).

This can both be the cultivation and managing of natural seaweed communities as introduced seaweed cultures. With intensive cultivation, often both the environment as the conditions will be either artificial or manipulated. Examples are seaweed cultivated in land-based ponds and with artificial light. Therefore the growing conditions are more controlled, which will lead to higher yields but also to a higher energy input. There are also hybrid methods, where the seaweed is cultivated in a natural environment, with external nutrient supply.

2.3.1 Extensive cultivation methods

A very common cultivation method is the cultivation on lines or ropes. These ropes are commonly made from polypropylene, which can be hundreds of meters long and are anchored to the bottom. When the seaweed becomes heavier, they will sink deeper below the water surface (Titlyanov & Titlyanova, 2010). This cultivation method is quite common, for example for the widespread *Eucheuma* and *Saccharina* genera, and for the cultivation of *Macrocystis pyrifera* (Kraan, 2010). Some other genera are cultivated with the help of nets. The mesh size is dependent on the species, and the net is often fixed on structures made from bamboo, the so-called floating raft method (FAO, 2003). An option to keep the net in plas is making use of buoys (Titlyanov & Titlyanova, 2010). Some species need much sunlight to grow; for example for the cultivation of *Porphyra* the nets are above the water level when it is low tide. Other genera to which net cultivation is applied to are *Ulva*, *Caulerpa* and *Gracilaria* (Kraan, 2010; Titlyanov & Titlyanova, 2010). *Gracilaria* can also be grown in sea beds of shallow bays and lagoons. The seaweed is attached to the bottom, and when they are harvested they will occupy the full surface area (Titlyanov & Titlyanova, 2010).

2.3.2 Intensive cultivation methods

With intensive cultivation the growing conditions will be more controlled, and there is a lower risk of losing the seaweed. The macroalgae will encounter less rough weather conditions. The costs of cultivation will generally be much higher due to high energy and material inputs. The macroalgae can be cultivated in tanks, where the nutrients are supplied in the exact right amounts. Tank cultivation gives the highest yield per square meter, but will be not be viable for large-scale cultivation (Titlyanov & Titlyanova, 2010). Tank cultivation can be very practical for the cultivation of *Sargassum*, since this genera is free-floating (Lüning & Pang, 2003). Intensive cultivation can also be applied when growing the species in small natural water bodies making use of artificial nutrient supply and the application of fertilizers (Titlyanov & Titlyanova, 2010). Examples of such aquatic areas are shallow bays or lagoons. A different interesting example of intensive cultivation does not make use of aquatic environments, but of arid lands. The seawater is sprayed on the seaweed (for example at *Ascophyllum spp*.), with high growth rates as a result (Chynoweth, 2002). Another option is to grow the seaweeds in ponds where nutrients are often introduced to the system; this happens for species of *Gracilaria, Kappaphycus* and *Caulerpa*. In this case the water can be supplied using seawater, river water, water where fish was cultivated in, or a mix (Titlyanov & Titlyanova, 2010). This leads to another successful method for intensive cultivation, which is integration of seaweed cultivation with fish cultivation. This can also be applied as a hybrid method. Seaweeds are effective in the absorption and accumulation of inorganic nutrients and heavy metals (Kraan, 2010). The nutrient runoff from fish cultivation can be diminished up to 90% (Reith et al., 2005; Titlyanov & Titlyanova, 2010). This expands the possibilities to waste-water treatment by growing seaweeds. The method can be applied both to intensive as extensive cultivation, and is widely tested and applied. The seaweed can be cultivated in environments where they receive the effluents, they can be co-cultivated in ponds or they can be cultivated in the sea, in the proximity of cages with animals (Titlyanov & Titlyanova, 2010).

2.3.3 Large-scale cultivation concepts

Some of the cultivation methods mentioned before can also be incorporated in larger-scale concepts for seaweed cultivation. Chynoweth (2002) analyzed many of these concepts. A subdivision can be made in near shore and offshore concepts, smaller and larger concepts (see Figure 4).

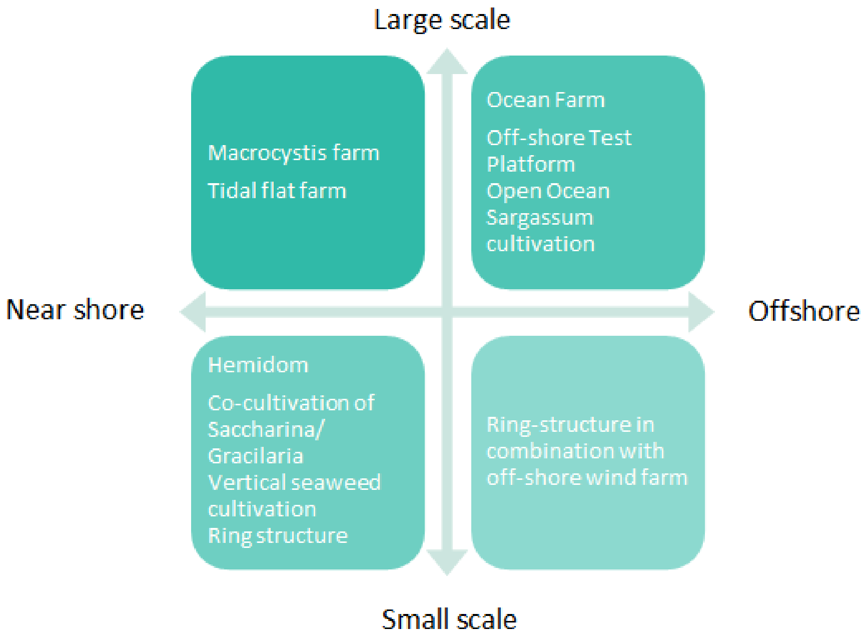


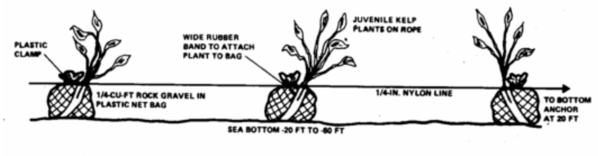
Figure 4. Subdivision matrix of the different seaweed cultivation concepts, divided in small scale and large scale concepts, near shore and offshore.

Roesijadi (2008) mentions that during World War I, acetone and butanol was produced from Macrocystis pyrifera. In order to do this, 400.000 tonnes of weed was processed per year. This shows that large-scale conversion is possible. Large-scale farms were developed as a part of the Marine Biomass Program in the seventies, as a reaction to the oil crisis (Roesijadi et al., 2008). Many concepts were tested on a pilot scale in these years.

The ocean farm would have a large surface area and makes use of lines that are 10-30 m below the surface. The nutrient supply would come from the ocean itself or from effluents. A concept drawing of such a farm is presented in Figure 5, here the processing and conversion component is part of the plant. Test farms were built in the seventies, but they could not withstand the high waves (Chynoweth, 2002). At the Offshore Test Platform, an umbrella structure was used for cultivation. However, the kelp plants were not attached well enough and were lost. After these setbacks, the near shore Hemidome was designed. This floating ring with a diameter of 15 meter performed quite well (Chynoweth, 2002). Another near shore system was developed specifically for *Macrocystis pyrifera* cultivation. This farm occupied a surface area of more than 2500 hectares; the plants were attached to bags that would lower them in the water (Figure 6). The seaweed would be harvested by a harvester in the center of the farm. Another offshore cultivation concept is the use of a large enclosing structure in the open ocean (Chynoweth, 2002; Florentinus et al., 2008). In this structure, floating seaweeds like *Sargassum* could be cultivated. This option could has a large potential, but this is not based on trials yet. Roesijadi (2008) summarizes the main issues related to off-shore seaweed cultivation:

- Containment, protection and distribution. Protection from storms is a major issue for the tested concepts so far;
- Productivity. Low productivity does not have to be a problem in itself, but the costs per square meter should be low enough;
- Nutrient supply and uptake. Nutrient upwelling may not be enough for the seaweed to grow sufficient.

These issues are interesting for further research. Now that the research interest in macroalgae farms has increased, it might be a good time to study new concepts.



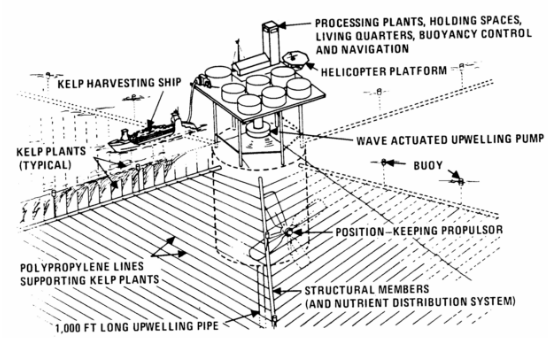


Figure 5. Macrocystis planting system (Chynoweth, 2002)

Figure 6. Conceptual design of Ocean Farm (Chynoweth, 2002)

Another possibility is to co-cultivate several species. *Saccharina* and *Gracilaria* could be cultivated in different times of the year, with help of a 'hanging rope curtain cultivation system'. *Saccharina spp.* performed well in this model, but the *Gracilaria* was not able to survive (Chynoweth, 2002). In a tidal flat farm, there will be harvesting of the seaweeds each day. Small areas would be enclosed by using nets. In densely-populated near shore areas, vertical seaweed cultivation could offer a solution (Florentinus et al., 2008). Seaweeds with different light requirements could be cultivated on these lines in order to make us of the space as efficiently as possible. Another extensively reviewed method by Reith (2005) is the cultivation of seaweed in the proximity of off-shore wind farms, so that the infrastructure for both practices can be shared. One of the concepts he uses is the so-called ring structure. This small ring was designed by Buck and Buchholz (2004) and delivers very good results due to the firm structure. However, this type of cultivation might be too costly to apply on a larger scale. Reith suggests to use layered ring cultivation, where again seaweeds with different light requirements are cultivated underneath each other. He selected three genera suitable for cultivation in the North Sea, which are *Ulva spp.* (green); *Saccharina spp*. (brown) and *Palmaria spp*. (red seaweed).

2.4 Main cultivated genera and products

In order to define the most suitable genera or species for application in a biorefinery, it is important to have knowledge about the cultivation methods and products of potential candidates. In this Section, details on genera, cultivation and main products are provided. Besides for food applications, many of the genera below are cultivated for the production of hydrocolloids; agar, agarose and carrageenan. A more detailed discussion on the applications of hydrocolloids will follow in Section 2.5.2. FAO defines hydrocolloids and its applications as follows:

"*A hydrocolloid is a non-crystalline substance with very large molecules and which dissolves in water to give a thickened (viscous) solution. Alginate, agar and carrageenan are water-soluble carbohydrates that are used to thicken (increase the viscosity of) aqueous solutions, to form gels (jellies) or varying degrees of firmness, to form water-soluble films, and to stabilize some products"* (FAO, 2003; p. 2).

2.4.1 Saccharina japonica and Laminaria

'Japanese Kelp' is cultivated at a large scale in Asia; specifically in China, Korea and Japan. Saccharina japonica is mainly used for food production. The species can grow up to ten meters in length when the conditions are favorable. Earlier China imported the 'Haidai' or Japanese Kelp from Korea or Japan, but they found ways to cultivate this species mainly with raft cultivation. The *species L. hyperborean, L. digitata* and *L. saccharina* grow in cold temperate water and are feedstocks for the production of alginate (FAO, 2003).

2.4.2 Eucheuma

*Eucheum*a is often cultivated with the fixed-line method and with the floating raft method. The main countries where *Eucheuma* ánd *Kappaphycus* cultivation is taking place are Indonesia, the Phillipines and Zanzibar. The seaweed should not be exposed to direct sunlight, but needs a lot of light for growing. It should therefore be cultivated in shallow waters, then the fixed-line method can be used which also ensures easy access for the farmer. The seaweed is quite sensitive for temperature and salinity levels. The water temperature should be high, between 25-30 °C. With the floating raft method, the seaweed is suspended around 50 cm below the water surface. This method can be used when the water is too deep for fixed-line cultivation. *Eucheuma* can be cultivated on a small-scale; when the many growing conditions are met it can grow to ten times its original size in only a couple of weeks. After harvesting, the seaweed needs to be dried, in order to maintain the value. *Eucheuma* is a feedstock for iota carrageenan, which means that it forms a clear, freeze and thaw stable gel, which becomes elastic with calcium salts (FAO, 2003).

2.4.3 Kappaphycus alvarezii

Previously, *Kappaphycus alvarezii* was part of the genera *Eucheuma*, and many of the growing conditions for *Eucheuma* apply to this species as well. It can be cultivated with the same methods as used for *Eucheuma*. But in Viet Nam also pond cultivation is applied to cultivate this species. *Kappaphycus alvarezzii* is a feedstock for kappa carrageenan. Kappa carrageenan forms strong gel with potassium salts and brittle gel when adding calcium salts (FAO, 2003).

2.4.4 Gracilaria

The main feedstocks for agar production are *Gracilaria* and *Gelidium*. *Gracilaria* can withstand a wide range of conditions, therefore it is found at many locations globally. However, the water temperature needs to be 20 °C or higher at least three months a year.

Gracilaria chillencis is cultivated in Chile and it delivers high-quality agar. In China and Indonesia, this seaweed is mainly cultivated by intensive cultivation in ponds. Besides this there are many different methods possible, including growing them on the bottom of open waters, line cultivation, co-cultivation and in tanks. Pond cultivation is less labor-intensive, since the seaweed does not have to be fixed to a substrate. However, with strong winds, the seaweed will float to one side of the pond which is unfavorable for the growing process. Gracilaria is also cultivated for food production, it is mainly sold as a fresh sea vegeTable in Hawaii and parts of Asia (FAO, 2003).

2.4.5 Porphyra

Porphyra is better known under the name nori, which is the dried seaweed wrap for sushi rolls. It is mainly cultivated in China, Korea and Japan; but the demand is widespread partly due to the popularity of sushi in western countries. In China nori is often added to soups as an extra component. It is a nutritious type of seaweed, with high protein content and many vitamins. During cultivation it is important that the nets are exposed to air a couple of hours per day. It can be cultivated in both shallow and deeper water. The process of producing nori sheets from *Porphyra* species is comparable to the paper making process. There is a constant oversupply of nori in Japan, which increases potential for other applications of *Porphyra* (FAO, 2003).

2.4.6 Undaria pinnatifida

Undaria pinnatifida is again mainly cultivated in China, Korea and Japan, the demand for 'wakame' is by far the highest in Korea. Wakame is considered as luxury food, but sometimes there is oversupply with price reductions as a result. *Undaria* is a very nutritious type of seaweed as well. The cultivation cycle consists of different steps, due to the complicated biology (FAO, 2003).

2.4.7 Sargassum

Sargassum is a potential feedstock for alginate. Using this genus is considered as a last option, since the quality of the alginate extracted is quite low, as is the alginate content. It can grow in the warmer seas and oceans. Many of the species are free-floating (FAO, 2003), which gives both challenges and opportunities in the cultivation process.

2.4.8 Ulva

Ulva is one of the few green cultivated genera. It contains ulvan, an unique carbohydrate present mainly in *Ulva* and *Entheromorpha*. It is constituted mainly by the components sulfate, rhamnose, xylose and glucoronic acid (Lahaye & Robic, 2007). Ulvan is not commercially produced yet, and the properties are less well-known than the properties and applications of agar, agarose and carrageenan. However, it could be a potential feedstock for the production of polymers to be used for food-, pharmaceutical and chemical applications. It can be a precursor for the production of fine chemicals with a high value. The carbohydrate is also expected to have biological properties (Lahaye & Robic, 2007). Related to the biorefinery approach, there are many recent research papers available dealing with biofuel production and multi-product formation from *Ulva* species (see for example Bruhn et al., 2011; Sarker, Bruhn, Ward, & Møller, 2012; van der Wal et al., 2013). Besides this, *Ulva* is also produced for food production, better known as sea lettuce (FAO, 2003).

2.4.9 Caulerpa

Caulerpa is used as a salad vegeTable, the species mostly cultivated for this application are *Caulerpa racemosa* and *Caulerpa lentillifera*. The latter is often cultivated in ponds, where changes in salinity are disastrous for the survival of this species. The water in the ponds should be exchanged every few days, for which tidal water movement can be used. This shows that *Caulerpa* is a sensitive genus for cultivation (FAO, 2003).

2.4.10 Macrocystis pyrifera

Macrocystis pyrifera is only cultivated in Chile on a small scale for the last couple of years (FAO, 2013). Before that, there was much attention for this species as a feedstock for biofuel production under the Marine Biomass Program (mentioned before). It is better known under the name giant kelp, because it forms kelp forests in calm and deep waters. It can also serve as a feedstock for alginate production (FAO, 2003).

2.4.11 Gelidium

Also *Gelidium* is being used for the isolation of agar. Species of this genus are is almost completely harvested from natural stocks; further part of *Gelidium* is collected from the beach after storms. Because the plants are small and slow growing, there is currently no cultivated *Gelidium*. An option is cultivation in ponds, but this is not a feasible option to date. Only in Vancouver, one company cultivates *Gelidium* to produce high-grade agar and agarose products, with a sufficiently high market value (FAO, 2003).

2.5 Products from macroalgae

Macroalgae are versatile in their applications, there are being used in different sectors (visible in Table 2). Some of the uses are for very small niche-markets, while other applications are serving a large global market like the food-and hydrocolloid industry (Werner, Clarke, & Kraan, 2004). In this section many of these applications will be discussed. First there will be attention for the production of biofuels from macroalgae, a relatively undiscovered area. Thereafter the other applications will be treated, which can be traditional or potential.

Table 2. Categories of seaweed uses (Werner et al., 2004).

Categories of seaweed uses in the SeaweedAfrica 'Uses Database' (figure represent the number of reported uses)	
Aesthetics	6
Agriculture, horticulture & agronomy	13
Animal aquaculture	5
Cosmetics	18
Environmental health, monitoring and remediation	7
Food	17
Health, thalassotherapy and wellness	25
Industry	24
Pharmaceutical and pharmacology	101
Science, technology and biomedicine	14
Miscellaneous uses	8

2.5.1 Biofuels from macroalgae

There are several options for the production of biofuels from macroalgae. In this Section, the general ideas and concepts behind the fuel production will be explained. Besides this, the results of experiments will be reported. This will lead to a deeper understanding both of the theory and practical aspects of biofuel production from macroalgae. Because of the high moisture content of macroalgae, the 'wet' conversion methods are more suitable for conversion (Chynoweth, 2002), so this will be the main focus of this Section.

2.5.1.1 Biogas production

Some researchers consider the production of biogas from macroalgae as the most promising option for biofuel production from macroalgae (Hughes et al., 2012; Jung et al., 2013). Chynoweth (2002) found that macroalgae show high conversion efficiencies and rapid production rates. In the process of anaerobic digestion, the organic content will be converted by micro-organisms to yield methanol, hydrogen gas and CO_2. First, the different steps of the process will be explained (Romagnoli, Blumberga, & Gigli, 2010). All these steps need to be performed in an oxygen-free (anaerobic) environment (Chynoweth, 2002) and make use of their own type of micro-organisms to carry out the reaction (Romagnoli et al., 2010). Non-methanogenic bacteria (fast-growing) convert the conversion of the organic components into smaller molecules, these compounds are utilized by methanogenic bacteria (slow-growing) with the production of methane and carbon dioxide (Chynoweth, 2002). A crucial element of this process is the optimal utilization of different micro-organisms. The process is divided in four stages:

- Hydrolysis. In this step the proteins, carbohydrates and lipids are converted into smaller monomeric units.
- Acidogenesis. The compounds are converted in volatile fatty acids and CO_2.
- Acetogenesis. The volatile fatty acids are converted into acetate and hydrogen gas in this step.
- Methanogenesis. Finally, the acetate and CO_2 are converted into methane gas.

The production of enzymes for the first two processes is energy-demanding, therefore this process will happen only when there is no easier accessible carbon source available (Horn, 2000). Figure 7 explains these processes further. Most fractions from macroalgae can be converted (e.g. proteins, carbohydrates and lipids), this illustrates that anaerobic digestion is a relatively unselective conversion method. When other products are meant to be extracted from the biomass, it could be a sensible decision to do this first (Roesijadi et al., 2008).

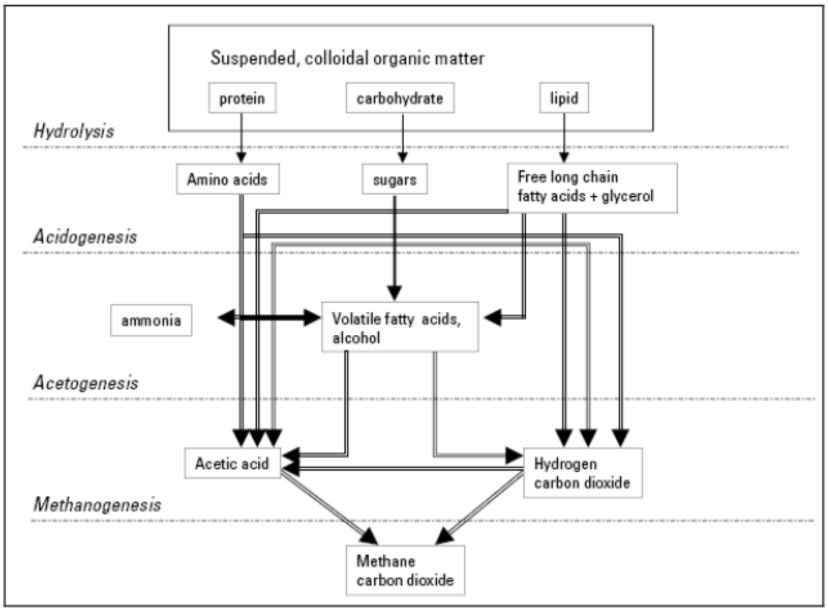


Figure 7. Different stages of anaerobic digestion (Romagnoli et al., 2010)

Chynoweth (2002) identified some indicators for the successful course of the process. According to his analysis, the mannitol content has a positive correlation with the methane yield. A higher algin to mannitol ratio will result in lower methane yields. A long solid retention time[3] will promote a higher methane yield.

There are no major technical barriers to utilize macroalgae for biogas production. The feedstock could potentially be used in current anaerobic digestion plants (Bruton et al., 2009). However, the price of the feedstock will continue to be the main economic barrier. Roesijadi (2010) introduces the process to convert seaweed to gasoline by anaerobic digestion and methanol-to-gasoline (MTG). A block diagram of this process is illustrated in Figure 8.

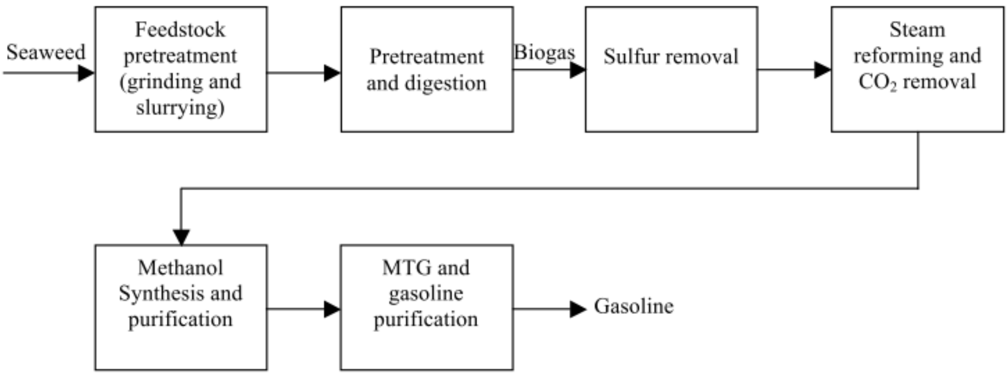


Figure 8. Seaweed to gasoline, a block diagram (Roesijadi et al., 2010)

2.5.1.2 Bioethanol

Another conversion option often studied is the conversion from macroalgae to bioethanol (Borines et al., 2013; Kumar et al., 2013; Pilavtepe et al., 2012). Basically, ethanol can be produced from any feedstock that contains carbohydrates that are convertible into sugars (Horn, 2000). In this process, firstly the carbohydrate polymers are converted into monomeric sugar units. Subsequently special yeasts or bacteria convert the sugars into ethanol by a fermentation reaction. In Figure 9 this process is summarized in a block diagram (Roesijadi et al.,

[3] Time that the feedstock spends in the reactor

2010). This process is commonly used for the conversion of terrestrial biomass, but it becomes different when making use of macroalgae.

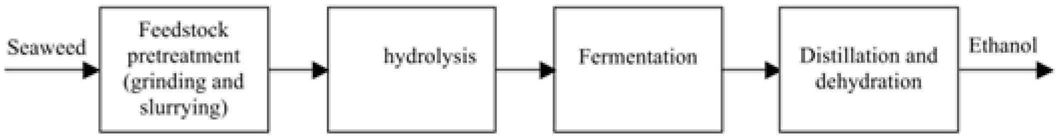


Figure 9. Seaweed to ethanol, a block diagram (Roesijadi et al., 2010)**.**

In Table 3, the different carbohydrates present in macroalgae, microalgae and 'terrestrial' biomass is listed; which illustrates the high number of different carbohydrates. A major issue is that not all types of carbohydrates are easily utilized in this process. There are two main functions of carbohydrates: energy storage and the provision of structure to the plant. In terrestrial plants the structure is provided by lignin and cellulose, and the energy storage by starch. Lignin and cellulose are almost absent in macroalgae, while alginate is an example of a structural component for macroalgae (Horn, 2000). The structural carbohydrates are harder to hydrolyze than the carbohydrates present to provide energy. Therefore, the energy storing carbohydrates lammitol and lammarin are relatively easy to convert (Bruton et al., 2009; Horn, 2000; Jung et al., 2013). Many of the other carbohydrates are composed of C5-sugars, or mixed sugars, which will give difficulties in the conversion (Kraan, 2010). Some of the complicated carbohydrates, like fucoidin, have a certain economic value that should be considered in the economic analysis (Roesijadi et al., 2008).

Table 3. Carbohydrates present in green, red and brown algae, microalgae and terrestrial biomass (Jung et al., 2013). **Mind the division in polysaccharide and monosaccharide for macroalgae.**

Macroalgae[a]			Microalgae[b]	Lignocellulosic biomass
Green algae	Red algae	Brown algae		
Polysaccharide	*Polysaccharide*	*Polysaccharide*	Starch	Cellulose
Mannan	Carrageenan	Laminarin	Total carbohydrate	Hemicellulose
Ulvan	Agar	Mannitol	Arabinose	Lignin
Starch	Cellulose	Alginate	Fucose	
Cellulose	Lignin	Fucoidin	Galactose	
Monosaccharide	*Monosaccharide*	Cellulose	Glucose	
Glucose	Glucose	*Monosaccharide*	Mannose	
Mannose	Galactose	Glucose	Rhamnose	
Rhamnose	Agarose	Galactose	Ribose	
Xylose		Fucose	Xylose	
Uronic acid		Xylose		
Glucuronic acid		Uronic acid		
		Mannuronic acid		
		Guluronic acid		
		Glucuronic acid		

[a] Adjusted from Jang et al. (2012), Roesijadi et al. (2010), Turvey and Christison (1967), Wegeberg and Felby (2010).
[b] Adjusted from Brown (1991).

By making use of different pre-treatments, the carbohydrates can be hydrolyzed to yield sugars more effectively (Bruton et al., 2009). The term 'pre-treatment' is used in different contexts, but here is referred to the process of hydrolysis. This can be achieved by using chemical, enzymatic and physical methods; sometimes combinations of these processes are even more effective (Jung et al., 2013; Kraan, 2010). There are different organisms able to hydrolyze and convert the carbohydrates into ethanol (Jung et al., 2013; Wei et al., 2013). The biodegradability in general will be favourable for seaweeds with a high carbohydrate content, and a low ash and water content. Polyphenols and salt are disadvantageous factors for the conversion into bioethanol (Horn, 2000). It has to be noted that the composition can vary drastically between seasons and growing conditions (Bruton et al., 2009).

2.5.1.3 Biodiesel

Some research is focused on the production of biodiesel from macroalgae (Fragale et al., 2005; Maceiras., 2011). For this conversion to take place, first the oil needs to be extracted. Then, the biodiesel is produced by the process of transesterification. While this process is relatively simple to carry out, it does not seem to be very useful for biofuel production from macroalgae. Most microalgae contain more lipid than macroalgae and therefore it is generally accepted that microalgae are much more interesting as a feedstock for the production of biodiesel (FRM Ltd, 2010; Jones & Mayfield, 2012).

Another option for the production of both diesel and gasoline, is the process hydrothermal liquefaction (HTL) (Roesijadi et al., 2010). A block diagram is presented in Figure 10. Here, seaweed slurry is introduced to a HTL reactor, where the pressure is set at 120-180 bar and 300-350 °C. This high pressure keeps the water in the liquid phase. After the reaction there is an oil phase, aqueous phase and gas phase. The oil-and gas phase is treated further to yield gasoline and diesel oil. While this process is interesting for seaweed, it is not demonstrated in real-life conditions yet. The economic analysis presented in Section 2.4.3 is therefore based on assumptions and not on real experiments.

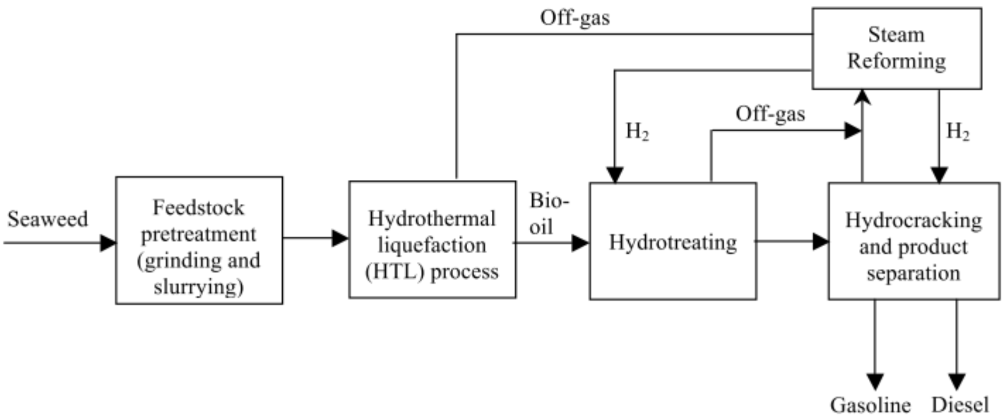


Figure 10. Block flow for seaweed to gasoline and diesel via HTL and upgrading (Roesijadi et al., 2010).

2.5.1.4 Biohydrogen

One of the products of anaerobic digestion described in Section 2.4.1.1 is hydrogen. Since it is an intermediate product (see Figure 7), it should be separated in the methanogenesis stage which can be quite complicated. Garofalo (2011) discusses the production of several types of biofuels from a wide range of micro-and macroalgae genera. The production of biohydrogen is only presented as an option for microalgae. He does not elaborate on the reasons for the ability to produce hydrogen. Jones and Mayfield (2012) mention the species *Gelidium amansii* and *Laminaria japonica* as potential species for the production of biohydrogen by anaerobic fermentation. However, during experiments with *Gelidium amansii*, the hydrogen production rate was decreased substantially with 50% due to an inhibitory by-product of the acid hydrolysis process. This article is providing a more specific reason of macroalgae being less suitable for biohydrogen production, however the literature is very limited to this regard.

2.5.1.5 Biobutanol

According to Oilgae (2010), biobutanol is another interesting biofuel, due to its favorable characteristics. Butanol can be easily added to gasoline due to its low vapor pressure and energy content which is closer to gasoline than ethanol. The fuel can be produced by applying the acetone-butanol (AB) fermentation making use of certain bacteries like *Clostridium spp*. These bacteria are able to produce different products from several carbon substrates, including butanol, acetone, ethanol and organic acids. It is not able to utilize all the carbohydrates present in macroalgae (Jung et al., 2013). This process received scientific attention recently, in several experiments the production of acetone and butanol from macroalgae as a feedstock was demonstrated (Huesemann et al., 2012; van der Wal et al., 2013). Huesemann for example, used *Saccharina species* as a substrate; the glucose, laminarin and mannitol was utilized by the micro-organisms. One of his main conclusions was that effort must be taken in the conversion of alginate as well, to make this process feasible.

2.5.2 Non-energy products from macroalgae

The production of biofuels from macroalgae is still a quite undeveloped field of research, while seaweed has been used for numerous other applications over the centuries. In this Section, the production of these compounds products will be discussed, some of which are still in a research phase.

As mentioned before, seaweed is mainly used as a healthy food product, particularly in Asia (FAO, 2003). Further, also the hydrocolloid industry is of considerable size. An indication of the total seaweed market is often retrieved from FAO (2003), which provides still the most complete overview (see Table 4). This indicates that there is a lack of up-to-date information on the seaweed industry. According to this report, the total seaweed industry has a value of 5,5-6 billion US$ in 2002, which is divided in food (5 billion), hydrocolloids (0,5 billion) and a negligible share for other applications as fertilizer, animal feed and biofuels. A more recent estimate of the total hydrocolloid industry is made by Bixler & Porse (2010), they report a total sales value of about one billion dollar in 2009. The difference can be explained by a doubling of the hydrocolloid industry in this period, or difference in data sources and assumptions. Since Bixler reports a sales value of 0,6 billion in 1999 already, the latter is probably part of the explanation.

Hydrocolloids have their main applications as food stabilizers, ingredients in cosmetics, biopolymers and nutrient substrates (FRM Ltd, 2010). These products are often more expensive than other alternatives like cellulose derivatives. But some of the characteristics are very important for a certain product, which can offset the price difference. Since hydrocolloids are natural products, the quality can differ for different batches. The companies that are considered trustworthy often have a strong market position. Therefore it can be challenging to enter the hydrocolloid market as a newcomer (FAO, 2003).

Table 4. Overview of the seaweed market (US Department of Energy, 2010; referred to FAO, 2003)

PRODUCT	VALUE
Human Food (Nori, aonori, kombu, wakame, etc.)	$5 billion
Algal hydrocolloids	
Agar (Food ingredient, pharmaceutical, biological/microbiological)	$132 million
Alginate (Textile printing, food additive, pharmaceutical, medical)	$213 million
Carrageenen (Food additive, pet food, toothpaste)	$240 million
Other uses of seaweeds	
Fertilizers and conditioners	$5 million
Animal Feed	$5 million
Macroalgal Biofuels	Negligible
TOTAL	**$5.5-6 BILLION**

Seaweeds are also used as fertilizer or soil additive, animal or fish feed (FAO, 2003). Some species can provide useful compounds as omega fatty acids or co-enzyme Q10 (FRM Ltd, 2010). Besides this, specific species are thought to have certain antiviral, antibacterial or other bioactive properties for pharmaceutical and medical applications (FRM Ltd, 2010). Smit (2004) and Holdt & Kraan (2011) wrote extensive reviews of these current and future applications for seaweed.

2.5.2.1 Agar

Agar is able to form gels; the applications of agar are revolved around this property. The melting temperature of agar gel is much higher than that of gelatin (FAO, 2003). The major part of the agar produced is used in food applications, mainly as stabilizer and thickener. Other applications are in the biotechnology, where it is used as gel for populations of bacteria. Agar can form a suitable medium with the right nutrient composition for the production of clones from plants (FAO, 2003).

Basically agar can be extracted from the seaweed with the use of water alone. The seaweed is washed and heated with water, the agar will dissolve in the water and the seaweed is filtered out the solution. After cooling, this will form a gel with one percent agar. This can be washed or bleached, afterwards the water will be pressed out and it will be oven-dried. Subsequently the agar is milled in the appropriate size. For specific species there will be some alterations on this production process (FAO, 2003).

2.5.2.2 Alginate

Alginates have several useful properties that are applied in different industries (FAO, 2003):

- The ability to increase viscosity of an aqueous solution;
- The ability to form gels, without the requirement of heat;
- The ability to form sodium or calcium alginate films, and calcium alginates.

The specific characteristics of the formed gels, films and fibres are different for each species used. This is related to the composition and ratios of mannuronate- and guluronate units of the long alginate polymers. The characteristics aimed for in the production process are dependent on the desired application. Also alginate can be used as thickener, stabilizer or gelling agent for food applications. About fifty per cent of the alginate market is dedicated to the textile printing industry (FAO, 2003). Here, alginate will serve to thicken the dying paste. Alginates do not react with the dye, which is considered as an important advantage. Furthermore, alginate has various applications in the pharmaceutical industry, the alginate fibers are applied in wound dressings, and calcium alginate beads can be used for the controlled release of drugs. Other examples of the diverging applications of alginates are films on paper and electrodes, and alginate serving as fish feed binder (FAO, 2003).

Alginate is a component of the cell wall in brown seaweeds; it is present in the form of calcium, magnesium and sodium salts of alginic acid. Since the magnesium and calcium variations do not dissolve in water, and sodium alginate does, all the alginate salts are to be converted into sodium salts. The sodium alginate is dissolved in water and the seaweed can be filtered out of the solution. The sodium alginate can be retrieved in two ways (FAO, 2003):

- Acid is added to the solution, which will make the alginate to precipitate so that it can be separated from the water. The addition of sodium carbonate will react with the alginate acid to form sodium alginate, which will be dried and milled.
- A calcium salt is added to the solution, which will react with the alginate to form the insoluble calcium alginate which can be separated from the water. Subsequently, sodium carbonate is added, to produce the desired sodium alginate. The pellets are dried and milled.

2.5.2.3 Carrageenan

Also carrageenan is characterized by its ability to form gels or viscous solutions. The specific properties are different for the different types of gels, indicated by kappa, iota and lambda carrageenan (FAO, 2003). Different seaweeds are used to extract the different types of carrageenan.

- Kappa carrageenan forms a rigid, elastic gel with potassium and a brittle gel with calcium. Kappa gives the strongest gels of all types.

- Iota carrageenan forms a soft and resilient gel with calcium. It can easily be stirred and will afterwards return to its initial strength, which is called thixotropic behaviour.
- Lambda carrageenan is able to form a solution with high viscosity.

Besides this, carrageenan molecules are negatively charged, which make them bind with positively charged molecules including proteins. The main application of carrageenan is in the dairy industry, here it is added to the products to prevent separation. Examples of these products are cottage cheese, ice cream and chocolate milk. When produced well, carrageenan can form an alternative to gelatin. Furthermore it finds its applications in other food industries, such as the meat industry and pet food. It also has some non-food applications, like air fresheners and tooth paste.

Carrageenan can be produced in two ways. It is easily extracted from seaweed by adding water, which is the procedure of the first and oldest method. For the extraction of carrageenan, the seaweed is heated in an aqueous solution together with an alkali. After the seaweed is removed, the solution is filtered by ever finer filters. Carrageenan will precipitate after addition of alcohol. The downside of this method is that it is expensive and energy-intensive to retrieve the carrageenan from the solution. Therefore the second method most-commonly applied nowadays. In the second method, the carrageenan is not extracted, but everything else is dissolved in alkali and water. This process will yield a mixture of cellulose and carrageenan, which can be sold as semi-refined carrageenan.

2.5.2.4 Ulvan

Ulvan can be extracted from the genera *Ulva* and *Enteromorpha* (Lahaye & Robic, 2007). Ulvan is not a commercial hydrocolloid yet, but is considered as a compound with comparable structural characteristics as alginate, carrageenan and agar. According to Chiellini and Morelli (2011), it is an interesting candidate for technology, biomedical and industrial-related applications. Examples of biological properties are antitumor activity, anticoagulant activity[4] and anti-influenza activity (Lahaye & Robic, 2007). Like most other hydrocolloids, it has an ability to form gels (Morelli & Chiellini, 2010). Furthermore, ulvan could be used as a source of rare sugar precursors for the production of fine chemicals (Lahaye & Robic, 2007)

2.5.2.5 Fertilizer

Seaweed is used for centuries already as a fertilizer; often beach-washed seaweed was collected and applied to the crops directly. Nowadays, the seaweed is composted first, or applied in the form of seaweed meal (dried and milled seaweed). The latter is used as fertilizer or soil conditioner. Alginate containing weeds can be composted, during this process the alginate polymers break down into smaller chains. This results in a product with 20-25% water which is easily stored before use (FAO, 2003). Seaweed extracts can be applied as soil conditioner, or as fertilizer in the horticulture. However, there is some doubt of the real effects of seaweed fertilizer. The most realistic option is to combine seaweed fertilizer with NPK fertilizers (nitrogen-, phosphor- and calcium fertilizers (FAO, 2003).

2.5.2.6 Animal feed

Seaweed meal has also found its application in animal feed. Seaweed meal is produced by cutting up the seaweed with ever smaller hammers. Subsequently the particles are dried to reduce their moisture content to below 15% (FAO, 2003). After this process it is milled and stored in bags, to prevent the seaweed to come into contact with water. The meal contains minerals, vitamins, trace elements and protein. The industry became smaller since the seventies, but seaweed meal has most certainly promising applications as an animal feed additive, mainly for horses (FAO, 2003). Often the application of seaweed extracts in animal feed resulted in positive effects, like a higher milk rate and an increased growth rate of lambs (Holdt & Kraan, 2011). Powder

[4] Coagulation: red blood cells clump together when there is a wound.

and extracts of seaweed have shown bioactive effects such as antioxidant, peroxidation of fatty acids, antibacterial, anti-fungical and anti-inflammatory. In several of the experiments, growth performances are increased or at least there are no negative effects. Seaweed species are potentially good candidates as feed supplements, with beneficial effects on health or the desired properties of the animal and product. However, seaweed is not widely applied yet in this market, due to the existence of cheaper alternatives.

2.5.2.7 Platform chemicals

Reith et al. (2005) addresses the idea to produce 'platform chemicals' from the abundant carbohydrates present in most seaweeds. The chemicals contain mainly the elements C, H and O and can have direct applications, or are able to function as a starting material for bio-derived products (Foley, Beach, & Zimmerman, 2011). Currently, most of these chemicals are produced from oil. The naphtha fraction forms a feedstock for the platform chemicals, of which most of the commonly used chemicals are derived from (see Figure 11; Cherubini, 2010).

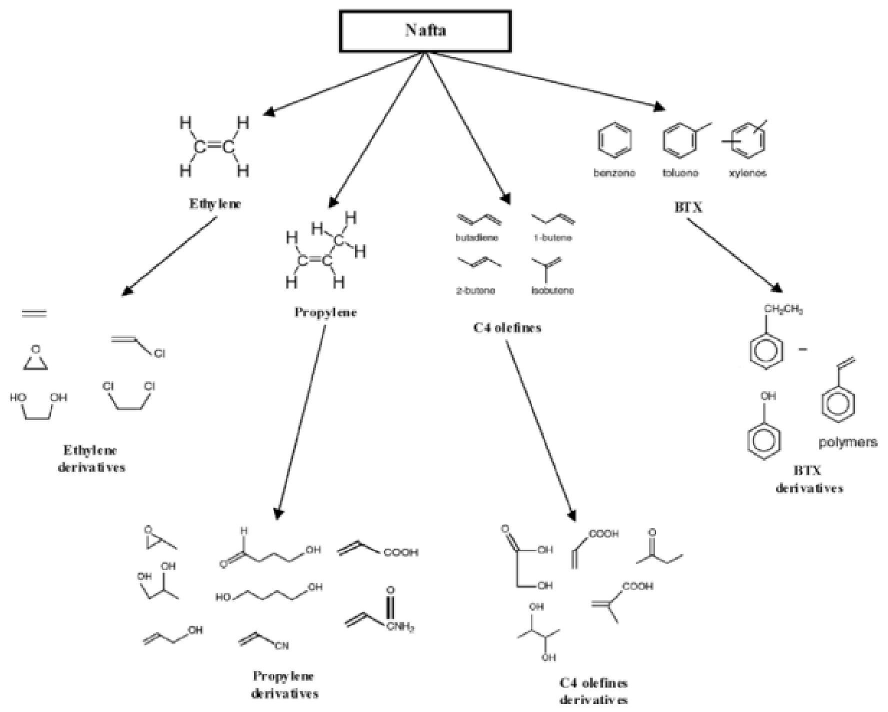


Figure 11. Production of platform chemicals from naphtha (Cherubini, 2010)

There is a lot of on-going research on the production of platform chemicals from land-based crops, but seaweed could form an interesting feedstock as well. The same problem occurs with the production of these chemicals as which the production of bioethanol; some carbohydrates are difficult to hydrolyze. There is not an industrial process available yet for this type of products. Reith (2005) stresses the research needs in this field. Economically this makes a strong case, because there is a high demand for such chemicals. His estimate of the potential profits is presented in Section 2.5.3.2.

2.5.2.8 Pigments

Pigments give the colour to macroalgae. When isolated, they have certain industrial applications (see Table 5 for an overview). This could be a potential product from seaweed, however it is not discussed extensively in literature and is more associated as an application for microalgae (Foley et al., 2011; Spolaore, Joannis-Cassan, Duran, & Isambert, 2006; Werner et al., 2004). A specific reason for this observation is not provided.

Table 5. Examples of pigments; with genera, colour and application (Holdt & Kraan, 2011)

Pigments		Genus	Colour	Application
Cartenoids	β-carotene	*Laminaria, Sargassum, Ulva, Porphyra*		Natural colouring of margarine and fish
	Astaxanthin	*Laminaria, Undaria, Sargassum*	Orange-red or pink	
	Fucoxanthin			
Phycobiliproteins		*Palmaria, Gracilaria*		Natural colouring: chewing gums, dairy products, cosmetics etc
Chlorophylls	Chlorophyll *a*	*Laminaria*		Food and beverages

2.5.2.9 Medical and pharmaceutical applications

Seaweed extracts are being used currently for applications in health products, cosmetics and pharmaceutical products on a small scale (Reith et al., 2005). There are other possibilities, and a lot of further research might be needed to discover the full potential of compounds present in seaweeds. Seaweeds contain bio-active compounds with many applications. These compounds probably developed in seaweeds because of the many challenges they had to overcome; like competition for space and tolerance for extreme conditions (Smit, 2004). The interesting molecules can potentially be useful for medical applications. There is a lot of research on these compounds, and it is complicated to summarize this range of applications and activities. Smit (2004) categorizes these activities in different functions:

- Anti-viral;
- Anti-biotic;
- Agglutination, coagulation[5];
- Related to cellular growth;
- Antithrombic and anticoagulant;
- Toxins;
- Anti-inflammatory;
- Enzyme inhibitors and stimulants;

Besides this review, there are some more reviews attempting to summarize the numerous activities. (Andrade et al., 2013; Australian Government, 2011; Holdt & Kraan, 2011; Smit, 2004). A summary of these applications is presented in Appendix B (Holdt & Kraan, 2011).

Besides carbohydrates, there are more bio-active compounds present in macro-algae. For example, some pigments have presumed effects (Holdt & Kraan, 2011), which are comparable to the effects presented in Appendix B. Seaweeds also contain vitamins like vitamin E (Holdt & Kraan, 2011). Compounds could be used as a bioactive component in natural health foods. Other compounds could be applied during treatment for cancer, diabetes or aids. Lipids present in macroalgae contain much ω-3 fatty acids, which have numourous positive health effects (Holdt & Kraan, 2011). Concluding, there are many potential medical and pharmaceutical applications of macroalgae compounds; but these applications are hard to market. There are a lot of regulations which is a main barrier for the marketing of these products, and many of the presumed effects are not completely proven.

[5] Agglutination: red blood cells clump together. Coagulation: red blood cells clump together when there is a wound.

2.5.3 Environmental analysis of macroalgae-based products

When products are produced from macroalgae, there should be clear environmental advantages compared to the conventional production technique. The studies containing environmental analyses are very scarce. This is partly caused by a lack of data, since the production of macroalgae-based products is still in a conceptual phase. In this section, the few environmental analyses that have been published will be reviewed. In Section 2.6, the environmental study dealing with the biorefinery more specifically will be discussed.

The production of the seaweed is important to analyze from an environmental perspective. Florentius et al. (2008) studied several concepts (which are called sets) for the cultivation of macroalgae from an environmental perspective. The results are also compared with the greenhouse gas emissions from biogas from manure, municipal solid waste and by simply using natural gas (see Figure 12). In this analysis, the necessary calculations are missing and the results are therefore hard to check. The authors did mention some of the important assumptions though. This makes this analysis only partly useful. The results are not very critically discussed, since the large uncertainties in the analysis are briefly addressed only.

Set 3 and set 5 are considered very positive in this analysis. For set 5 (vertical lines, near-shore) the external nutrient supply is assumed to be zero, because there will be sufficient nutrients present in the water. Set 6 is performing poorly in this analysis. In this concept, floating Sargassum is cultivated in large floating structures in the middle of the ocean. Because the transport distance is large and there is a need for external nutrient supply in this infertile area, the GHG emissions will be large. However, the amount of biomass that can be produced in this concept and therefore the amount of energy is very large. Mainly in this concept, the uncertainty is high. This type of ocean cultivation is not demonstrated yet, unlike the other concepts. For set 3 (line cultivation near offshore infrastructure like windparks), the energy for harvesting is not included, for unclear reasons. For set 4 a considerable amount of energy is invested in the harvesting step, therefore the greenhouse gas balance is less positive. From this study set 3 seems to be the best option, both from an environmental as from an economic perspective. The combination of macroalgae cultivation and offshore windparks could offer an interesting possibility for the future (Reith et al., 2005).

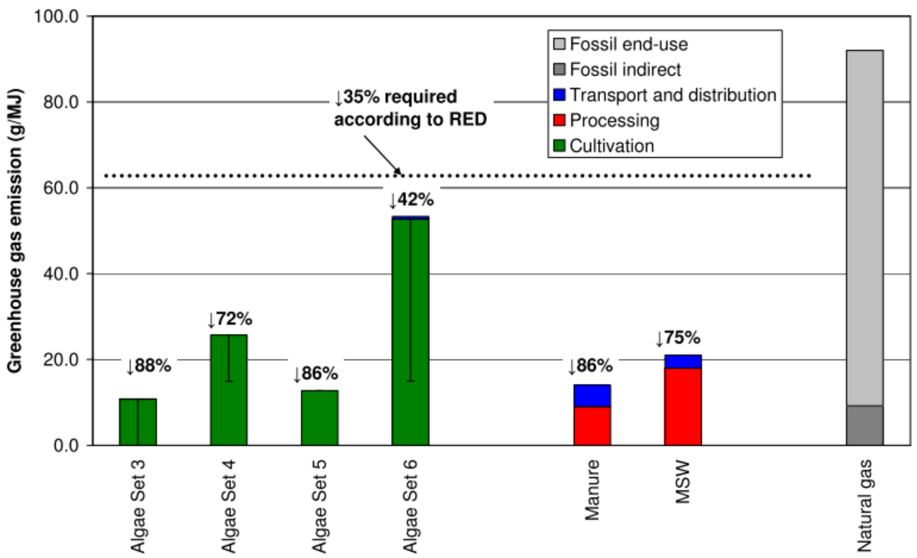


Figure 12. Greenhouse gas emissions for different concepts compared with a reference scenario (Florentinus et al., 2008). **Set 3: horizontal lines between offshore infrastructure; set 4: ring system in rougher near shore areas; set 5: vertical lines nearshore in densely used areas; set 6: bounded floating structure in open sea.**

There is a need for a solid life cycle analysis (LCA) to determine the environmental effects of the biofuel production from macroalgae (Roesijadi et al., 2008). Romagnoli (2010) is attempting to make a life cycle inventory that could be used for such an analysis. The system studied in this article was the production of *Ulva* *prolifera* with poultry manure as a carbon source, with biogas production as the product. One of the main results is that the CO_2 balance of this specific type of biogas plant is positive, which means that more CO_2 is emitted in the atmosphere than is absorbed. However, the very specific system description makes this result hard to generalize to other macroalgae-based systems.

2.5.4 Economic analysis of conversion to products

The economic analysis of processes is based on many assumptions, both from costs perspectives as from technical perspectives. So the cost Figures reported in this Section are useful to get an idea of the costs, but bear large uncertainties. Sometimes the estimations are based on old data, which will affect the analysis even more. However, these limited cost estimations are needed to research the economic feasibility of the conversion of macroalgae into products.

2.5.4.1 The cost estimations for the production of biofuels

Many reports include an economic analysis, some more extensive than others. However, most of these analyses refer to the reports from Chynoweth (2002) and Reith (2005). Before the other reports are discussed, their findings will be summarized shortly.

The study from Reith is focused on macroalgae cultivation in combination with offshore wind farms. In this way, the infrastructure of both activities can be combined. This could give economic and practical advantages. The system description in this report is adjusted to this situation. The productivity assumptions will vary between twenty tonnes dry matter per hectare per year for one-layer cultivation and fifty tonnes dry matter per hectare per year for multi-layer cultivation. Energy use for harvesting and transporting the seaweed is deduced from other reports. For two cases with different scales and for different conversion technologies for seaweed to biofuels, the energy production and avoided CO_2 emissions are calculated. For the cultivation methods, different cost estimations are presented for different seaweeds and productivities, most of which are from the Marine Biomass Program. The investments of the cultivation system will be the largest part of the total investment costs. Also the costs for harvesting are found to be high. The cultivation ring mentioned in Section 2.3 (Buck & Buchholz, 2004) will result in the highest cultivation costs, while this ring structure is the most sTable cultivation method so far. This result is also found by Florentius et al. (2008), see Figure 13 below. Reith concludes his analysis by saying that the costs of offshore cultivated seaweed will probably be too high for the production of energy alone. Near shore cultivation has more potential in this context. The underlying foundation of these statements is provided by calculations on the American Marine Biomass Program, where cost estimations for large-scale cultivation are made. Chynoweth (2002) analyzed these large scale cultivation methods. In Table 6, the costs for cultivation used in his economic analysis, as in the analysis from Reith (2005) is presented.

Table 6. Cultivation costs of several genera and cultivation systems (Chynoweth, 2002; referred to Bird, 1987)**. The numbers are expressed per dry-and ash free metric tonne (DAFMT) and for different assumptions of the yield.**

System	Yield (DAFMT/ha/yr)	Feedstock ($/DAFMT)	Cost ($/GJ)	Feestock cost ($/DAFMT)
Nearshore Macrocystis	34	67	5,5	72
	50	42	3,5	41
Rope farm Gracilaria, Laminaria	11	538	44	-
	45	147	12	-
Tidal flat farm, Gracilaria, Ulva	11	44	3,6	48
	23	28	2,3	23
Floating seaweed, Sargassum	22	73	6	71
	45	37	3	36

As can be seen, the source where the values are coming from is from 1987. Therefore it is safe to say that these results are outdated. However, important economic analyses are based on this data, and other reports are basing their economic estimations on these reports (an example is the study from Reith et al., 2005). This could cause large inaccuracies in these analyses; there is a need for more recent cultivation data. Table 6 shows that the rope farm is a very expensive cultivation method, while the tidal flat farm is a more reasonable alternative from an economic perspective. Also the floating cultivation of Sargassum could offer interesting possibilities, while this cultivation method is still subject to large uncertainties (Florentinus et al., 2008). The concept was already introduced in the study from Bird (1987; reffered to in Chynoweth, 2002), but in 2008 it was still not tested under real conditions.

In order to get a better idea of the way how different reports retrieve their economic data, in Table 7 the cultivation costs and references of some reports are summarized. Some reports refer (indirectly) to Chynoweth (2002) as mentioned before. Unfortunately, no clear calculations or methods for these numbers are provided.

Table 7. Summary of different cost Figures of cultivation systems.

Report	Lowest costs ($/tonne dry matter)	Highest costs ($/tonne dry matter)	Referred to	Comments
Chynoweth (2002)	21	409	Bird (1987)	
Reith et al. (2005)	21	409	Chynoweth (2002)	
Oilgae (2010)	100	300	No sources	Unclear how these numbers are retrieved.
Roesijadi (2010)	21	112	Reith (2005)	Assuming the best productivities from Chynoweth.
Bruton et al. (2009)	223	458	No sources	Converted from € to $ (2009)
Florentius et al. (2008)	413	863	Own research	Converted from € to $ (2008). Different cultivation systems studied.
Kelly & Dworjanyn (2008)	148	-	Several sources	Converted from £ to $ (2008). Cultivation of *L. saccharina*.
Roesijadi et al. (2008)	500	-	Personal communication	Prices for dried kelp.

In Figure 13, the cost estimations of different cultivation concepts from (Florentius et al. (2008) are illustrated. Here it becomes visible that set 3 is also performing quite well from an economic perspective, like mentioned in Section 2.5.3.

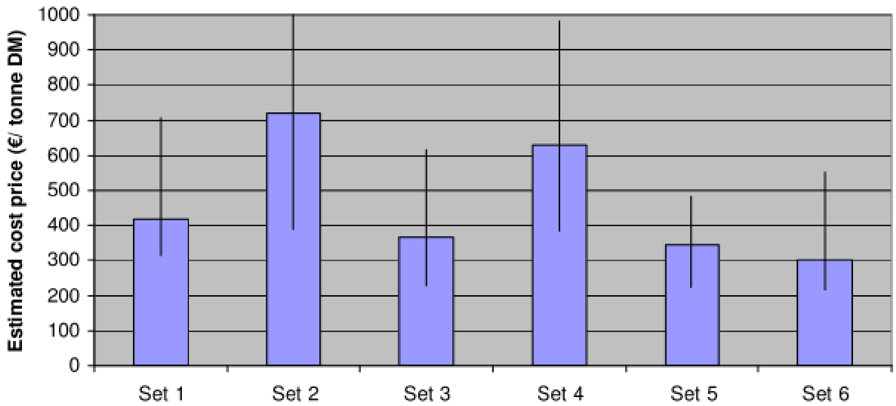


Figure 13. Cost price ranges for investigated sets (Florentinus et al., 2008)**. Set 3-6 are macroalgae cultivation concepts. Set 3: Horizontal lines between offshore infrastructure; set 4: ring system in rougher near shore areas; set 5: vertical lines near shore in densely used areas; set 6: bounded floating structure in open sea.**

Besides using the feedstock price as a starting point for the economic analysis, another option is to calculate the different costs for the conversion technologies, and to calculate the 'break-even' price: the maximum allowable price that the raw feedstock could have, in order to produce biofuels with the current market price. Chynoweth (2002) sets the conversion costs component for conversion from macroalgae to biogas at $1,50-3,50 per GJ. When this gas will be upgraded[6], this will add another $1-2 to the price per GJ produced. The factor influencing these prices mostly is the assumed methane yield. This is important to keep in mind when analyzing the economics of a certain system. Regarding the conversion to bioethanol, the amount of soluble carbohydrates as a percentage of the total carbohydrates is an important factor[7] and should be as high as possible, as is the ratio of hexose to pentose sugars which should be as low as possible. The price of ethanol is ranging from $0,50-0,75 per liter for baseline technologies and from $0,25-0,30 for advanced technologies (Chynoweth, 2002). However, the author mentions that these estimates are not based on large-scale conversion and that care should be taken when using these values.

According to Roesijadi (2010), the methane yield assumed by Reith is very conservative. Reith uses a yield of 0,17 m^3/kg of volatile solids[8] (VS); while other sources report yields ranging between 0,22-0,43 m^3/kg VS (Kelly & Dworjanyn, 2008). He also stresses the large influence of the methane yield on the total cost balance of the different scenarios. None of the discussed techniques for macroalgae conversion have been applied at an industrial scale yet (e.g. methanol-to-gasoline (MTG) and hydrothermal liquefaction (HTL)). The block diagrams of these two processes are represented in Sections 2.4.1.1 and 2.4.1.3 (Figure 8 and 9). In Table 8, his economic analysis is presented.

Table 8. Fuel product cost results reported in 2008 dollars (G Roesijadi et al., 2010).

Product	**Gasoline**	**Ethanol**	**Gasoline/ diesel**
Main technology	Fermentation and MTG	Fermentation	HTL and upgrading
Feedstock (dry metric tonne/day)	500000	500000	500000
Intermediate products	Methane	n/a	HTL bio-oil
Final products	Gasoline	Ethanol	Gasoline and diesel
Final product yield, million gallon/year	11	42	39
Production costs ($/gallon final product)			
Seaweed to intermediate product	1,4	1,8	1,5
Intermediate to final product	1,5	n/a	1,2
Final product 2008 market average price ($/gallon)	2,6	2,2	2,8
Maximum allowable feedstock price ($/dry metric tonne)	-6	28	6

By making use of the average market price, the maximum allowable feedstock price was calculated. In the first case, this feedstock price is negative. Roesijadi addresses that this is partly caused by the low conversion factor he used in his analysis, retrieved from Reiths report. The conversion rate to ethanol is higher than is demonstrated so far (50% conversion rate), therefore this outcome might be too positive. A similar analysis was done by Reith (2005), his results are reported in Table 9. The two results are quite different from each other.

[6] This means that the mixture of CO_2 and methane will be separated, to yield methane gas. This will result in gas of 'pipeline quality' (Chynoweth, 2002).
[7] Soluble carbohydrates are easier to convert into bioethanol.
[8] Volatile solids is also called: ash-free dry weight (Roesijadi et al., 2010), this indicates the organic carbon fraction in a certain compound.

Table 9. **Estimated production and "break-even" cost for methane and electricity from anaerobic digestion of seaweed** (Bruton et al., 2009; retrieved from J. H. Reith et al., 2005)**. Case 1 and case 2 differ only in scale of the project.**

Item	Remarks	Case 1	Case 2
Scale (tonnes/year d.b.)		100000	500000
Hydraulic residence time (HRT) in days	30 days, also in model	20	20
Investment cost (€m)		9,6	31,9
Operational costs (2005) (€m/yr)		0,96	3,2
Gross methane production (million m3/yr)		14,8	74
Net methane production (million m3/yr)	After upgrading to natural gas	12,4	61,8
Production cost methane (€/GJ)	Excluding raw material cost	2,29	1,53
Production cost methane (€/GJ)	Excluding raw material cost	0,08	0,05
Break-even cost of seaweed (€/t d.b.)	Based on 58/GJ and 4,93 GJ/t	21	25
Production of electricity (MWh)	At 40% elec. efficiency	60570	302850
Production costs of electricity (€/MWh)	Excluding raw material cost	16	11
Break-even cost of seaweed (€/t d.b.)	Based on €120/MWh	63	66

2.5.4.2 *The cost estimations for the production of other products*

In this Section an overview of the different values of products that can be produced from macroalgae is provided. The economic overview for the macroalgae-based biorefinery concept is presented later in Section 2.6.5. Like explained in Section 2.5.2, the market for food is especially large, followed by the hydrocolloid market. There are also small markets for other applications, like fertilizer, cosmetics and animal feed (FAO, 2003). In Table 10, an overview is given of the potential value of several products when extracted from seaweed. It shows that the production of alginates, mannitol, fucoidan and human protein could give substantial profits.

Table 10. High-value co-products from ethanol production of macroalgae (Kraan, 2010; referred to Reith et al. 2005 and Wijfels 2009)**.**

Product	Market value ($/tonne)	Content (% of dry weight)	Value ($/tonne d.w.)
Alginates	6000	23	1380
Mannitol	6000	12	720
Fucoidan	12000	5	600
Iodine	14500	0,45	65,25
Potash	60	9,5	5,7
Phosphorus	1000	0,3	3
Protein human	5000	12	600
Protein feed	750	12	90
Lipids human	2000	3	60
Lipids feed	500	3	15
C-removed	15	33	4,95
N-removed	2000	3	60

Reith (2005) provided an overview of interesting products that could be produced from seaweed using certain assumptions for the concentration and extraction yields for seaweeds (see Table 11). This is his economic analysis of the production of platform chemicals. He presents an average value of $274 per tonne d.w., while the extraction of citric acid, butanediol, succinic acid and adipic acid would provide substantially higher values to the seaweed. Like mentioned before, the production methods for these platform chemicals are not established yet. In Reiths analysis, also the combination or exclusion of products is not addressed, like the potential seaweed species for this type of conversion.

Table 11. Platform chemicals that can be produced from seaweed making use of fermentation. Assumptions: 60% carbohydrates, 90% conversion efficiency (Reith et al., 2005)

Product	Market value	Production	Value	100000 tonnes/year		500.000 tonnes/year	
	$/tonne	kg/tonne seaweed	$/tonne seaweed	ktonne product	sales volume (M$/yr)	tonne product	sales volume (M$/year)
Ethanol	331	255	84	25400	8,4	127000	42
Acidic acid	728	247	179	24600	17,9	123000	89,5
Butyraldehyde	948	123	117	12300	11,7	61500	58,3
Adipic acid	1433	370	530	36900	52,9	184500	264,4
Butanol	904	123	111	12300	11,1	61500	55,6
Lactic acid	300	486	146	48600	14,6	243000	72,9
Succinic acid	772	429	331	42800	33	214000	165,1
Propylene glycol	1279	133	170	13300	17	66500	85
Glycerol	1279	247	315	24600	31,5	123000	157,3
Citric acid	1808	429	775	42800	77,4	214000	386,9
Proprion acid	904	227	205	22600	20,4	113000	102,1
2,3-Butanediol	1984	163	323	16200	32,1	81000	160,7
Average value	1056						
Average value seaweed (d.m)			274				

2.6 The macroalgae-based biorefinery

The production of single products from macroalgae is often not economically feasible, due to the high costs associated for the cultivation and harvesting of seaweed (Reith et al., 2005). Currently, there is a market of seaweed for consumption and for the production of hydrocolloids. But the prices of biofuel are too low to utilize seaweed as a feedstock for biofuel production. Therefore, the widely supported point of view of the scientific community is that there should be production of several products from macroalgae in order to make the production process economically feasible (see for example Burg et al., 2013; Reith et al., 2005). In this way, the feedstock can be used as efficient as possible and seaweed will be able to function as an alternative with many advantages compared with the conventional biological feedstocks for the production of biofuels and chemicals (Reith, Steketee, Brandenburg, & Sijtsma, 2006). The whole seaweed crop can be used, which is an important factor in the bio-based economy.

In this Section, the macroalgae-based biorefinery concept is studied further. First, the main ideas of the biorefinery concept will be presented. These ideas will be applied to macroalgae, and a so-called value pyramid will be composed. There will be a review of the studies on the macroalgae-based biorefinery. First, the proposed configurations and product mixes will be analyzed, and then the technical, economic and environmental aspects will be studied where possible. The analysis will reveal certain knowledge gaps that are still present.

2.6.1. The biorefinery concept

The discussion of the biorefinery concept is started with two definitions:

"*Biorefining is the sustainable processing of biomass into a spectrum of markeTable products and energy* (Cherubini, 2010, p. 1414; referred to IEA Bioenergy Task 42)".

"*A biorefinery is a facility (or network of facilities) that integrates biomass conversion processes and equipment to produce transportation biofuels, power, and chemicals from biomass* (Cherubini, 2010, p. 1414)".

This implies that the biomass will be converted into their main building blocks by a variety of different technologies to produce these compounds. The biorefinery is therefore not only focused on the production of biofuels, but also on the production of other valuable co-products. There is a strong analogy with a petroleum biorefinery, as mentioned in Section 1.4. Kafarov (2011) agrees that that there are similarities between a biorefinery and petroleum refinery, but also stresses the important differences between the two types of refineries. A similarity is that several products are produced from one feedstock or mixture. However, because biomass was not subjected to biodegradation to the extent that it happened to oil, there are more potential products to retrieve from biomass, as is shown in Figure 14 (Kafarov, 2011). The order in which this happens is important, because there is the possibility that some products can not be produced anymore after extraction of another product.

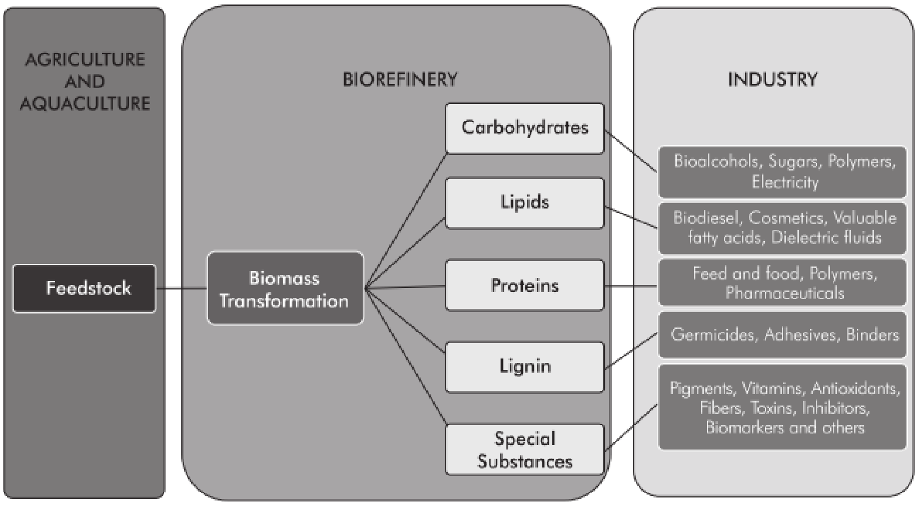


Figure 14. General outline of the biorefinery concept (Kafarov, 2011).

The conversion methods can be very different for the types of refineries. That is, for the petroleum refinery, the elements in the oil mixture are separated by making use of differences in boiling points in a distillation unit. After separation, the different elements are processed further. The conversion of the biomass in a biorefinery happens either by applying a thermochemical process, or by applying a biological conversion method. Qin, Müller and Cooper (2011) add that the reaction conditions should be relatively mild; otherwise the characteristics of the aimed products can change. Therefore some new processes and conversion techniques need to be developed. Subhadra (2010) mentions some other differences between feedstocks for an oil refinery and for a biorefinery. Biomass contains a lot of moisture, while oil is a very concentrated mixture of different hydrocarbons with a high energy density. Oil is often extracted from large reserves and has a high energy density, while there is a higher land requirement for the production of biofuels (due to the lower energy density). This can have consequences for the size of a production facility, and the way how the biomass is collected (e.g. transportation distance). Oil is a mixture of which the composition is often well-known, while biomass is subject to large seasonal variations (Cherubini, 2010).

Kerton et al. (2013) distinguishes three different types of biorefineries

- The first type: one feedstock is used to produce a single product using one process;
- The second type: one feedstock is used to produce a number or range of different products making use of multiple conversion methods;
- The third type: a mixed feedstock or low-value biomass is utilized to produce a range of products, making use of different conversion methods.

Strictly speaking the first type should not be called a biorefinery, because there is only one product produced. In this study, the focus will be mainly on the second type of biorefinery.

2.6.2 Macroalgae-based biorefinery scenarios

Subhadra (2011) states that in a biorefinery scenario at least one low-volume high-value chemical should be produced, together with at least one high-volume low-value transportation fuel. This way, the value from the feedstock can be maximized. The US Department of Energy (2010) explores the search for valuable co-products as bit further. The authors claim that a co-product should comply with one of the following criteria in order to have a business case:

- It should be identical to the (functional performance of the) existing product; in order to be competitive it should be at least 30% cheaper than the existing product. However, the natural origin could offer an additional advantage;
- It should be a new material with unique and useful characteristics.

This idea is developed further for microalgae. The writers present five different options on how to retrieve as much economic value from microalgae as possible. This is presented graphically in Figure 15. The different scenarios can be analyzed and compared to each other. Not all the products can be produced from macroalgae; for example the production of biodiesel would be less suitable.

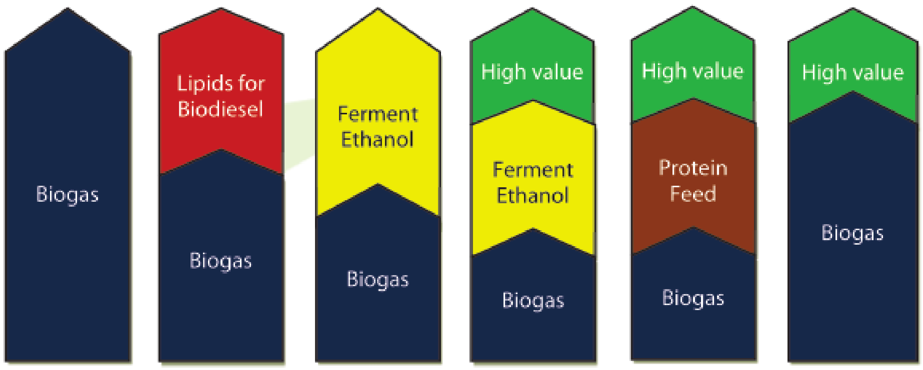


Figure 15. Different scenarios for algae biorefineries, more specifically aimed at microalgae (Bruton et al., 2009).

2.6.3 The value pyramid

While composing scenarios for the biorefinery concept, it could be helpful to use the value pyramid as a concept (Subhadra, 2010). A value pyramid shows the different products that can be produced from a feedstock, with the small-volume high-value products on top and the large-volume low-value products at the broad base of the pyramid. A value pyramid for microalgae is presented in Figure 16. This value pyramid nicely shows the different products that can be produced from a certain feedstock. It does not imply that all these products can be produced together.

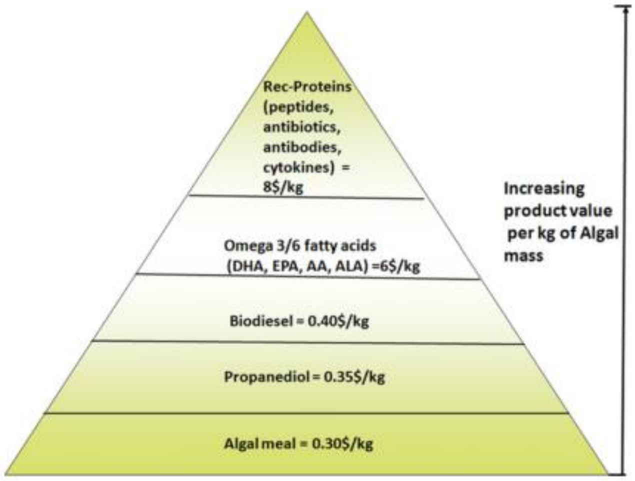


Figure 16. Value pyramid for multiple products from microalgae (Subhadra, 2010).

A similar value pyramid can be constructed for the case of macroalgae, which was not done before. This pyramid is presented in Figure 17. This value pyramid can be used for the determination of the optimal product mix. It becomes clear that the different fuels have a relatively low value. This is something to take into account when designing a case-study.

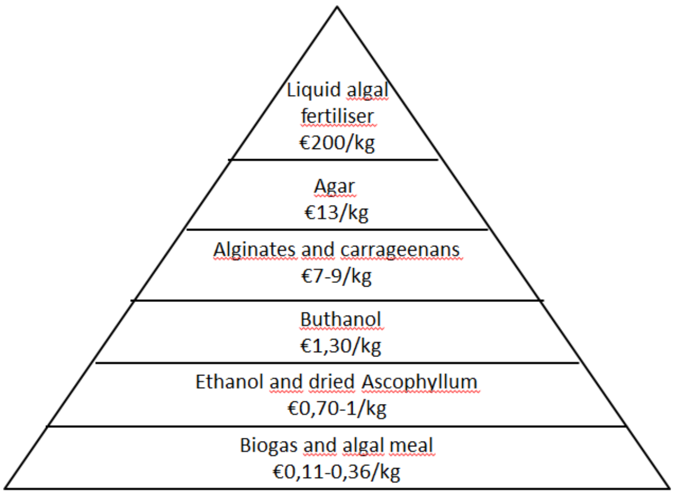


Figure 17. Concept of value pyramid for macroalgae. Data retrieved from Schlarb (2011), **numbers from 2008-2010.**

2.6.4 Macroalgae-based biorefinery configurations

In some studies, macroalgae-based biorefinery scenarios are presented. Some of these scenarios are presented in this section. Two examples are presented in Figure 18 and 19 (Hal & Huijgen, 2013). In the first case (Figure 18) mannitol is extracted from kelp. From the remaining part of the seaweed, the fucoidan is retrieved. Alginate is produced for the hydrocolloid industry. In the second case, the carbohydrates from Palmaria palmata are hydrolysed with a mild acid treatment method, to yield monomeric sugars. These sugars are converted into acetone, butanol and ethanol. The resulting fraction can be converted into biogas to yield a mixture of methanol, carbon dioxide and hydrogen gas.

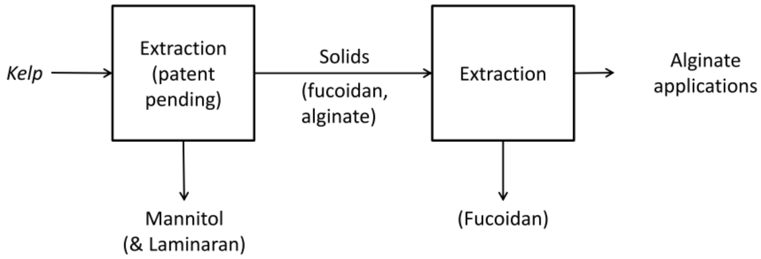


Figure 18. Product mix for kelp (Hal & Huijgen, 2013).

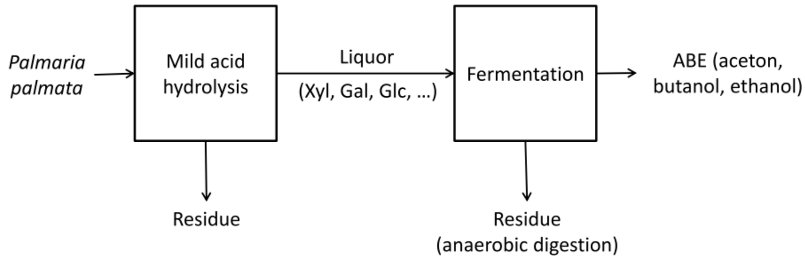


Figure 19. Product mix for *Palmaria digitata* (Hal & Huijgen, 2013)

Figure 20 (Horn, 2000) also shows a potential process scheme, in this case for Laminaria hyperborean. Here, firstly the methane is produced. Since the alginate is not hydrolyzed, this is extracted in a second step as a commercial product. According to Horn, this is the most economic decision when producing methane gas from seaweed. Horn considers mannitol and laminaran as a waste product of this process, but not everybody will agree on this. These carbohydrates could potentially be used for the production of other products or fuels.

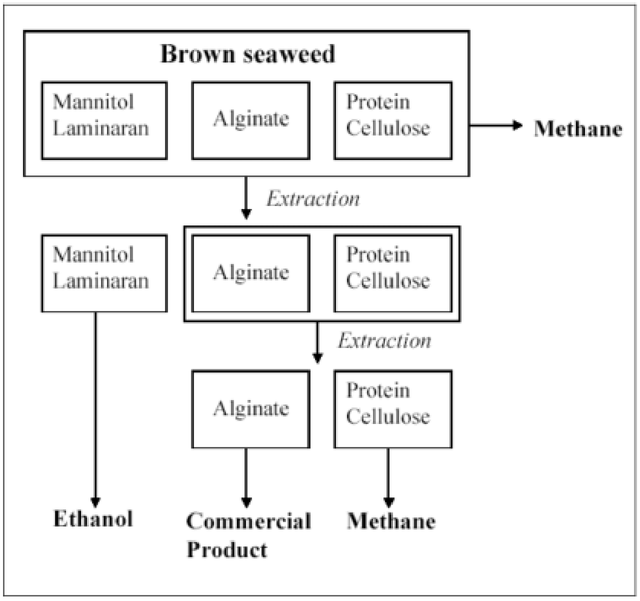


Figure 20. Processing scheme for the macroalgae-based biorefinery (Horn, 2000).

2.6.5 *Environmental analysis macro-algae based biorefinery*

The studies on the environmental impacts of biofuels produced from macroalgae are already scarce, the studies on the macroalgae-based biorefinery even more. An environmental analysis of the production of several products from macroalgae is complicated due to large gaps in the available literature. One exception is the study of Langlois et al. (2012), who considers the production of biogas ánd alginate in an LCA study.

Also Langlois et al. (2012) attempted to apply an LCA to the production of biomethane from offshore cultivated macroalgae. The strong aspect of this study is that two systems were compared with each other, and also a fossil reference system was included:

- Methane from anaerobic digestion of whole seaweeds
- Methane from anaerobic digestion of alginate extraction residues
- Natural gas from the EcoInvent database as a reference system

Furthermore, the macroalgae used for the analysis was cultivated by offshore cultivation, which could be more relevant to many production systems. The authors concluded that biofuel production from macroalgae could be interesting; however with current techniques the impacts are higher than the impacts of natural gas. Therefore there is a need for technical improvement before this biofuel production becomes beneficial from an environmental point of view. Suggestions made are to provide the electricity by a clean source (for example from offshore wind farms). For the production of methane from alginate extraction residues, the extraction process itself should be improved. An example of the different impact contributions of the biogas production from whole seaweeds is illustrated in Figure 21.

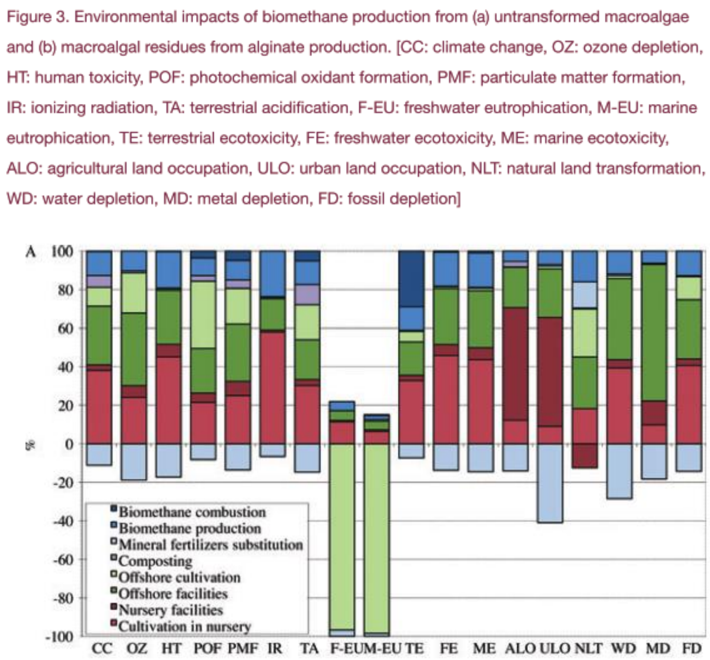


Figure 21. Impact distribution for biogas production from whole seaweeds (Langlois et al., 2012)

2.6.6 *Economic analysis macro-algae based biorefinery*

In many research reports, the conclusion was that the production of biofuels from macroalgae is not economical feasible with the current techniques (see for example Chynoweth, 2002; Reith et al., 2005; Roesijadi et al., 2010). In this section the biorefinery approach, where several products are produced, is analyzed from an economic perspective.

Reith (2005) did not only focus on the production of biofuels from macroalgae, but also paid attention to the potential of other products. In Table 12, the cost Figures for different products produced from seaweed, as two combinations of products are estimated. The first part of this Table was presented earlier in Section 2.4.3.2. It shows that it is a better option to produce both energy products and other products from seaweed, otherwise the value of the seaweed will be very low. The value of food products produced per tonne of seaweed has a higher value than the different combinations analyzed by Reith.

Table 12. Values of different products and product combinations. Retrieved and translated from Reith (2005)**.**

Application	Value end product $/tonne	Value fresh seaweed $/tonne	Value dry seaweed $/tonne
Food	$1.600	$1.600	$13.333
Phycolloids	$6.000	$264	$2.200
Platform chemicals	$1.050	$32	$270
Dyes (4%; extraction yield 90%)	$100.000	$264	$2.200
Farmaceuticals (1%; extraction yield 90%)	$500.000	$540	$4.500
Electricity by anaerobic digestion	Other Chapter	$8	$70
Bioethanol + electricity	Other Chapter	$5	$44
Electricity by Hydro Thermal Upgrading	Other Chapter	$7	$59
Phycolloids + methanol production remaining biomass			
Phycolloids (20%; extraction yield 90%)	$6.000	$130	$1.080
Electricity by anaerobic digestion	Other Chapter	$7	$56
Total			*$1.136*
Dyes + methanol production remaining biomass			
Dyes	$100.000	$432	$3.600
Electricity by anaerobic digestion		$8	$67
Total			*$3.667*

Table 12 shows that the production of fuels will result in a much lower value of the feedstock that the production of other products. The value of pharmaceuticals will give the highest value after food production. The production of pharmaceuticals is not established yet, thus this result should be considered as an indication. Reith also suggests producing platform chemicals from macroalgae, as discussed in Section 2.4.2.6. The economic aspects of producing these chemicals are quite positive (see Table 10). The value of the products will probably exceed the production costs of the seaweed. But as mentioned in Section 2.4.2.6, there is not a production method available to produce these chemicals.

2.7 The knowledge gap

The aim of this literature review was to give an overview of the available literature and reports about the cultivation, processing, market and biorefinery options of the macroalgae-based biorefinery. Also the environmental and economic performance was addressed.

The production of seaweed could offer advantages. The potential resource base is large. However, the production and harvesting of seaweed is still an expensive process. There is a need for efficient methods for the harvest and processing of the macroalgae. Furthermore, the carbohydrates from macroalgae are quite different than the carbohydrates of land-based crops. This introduces new challenges for conversion techniques already established for biofuel production from terrestrial crops. Not all these challenges are addressed by the available literature yet. Many authors agree that the production of fuels from macroalgae will only become economically feasible when more valuable products are produced from the feedstock. The scientific community is still struggling with the best options for this 'biorefinery concept'. The option suggested by Reith (2005) to produce platform chemicals from macroalgae could be very interesting. The market for these chemicals is big, but the industrial processes are not always established.

This is a common problem in the literature on macroalgae-based biorefineries. Very interesting ideas are introduced and researched, but the practical demonstrations are missing. This is a complicating factor for the analysis of the economics and the environmental effects of the biorefinery. In the next chapters, three case-studies will be presented, that might give novel insights in the macroalgae-based biorefinery.

3. Methods

In this section, the methods for the selection of appropriate case-studies, the economic and the environmental analysis are presented.

3.1 Species selection

In order to select suitable species as the studied feedstock for the different case-studies, concise and quantifiable criteria needs to be applied. After an extensive literature review of the available articles addressing these criteria, the most important criteria are selected. As an additional criterion the data availability is added. This is important, since there is a need for sufficient information to study a certain species in a case-study. The selection criteria are retrieved from different articles and reports (Australian Government, 2011; Chynoweth, 2002; Garofalo, 2011; Kelly & Dworjanyn, 2008; Lawton, de Nys, & Paul, 2013; Roberts & Upham, 2012; Roesijadi et al., 2008; Werner et al., 2004). Roughly, these criteria can be divided in three categories, which are cultivation criteria, harvesting criteria and criteria considering the conversion into products (see Figure 22). The first three criteria are being used as the main selection criteria. The criteria 4-8 are considered as supporting criteria. In Box 1, the criteria are explained and motivated further.

	Main criteria	**Measured as /from**
1.	Display high productivity	Kg d.w./ha/year
2.	Have a chemical structure with large potential for conversion to fuels	Composition data
3.	Have a high concentration of co-and by-products of value	Composition data
	Suppporting criteria	
4.	Have a rapid nutrient uptake	Results from studies
5.	Be robust, and should be able to withstand several conditions	Growing conditions
6.	Already be cultivated elsewhere at significant scale	Cultivation data
7.	Be easily harvested by mechanical techniques	Qualitative information
8.	Occur in the ecosystem under question already	Distribution and cultivation data

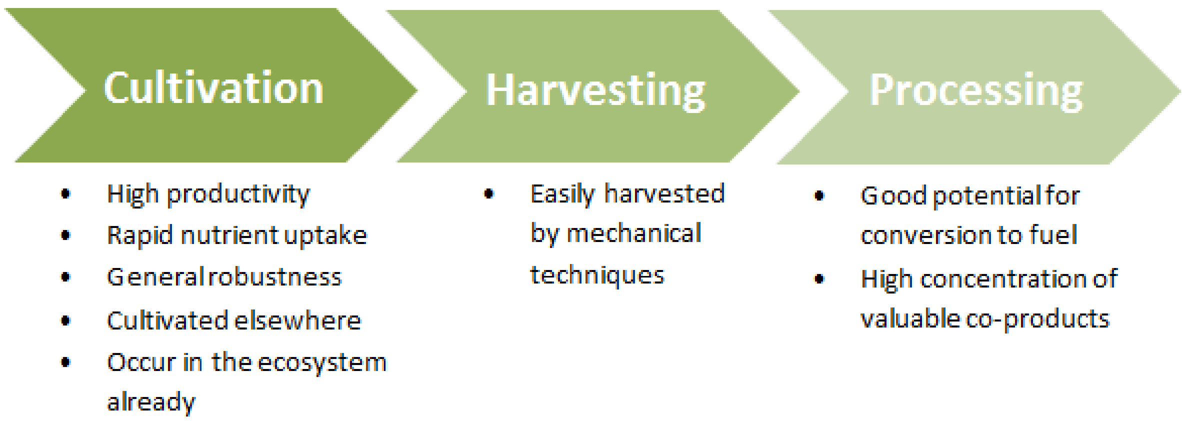


Figure 22. Main criteria for the selection of species, in the cultivation, harvesting and conversion stages

Main selection criteria

1. **Display high productivity**

High productivity will mean more feedstock to process and with the right composition more biofuels and co-products. A typical seaweed species with high productivity is Giant Kelp or *Macrocystis pyrifera*, already selected for biofuel production during the Marine Biomass Program (Brunswick, Columbia, & Korea, 2006). Thus, the productivity of a species can be an important decision factor for the selection of species. However, productivity in different seasons will fluctuate largely, which makes the data hard to compare. The climate where the seaweed will be cultivated is an important factor. The productivity will be measured as kg/ha/year. The photosynthetic efficiency[9], or quantum efficiency (Frost-Christensen & Sand-Jensen, 1992) could be treated as an additional measurement, since this factor is not dependent on the chosen cultivation location. Therefore this measure could be more reliable to use, but is often not available.

2. **Have a chemical composition with good potential for conversion to fuel**

The carbohydrate content is an important parameter of the potential for biofuel production of a certain species. The different types of carbohydrates are also very important, since some of the carbohydrates are hard to digest for micro-organisms. Therefore, as a first measure for the biofuel production potential, the carbohydrate content will be reported, since this is an important factor for bioethanol and biogas production. Furthermore, the lipid content will be reported, which is related to the production of biodiesel.

3. **Have a high concentration of co-and by-products of value**

This criterion is twofold, both the concentration of co-products as the value of the co-products should be as high as possible. For this criterion, the sales volume from the production of hydrocolloids from the genus in question in 2009 will be reported (Bixler & Porse, 2010). When possible, an indication of the concentration of these products present in the genera will be given. Also, the protein content is reported, since macroalgae could be a feedstock for the production of animal feed (Florentinus et al., 2008). Lastly, the potential products for medical applications will be listed (see Appendix B). Often these products will still be in a R&D stage.

Supporting selection criteria

4. **Have the potential for rapid nutrient translocation**

There is an important relation between nutrient uptake rates and productivity. Mainly nitrogen uptake is an important factor (Alwyn & Rees, 2003). A high uptake rate will make the plant grow faster, and can possibly extend the possibilities for cultivation systems. If a species can take up nutrients efficiently, there is less need for external nutrient supply. A basic theory for nutrient uptake is that with a higher surface area to volume ratio (SA:V), the nutrient uptake will be higher (Alwyn & Rees, 2003). When this information is not available (which is very common), the ease of nutrient uptake will be measured by using the Michaelis-Menten parameters V_{max} and K_m (see Figure 22). The value of V_{max} divided by K_m gives the affinity (A) for the nutrient under question (Runcie, Ritchie, & Larkum, 2003). It describes the uptake rate versus the substrate concentration, where higher values are suggesting a competitive advantage (Runcie et al., 2003). This affinity will be reported for the nutrients ammonium, nitrate and phosphate.

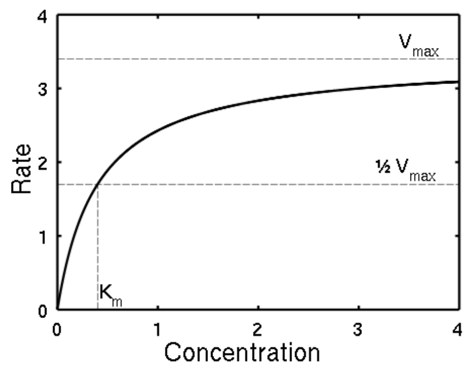


Figure 12. Michaelis-Menten curve. V_{max} is defined as the maximum uptake rate of a certain nutrient for a certain organism. K_m is the substrate concentration which leads to half of the maximum uptake rate by that organism.

5. **Be robust**

This criterion is hard to measure, mainly because the robustness of a genus is a very general term. It is important, because the species should be suitable for large-scale cultivation and shouldn't be floated away (Chynoweth, 2002). The robustness can't be measured in a purely quantitative way. Based on the information on cultivation conditions from FAO (2003), the genera will receive two scores on the general nutrient requirements and on the area and ease where the genera can grow. Therefore this is a qualitative criterion that will be used only as supporting information.

[9] Defined as the percentage of available light that is converted into biomass (Garofalo, 2011).

6. Are successfully cultivated elsewhere

When the selected genus is cultivated on a large scale, there is apparently already a large body of knowledge available on cultivation, biology, harvesting and processing of the genus. This could form an important advantage for a certain genus. Therefore, the production Figures of the last years can give a good indication of the opportunities of a certain genus. The statistical program FishstatJ (FAO 2013) will be used to report the quantities and values of the genera for the year 2010.

7. Can be easily harvested by mechanical techniques

For this criterion qualitative information on harvesting techniques and cultivation trials will be needed. Some of this data is available at FAO (2014), and in several articles (Florentinus et al., 2008; Garofalo, 2011; Rote et al., 2012; Titlyanov & Titlyanova, 2010). Often, if mechanical harvesting can be applied, this will have a positive influence on the economic viability of cultivation of a species. The genera will receive a score from 1 to 10. This grade is based on wheter it is known that the genus can be harvested mechanically. When there is no information available, the genus will not receive a score. Like criterion 6, this criterion is qualitative.

8. Occur in the studied ecosystem already

This factor is included, because there will be a preference for species that are present in an ecosystem already. Newly introduced species could affect ecosystem dynamics in unknown and sometimes unwanted ways (Florentinus et al., 2008). For this criterion, data from FishstatJ will be used. This statistical program also shows the specific countries where a genus is cultivated. For further distribution data, the database Algaebase is used. With this information, the continents where the genera occur will be indicated. This measure is very broad, and is less important than most of the other criteria.

First, the genera to be considered are selected on the basis of cultivation figures from FAO (2013). The nine genera globally cultivated in the largest quantities are studied further. Besides this, two additional genera that seemed to be interesting according to the literature are added to the list. Subsequently the genera are analyzed according to the criteria presented in Box 1.

3.2 Selection of products, product configurations and technologies

The aim of this Section is to select products, product configurations and technologies, in order to construct the case-studies (methods Section 3.3). These products will be adjusted to the species that are selected (see Section 3.1).

An important factor of the biorefinery concept is that most of the components of the feedstock can be utilized, aiming for only a minor waste flow. In order to determine the products and product mixes for the biorefinery, detailed composition data of the selected species is used. On the basis of this data, potential products can be determined, different product mixes can be proposed and the technologies can be studied. This will form the back-bone of the case-studies that are presented thereafter.

3.2.1 Selection of products

While considering data availability, different suitable products are selected. This happened on the basis of available production processes and economic data. When possible, the specific composition of the species is used for the analysis.

Both energy products (biofuels) as non-energy products will be analyzed here. For some products the exact conditions or conversion technology are not clear. These products cannot be analyzed in this stage and will not be considered further.

3.2.2 Selection of the product mixes

When different products are produced from one species, the production of one product has consequences for the quantity that can be produced for another process. This is considered for the different species. The most suitable combinations of products are selected. When possible, the product mixes will be based on a specific article or study which will form the basis of the case-study (Potts et al., 2012; Langlois et al., 2012; van der Wal et al., 2013).

3.2.3 Selection of the production technologies

Dependent on the data availability and quality, the most appropriate production technologies are selected. The information gathered will be presented as follows:

- A process flow chart, for the overview of the total process;
- Process conditions for the different steps; including temperature, pressure, compounds needed, energy input etcetera.
- Yield of the process, derived from literature.

Often, there are not industrial process conditions available for the selected products, especially when this is a specific combination of several products. When this is the case, the lab-study conditions will be adapted to an industrial process supported by literature.

3.3 Selection of the case-studies

The selected species, products and processes functioned as the basis for the case-studies. The case-studies consist of the following components (Figure 23). All these components are addressed in the case-studies and are also used in the following sections (the environmental and economic analysis).

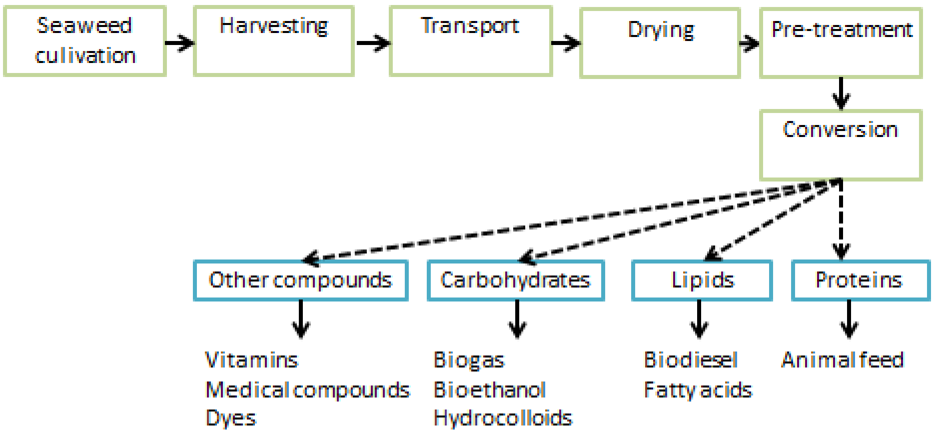


Figure 23. Overview of the different steps in the macroalgae-based biorefinery (based on Bruton et al., 2009; Linshiz, Berkeley, & Labs, 2013).

3.4 Environmental analysis

In the environmental analysis the largest environmental impact factors of the case-studies are analyzed. The different case-studies are compared with each other, in order to construct an LCA. Therefore, the principles and frameworks of ISO 14040 and the requirements and guidelines of ISO 14044 are being used (Goedkoop, Oele, Leijting, Ponsioen, & Meijer, 2013). The LCA consists of the following steps (Goedkoop et al., 2013):

- Defining the goal and scope. The reason to carry out the analysis, the functional unit to compare, the system boundaries and co-products.
- Life cycle inventory (LCI). All the material and energy inputs and outputs for the system are included in this database.
- Life cycle impact assessment (LCIA). Find out the environmental relevance of these inputs and outputs using pre-defined impact factors.

- Interpretation of the results and comparison.

The studies on the environmental aspects of the macroalgae-based biorefinery are scarce. The couple of existing LCA studies formed the basis of this Section (Aresta et al., 2005; Langlois et al., 2012; Romagnoli et al., 2010). The database used is EcoInvent. When the required information was not present, reasonable assumptions for the inventory were made.

3.4.1 Goal and scope

By studying three different case-studies, the most important environmental impacts will be identified. The available data is not always reliable (with Langlois et al., 2012 as an important example). Therefore, the goal of the study is to construct Life Cycle Inventories which could function as an example for further research and to identify the main environmental impacts of the processes. The systems of the case-studies will be compared with each other.

The impact of the cultivation of the seaweed is very relevant for the environmental performance. Therefore, making use of a cradle-to-factory-gate approach is justified.

3.4.2 Functional unit and allocation

Because the products of the different case-studies differ from each other, the functional unit used is 1 MJ of energy content. The biorefinery concept allows to produce more than one product, besides the production of energy. Therefore, allocation is a crucial part of the analysis.

When there are also non-energy products, an economic allocation will be applied. This is the last option according to the ISO standard, but it can be the best available method when other data is missing. For example, when both energy-and other products are produced, energy content allocation or allocation based on other physical properties is not possible (Goedkoop et al., 2013). Another option would be to apply mass allocation, but this would be unfavourable since a large part of the impacts could be allocated to a heavy waste product.

Economic allocation does reflect the value of an output and distinguishes waste from an output. However, the impact of price fluctuations could change the allocation significantly, which is regarded as a major weakness of the method (Goedkoop et al., 2013). The economic allocation is constructed by making use of the most recent and reliable price information. The quantities produced per kg dry weight are multiplied with the value per unit of the product. The percentage of the total value per kg dry weight shows how the effects are attributed to that product.

3.4.3 Impact factors

The impact factors that are studied are non-renewable energy use (NREU), renewable energy use (REU) and global warming potential (with a time horizon of 100 years, GWP100) (Romagnoli et al., 2010). NREU and REU are interesting from an energy perspective, because there is energy production in the case-studies as well. The effects of climate change differ between the short and the long run. Other time horizons that can be used are 20 and 500 years. Since 100 years is also used as a time horizon by the IPCC, this is being used here as a default (Roes, 2011).

3.4.4 Life cycle inventories

The life cycle inventories for the different cases are presented in Appendix D. Some simplifications are applied, since not all the required information is available. Parts of the LCI are adopted from the excisting study of Langlois (2012). In this article, the most complete LCI to-date is presented. For the case-studies that are not similar to the case-study presented in Langlois and where parts of the inventory is missing, the data will be calculated or estimated on the basis of assumptions.

- The material requirements are adapted to the difference in productivity of the different species;
- The heating and cooling requirements are calculated on the basis of the heating requirements in Langlois (2012). This requirement will be calculated using the known temperature difference and mass of the solution, so that a value expressed in J/K/kg will be retrieved.;
- The energy requirements for processes other than heating and cooling (like crushing and stirring) are roughly adapted from Langlois (2012);
- The materials for the buildings and facilities are also roughly adapted from Langlois (2012);
- When parts of the LCI from Langlois et al. (2012) do not seem to be realistic, these entries are adapted or removed. This will be indicated in the LCIs in appendix D.
- The energy requirements for centrifuging are adapted from the BREW report (European Commission, 2006);
- The specific quantities of substances to be added to the process are retrieved from literature studies and are described in section 4.2 and 4.3.
- The energy requirements for the separation of products (only applicable to case-study 3) are down-scaled from Wu et al. (2007), an LCA study for a corn-based ABE fermentation plant.

3.5 Economic analysis

In this section, the methods for the prospective economic analysis are presented. This gives an idea of the largest cost factors, but also of the economic inefficiencies of the studied processes. All the numbers were updated to 2014 Euros. The economic performance will be presented in several ways (the abbreviations are explained at page 4):

- A contributional analysis of the different stages of the case-studies
- A specification of the prices of the utilities and compounds used during the processes
- The NPV of the project (Blok, 2007). The annuity factor α was calculated using a discount rate (r) of 5 % and a lifetime (L) of 20 years (see equations 3.5.1 and 3.5.2).
- The simple Pay-Back Period of the project

Equation 3.5.1 (Blok, 2007)

$$NPV = -I + \frac{B - C}{\propto}$$

Equation 3.5.2 (Blok, 2007)

$$\propto = \frac{r}{1 - (1 + r)^{-L}}$$

Equation 3.5.3 (Blok, 2007)

$$PBP = \frac{I}{B - C}$$

Equation 3.5.4 (Ereev & Patel, 2012)

$$(Cost\ equipment)_X = (Cost\ equipment)_{base} \times \left(\frac{Capacity\ X}{Capacity\ base}\right)^{EXP}$$

The costs for the different stages will be retrieved or estimated in several ways as presented below. All the prices used are updated to 2014 Euros using exchange rates and inflation calculators.

Cultivation and Not enough data is available to make a concise and well-founded calculation for the

harvesting	cultivation costs. Therefore a literature review will be done in order to find the best estimates possible. For harvesting, a value per hectare is chosen, to account for the large differences in cultivation area.
Drying	The costs for drying are not considered separately, because it is assumed that the biomass would be dried naturally.
Utilities	By making use of the life cycle inventories, the total gas and energy requirements are retrieved. For the electricity price, different price levels are used depending on the electricity requirement. One gas price was used (European Commission, 2014).
Chemicals and other compounds	By making use of the life cycle inventories, the requirements for chemicals and compounds are calculated. For most of the prices for these compounds indicative prices were used (ICIS, 2006).
Equipment for extraction process	The costs of the equipment required for the biorefineries is estimated making use of the equipment database in SCENT (ProSuite, n.d.). First, an inventory of the required equipment will be prepared. With help of a scaling law with 0,65 as a scaling exponent, the price could be calculated for the appropriate scale (Ereev & Patel, 2012). Since there is no additional information available for the appropriate scaling factors for different types of equipment, this number will be used as a default factor. The other costs besides equipment will be calculated using cost category percentages for an ABE batch fermentation plant, to yield the total investment costs and O&M costs (Gapes, 2000).
Biogas plant	For the cost estimation of the biogas plant, a paper reviewing different plant sizes was used (Walla & Schneeberger, 2008). By calculating the substrate flow per hour of the different plant-sizes and case-studies, the appropriate size was determined. Because the biogas plant treated in Walla produced electricity, the costs were divided by a factor of 1.2, to account for the simpler design of the plants in the case-studies. Both the investment and O&M costs were based on this study.
ABE plant	For the ABE plant of case-study 1, the costs estimations reported in Gapes (2000) were used. A graphical representation of the investment cost is presented in Figure 23.
O&M costs	The O&M costs are also retrieved from literature. These costs are indicated in Gapes (2000) and Walla and Schneeberger (2008) and will be used as an estimation.
Profits	For the profits of the different products, the prices and quantities indicated in the economic allocation tables will be used.

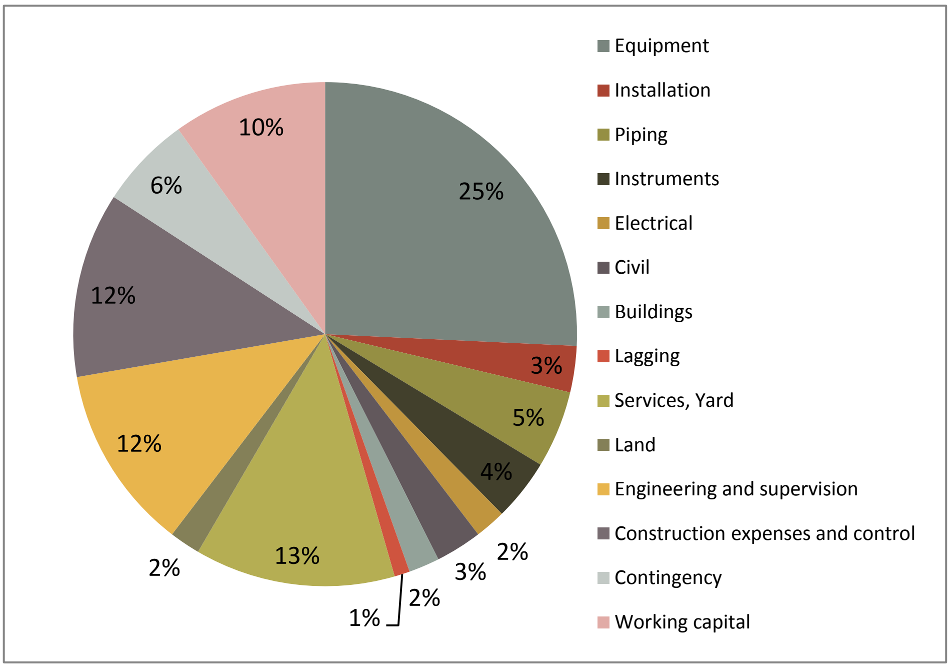


Figure 23. Distribution of investment costs for an ABE fermentation plant (Gapes, 2000)**. Total costs for this facility are €3,17 million (2014 Euros).**

3.6 Sensitivity analysis

The aim of the sensitivity analysis is to determine what the influence of a variation in different variables will have on the economic and environmental analysis. This is important, because some variables will have large effects on the outcomes. Especially the parameters that are based on assumptions will have to be checked in order to see what the influence is of another assumed value. These assumed parameters bear a significant uncertainty, which will have it's effect on the outcomes. The factors that will be studied will be determined after the establishment of the case-studies. Some of these parameters have already been identified as critical parameters for the performance of the macroalgae-based biorefineries:

- The influence of the assumed productivity of the species;
- The influence of the yield assumed in the conversion processes;
- The influence of cultivation costs on the economic performance.

The sensitivity analysis will be done in Excel, by using a 'what-if analysis' with one variable. This means that for a certain outcome, one of the input variables will be varied in a certain range. Excel calculates the effect this has on the outcome.

4. Results and discussion

In this Chapter, the results of the case-studies are presented. The calculations for the economic, technical and environmental analysis are performed and explained. The results will be discussed at the same time to end with a general discussion in Section 4.7.

4.1 Species selection

The genera that are studied were selected by production volume and value in 2010, based on Fishstat data (FAO, 2013). These genera were listed in Table 1 (Section 2.2). Besides these 9 genera, *Macrocystis* (more specifically *M. pyrifera)* was included in the analysis as well. This species was suggested as promising species for mass cultivation in the Marine Biomass Program from the American Government in 1986-1990 (Chynoweth, 2002; Reith et al., 2005). *Gelidium* is widely used for agar production besides *Gracilaria*, and was therefore included in the analysis (Bixler & Porse, 2010). This genus is currently not cultivated due to economic reasons; instead it is harvested from natural stocks. The genera were analyzed on the basis of the criteria explained in box 1. The results of the main criteria are presented in Table 13. The data is from many different sources. Often, numbers are reported for specific species. The differences between species within genera can be quite big, so care must be taken when using these numbers.

Table 13. Results of criteria 1-3. Productivity, fuel potential and co-products. Sources are various research articles and reports.

Criterion	**1. Productivity**		**2. Fuel potential**				**3. High-value products**		
Measurement	Average productivity	Range in productivity	Average carbohydrate content	Range carbohydrate content	Average lipid content	Range lipid content	Sales volume in 2009 from hydrocolloids	Average protein content	Range protein content
Unit	Tonne d.w./ha/yr	Tonne d.w./ha/yr	% d.w.	% d.w.	% d.w.	% d.w.	Million US$	% d.w.	% d.w.
Genus									
Laminaria	52	15-131	36,0	30,3-41,7	1,3	0,7-2	168,5	8,9	2,5-15
Eucheuma	36		23,4	15,2-26,5	0,5	0,2-1,1	59,9	9,0	2-12,6
Kappaphycus	32	13-42	27,4		0,7	0,7-0,8	416,3	16,2	16,2-16,3
Gracilaria	40	3-127	39,1	25,1-63,1	1,3	0,3-3,3	137,7	9,9	5,0-23,0
Porphyra	3		46,0	40,7-56,4	1,7	0,7-3,8		30,5	19,7-43,6
Undaria	24		38,4	28,6-47,4	3,1	1,1-5,2		19,3	9,1-28,7
Sargassum	35	25,6-43,8	3,7	3,4-4,1	0,1	0,07-0,09		8,7	8,0-9,4
Ulva	105	22,5-265	44,9	19-67	3,2	0-8,0		17,5	8,5-27,2
Caulerpa			3,6	3,3-3,9	0,1	0,06-0,12		4,0	3,8-4,2
Macrocystis	31	12-62					19,1		
Gelidium			41,9	40,6-43,1	1,7	0,9-3,2	35,1	11,5	10,3-12,3
Average of all genera	**40**		**30**		**1**		**139**	**14**	

4.1.1 Productivity

The average productivity of all genera together was 40 tonnes dry weight per hectare per year. Note that not for all genera data is available. For the cultivation of *Caulerpa* no productivity data was found at all. This was also the case for *Gelidium*, but this is expected since *Gelidium* is not cultivated on a commercial scale. For some important genera only one value was found, which is interesting because for example *Eucheuma* is the second most cultivated genus in quantity (FAO, 2013).

High productivity was found for *Ulva, Laminaria* and *Gracilaria*. Care must be taken when interpreting these numbers because of two reasons. Firstly the ranges are often quite big for some of the species. This is also caused by the second reason. The sources used sometimes report commercial rates, and sometimes experimental rates under optimal and very energy-intensive conditions. An example of this is the cultivation of *Ulva*, which is occasionally very high. Many of the ranges are from projects where the *Ulva* species are co-cultivated with fish species (Bruton et al., 2009; Garofalo, 2011). It could be that this type of cultivation is less suitable for large-scale cultivation.

According to these numbers*, Laminaria* seems to be a good option for large scale production. *Kappaphycus* has a reasonable productivity range as well (13-42), which is also true for *Macrocystis* (12-62) and *Sargassum* (25,6-43,8). The reported range for *Gracilaria* is very large, as well as for *Ulva* species. While productivity is a very important factor for the species selection, the prevalence of productivity data is not always sufficient to compare genera with each other. Interestingly enough, the productivity of Porphyra is very small. The source of this number was a personal communication (Kelly & Dworjanyn, 2008), and therefore it cannot be checked. There were no other sources reporting productivity numbers for this genus.

4.1.2 Fuel potential

For the fuel potential, the carbohydrate content was used as a rough measure (this determines partly if the seaweed can be converted into bioethanol). This fuel potential is also dependent on the type of carbohydrates present in the macroalgae, but there was not enough data available to report this for all the genera. Besides the carbohydrate content, the lipid content gives information on the possibility of biodiesel production. Finally, the carbohydrate, lipid and protein content together is an important measure for the biogas production potential (Chynoweth, 2002).

The data availability for the composition of the genera was better than for the productivity of the genera. The average carbohydrate content was 30%. High carbohydrate contents were found for *Porphyra* (46,0%), *Ulva* (44,9%), *Gelidium* 41,9%) and *Gracilaria* (39,1%). So species from these genera are potential candidates for bioethanol production. For *Sargassum* and *Caulerpa*, notable low carbohydrate contents were reported. These contents where both reported in the same source (Robledo & Freile Pelegrín, 1997). In this report, the compositition of six species was analyzed; compared with the other four species the values for *Sargassum* and *Caulerpa* was low.

Besides the carbohydrate content, also the lipid content was reported. This was often found to be very low. The average percentage was 1%, and *Ulva* and *Undaria* stood out with an average value of respectively 3,2% and 3,1%. Also for *Porphyra* and *Gelidium* moderately high contents were reported (for both genera 1,7%). Like mentioned in section 2.5.1.3, the production of biodiesel is most-often more suitable for microalgae than for macroalgae (Jones & Mayfield, 2012).

For the production of biomethane, the carbohydrate content as the lipid and protein content is an important factor (Chynoweth, 2002). Based on table 13, the genera Ulva and Undaria have high contents for all these three components.

4.1.3 High-value metabolites

For the production of co-products, it is complicated to find indicators which are available for most of the genera. Here, the sales volume of the hydrocolloids was used to give an indication of the market size for these products. The sales volume was deduced from Bixler & Porse (2010). The value for carrageenan production from *Kappaphycus* was the highest in 2009, followed by *Laminaria* for agarose production and subsequently by *Gracilaria* for agar production. The genus *Ulva* could be used for the production of ulvan, which is thought to have potential pharmaceutical applications (Alves, Sousa, & Reis, 2012; Lahaye & Robic, 2007). However, the applications of ulvan are still in an experimental phase. The ulvan content is reported as 8-30% (Bruton et al., 2009).

Another indicator used here is the protein content. Protein can be converted to biogas in the process of anaerobic digestion (Romagnoli et al., 2010); but it also gives an indication of the suitability of a genus for the production of animal or abalone feed (FAO, 2003). The average protein content is 14%, but mainly *Porphyra* has a much higher protein content (30,5 %). Genera with reasonable protein contents are *Undaria* (19,3%), *Ulva* (17,5%) and *Kappaphycus (16,2%)*. Other reported species for animal or fish feed are *Macrocystis* and *Gracilaria* (FAO, 2003). However, there was no composition data available for *Macrocystis*, and from this data *Gracilaria* does not show to have a high protein content (9,9%).

Besides these products, the macroalgae could be used for the production of platform chemicals as well, as described in Section 2.5.4.2 (table 11). There is not a production method available for these chemicals yet (Reith et al., 2005). The carbohydrate content was applied as a rough indicator for the viability of this process, since the chemicals could be produced from carbohydrates.

Preliminary conclusion

For most of the genera, the data availability was not sufficient. These genera could be suitable for the macroalgae-based biorefinery, but there is currently not enough information available. This is mainly true for *Eucheuma, Porpyra, Undaria, Sargassum, Caulerpa* and Gelidium. This observation already excludes a number of options. *Laminaria, Kappaphycus, Gracilaria, Ulva* and *Macrocystis* are genera for which enough data seems to be present.

Ulva seems to be a very interesting option to consider as a feedstock for a macroalgae-based biorefinery. High productivity values are reported, and the potential for fuel production seems to be good. The high protein content reported is also an interesting factor. The production of ulvan from *Ulva* species is still a factor of uncertainty, since it is not completely clear for what applications ulvan can be used.

The big advantage of *Laminaria* is that it is already produced on a large scale. The reported productivity values are based on commercial production, which makes these values probably more realistic than others. Also the production of alginate from *Laminaria* species could be an interesting option. *Laminaria* is not characterized by an outstanding high carbohydrate content.

Gracilaria is characterized by a sufficient productivity and a high carbohydrate content. The genus is well-known due to its applications in the hydrocolloid industry (for agar production). So there is also quite some data available for *Gracilaria*. Therefore it is also considered as an interesting candidate for the macroalgae-based biorefinery.

Kappaphycus offers opportunities, since the market for carrageenan is quite big. However, the other reported values for this genus are not notably high.

Because of the use of Macrocystis during the Marine Biomass Program, this genus was considered as an option. However, the data availability is not sufficient to draw conclusions on the suitability of this genus as a feedstock for the biorefinery. Unfortunately, many of the reports are not accessible, and are only discussed to a limited extent in the report by Chynoweth (2002)*. The composition data for Macrocystis is very limited.*

The criteria described above will be the main decision factors. The findings of the resulting criteria (criteria 4-8) are summarized in Table 14. These criteria offered additional data for the genera selection.

Table 14. Results of criteria 4-8.

Criterion	4. Nutrient uptake			5. Robustness	6. Cultivated elsewhere		7. Harvested mechanically	8. Occur in eco-system	
Measurement	Average affinity index (Vmax/Km) ammonium	Average affinity index (Vmax/Km) nitrate	Average affinity index (Vmax/Km) phosphate	Based on possible growing locations and conditions	Quantity 2010	Value 2010	Based on potential or current	Cultivated in number of continents	Distribution in number of continents
Source	Alwyn and Rees (2003)			FAO (2003), Florentinus (2008)	FishstatJ (2013)		Chynoweth (2002), Bruton (2008) Garofalo	Algaebase. org	
Unit	(Micromol/g d.w./h)/micromol	(Micromol/g d.w./h)/micromol	(Micromol/g d.w./h)/micromol	Score out of 10	Tonnes	Thousands US$	Score out of 10	Out of 7 continents	Out of continents
Genus									
Laminaria	0,4	7,3	0,4	7	5146883	300868	8	1	4
Eucheuma				5	3748000	1143474	4	4	4
Kappaphycus				5	1874577	265077		3	4
Gracilaria	5,2	13,3		9	1717474	540458	5,5	3	4
Porphyra				6	1647734	1162837		1	7
Undaria	10,1			6	1537339	666865		1	3
Sargassum	2,7		1,7	6	78210	35977	7	1	6
Ulva	7,7	45,9		6	4531	3691	6,5	1	7
Caulerpa	0,2			4	4309	2562		1	5
Macrocystis	4,1	2,0		7	12	12	8,5	1	4
Gelidium				8	0	0	6,5	-	6
Average of all genera	**4,4**	**17,2**	**1,0**	**6,3**	**1432643**	**374711**	**6,6**	**1,7**	**4,9**

4.1.4 High nutrient uptake

To measure the nutrient uptake, the affinity index was used[10] (Runcie et al., 2003). The experiments used for the determination of this index, were done on different species with sometimes diverging values (Runcie, 2003). Therefore, it was interesting to see whether the genera with a high average affinity index, also show to have a high average productivity. Not for all the genera the affinity index could be determined, for phosphate it is only determined for two genera and therefore it will not be considered.

Ulva species and *Gracilaria* both received high scores on ammonium and nitrate uptake, which corresponds with the high productivity of these species. *Laminaria* however, also showed to have a high annual productivity, but did not stand out in the numbers of nutrient uptake. Furthermore, the genera *Sargassum, Caulerpa* and *Macrocystis* do not show a rapid nutrient uptake potential according to this indicator. The indicator showed to be partly useful as a supportive criterion, since for some genera it correctly corresponded with the productivity. However, the experiments were based on one source only, and were done for a limited number of species. Therefore it did not serve as an important decision factor for the genera selection.

4.1.5 General robustness

The general robustness of a genus could be important when comparing different cultivation systems and locations with each other. The grade gives some information on the different locations and water temperatures where the genera could grow, and also about the growing conditions and nutrient requirements. However, the grade was given based only on qualitative information, and could be subject to discussion. Therefore this criterion could be used as an additional advantage or disadvantage for a genus.

Gracilaria (9/10) is a robust species which is easy to grow, and *Gelidium* (8/10) is able to survive with low nutrient concentrations. Also *Laminaria* (7/10) can grow on different sea bottoms and in a big range of temperatures. A low grade is reserved for *Caulerpa* (4/10), which grows in a small range of temperatures, is susceptible for changes in salinity and can only grow in protected areas. *Eucheuma* (5/10) needs to be exposed to high-temperature water, bright light and moderate to strong water currents. This is also the case for *Kappaphycus* (5/10), which needs slower water flows.

4.1.6 Cultivated elsewhere

The quantity of cultivation of the different genera ranked the list of considered genera in the first place. The reasoning behind this is that on average there will be more knowledge on the cultivation of largely cultivated genera. *Laminaria/Saccharina* and *Eucheuma* are cultivated in very large quantities. The genera *Kappaphycus, Gracilaria, Porphyra and Undaria* are also cultivated in significant numbers. Unfortunately, there is not always sufficient scientific literature available for the genera listed here.

Comparing the most important genera in quantity and value in 2010 is interesting. The most cultivated species in weight were *Laminaria, Eucheuma* and *Kappaphycus* respectively, while the genera with the highest value were *Porphyra, Eucheuma* and *Undaria.* The average value per kg harvested was the highest for *Ulva* and *Porphyra*. The database does not offer information on the specific products and values of the genera.

4.1.7 Harvested mechanically

For some genera there was no information available on the possibility of mechanical harvesting. For others there are some concepts available, or methods that are functioning well. The main example is *Macrocystis*, earlier *Macrocystis pyrifera* was harvested mechanically for biofuel production. This could happen on a big scale, since the growing pattern of the species is suitable for mechanical harvesting (Chynoweth, 2002). Special

[10] The value of V_{max} divided by K_m provides the affinity (A) for the nutrient under question

ships were designed to harvest this species, which was pumped up through pipes (Kelly & Dworjanyn, 2008; Roesijadi et al., 2010; Rote et al., 2012).

This puts this species in a more important position than before. For *Laminaria*, mechanical harvesting is also taking place, mainly in Asia. In France, so-called scoubidou devices are used, while in Norway trawlers operated from a boat were developed specifically for the hydrocolloid industry (Bruton et al., 2009). Interesting concepts for the harvesting of *Sargassum* do exist, but these concepts are not in use yet. Gelidium is harvested by divers, manually or with help of special machines (FAO, 2003). *Ulva* can be harvested from the wild using mechanical harvesters (Garofalo, 2011). For many genera, no specific harvesting methods were mentioned in literature, however there are some general ideas. The US Department of Energy (2010) stresses the need of technology transfer from the important seaweed cultivation countries in Asia for successful cultivation trials. In the article, no specific reasons are mentioned why certain harvesting concepts couldn't be used for other genera. In order to establish large-scale harvesting, large ships should be developed involving mowing or dredging (US Department of Energy, 2010). Generally speaking, there is not much information available about the possibilities for mechanical harvesting.

4.1.8 Occur in the ecosystem already

This criterion becomes more important when a specific location for cultivation is known. When species are introduced that are not native in the ecosystem, they could cause unwanted effects or a change in the equilibrium. Widespread genera could offer a small advantage in the species selection, because the chance will be smaller that they will cause these potential effects. When elaborating on a certain species it becomes more important if this species is already present in the ecosystem. Widespread genera are *Ulva, Porphyra* and *Gelidium*; while *Undaria* is less widespread.

Concluding remarks

Also after analyzing the resulting criteria, *Laminaria/Saccharina, Ulva* and *Gracilaria* still seemed to be promising genera to study further. There is a lot of data available for *Laminaria* cultivation and conversion, since it is cultivated in large quantities. It has a considerable productivity and an interesting composition. *Ulva* stood out as well, with a high potential productivity and a beneficial composition. The same was true for *Gracilaria,* but there was not all the required data available to study this genus further. Therefore, the focus will be mainly on these two genera.

Macrocystis used to be a well-studied genus, mainly in the sixties in the USA. It still seemed to be a suitable genus for a biorefinery, but many of the reports with useful information are not accessible. The lack of data issue is also important for *Eucheuma, Caulerpa, Sargassum* and *Gelidium. Undaria* could be interesting, but does not stand out in most of the criteria. *Porphyra* has a favorable composition with a high carbohydrate and protein content.

4.2 Selection of products, product mixes and technologies

For the elaboration of the case-studies, the technologies that will be used needed to be described. The reaction conditions and type of reactors need to be clear. Also, there was a requirement for information of the economic aspects of these technologies and products. Therefore the data availability of the different processes was an important factor for determining the product mixes.

Many of the articles describing methods and results for the production of a certain product from seaweed are based on experiments on a small scale. These results needed to be extrapolated, to apply this to a larger scale. The studies from Reith et al (2005), Roesijadi, Copping, & Huesemann, (2008) and Chynoweth (2002) were very useful in this respect, since in these studies assumptions are made for larger-scale plants which could form the foundation for the case-studies proposed here.

4.2.1 Selection of products

For the production of many products there was not enough information available in order to use the process in a case-study. An important example is the production of platform chemicals from carbohydrates introduced in Reith (2005); the author admits that there is currently not a production method available. The same is true for the potential medical and pharmaceutical applications, reviewed by several authors (Australian Government, 2011; Smit, 2004). This reduced the number of potential products drastically, since there is also a need for environmental and economic parameters to study the processes. This means that the research on these products is not advanced enough to apply in these case-studies.

The main commercial products produced from macroalgae are the hydrocolloids agar, alginate and carrageenan (FAO, 2003). These processes are described in literature, but the exact processing conditions are only seldom explained due to confidentiality. Another recently introduced option is the production of ulvan, a polysaccharide from *Ulva species*, however the commercial value and applications remain to be unclear (Alves et al., 2012; Chiellini & Morelli, 2011). Besides these products, some sources also mention the commercial production of liquid fertilizer and animal feed from macroalgae (Roesijadi et al., 2010), while this process is not very clearly described in literature.

The production of biofuels is discussed more extensively in literature. There are basically four different options which were reviewed earlier in Section 2.5.1. It became clear that the conversion to biodiesel (Fragale et al., 2005; Maceiras et al., 2011) and biohydrogen (Lee, Park, Sim, & Lee, 2009) is not very suitable for macroalgae. The production of biogas and bioethanol on the other hand seems to be a better option (Borines, de Leon, & McHenry, 2011; Chynoweth, 2002; Kumar et al., 2013). Concluding this, the following products were considered: agar, alginate, carrageenan, ulvan, liquid fertilizer, compost, animal feed, biogas and bioethanol. These potential products need to be translated into case-studies where a combination of products is produced from one species.

4.2.2 Selection of product mixes

In this section, the product mixes will be described making use of the two proposed species; *Ulva lactuca and Saccharina latissima.* In order to have a clear overview of the composition of the species, detailed composition data is provided in Appendix C. For the three case-studies, some articles formed the basis for the design of the case-study. An overview of the different product mixes and studied species is provided in Table 15.

According to Jard et al. (2013) the methane potentials of *Saccharina latissima* and *Ulva lactuca* are 0,209 and 0,241l CH_4/g VS. This potential is dependent mainly on the amount of components that can be degraded to CH_4 and CO_2, which are protein, lipid and carbohydrates (Jard et al., 2013). For the first case-study, three products will be studied. As a high-value product sodium alginate will be produced. The residues are sent to a biogas plant for biomethane production. The waste is converted into compost and liquid fertilizer (used during the cultivation stage). For the second case-study, ulvan is extracted from *Ulva lactuca*. The residues are utilized for biogas production as well, combined with compost production. In the third case-study, *Ulva lactuca* is subject to ABE fermentation.

Table 15. Overview of product mixes that will be studied in the different case-studies.

Case-study	1A, 1B	2A, 2B	3
Species	*Saccharina latissima* (without and with cellulose)	*Ulva lactuca* (without and with cellulose)	*Ulva lactuca*
Product 1	Sodium alginate	Ulvan	Butanol
Product 2	Biogas	Biogas	Acetone
Product 3	Compost	Compost	Ethanol
Main source	Langlois et al. (2012)	Yaich et al. (2013) Langlois et al. (2012)	Potts et al. (2012) Wu et al. (2007)

4.2.3 Selection of technologies and protocols

It is not uncommon that extraction or conversion methodologies are only described on a small scale in literature. The industrial processes are often not publically available, therefore by using reasonable assumptions the lab protocols have to be adjusted to larger-scale processes. The protocols are explained here in their original form, while the adjustments are explained in Section 4.3 (selection of the case-studies).

4.2.3.1 Extraction of alginate

For the extraction of sodium alginate, the protocol from Langlois (p. 393, 2012) was used, partly because there is a lot of data provided in this LCA study which can be adopted for this study. Besides this, there are not many extraction processes publically available. Some major adaptations were applied to the process, because it did not seem feasible at a larger scale.

- The biomass is washed and crushed.
- The biomass is treated with alcohol (which is recycled).
- Subsequently the soluble fraction is extracted using HCl[11] and dewatered using a vibrating sieve.
- For the alkaline extraction, Na_2CO_3 solution is used. This causes the alginates to solubilize with sodium cations.
- A second dewatering step is performed.
- The extraction residues are recovered using a filter press.
- The remaining solution is cooled to room temperature.
- By using HCl for acid precipitation, a gel of alginic acid is obtained.
- A third dewatering step is performed using a vibrating sieve at 4 °C.
- Sodium carbonate is added to yield sodium alginate.
- The sodium alginate is dried in a convective drier.

4.2.3.2 Extraction of ulvan

The protocols for ulvan extraction were scarce, since ulvan received research interest only recently (Chiellini & Morelli, 2012; Alves et al., 2012). The protocol for ulvan extraction was adopted from Yaich et al (p. 376; 2013), where different extraction methods were tested. The most successful extraction conditions are reported here.

- 60 grams of the dried algae is heated at 90 °C in 1 L HCl solution (pH 1,5) and stirred at 250 rpm.
- Samples are extracted every hour, during three hours.
- The suspension is filtered and cooled at room temperature.
- The filtrate is centrifuged at 10 °C for 20 minutes at 10.000 rpm in order to separate solid particles. It was filtered again, to yield the 'extract juice'.
- pH of extract juice is adjusted to 3,5 with 1 M NaOH.
- Ethanol is added, to make the ulvan to precipitate. This alcohol precipitate is separated by centrifugation at 5000 rpm for 20 minutes at 10 °C.
- The precipitate is washed three times with ethanol solutions and centrifuged again for 10 minutes at 10 °C.
- The preticipitate is dried in a vacuum oven at 40 °C.

[11] This process is called lixiviation.

4.2.3.3 Conversion to biogas/compost/liquid fertilizer

The process of anaerobic digestion where methane can be produced, as liquid fertilizer and compost, is described on the basis of a larger scale in Reith (2005). In this Section this process is described (see Figure 24), and because the production of liquid fertilizer and compost are logical steps after biogas production they will not be described separately.

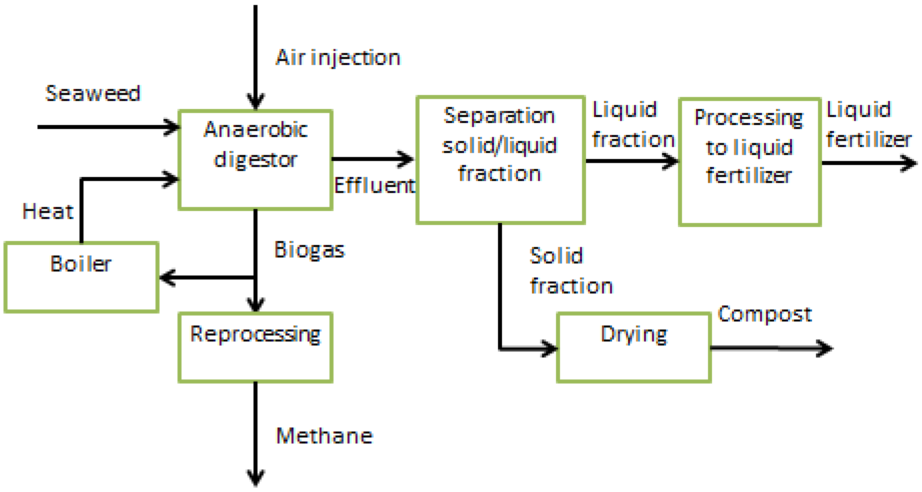


Figure 24. Schematic representation of biogas facility. Adjusted from Figure 4.3 (Reith et al., 2005).

In this system, the seaweed is introduced in the anaerobic digester. There is also the option to make use of several modular digesters, with a volume of 5000 m^3 each. The seaweed slurry can reside either 20 or 30 days in this anaerobic digester. After introducing heat and air in the digester, biogas can be produced. Part of the gas is used for heating of the digester; the other part will be reprocessed to introduce it in the natural gas network as methane. During the reprocessing step, the gas which contains 65% methane and 35% CO_2, is treated to remove nitrogen and sulfur particles and is dried subsequently. The effluent is separated by centrifugation in a liquid and a solid fraction. The liquid fraction can be sold as liquid fertilizer; the solid fraction will be dried and can function as compost.

4.2.3.4 ABE fermentation

For this process, the protocol from Potts (2012) was used. For the separation of the different products, the life-cycle inventory from Wu (2007) was down-scaled to the appropriate scale (with a factor of 72,5).

- Per 2 kg of dry algae, a 1% sulfuric acid solution with a total volume of 12 L is prepared.
- This solution is hydrolyzed at 100 °C (other than in Potts), for 70 minutes.
- The pH is adjusted to 4,5 with NaOH.
- For the fermentation step, 0,0024 kg of Clostridium saccharoperbutylacetonicum (yeast) is added to the solution. The batch-fermentation process takes place at a temperature of 35 °C (Wu et al., 2007). The sugar concentration in the solution will be 45,4 g/L, the minimum concentration required for fermentation (Wu).
- The fermentation broth will be separated in various fractions, making use of distillation. It is separated in butanol, ethanol, water, homogeneous ethanol-water azeotrope and heterogeneous water-butanol azeatrope (Wu et al., 2007). In the first distillation tower is butanol recovered, in the second one acetone. In the third tower ethanol is recovered, and the resulting mixture is sent to an adsorption unit where water is recycled and sent back.

4.3 Selection of the case-studies

The four case-studies are summarized in Table 16 below. The boxes following subsequently explain the case-studies further. In order to design the case-studies in a way that they can be compared with each other, the energy output of the different biorefinery configurations is the same. This energy output was found by using the dimensions of a typical commercial biogas plant. Together with the assumptions of case-study 1A, this yielded a certain volume of biomethane. The inputs for the other case studies (1B-3) were adapted according to this energy content.

The life cycle inventories were constructed according to the industrial process that could be used for the case. The techniques and processes described before will form the basis for the processes; the adaptations will be indicated in this section.

Table 16. Summary of the case-studies

Description	Unit	Case 1a	Case 1b	Case 2a	Case 2b	Case 3
Seaweed species		*Saccharina latissima*	*Saccharina latissima*	Ulva lactuca	*Ulva lactuca*	*Ulva lactuca*
Cellulose filter	Yes/no	No	Yes	No	Yes	No
Type of cultivation system		Long-line cultivation	Long-line cultivation	Long-line cultivation	Long-line cultivation	Collection
Assumed productivity	tonne d.w./ha/year	1,75	1,75	20	20	0,024
Size of cultivation system	ha	3577	2047	186	129	203000
Total amount of biomass	tonne d.m/year	6278	3593	3728	2582	4942
Harvesting method		Mechanical	Mechanical	Mechanical	Mechanical	Mechanical
Distance to the shore	km	166	166	166	166	300
Energy carrier produced		Biomethane	Biomethane	Biomethane	Biomethane	Butanol
Co-product 1		Sodium alginate	Sodium alginate	Ulvan	Ulvan	Acetone
Co-product 2		Compost	Compost	Compost	Compost	Ethanol
Total annual energy production	GJ/year	11289	11289	11289	11289	11289
Energy yield by algae alone	MJ/kg d.w.	1,80	1,80	3,03	3,03	2,28
Energy yield of algae and cellulose	MJ/kg d.w.	1,80	3,14	3,03	4,37	n.a.
Required volume for biomass in digestor	m^3	10750	6153	6384	4422	
Load factor facilities	Hours per year	4380	4380	4380	4380	4380
Land requirement for drying	m^2	12038	6891	7150	4953	9476

The productivity assumed for *Saccharina latissima* was not explicitely mentioned (Langlois et al., 2012); therefore it needed to be calculated. The cultivation area was mentioned for the whole seaweeds (the base-case in Langlois (2012), so only biogas production from seaweed). The production facilities would have a production capacity of 2MW, meaning that they would have a constant energy output of 2 MW. Together with the assumed biochemical methane potential (BMP), the productivity per hectare cultivation area could be calculated. This value was much lower than the values from literature, which gives some doubt about the assumptions made here. The productivity for *Ulva lactuca* was retrieved from literature (Bruhn et al., 2011). For case-study 3, there was no cultivation but collection of the biomass from heavily accumulated areas. The collection area was based on Potts (2012), and scaled-up with a factor of 20. This causes the collection area to be very large, and the productivity of the biomass expressed per hectare is quite low compared to the case-studies where the seaweed is cultivated.

The amount of energy production per year was fixed for all the case-studies. This value was calculated by applying the size of a typical commercial biogas plant, which is 10750 m^3 (Samer, 2012) to the values of case 1A. In Langlois (2012), both the production of biogas from whole seaweeds as from alginate residues was studied. The BMP for the alginate residues was assumed to decrease with a factor of 2,86 compared with the whole seaweeds (Langlois et al., 2012). By using the loading rate per day (3,2 kg d.w./m^3/day (Langlois et al., 2012)), the load factor (4380 hours per year) and the biochemical methane potential (BMP) (51 Nm^3/tonne d.m. for the alginate residues (Langlois et al., 2012)), the amount of biogas produced per year was calculated. This was multiplied with the energy density of the biogas (assumed 35,26 MJ/Nm^3 (calculated from Langlois (2012)) to yield an annual energy output. The other case-studies were designed to yield the same energy output. For Ulva lactuca the BMP was higher, and expected to decrease for the ulvan residues with the same factor as in case-study 1 (2.86). This resulted in a BMP of 85,87 Nm^3/tonne d.w.

Because the addition of cellulose (as a filter during the alginate and ulvan extraction process) has a substantial effect on the amount of biogas produced (Langlois et al., 2012), two scenarios were formulated for case-study 1 and 2. In scenario 1A and 2A, no cellulose was added to the process. In scenario 1B and 2B a cellulose filter was present. Based on the data presented by Langlois (2012), the additional energy production by the cellulose was calculated. This will result in a higher energy productivity expressed per kg d.w., which will have effects on the environmental and economic performance (section 4.4 and 4.5). While the products of case 3 are chemicals rather than energy products, the same output expressed in energy was assumed by using the energy densities of the products. The energy densities used, where 23, 28 and 21 MJ/L respectively for acetone, butanol and ethanol (Wu et al., 2007).

The distance from the shore was calculated from Langlois (2012). In the life cycle inventory (LCI), an amount of diesel per kg d.w. was reported. Together with the value of 0,11 L diesel/km/tonne transported (Langlois, 2012), the transported distance of 166 km was calculated (in accordance with Reith et al., 2005). For case-study 3, the distance was assumed to be higher (300 km) because it needs to be collected from different accumulation spots (Potts et al., 2012).

For the drying area for the sundrying of the seaweed, assumptions from Potts (2012) were used. A drying cycle of 4 days was assumed, and a drying season of 182,5 days (half a year). The thickness of the layer was assumed to be 3 inches (7,6 cm) and the dry weight percentage 15%. This resulted in a required volume of seaweed to be dried per cycle and therefore in a surface area. Besides the explanation for table 16, some additional assumptions were used:

- The facilities of all the case-studies are only used during half of the year, due to the requirement that the biomass needs to be sundried for economical- and energy reasons. The capacities of the facilities are adapted to this assumption. This will mean that the load factor of the facilities is 4380 hours.
- For the cultivation of *Ulva lactuca* is assumed that parts of Ulva plants are inserted in the ropes (vegetative reproduction). Therefore there is no need for nursery facilities for this case-study.
- To account for the difference in productivity of *Saccharina latissima* and *Ulva lactuca*, the material requirements for the offshore cultivation facilities are assumed to be scaled down according to the difference in productivity (20/1,75 = 11,4) when expressed per kg d.w.
- Many energy requirements for case-studies 1 and 2 are adapted from Langlois (2012), however some of the values are adapted according to other reports or protocols.
- The retention time in the biogas plant (case-study 1 and 2) is assumed to be 43 days, the loading rate is 3,2 kg d.w./m^3/day.
- The heating requirements for the case-studies 1 and 2 are provided by gas burnt in a large-scale industrial furnace, while the cooling requirements were provided by an absorption chiller operated by natural gas (Langlois et al., 2012).

- The energy requirements for the downstream processing of case-study 3 is adapted to the study from Wu (2007). In this study, much more biomass is converted per year. The carbohydrate stream processed in Wu (2007) was 73 times larger. Therefore, the energy requirements are divided by this factor and multiplied with a factor of 1,2; to account for the lower energy efficiency for a smaller facility.
- In case-study 3, the stream to the fermentor is adapted to contain a sugar concentration of 0,043 kg/L of fermentation medium. This is the minimum sugar concentration in order to produce ABE products (Wu et al., 2007).
- The construction requirements for case-study 3 are unknown. Since the construction requirements have a limited environmental impact, the assumption is that they will be comparable to the material requirements for the processing of whole seaweeds (Langlois et al., 2012).

4.3.1.1 Case-study 1A and 1B – overview

In this case-study will *Saccharina latissima* be the feedstock for the production of sodium alginate, biomethane and compost. A rough overview of the case-study is presented in Figure 25. The seaweed plantlets are produced first in a nursery, after which they are attached to ropes. The seaweed is cultivated off-shore, using long-line cultivation. The area required for cultivation is large, mainly because of the low productivity assumed by Langlois (which is 1,8 tonne d.w./ha/year). Harvesting will happen mechanically by using a dedicated harvester. Since it is not economically feasible to dry the biomass artificially, the seaweed will be sundried. This is the reason that the load factor for this system is only 0,5 (4380 hours per year), because it is assumed that the seaweed is cultivated in a temperate area (with a substantial amount of sun hours per year). In a biorefinery facility the alginate extraction process will take place. This is discussed in more detail below. The difference of case A and B is the use of a cellulose filter in case B, which will have a larger energy yield as a result, but will also have higher costs and environmental impacts as a result. The differences will become clear in the sections 4.4 and 4.5. Subsequently, the biogas is produced from the alginate residues in an anaerobic digestor. The required heat for the digestor is provided by part of the biogas produced. Because the alginate residues are being used, the biogas potential is much lower than for whole seaweeds (Langlois et al., 2012). The biogas will be upgraded in order to yield the required amount of biomethane. The digestion residues are separated in a liquid and a solid fraction. The liquid fraction is used as a fertilizer for the plantlets. The solid fraction is converted into compost. The life cycle inventory for this case-study is presented in Appendix D.

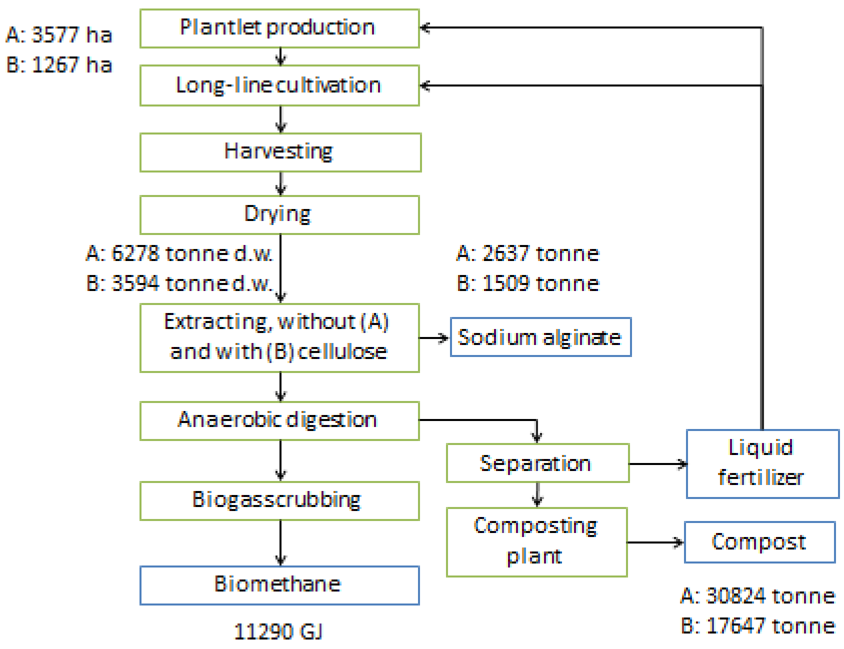


Figure 25. Overview of case-study 1A and 1B. A: without addition of cellulose; B: with addition of cellulose.

4.3.1.2 The economic allocation

In Table 17 and 18, the economic allocation assumptions are presented. It can be seen that by far the largest part of the environmental impacts will be attributed to the sodium alginate. The profits of the biogas are very small, for case-study 1A these profits are even smaller than for the compost.

Table 17. Economic allocation case 1A

Product	Price		Source	Amount produced	Unit	Revenue per kg d.w. Algae ($)	Impact (%)
Sodium alginate	12	USD/kg	Bixler & Porse	0,42	kg/kg d.w. Algae	5,04	98,9
Biogas	55,5	USD/MWh	Langlois	0,50	kWh/kg d.w. Algae	0,03	0,5
Compost	5,9	USD/tonne	Langlois	4,91	kg/kg d.w. Algae	0,03	0,6
Total						5,10	100

Table 18. Economic allocation case 1B

Product	Price		Source	Amount produced	Unit	Revenue per kg d.w. Algae	Impact (%)
Sodium alginate	12	USD/kg	Bixler & Porse (2010)	0,42	kg/kg d.w. Algae	5,04	98,5
Biogas	55,5	USD/MWh	Langlois (2012)	0,87	kWh/kg d.w. Algae	0,05	0,9
Compost	5,9	USD/tonne	Langlois (2012)	4,91	kg/kg d.w. Algae	0,03	0,6
Total						5,12	100

4.3.1.3 The extraction process

The process is based on several sources (Langlois et al., 2012; Vauchel, Kaas, Arhaliass, Baron, & Legrand, 2008*;* "Method for producing sodium alginate and co-producing ethanol and seaweed organic fertilizer," 2013)

- The biomass is crushed in small particles. Ethanol is added, in order to bleach the biomass (to avoid the production of coloured sodium alginate). A high recycling rate is assumed for the ethanol.
- During acidification, a small amount of acid is added to the solution. This makes alginic acid to be formed, which is insoluble to water.
- Subsequently, sodium carbonate is added for the extraction step, which solubilizes the alginates with the sodium cations in the solution.
- This process takes 3 hours. By making use of filtration (without (A) or with (B) cellulose), the sodium alginate is recovered from the aqueous solution.
- Again, HCl is added to the solution to promote the formation of a gel of precipitated alginic acid.
- Finally a smaller amount of sodium carbonate is added to the gel to form sodium alginate. The drying occurred by a convective dryer.

4.3.2.1 Case-study 2A and 2B - overview

In this case-study, there will be production of ulvan, biogas and compost from the green seaweed *Ulva lactuca* (see Figure 26). The productivity of this seaweed is assumed to be much higher than for *Saccharina latissima*. A productivity of around 20 tonne d.w./ha/year reported by Bruhn (2011) is assumed here. This makes the cultivation area for the production of the same energy output much smaller. Also the *Ulva lactuca* is assumed to be cultivated and converted in a temperate climate. Therefore the facilities will be used only half of the year. After drying, the ulvan will be extracted. The details of this process are explained below. Because this process is not commercialized yet, the yield is much lower than for the alginate extraction from *Saccharina latissima*. The ulvan residues are used for the production of biogas, where also part of the biogas will be used for the heat requirements of the biogas plants. The biogas potential of *Ulva lactuca* is higher than for *Saccharina latissima* (Bruhn et al., 2011). The biogas is upgraded in a purification system. The residues are separated in a liquid and a solid fraction, the liquid fertilizer will be used for the seaweed production, and the solid fraction is converted into compost. The life cycle inventory for this case-study is presented in Appendix D.

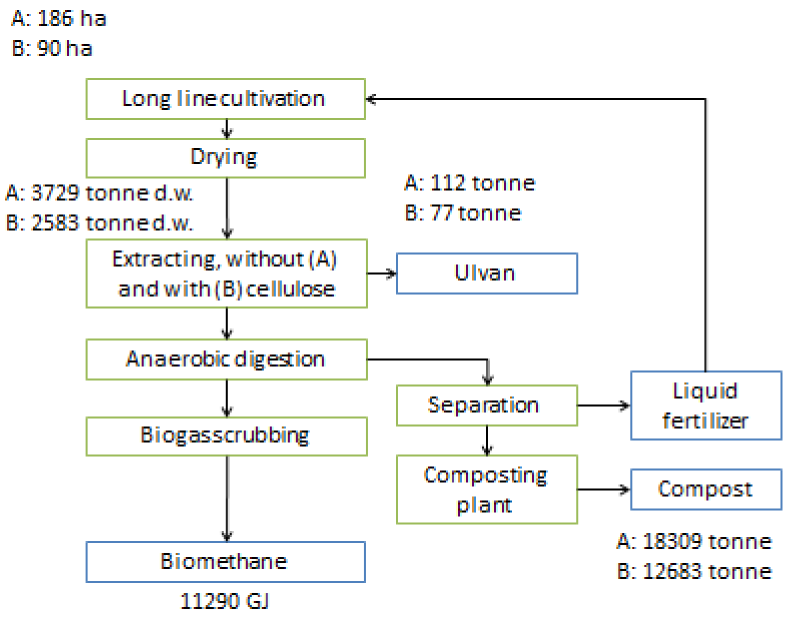


Figure 26. Overview case-study 2A and 2B. A: without addition of cellulose; B: with addition of cellulose.

4.3.2.2 The economic allocation

The economic allocation factors of case-study 2A and 2B are presented in Table 19 and 20. Because the estimated value of ulvan is lower than the value of alginate, the environmental impacts will be more distributed among the different products. However, this value is only based Also the assumed yield of this process is much lower than for alginate. Besides this, *Ulva lactuca* produces more biogas, which also has its effect on the economic allocation.

Table 19. Economic allocation case 2A

Product	Price		Source	Amount produced	Unit	Revenue per kg d.w. Algae ($)	Impact (%)
Ulvan	6,75[12]	USD/kg	Bixler & Porse (2010)	0,03	kg/kg d.w. Algae	0,21	73,1
Biogas	55,5	USD/MWh	Langlois (2012)	0,84	kWh/kg d.w. Algae	0,05	16,6
Compost	5,9	USD/tonne	Langlois (2012)	4,91	kg/kg d.w. Algae	0,03	10,3
Total						0,28	100

[12] Value is based on average market price of hydrocolloids (agar, alginate and carrageenan) in 2009; and divided by 2 (an estimation), because the commercial value is not certain yet (Bixler & Porse, 2010).

Table 20. Economic allocation case 2B

Product	Price		Source	Amount produced	Unit	Revenue per kg d.w. Algae	Impact (%)
Ulvan	6,75	USD/kg	Bixler & Porse (2010)	0,03	kg/kg d.w. Algae	0,21	68,1
Biogas	55,5	USD/MWh	Langlois (2012)	1,21	kWh/kg d.w. Algae	0,07	22,3
Compost	5,9	USD/tonne	Langlois (2012)	4,91	kg/kg d.w. Algae	0,03	9,6
Total						0,30	100

4.3.2.3 The extraction process

Ulvan can be extracted both by hot water extraction (Paradossi, Cavalieri, Pizzoferrato, & Liquori, 1999) as by acid extraction (Yaich et al., 2013). In this case-study a combination of these two methods are being used, with the appropriate quantities from both methods.

- The biomass is crushed in small particles in order to increase the reaction surface (Langlois et al., 2012).
- HCl is used for the acid extraction, which takes place at 90 °C under continuous stirring for an hour.
- The solution is cooled and centrifuged. Subsequently it is filtered to separate the ulvan from the water. This happens without (A) or with (B) a cellulose filter.
- An alkali is used to neutralize the resulting solution.
- Ethanol is added for ulvan precipitation at a 1:1 weight ratio (Paradossi et al., 1999). A recycling rate of 90% is assumed. This is followed by another centrifuging step.
- The resulting ulvan is dried with a convective dryer.

4.3.3.1 Case-study 3- overview

In this case-study, also *Ulva lactuca* will be the feedstock. However, here the *Ulva* will be collected from waters where large floating algae blooms are present. This algae accumulation has negative effects for the water quality, therefore the collection and conversion of the blooms will have additional positive environmental effects. This idea is based on the study from Potts et al. (2012), where the *Ulva latuca* is collected in Jamaica Bay, near New York City. In this case-study the biomass will be the feedstock for the simultaneous production of the chemicals acetone, butanol and ethanol (ABE fermentation). The yields of these products in this prospective analysis are not very high. This causes the amount of required biomass in order to reach the same energy output as in case 1 and 2 to be quite high, especially when compared to the scale assumed by Potts. See Figure 27 for an overview of the process.

The seaweed is collected with waste collection boats and transferred to the biorefinery. It will be sundried, and subsequently transferred to the biorefinery facilities. ABE fermentation will occur when yeast is added in the system. The details of this process are explained below, the life cycle inventory for this case-study is presented in Appendix D.

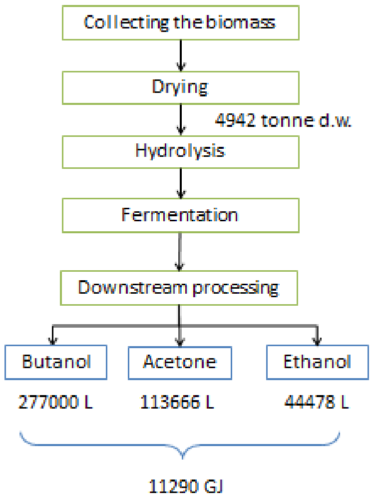


Figure 27. Overview of case-study 3 (Potts et al., 2012)

4.3.3.2 *The economic allocation*

The economic allocation is presented in Table 21. The largest part of the environmental impacts will be attributed to the butanol. Because the yields of the process are not very high, like the assumed price level for the products, the revenue per kg d.w. will be much lower than for the other case-studies.

Table 21. Economic allocation of case-study 3.

Product	Price		Source	Amount produced	Unit		Revenue per kg d.w. Algae ($)	Impact (%)
Acetone	1,37	USD/kg	ICIS, 2006	0,02	kg/kg Algae	d.w.	0,02	17,5
Butanol	1,71[13]	USD/liter	Chemical Strategies Group, 2013	0,06	L/kg Algae	d.w.	0,10	76,6
Ethanol	0,793	USD/liter	ICIS, 2006	0,009	L/kg Algae	d.w.	0,01	5,9
Total							0,13	100

4.3.3.3 *The fermentation process*

This process is based on several sources (Potts et al., 2012; Wu et al., 2007).

- The biomass is first crushed into small particles (Langlois et al., 2012).
- Then, the biomass is hydrolyzed using sulfuric acid (1%). The hydrolysis happens at a high temperature (100 °C).
- Sodium hydroxide is added for neutralization, to bring back the pH to a value of 3,5.
- For the fermentation process, a minimum sugar concentration of 45,4 g/L is required (Wu et al., 2007). This minimum value is assumed here.
- For the fermentation process to occur, the yeast C. saccharoperbutylacetonicum is added (Potts et al., 2012). This yeast is able to produce acetone, butanol and ethanol.

[13] Prices ranged between $5 to $10 per gallon ($1,32-$2,64 per liter) in recent years (Chemical Strategies Group, 2013)

- For the downstream processing, the energy requirements for a corn-based ABE facility are used (Wu et al., 2007). The products are recovered making use of distillation.

4.3.3.4 *The downstream processing*

Wu et al. (2007) described the distillation process for a corn-mill anaerobic digestion plant and provided a life cycle inventory for the analysis of this plant. The scale at which this happened was much bigger than the scale of case-study 3. The feeding rate to the distillation configuration and load factor described in Wu (2007) was converted into a feeding rate for the load factor used in case study 3. Subsequently, the feeding rate of case-study 3 was calculated, based on the appropriate concentration of glucose in the solution. The feeding rate presented in Wu (2007) was 72,5 times larger. This factor was used. The energy requirements (of steam and electricity) presented in Wu (2007) were converted into the right units and expressed per year. Finally the energy requirements expressed in Wh/kg d.w. could be retrieved from this data. The results are presented in Table 22.

Table 22. Energy requirements for the distillation process used in case-study 3 (Wu et al., 2007).

Element	Steam (Wh/kg d.w.)	Electricity (Wh/kg d.w.)
Fermentor agitator	0.0	
Condenser		78.6
Gas pump		1.5
Gas stripper		0.0
Adsorption feed pump	0.0	
Distillation column 1		0.0
Distillation column 2	465.2	
Distillation column 3	42.5	
Distillation 2 feed pump	0.0	
Distillation 3 feed pump		0.0
Adsorbent regeneration	-5.4	6.0
Total	**502,3**	**86,1**

4.4 Environmental analysis

In this Section, the results are presented in a comparable basis. This means that the results of the different cases are presented in the same graphs. All the impacts are measured using the same functional unit, e.g. 1 MJ of energy output. The three impact factors (non-renewable energy use, renewable energy use and global warming potential) are presented. Table 23 provides an overview of the products and yields produced in each case-study, expressed per MJ energy output. This means that for case-study 1 and 2, the biogas output is 1 MJ, and the other products are expressed per MJ energy output. For case 3, the three products together contained an energy content of 1 MJ in total. Therefore these quantities are presented both in volume as energy content in table 22. A couple of things are remarkable about this overview. Firstly, the amount of compost that is produced in case-study 1 and 2 is very large. This value was adapted from the economic allocation of Langlois et al. (2012). It was not justified in this study, and it seems to be very large. Secondly, the yield of ulvan production in case-study 2 is quite low compared to the yield of the alginate production from case 1. The yield of case 1 was adapted from Langlois (2012), while the yield of case 2 (0,03 kg/kg d.w.) was retrieved from an experimental lab-study (Yaich et al., 2013). For further research it is probably better to work with a different yield for ulvan extraction. Alves (2012) reports a range of extraction yields of 0,1-0,28 kg/kg d.w., so the yield used in this study might be too low. The results of the LCA are discussed in the next sections.

Table 23. Overview of products, quantities and the environmental analysis

	Unit	1A	1B	2A	2B	3
Species		Saccharina latissima	Saccharina latissima	Ulva lactuca	Ulva lactuca	Ulva lactuca
Addition of cellulose		No	Yes	No	Yes	No
Focus of case-study		High-value products	High-value products	Energy	Energy	Chemicals
Products produced	Per MJ (functional unit)					
Biomethane	MJ	1,0	1,0	1,0	1,0	
Alginate	kg	0,2	0,1			
Compost	kg	2,7	1,6	1,6	2,3	
Ulvan	kg			0,010	0,007	
Acetone	l/MJ					0,010/ 0,23
Butanol	l/MJ					0,024/ 0,68
Ethanol	l/MJ					0,004/ 0,09
Total scores environmental analysis	per MJ (functional unit)					
NREU	MJ-equivalent	22,4	18,5	6,22	8,42	3,71
REU	MJ-equivalent	1,30	11,5	0,15	7,83	0,04
GWP	CO2-equivalent	26,1	21,1	8,85	11,7	3,71

4.4.1 Non-renewable energy use (NREU)

Figure 28 shows the scores for the different case-studies on NREU. It can be seen that all the case-studies received high scores, considering that the values are expressed per MJ energy output. It becomes clear that a very large part of the scores for case 1A/B and 2A/B is caused by the extraction process. For case 2A and B the extraction causes about 90% of the total score of NREU, for case 1A and B more than 65% (see also Figure 29 with the contributional analysis of the NREU). The large amount of sodium carbonate needed for the alkaline extraction step is a major cause of this score in case 1A and B. In case 1B, the cellulose also has a large impact. But because of the cellulose addition, there is more energy production per kg of d.w., which means a lower overall score expressed per MJ produced. Furthermore, there are large energy requirements with considerable impacts for this process, associated with the alkaline extraction as well. This is caused by heating and cooling requirements, but also the electricity requirements for the alcoholic pre-treatment and alkaline extraction are considerable. Also the scores for cultivation and harvesting are quite large. This is mainly caused by the plantlet production, which is an energy-intensive process. The ammonium nitrate added as a nutrient has a large impact as well. The offshore seaweed cultivation itself is less energy-intensive.

For case 2, the main impact of the ulvan extraction is caused by the ethanol added in the process. A high recycling rate of ethanol (98%) was assumed, but the total amount to be added and the impacts per unit are still considerable. The energy requirements for heating and cooling the biomass also have a large impact on the total score. The addition of cellulose in process does not lower the score on NREU much. The cellulose received a relative high score, compared with the other substance requirements. This is also visible in Figure 29, the extraction process for case 2A received relatively a much lower score than for case 2B (87 compared with 93% of the total score). The scores for cultivation and harvesting are almost negligible, which is due to the assumption that Ulva lactuca can be cultivated vegetatively, and there is no need for the energy-intensive plantlet production (unlike in case-study 1).

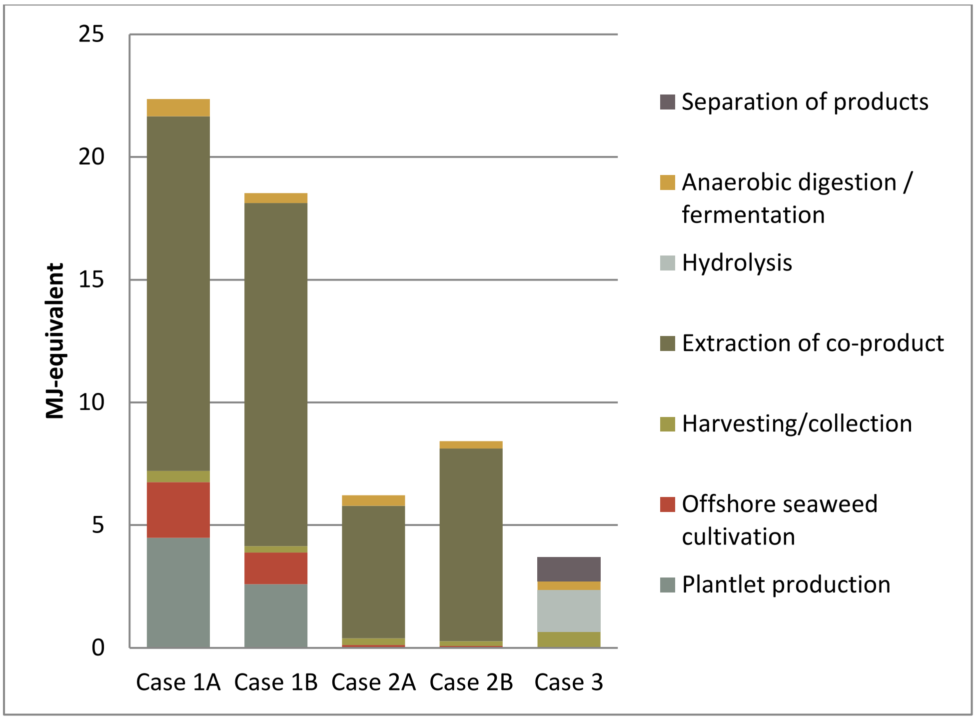


Figure 28. Non-renewable energy use, in MJ-equivalent per MJ energy output

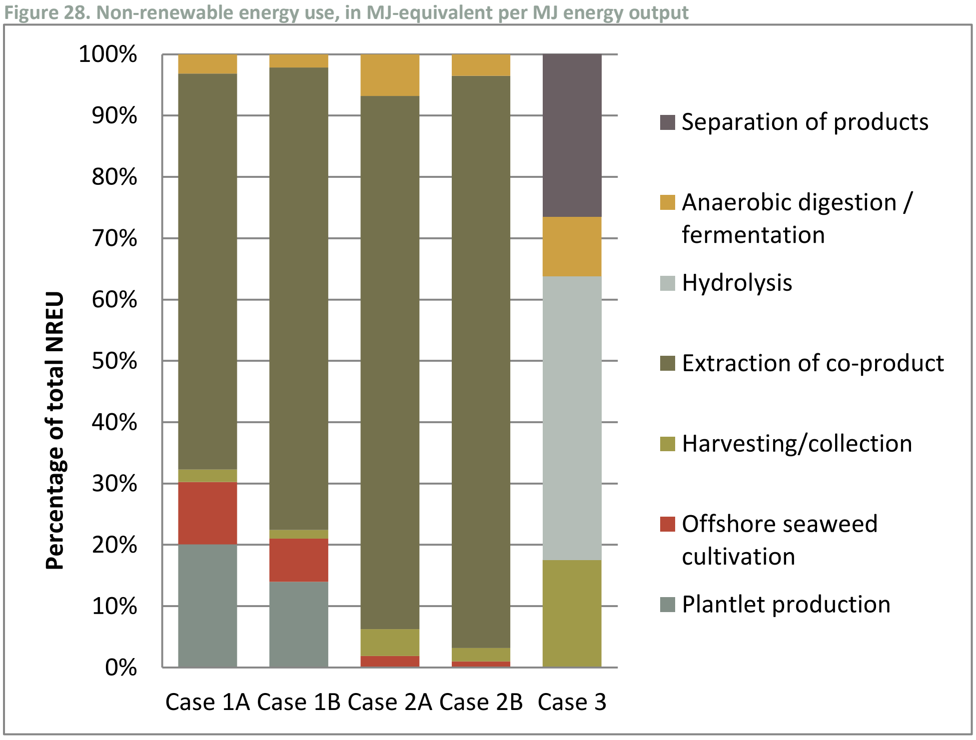


Figure 29. Contributional analysis of the NREU

Also case-study 3 received a considerable score on NREU. The most important causes of this score are the processes of hydrolysis and the separation of the products. For hydrolysis the impact is caused by the natural gas requirement of the heating process. For the separation of the products there are also significant energy requirements, since the products are separated using a disitillation process.

For case-study 1, the impacts are mainly attributed to the alginate extraction (about 98%). In fact, the extraction process was causing the main impacts for the NREU, but less than 98%. The allocation to the biogas production were less than 1% for case-study 1A and B. For case-study 2, the total impacts were also mainly attributed to the ulvan extraction (about 70%), while the extraction process caused more than this to the total score (around 90%). For case 3, the impacts are mainly attributable to the butanol production (about 75%), while in this case all three products are produced at the same time. The products are produced simultaneously during the ABE fermentation; while in case-study 1 and 2 the co-product is extracted befor the biomethane is produced.

4.4.2 Renewable energy use (REU)

See Figure 30 for the total scores on REU. It is remarkable that case-study 1B and 2B scored very high on REU. For case-study 1A, 2A and 3, the scores were much lower. The main causes of the scores for these case-studies was the electricity consumption during the processes. Because a part of the European electricity is generated by hydropower, each process powered by electricity will receive a small score on REU.

For case 1B and 2B the REU is very high, which is caused by the addition of cellulose in this process. The source of this cellulose is assumed to be chemi-thermomehanical pulp, a waste product from the paper industry (Langlois et al., 2012). These scores caused the total scores for energy use of case 1B and 2B (NREU and REU) to be higher than for case 1A and 2A. This becomes visible in Figure 31, where the total scores for the case-studies are presented. The addition of this large amount of cellulose to the process had significant effects on the energy use.

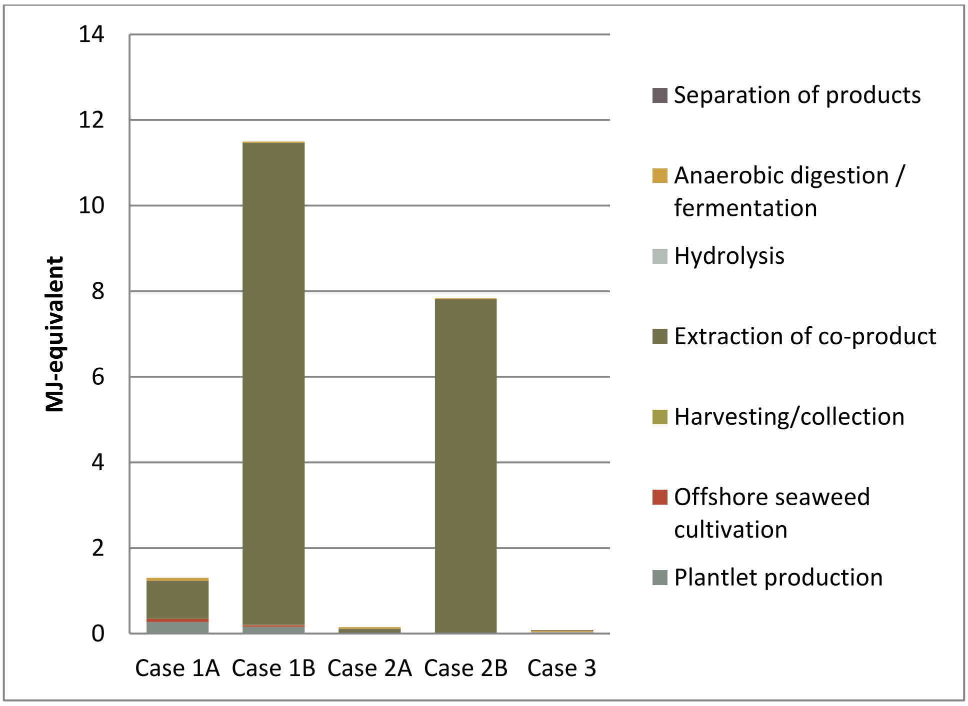


Figure 30. Renewable energy use, in MJ-equivalent per MJ energy output.

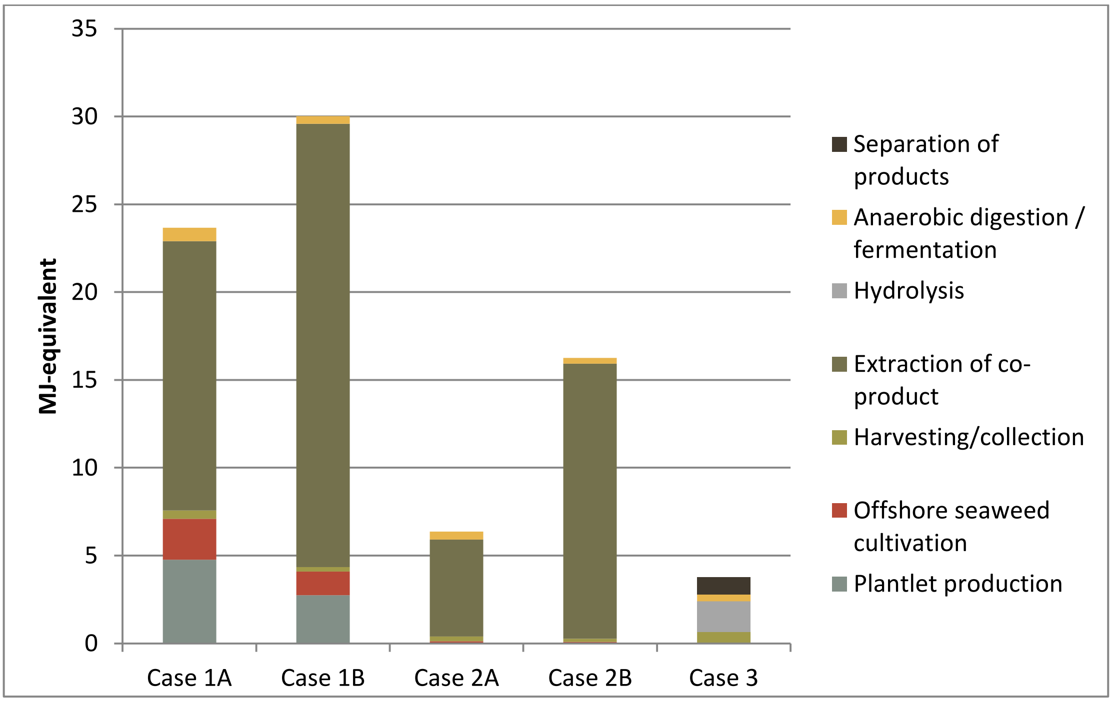


Figure 31. Total energy use (NREU + REU)

4.4.3 Global warming potential

The results for the GWP are presented in Figure 32. Case-study 1A received a score of 1,32 kg CO_2-equivalent, which is the highest impact of all the case-studies. The GWP of ammonium nitrate (required for the plantlet production) is one of the causes for this score. Besides this, the significant energy requirements for the alginate extraction caused the GWP score to rise. For case 1B, the addition of cellulose caused some impact as well. The remaining patterns are almost completely the same as for the NREU. This becomes visible in Figure 33, which shows the contributional analysis of the GWP. Besides this, the ratios between the total scores of the different case-studies are very comparable for NREU and GWP (see Table 24 for the comparison). Only the last ratio (between 2B and 3) the difference is relatively large. For case 1A and B, the impact of plantlet production was slightly higher. The GWP of harvesting is relatively smaller than the NREU, like the GWP for the extraction process.

For case 2A and B the relative scores on GWP and NREU are comparable. The addition of ethanol was an important impact factor, and also the energy-intensive extraction process caused a significant impact. Besides the impacts of the energy use, also the addition of the cellulose filter caused the GWP score to rise. For case 2A and B, the impact of harvesting the biomass is relatively smaller than the NREU. The impact of extracting the ulvan is relatively smaller, while the impact of anaerobic digestion is larger.

For case-study 3, the impact on the GWP of the hydrolysis and separation process is relatively larger than the NREU, while the process of harvesting is smaller. The steam requirements for the distillation process (as a separation method) was a major cause of the score on GWP. And also the energy requirements for the hydrolysis caused the GWP score to increase. Thus the energy-intensive processes where causing the relatively differences for the GWP compared to the NREU for case 3.

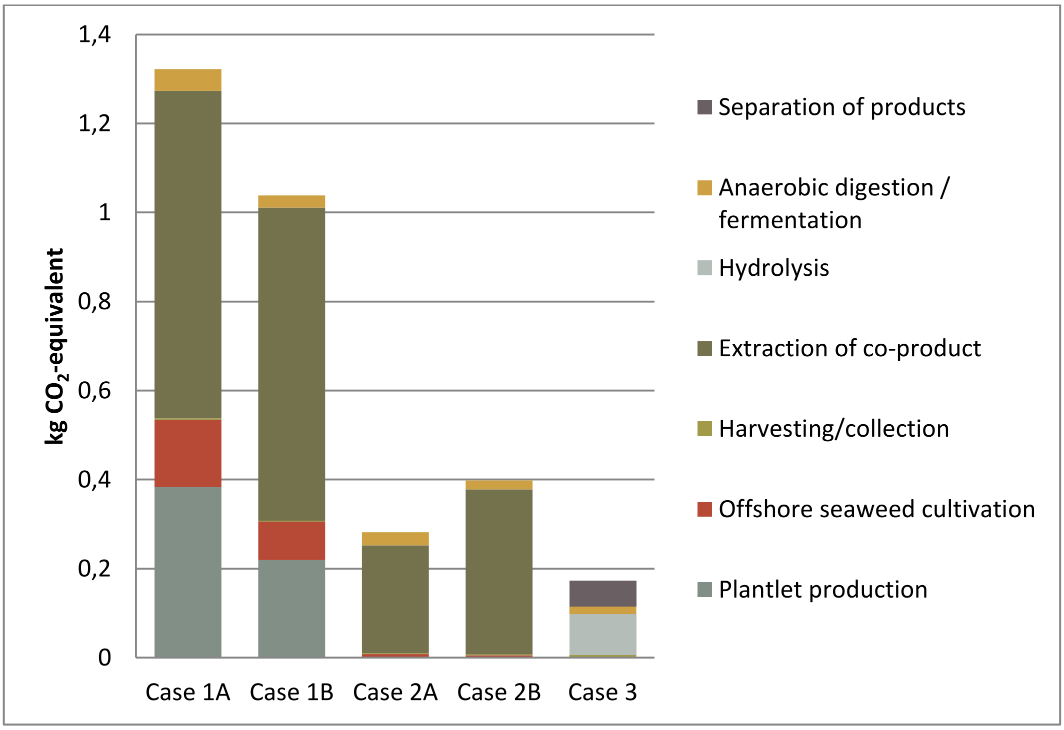


Figure 32. Global warming potential, in CO_2-equivalent per MJ energy output.

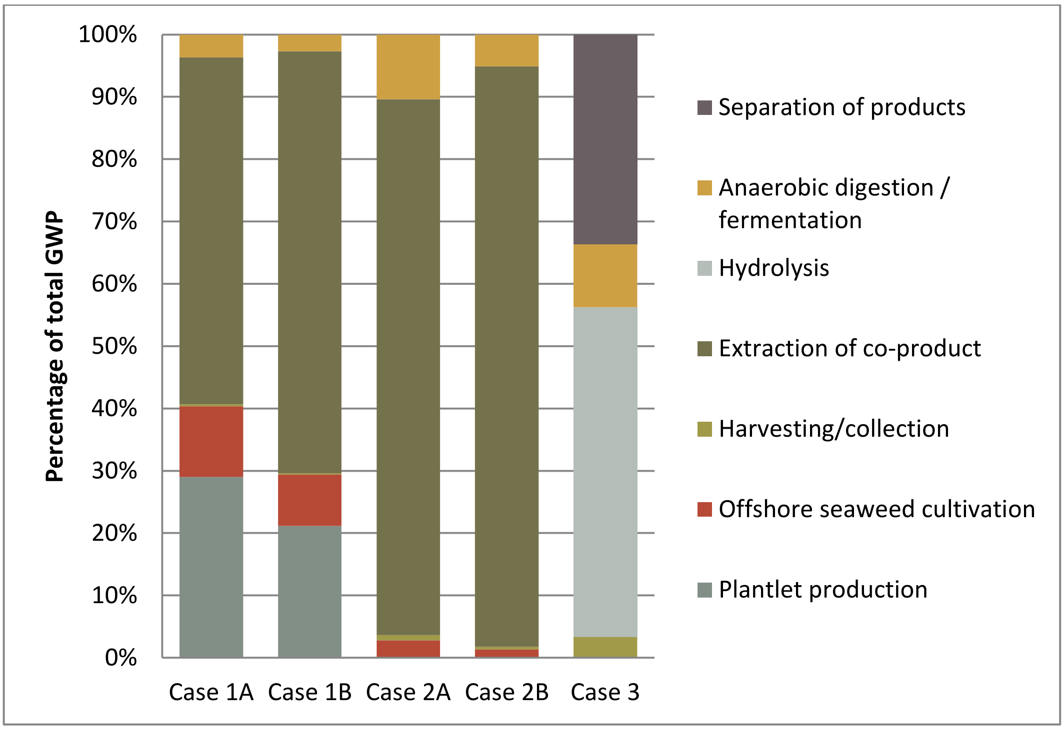


Figure 33. Contributional analysis of the GWP.

Table 24. Ratios between total scores NREU and GWP for all the cases.

	1A:1B	1B:2A	2A:2B	2B:3
NREU	1,2	3,0	0,7	2,3
GWP	1,3	3,7	0,7	4,9

4.4.4 Comparison with other studies

The fact that there were almost no studies available conducting an LCA for the production of biofuels and products from macroalgae, made that the results are complicated to compare and analyze. Also, the LCIs of the case-studies were based on assumptions, lab-study protocols and these scarce LCA studies, which made the results at least questionable. Therefore, the design of the case-studies and the results should be considered as a start for the LCA of the macroalgae-based biorefinery, rather than interpreting the results and values as comparable with other biorefinery systems. Hence the results will not be compared with a reference system, because this comparison will not be reliable.

The case study by Langlois et al. (2012) was the most complete LCA study to-date. However, the data in this study did not always seem right. During the extraction process, very large quantities per kg d.w. were reported (1601,6 kg 2M HCl). Many parts of the LCI were not justified sufficiently, and the energy requirements were adopted from a pilot plant which was also not ascertainable. Therefore, the values in the inventory were adapted for the case-study were needed (indicated in Appendix D). The results of the study were only reported in relative values (comparable with Figure 29, and 33, illustrated in Figure 20). This made the results not very transparent. The impact factors used were also different than the impact factors of this study (in Langlois (2012), the ReCiPe impact factors were used). In order to compare the results, the exact same inventory was used with the impact factors NREU, REU and GWP. The results of this analysis are presented in Table 25.

Table 25. Overview of absolute results study Langlois et al. (2012). All values are expressed per MJ energy output.

Impact factor	NREU	REU	GWP
Unit	MJ-equivalent	MJ-equivalent	Kg CO_2-equivalent
Score	2153	158	110
% extraction process for total score	99	99	99

This analysis shows very large numbers per MJ energy output. For all the impact categories, this score was mainly caused by the extraction process (for 99%). Like mentioned above, the addition of a large amount of strong acid was the main source of this large impact. Besides this, the facilities for chemical production (for upgrading the biogas) caused a relatively high impact compared to other material and construction requirements (7 MJ-equivalent for the NREU). The analysis illustrated the current state of the available literature for the macroalgae-based biorefinery.

Besides this study, it is also interesting to compare the results with the study from Florentinus et al. (2008). In this study, different cultivation concepts were compared with eachother to an environmental and economic respect. The results were presented before in Section 2.5.3 (Figure 12). In this study it was assumed that the seaweed would be converted into biogas using anaerobic digestion. For a green house gas balance, all the steps (from cultivation to end-use) were included. Included were the impacts of energy use, fertilizers and other energy-intensive products that can cause GHG emissions. Excluded were buildings and materials for construction. Two cultivation concepts considered by Florentinus (2008) were comparable to the case-studies analyzed here (set 3: horizontal lines between offshore infrastructure; set 5: vertical lines nearshore in densely used areas). In case-study 3, different products were considered and will therefore not be compared with this study. The inventories of the different in-and outputs of the systems and the specific methods were not mentioned in the study. Also the type of GHG considered in the study were not specified. In Table 26 the results are presented. In the first row, the GWP for all buildings and materials is reported, assuming the extraction of alginate or ulvan as well. In the second row, the GWP is reported when assuming that the whole seaweeds will be transformed into biogas without co-product extraction. The amount of biogas produced in this case could be calculated based on Langlois et al. (2012). In the third row, the impacts of the buildings, materials and the extraction process were excluded for the GWP. And finally in the fourth row, the GWP is reported with the exclusions assuming that the whole seaweed is converted into biogas. Here the comparison can be made between the two studies. It seems that Florentinus et al. (2008) might be too optimistic about the GHG emissions. However, the results are very comparable with case 2B. Since the methods and results of Florentinus (2008) are not transparent, the analysis cannot be extended. It would be very useful to have more of these comparisons for further research, in order to find the effects of different assumptions and analyses on the final result.

Table 26. Results of the comparison between this study and Florentinus et al. (2008). The comparable concepts of Florentinus (2008) are set 3 (horizontal lines between offshore infrastructure) and set 5 (vertical lines nearshore in densely used areas).

	Case	Unit	Case 1A	Case 1B	Case 2A	Case 2B	Set 3 (Florentinus)	Set 5 (Florentinus)
GWP per MJ (including everything)	With extraction	kg CO_2-eq/MJ	1.320	1.040	0.820	0.400		
GWP per MJ (including everything)	Without extraction	kg CO_2-eq/MJ	0.805	0.634	0.500	0.244		
GWP per MJ (without buildings, construction materials, extraction process)	With extraction	kg CO_2-eq/MJ	0.396	0.244	0.031	0.021		
GWP per MJ (without buildings, construction materials, extraction process)	Without extraction	kg CO_2-eq/MJ	0.242	0.149	0.019	0.013	0.012	0.014

4.5 Economic analysis

In this Section, the results for the economic analysis are presented per processing step. Finally, the economic performance of each case-study will be presented as the NPV and the PBP.

4.5.1 Cultivation and harvesting

The different values and ranges reported in the reviewed literature are presented in the long-list in Appendix E. Many of the estimations were discarded, because they did not seem useful for this analysis. This was caused by several considerations, like other cultivation systems, very old and untraceable estimations, calculations that did not correspond with the original source or the assumption of a different scale for cultivation. This resulted in a short list, presented in Figure 34.

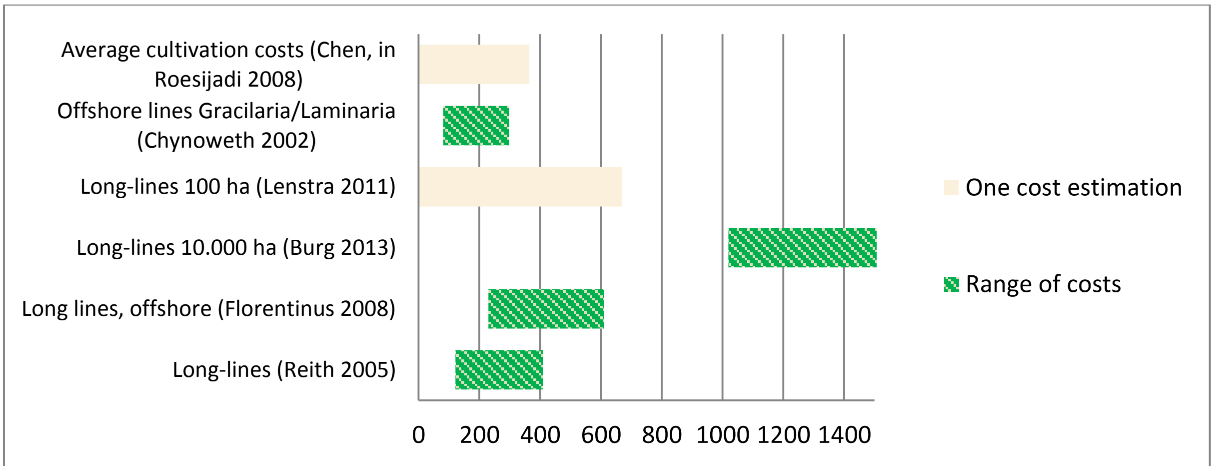


Figure 34. Short list of prices per tonne d.w. Light bar indicates one value, green bar indicates a range of prices.

Based on this review, the costs for long-line cultivation were set at €600 per tonne d.w. Because the assumed productivities of the species *Saccharina latissima* and *Ulva lactuca* are very different from each other (1,75 and

20 tonnes d.w./ha/year respectively), it seemed to be reasonable to express the harvesting costs per hectare. In this way, the difference in cultivation area is accounted for. The best estimate present for these costs is €104 per hectare (Lenstra, 2012). These two values will be used as an assumption for further calculations. Because for case 3 there is no cultivation but collection of the biomass, another number has to be used. The ratio between the price of the fuel requirement and the total cultivation costs for case 1A and 1B was used to find the total collection costs of *Ulva lactuca* in case 3. This resulted in a number of €107 per tonne of dry weight.

4.5.2 Drying

No additional costs for drying of the biomass were assumed. This is because it will not be economically feasible to dry the biomass on an industrial scale (Langlois et al., 2012). Therefore the drying of the biomass will happen outside, with natural drying. This is the basis for the assumption that the facilities will be used only half of the year. However, even when applying sun-drying, there needs to be a sufficient area of land available in order to dry the biomass. This area was presented before in Table 16 (section 4.3), taking into account the drying season (6 months), the amount of biomass, the drying cycle (4 days) and the thickness of the seaweed (3 inches) (Potts, 2012). This resulted in drying areas varying between 5000 m^2 (case-study 2B) and 12000 m^2 (case-study 1A). So for most case-studies, the required area is less than one hectare.

4.5.3 Utilities and compounds

A list of the applied prices for compounds and utilities is presented in Appendix E. The cellulose that is applied in the filter is a waste product from the paper industry; there was no price information available. Therefore there was need for an assumption here (€200/tonne). The price of yeast was derived from a chemical supplier (Sigma-Aldrich, 2014), and might be on the high side.

In Figure 35, the annual gas- and electricity expenses are displayed, while Figure 36 shows the annual costs for the compounds and substances that are required. The difference between case 1A and 1B is only caused by the difference in scale. In case 1, much more electricity than gas is consumed during the process. Electricity consumption is mainly large during the plantlet cultivation in the nursery, during the alcoholic pre-treatment and the alkaline extraction step during alginate extraction. The heat requirement for the extraction process is not very large.

Also for case 2, the difference in total costs is only caused by the difference of total scale (amount of biomass processed per case). For case 2, the gas requirement is much higher than the electricity requirement. During the ulvan extraction process, there is a need for heating and cooling at large temperature intervals. This is the main cause of the gas requirement during the whole processing chain.

Finally for case 3, also the gas requirement is much higher than the electricity requirement. This is due to two of the processes. Firstly, during the hydrolysis step, the solution needs to be heated at high temperatures. Secondly, during the separation of the products, there is a large gas requirement for the distillation process.

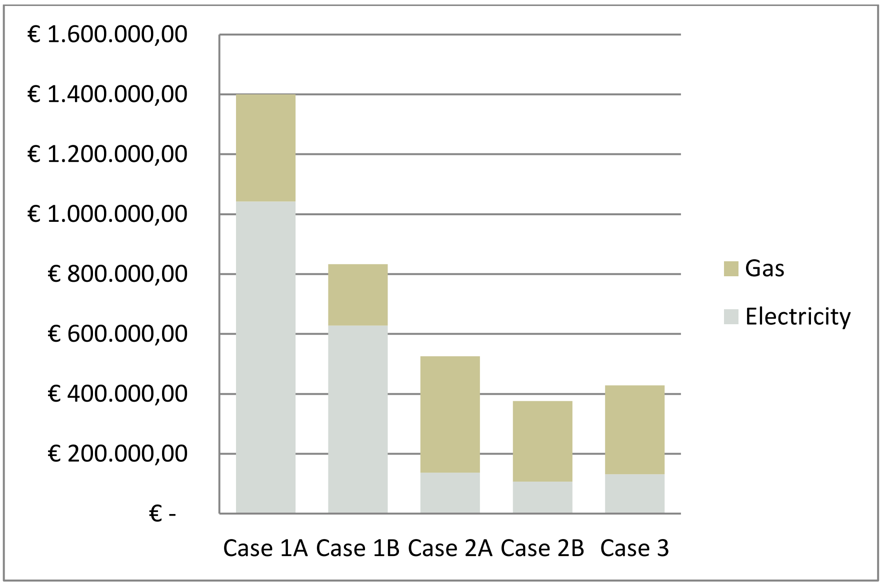


Figure 35. Annual gas-and electricity expenses

The water requirements for case 1 and 2 are very large. While the price of water is low (€1.36/tonne is assumed here), the large quantities still cause the water to have a major financial impact. Especially for case 1A, the costs of water are more than €1.000.000. For case 2A, water is the largest cost factor for all the compounds together. In case 3, the water requirements are much smaller and therefore have a very limited impact on the total costs.

For case 1, the large amount of required sodium carbonate is a major cost factor. Besides this, the sodium phosphate required for the plantlet cultivation is also significant. For case 1B the cellulose adds up to the costs. For case 2, the hydrogen chloride is an important cost factor, besides the water requirement. The addition of cellulose in case 2B almost doubles the cost. In case 3, the use of sodium hydroxide and the addition of yeast for the fermentation process are the main cost factors.

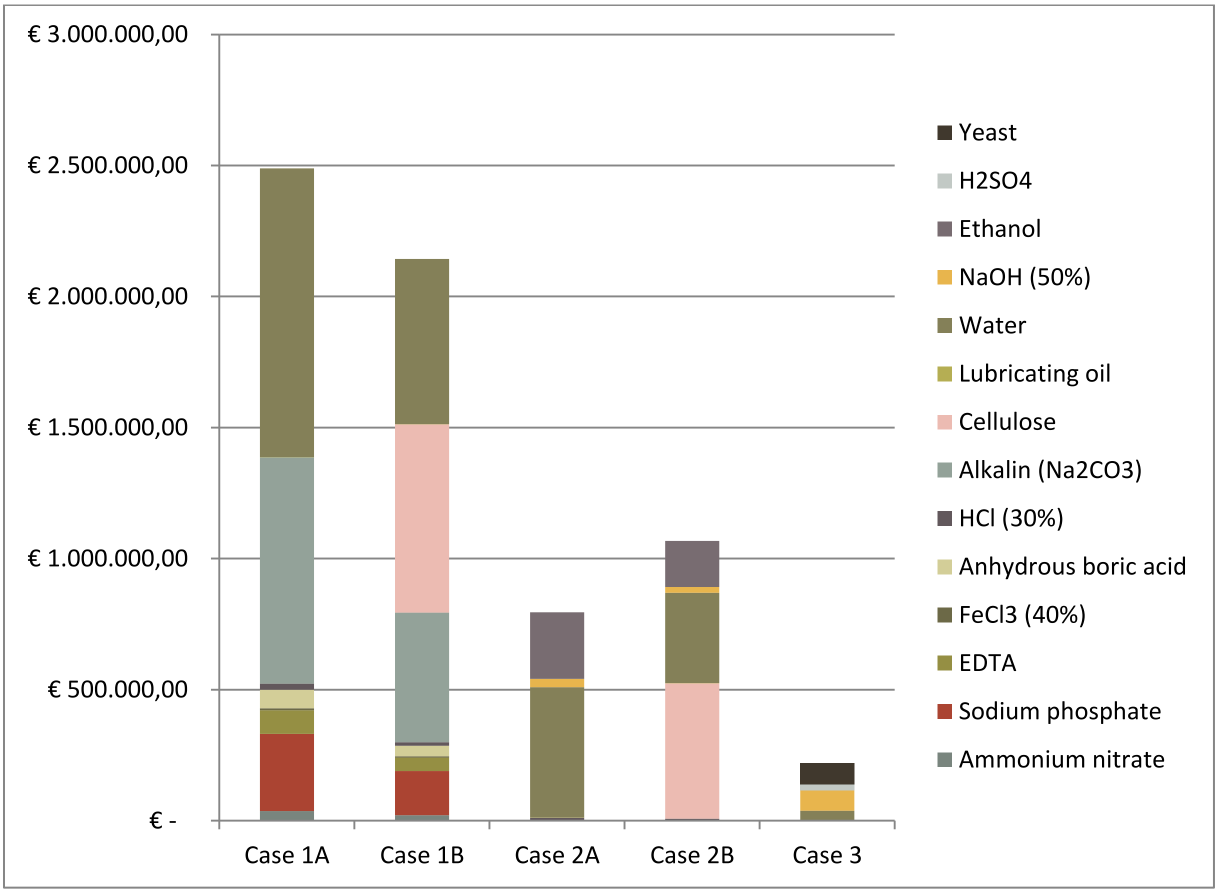


Figure 36. Total annual costs for compounds and substances.

4.5.4 *Annual profits*

Table 27 presents the annual profits, using the assumptions listed in the economic allocation tables before. The value of alginate is very high, in combination with the energy output of the case-studies and the low assumed productivity, this leads to large annual profits. Mainly in case 1A this effect is pronounced, because in this case the same amount of energy needs to be generated, but without the cellulose added. The annual revenue for the compost is even higher than for biomethane in case 1A. The profits for cases 2A and B are much smaller, due to the lower assumed value of ulvan, the lower yield of the ulvan extraction and the smaller amount of processed biomass. The annual profits for case 3 are the lowest, due to the low yield of the ABE fermentation.

Table 27. Annual profits for the case-studies

Case	Product	Annual profits (€/year)	Total profits (€/year)
1A	Alginate	€ 23,263,848.71	
	Biomethane	€ 127,966.82	
	Compost	€ 133,716.36	
			€ 23,525,531.88
1B	Alginate	€ 13,316,348.35	
	Biomethane	€ 127,966.82	
	Compost	€ 76,539.94	
			€ 13,520,855.10
2A	Ulvan	€ 564,395.25	
	Biomethane	€ 127,966.82	

	Compost	€ 79,416.96	
			€ 771,779.03
2B	Ulvan	€ 390,945.48	
	Biomethane	€ 127,966.82	
	Compost	€ 55,010.56	
			€ 573,922.86
3	Acetone	€ 79,641.50	
	Butanol	€ 347,922.91	
	Ethanol	€ 26,891.12	
			€ 454,455.53

4.5.5 Investment costs facilities

The investment costs of the biorefineries were calculated using the values of an ABE fermentation plant. The price of the equipment was calculated using the SCENT economic assessment tool. The most expensive parts will be the waste water treatment facility and the different stirred tank reactors. The costs for the biogas plant were calculated using the cost estimation of Walla (2008), while the cost of the ABE-facility was calculated according to Gapes (2000).

4.5.6 NPV and PBP

The net present value and simple pay-back period were calculated using equations 3.5.1 and 3.5.3. The results are presented in Table 28.

Table 28. Overview of NPV and PBP of the cases. Red and bold numbers indicate negative values.

Case	NPV	PBP
1A	€ 187.376.156,29	0,31
1B	€ 97.815.784,99	0,43
2A	**€ 39.743.597,54-**	**- 1,47**
2B	**€ 34.317.530,34-**	**- 1,48**
3	**€ 16.914.844,49-**	**- 3,36**

Only the NPV of case 1A and B is positive, and has a positive PBP. The PBP is even very low, especially when considering that many companies are looking for projects with a PBP less than five years (Blok, 2007). This is caused by the very high profits of these cases, which are even higher than the total investment costs. For cases 2A/B and 3, the annual benefits are lower than the costs. This causes a negative PBP, and also a negative NPV. A negative PBP does not provide information about the project, since the formula shows asymptotic behavior for negative vales. Therefore these value will not be used for the sensitivity analysis.

4.5.7 Overview of annual costs

In Figure 36, the different cost factors of the case-studies are presented. This way, the relative importance of the different cost factors compared with the capital costs will also become clear. Large differences between the cultivation costs are visible. In the cases 1A and 2A and 2B, the cultivation costs take up a large part of the total annual costs. For the A variations, the biomass requirement is much larger than for the B variations of the case-studies. In case 3 there are no harvesting costs, but only costs for the collection of the biomass. This influence on the overall economic performance is pronounced: here the costs of acquiring the raw biomass are only about one quarter of the total costs. The annual investment costs for all the cases are very small compared with the other costs. This again highlights the fact that the cultivation costs are important for the economic feasibility. It also indicates that the estimates of the investment costs are probably too low, when comparing this with cultivation costs, costs for compounds and utilities.

The costs for utilities are also large in all the cases, but the costs for compounds even more. Especially in case 1B and 2B this is clearly visible. In these cases the large costs are also associated with the costs of the cellulose. The total annual costs of case 3 are much lower than for the other cases. However, because the profits are small, the project is not economically feasible in this form.

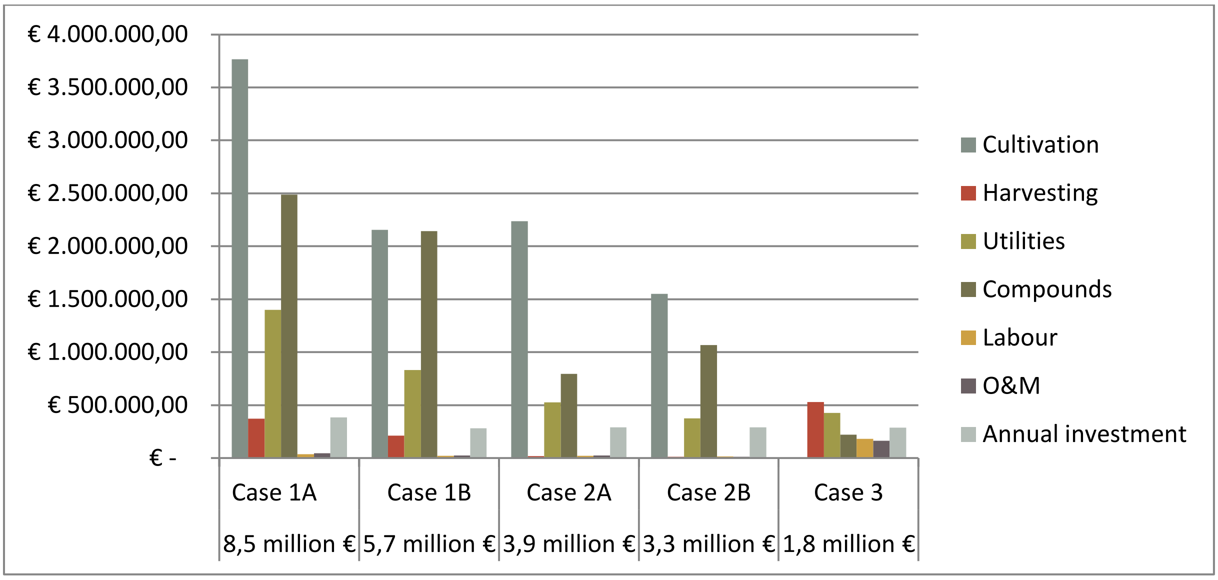


Figure 36. Overview of the annual costs per case-study. The total costs are indicated below the case-studies.

4.6 Sensitivity analysis

In this section, the influence of different parameters on the economic performance of the case-studies is presented. For most parameters, the NPV was used because of the asymptotic behavior of the PBP. When the value of benefits minus costs is negative, the PBP does not provide any information on the project.

The influence of the cultivation costs seemed to be large, and there is also a large uncertainty in the price factor since the costs were based on estimations from literature, but are far from certain. The results are presented in Figure 37, the values ranged from the lowest and highest price estimate presented in the shortlist before. The cultivation costs affect the NPV of case-study 1A the most. This is caused by the large amount of biomass required for this case-study. The effect on the NPV for case 1B and 2A is similar, also explained by the comparable amount of required biomass. From the graph it becomes visible that in this price range case 1A and B will remain to have a positive NPV, and case 2A and B a negative NPV. The break-even price for case 2A and B is therefore not reached in this range. With this trend line, the feedstock must be provided for a negative price in order reach a positive NPV for case 2A and 2B

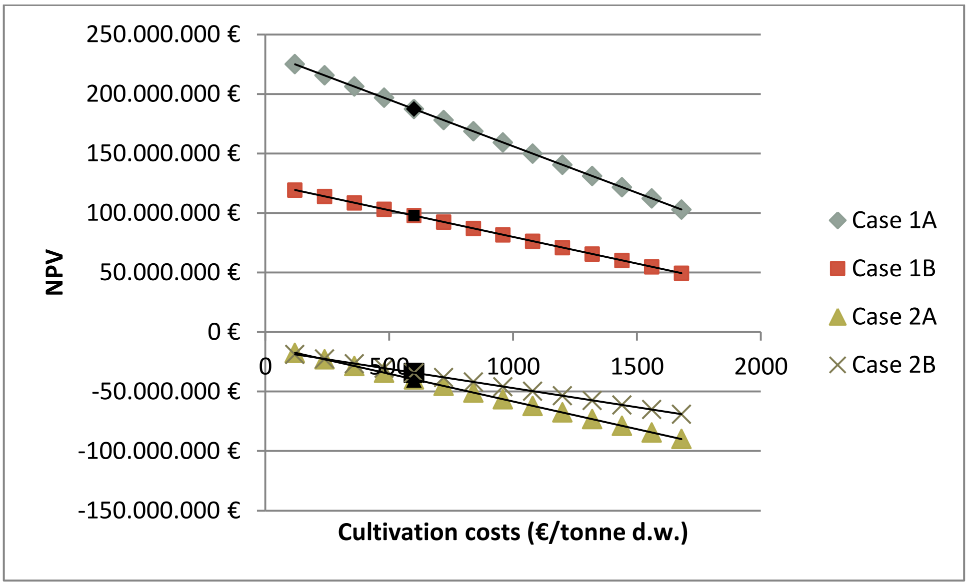


Figure 37. Influence of variation in cultivation costs on NPV. The assumed cultivation costs in this study were €600/tonne d.w., indicated as a black data point.

The influence of the yield of the extracted hydrocolloid is also an important parameter to study. The yield for alginate production was adapted from Langlois et al. (2012), which was 0,42 kg alginate per kg d.w.; while the yield for ulvan used In the case-study was only 0,03 kg ulvan/kg d.w. (Yaich et al., 2013). Most probably, the estimation of the yield for alginate extraction is too high. In Ostgaard et al. (1993) the alginate content was reported as 23% of the dry weight and in Vauchel et al. (2008) the extraction yield was 40% (these values would result in a value of 0,10 kg/kg d.w.). The industrial process could be more efficient, but this gives reason to believe that the assumed extraction yield from Langlois et al. (2012) might be too optimistic. Therefore, the range for the sensitivity analysis had 0,42 kg/kg d.w. as an upper value. The range assumed for ulvan extraction might be too low. According to Alves et al. (2012) the yield of extraction will range between 0.01-0.28 kg/kg d.w. This range was used for the sensitivity analysis for case 2.

Besides this, the assumed economic value of alginate is much higher than for ulvan. In Figure 38, it becomes visible that again the influence on the NPV is pronounced most for case 1A. This is because of the large amount of required biomass for this case-study. The extraction yield will have a large influence on the NPV, because there is a lot of biomass that will be used for the extraction process. It also becomes visible that the NPV of case 2A and 2B would be positive with a higher ulvan yield. This will happen quicker for case-study 2A. The effects on the NPV are higher for case 1B are larger than for 2A, because of the higher assumed value of alginate. Lastly, the trend lines of the different case-studies cross at the same yield, which is about 0,12 kg/kg.

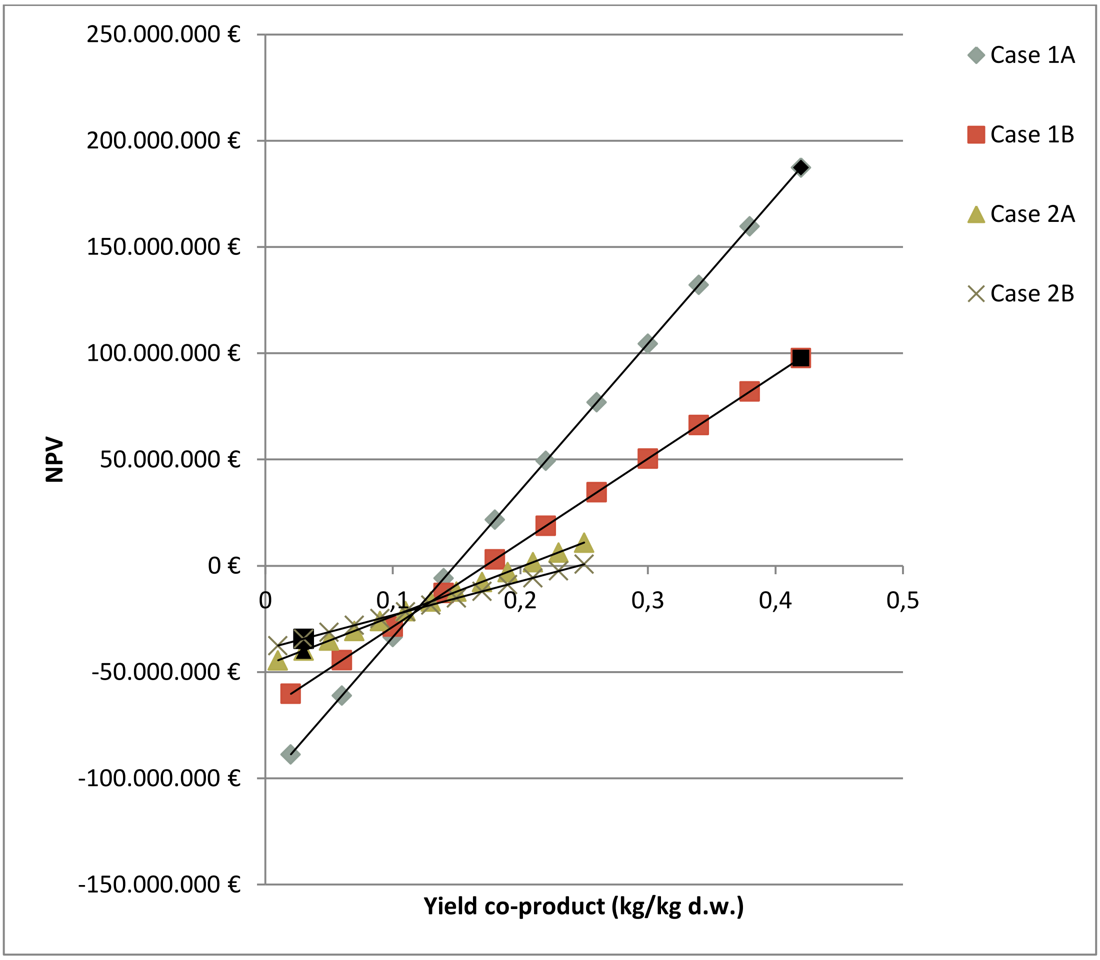


Figure 38. Influence of yield of co-product on NPV. The base-case is represented by a black data point, which is 0,03 kg/kg d.w. for ulvan production and 0,42 kg/kg d.w. for alginate production.

Like mentioned above, the assumed value of sodium alginate produced in case 1A and B is quite high ($12/kg, Bixler & Porse, 2010). Therefore the influence of a variation in this price was also analyzed in Figure 39. The range in prices was set between 7 and 18$/kg, which was the average price of hydrocolloids (agar, alginates, carrageenan) between 1999 and 2009. As expexted, the influence of the price is more important for case-study 1A (because of the larger biomass requirement and therefore the larger amount of profits from alginate).

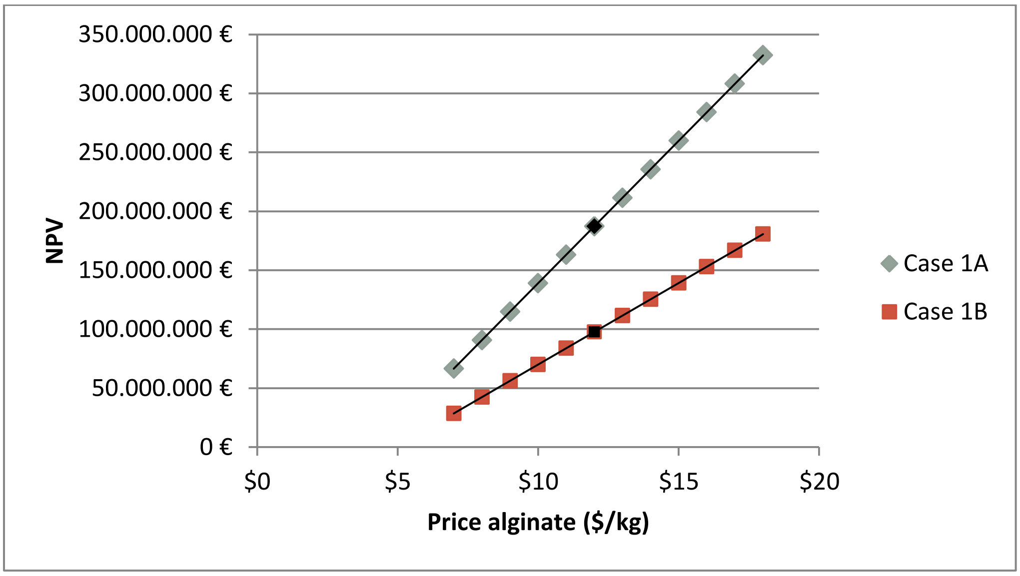


Figure 39. Influence of alginate price on NPV. The black data-points indicate the base-case of $12/kg (Bixler & Porse, 2010).

The productivity of *Saccharina latissima* assumed was only 1,75 tonne d.w./ha/year; compared with 20 for *Ulva lactuca*. After a sensitivity analysis, the effect of this parameter at the economic performance is very limited. With a range between 1,75 and 20 tonne d.w., the PBP remains to have a value around 0,30. Therefore, the productivity did not seem to have a very large influence on the economic performance of this case-study.

Figure 40 shows the influence of the price of cellulose on the NPV of case 2B. The price of the cellulose was estimated at 200€/tonne. The effect of this price is less pronounced than the effect of the ulvan yield, but is very comparable to the effect of the cultivation costs on the NPV of the project.

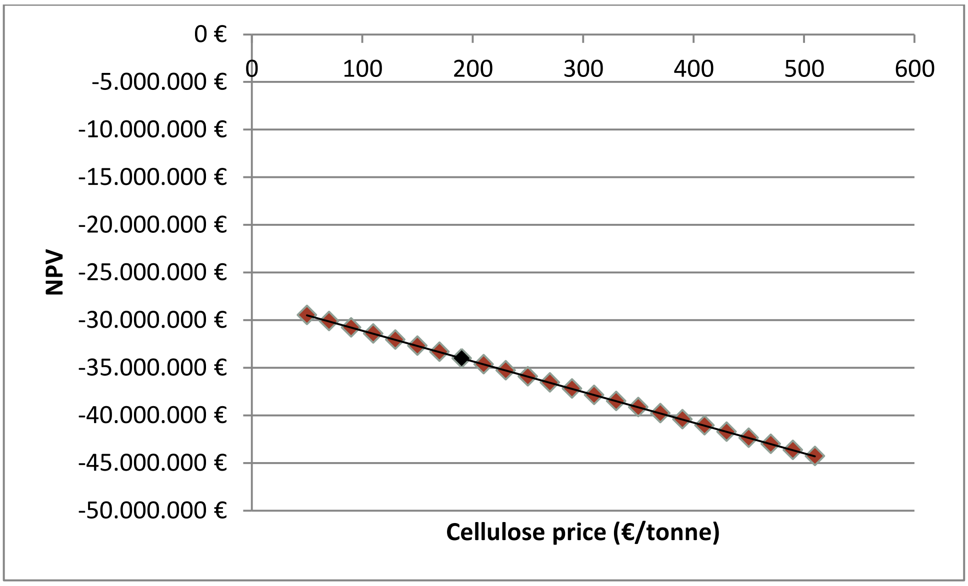


Figure 40. Influence of variation in cellulose price on NPV.The black data point indicates the base-case of €200/tonne cellulose.

Figure 41 shows the influence of the butanol yield on the NPV of case-study 3. Typical butanol yields are in the ragne of 0.15-0.23 kg/kg sugar. With a carbohydrate content of 0,407 kg/kg d.w. (Jard et al., 2013) this translated in a reasonable yield between 0,061-0,10 kg/kg d.w. A higher yield will result in lower collection costs for this case-study, but the energy output remains the same. This has to do with the design of the case-study. The products acetone, butanol and ethanol are produced in a ratio of 3:6:1. The energy contents of these three products together sum up to an energy production of 2,28 MJ/kg d.w. All the collected biomass together has to produce the fixed amount of energy, which was the same for all te case-studies (11290 GJ per year). When the yield of butanol increases, the ratio between the products stays the same and the other products will also be produced in larger quantities. The only effect this will have is that the biomass requirement will decrease. When the yield would be increased even more, the graph would show asymptotic behavior and the NPV would not become positive with a higher butanol yield.

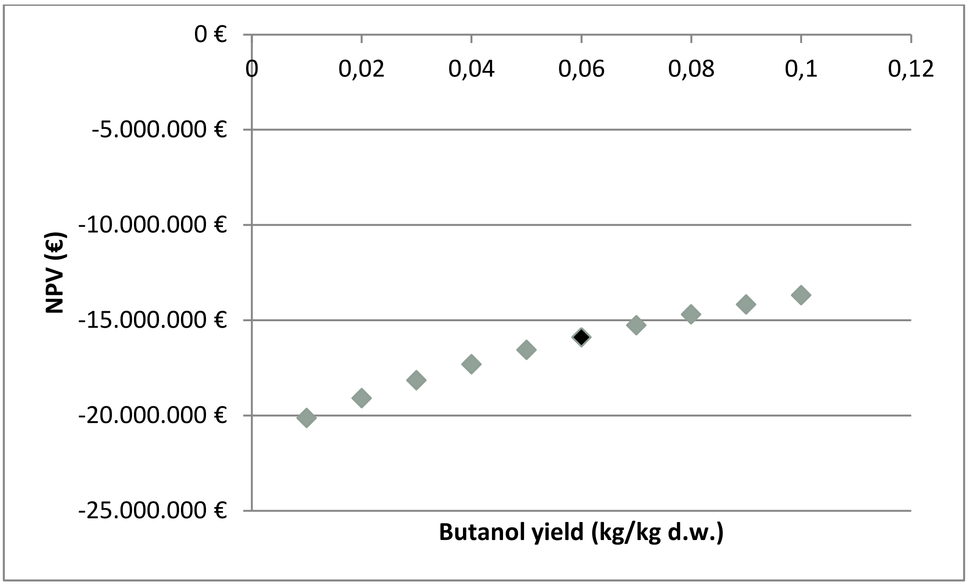


Figure 41. Influence of the butanol yield on NPV. The black data point indicates the base-case of 0.06 kg/kg d.w.

4.7 General discussion

4.7.1 Data-quality and availability

The research on the topic of the macroalgae biorefinery is still in an early stage. After the oil crises in the seventies, the interest in macroalgae as a potential feedstock for biofuel production ceased. Lately, there is a renewed interest in this topic, since there is a need for alternative feedstocks for biofuel production. Besides this, also the production of biobased products is an important research topic lately. Macroalgae are studied in the biorefinery context as well; however the extent to which this happened is very limited. There are some studies researching the technical potential; but economic and environmental studies are scarce, especially the combination of the two. The studies that are available, are often unclear in the assumptions, methods and calculations that were used (Reith et al., 2005; Langlois et al., 2012; Florentinus et al., 2008). Therefore this study could be very useful for the identification of future research needs and the gaps in the currently available data. The case-studies are not trustworthy enough to be used for absolute conclusions or reasonable estimates of the economic and environmental performance.

An important example of the lack of reliable data is the availability of reliable estimates for the cultivation costs of macroalgae. Many articles refer back to Bird & Benson (1987) for their estimations, a book which is hard to acquire, but also very outdated. Others refer to Chynoweth (2002), who also refers back to Bird. Some authors do not mention the weaknesses of this data. This makes the use of this type of data complicated, but sometimes unavoidable due to the lack of an alternative. Mainly for the large-scale cultivation concepts, there are many uncertain factors. While the cultivation of seaweed is common practice for ages, the lack of reliable data is striking.

Besides the uncertainties with regard to the seaweed cultivation, there are many more uncertainties in the production chain. For some potential products, the production methods are not established yet (examples are some platform chemicals, bio-active substances). This limits the choice for product mixes drastically to the more common products. Besides this, the industrial production methods for the more common product (like hydrocolloids) are often not publically available. Therefore lab protocols needed to be translated to an industrial process which did not increase the reliability of the study. Since the production of biofuels does not take place on a large scale yet, also these production methods are mostly available as a lab protocol. With regard to this, it was to early to formulate case-studies and conduct an environmental and economic analysis for the macroalgae-based biorefinery.

4.7.2 Design case-studies

The case-studies were designed based on the available data and literature. Several assumptions and calculations needed to be adapted in order to design realistic case-studies for the economic and environmental analysis. The case-studies were adapted in such a way that they all yielded the same energy output. This caused the biomass requirement and cultivation area of case 1A to become very large, also because of the relatively low methane yield of this species. Also the profits for case 1A and 1B became very large. The amount of sodium alginate annually produced in case 1A is 2600 tonne. The total sales volume for alginate in 2009 was 26.500 tonne (Bixler & Porse, 2010), so the biorefinery would provide in 10% of the global demand. This is not a realistic assumption. The assumed yield of 0,42 kg alginate/kg d.w. (Langlois et al., 2012) is high, and it is not an example of a high-value low-volume product (since there was 0,42 kg alginate produced per kg d.w.). Like mentioned before, the economic allocation applied here bears uncertainty due to price fluctuations. For most price estimations, only one data source was used.

For the cultivation of *Ulva lactuca*, the assumption was made that this species could be cultivated vegetative, and that plantlet production was not required. Whether this will work in practice is unknown, due to a lack of data. The yield for ulvan production was based on an experimental study (Yaich et al., 2013). The yield of alginate was adopted from the only LCA study (Langlois et al., 2012). These assumptions proved to be very important for the economic performance. The negative economic performance of case 2A and B could be explained partly by the low ulvan yield. The scale of the different case-studies appears to be very large (about 6300 tonne d.w. per year for case 1A), which will make the cases less realistic. However, there are reports where much larger scales are considered. The most relevant example is the report from Reith (2005), where scales of 100.000 and 500.000 tonnes d.w. per year were studied (compared with ±6000 tonnes d.w for case 1A). Concluding, the design of the case-studies could be changed, by making use of other yields and more reliable data from pilot plants.

4.7.3 Life-cycle inventories

The life-inventories were an important part of the case-studies. The inventory for case-study 1 is mainly adapted from the study from Langlois, who retrieved much of the data from a pilot plant. This data is not publicly available and can therefore not be checked. Also some assumptions are adapted from this study, like the productivity of *Saccharina latissima*. It was calculated that this productivity was 1,75 tonne d.w./ha/year, which is not corresponding with the literature. For example Laminaria japonica (a very common species, comparable with *Saccharina latissima*) could have a productivity of around 25 tonne d.w./ha/year (Bruton et al., 2009).

Some major adaptations were done to the inventory of Langlois (2012), where possible based on literature. But the exact conditions of production steps are often not published; therefore there is still room for improvement regarding this. Because the addition of cellulose to the process showed to have a major effect on the amount of biogas produced per kg of dry weight, the process was adapted both with and without addition of cellulose.

The inventories for cases 2 and 3 were based on the inventory for case-study 1, with adaptations were needed. Clearly the production methods were different, but the main available sources were lab studies. These small-scale experimental conditions needed to be up-scaled to an industrial process. Also here there is room for improvement, when possible with data from a pilot-plant. The products and amounts produced were adapted from Langlois et al. (2012). The amount of compost produced per kg d.w. seems to be very high. Unfortunately, there was no other source available to confirm this value.

4.7.4 Environmental analysis

While the LCA constructed in this study is a prospective one, there are some important aspects that can be used for future research. First, it became clear that the extraction process is an environmentally demanding process, which large energy- and material requirements. Especially when cellulose is added to the process, the REU of the extraction process increases compared to the process without cellulose addition. For case 1 the increased energy output makes that the B-variant (with cellulose) has a lower environmental impact per MJ produced than case 1A. But for case-study 2 the impact of the cellulose is relatively bigger, so that the environmental impact per MJ produced is larger for case 2B than 2A. According to Langlois, the alternative for the use of a cellulose filter is making use of diatomaceous earth. The environmental impacts for this filter aid were not considered in the case-studies, because a lack of data. This would improve the reliability of the case-studies.

For case 2, the impact of seaweed cultivation is much smaller than for case 1. This is caused by the assumption that Ulva lactuca could be cultivated vegetatively, combined with the low assumed productivity of Saccharina latissima. This could give a distorted image, since the low productivity of *Saccharina latissima* is probably not realistic.

The results in the study by Langlois are only presented with relative values, using all the ReCiPe impact categories. This causes that the results are hard to compare with this study. However, also in the study of Langlois it becomes visible that by far most of the environmental effects are to be attributed to the alginate extraction process. In the discussion of the study the authors also acknowledged that the process described in their inventory is far from ideal, and that the large quantities of water, cellulose and hydrochloric acid will have to reduce. They also suggested and tested some other improvements to the process. These include the use of electricity and heat produced by wind energy, material recycling, a less energy-intensive drying process, and less fuel consumption. The use of electricity of a renewable source was found to give the best improvements to the process.

For case-study 3, the separation of the products and the hydrolysis process caused the largest environmental impacts. The inventory of the energy-requirements for the separation process (distillation) is based on an LCA-study of an ABE fermentation plant with corn as a feedstock (Wu et al., 2007). Because of the large difference in size of the plants, it should be more convenient to use data from a plant with a smaller scale and a more comparable feedstock.

The environmental impacts were very large for all the case-studies. Case 3 received the lowest score on energy use (NREU + REU), with 3,78 MJ-equivalent per MJ produced, which is still a large number. Case-study 1B received a score of 30 MJ-equivalent. This means that from an environmental perspective, the case-studies in its present form do not seem to be a suitable alternative.

4.7.5 Economic analysis

The economic analysis showed some interesting results. Case 1A and B seem to be very attractive from an economic point of view. As discussed before, this is also caused by the design of the case-studies. The profits for these case-studies are very high. The very small PBP is caused by the fact that the profits per year are larger than the initial investment costs, which is an unrealistic assumption. Case-study 2A, 2B and 3 did not seem to be attractive in its current form. The sensitivity analysis showed that the assumed yield of alginate or ulvan is very important for the economic performance of the case-studies. With a higher yield, case-studies 2A and 2B could be economically feasible projects as well. The influence of the cultivation costs is mainly important for the case-studies with large biomass requirements. Within the studied range, case-studies 2A and 2B did not receive a positive NPV with lower cultivation costs. Therefore we can conclude that the yield of ulvan is much more important for these cases. The influence of the cellulose price showed to be as important as the cultivation costs. For case-study 3, the assumed butanol yield also showed to have an effect on the NPV. However, the NPV did not become positive for higher butanol yields. This is also caused by the fact that there is a fixed energy output for this study. So with an increased butanol yield, there is a lower biomass requirement for this case-study. The increase in yield does not lead to higher profits.

There are large uncertain factors in the economic analysis. An important example is the investment costs. These costs are retrieved from several sources (Gapes, 2000; Walla & Schneeberger, 2008) and were down-scaled where needed. Because of the lack of economic data, this was the best option. The costs for utilities and compounds where retrieved with an bottom-up approach; with help of the life-cycle inventories and common market prices (ICIS, 2006). This method can give substantial over-or under estimations. The fixed costs are very large compared with the investment costs for all the cases. This is an indication that the investment costs are estimated too low. Further research will be needed, to make more realistic cost approximations.

In the current form of the case-studies, only case 1A and 1B seem to be promising from an economic point of view. The assumed yield of alginate (0,42 kg/kg d.w.) is high, and is not an example of a high-value low-volume product. With slightly different assumptions case 2A and 2B could also have a positive NPV. The addition of cellulose does not seem to have a negative effect on the economic potential of case-studies 1B and 2B. Case-study 3 does not seem to be an economic feasible project. This is mainly due to the small profits that could be generated here. Clearly, reliable economic data would offer a more realistic image of the economic potential of the different case-studies.

4.7.6 Future research needs

Like indicated before, there is a large amount of missing information, required for the economic and environmental analysis of macroalgae-based biorefineries. Therefore there are some important research needs that are addressed as follows:

- There is a need for more detailed and trustworthy information on cultivation techniques and costs. While the seaweed cultivation takes place for centuries, there is surprisingly little reliable information available on this topic. Large-scale cultivation concepts should be studied further, for example the combination of macroalgae cultivation near offshore wind parks (Reith et al., 2005).
- The conversion techniques for macroalgae-based products are not well-established. It would be very useful if there are more studies on different conversion techniques, both for the production of common products as for products that are not commercially produced yet. Many production paths are only described on a lab-scale, while the data for production on an industrial scale would have much added-value. This would also give a more realistic image of the industrial yields of the processes.
- The type of study like it is presented in this thesis is scarce or even non-existent. There is a need for more integrated environmental and economic analyses treating the biorefinery concept. Langlois et al.(2012) took an important first step for an LCA study, but the study misses a lot of information and the values used are not always justified. The data from a pilot-plant in combination with expert interviews would improve the case-studies. The case-studies in this thesis had to be designed without much supporting, relevant and reliable literature, so a lot of improvement is possible here.

5. Conclusions

Due to the increase in demand for energy and chemicals and the effects of global climate change, there is a strong case for the use of alternative resources. One of these alternatives is the use of biofuels, which could cause issues related to food security, water- and land use. The production of fuels and compounds from seaweed could be an interesting option, because macroalgae can be cultivated in seawater in large quantities. However, there are many aspects that need to be addressed before the seaweed-based biorefinery can be established. In this thesis, an overview was given of certain issues and the concept was studied on the basis of case-studies.

One of the conclusions is that much crucial data is missing in order to study the biorefinery concept for seaweed. This limited the options drastically and therefore not all the questions could be answered. This was the case for cultivation concepts, and also for potential products to be produced. While there are different cultivation concepts presented in literature (Chynoweth, 2002; Florentinus et al., 2008), the cultivation assumed for the case-studies was large-scale long-line cultivation. For other potential cultivation methods, there was not enough available information to base the life-cycle inventories on. For the third case-study, the biomass was collected from heavy accumulated spots (Potts et al., 2012). The cultivation costs were retrieved from literature, and was based on reasonable estimates.

From the analysis based on selection criteria, several genera seem to be interesting to study further; these were *Ulva, Saccharina/Laminaria* and *Gracilaria*. The latter genus was dropped due to the data availability. *Ulva lactuc*a and *Saccharina latissima* formed the basis of the case-studies. With the available data, the best production methods were selected. This formed the basis for the life-cycle inventory. The production of biogas is one of the more viable options, without important technical issues (FAO, 2003). The production of hydrocolloids is serving an established market, which could generate the required profits (Bixler & Porse, 2010). The ABE-fermentation process was studied for the third case-study. A lot of work still needs to be done, because the inventories are based on many uncertain assumptions. The environmental performance of the case-studies in this form was not good, considering that the total energy use for case 1B was 30 MJ-equivalent per MJ output. A large part of this impact is caused by the extraction of alginate, but also without the extraction process the impact is too high.

The biorefinery concept showed that by producing a high-value product the project could be economical feasible. This was especially true for the first case-study. However, the assumed yield of the co-product is very important for the economic performance. The investment costs were lower than the profits for case 1, which is not realistic. From the analysis, it became clear that the data required for an environmental and economic analysis is not sufficient. The best possible estimates were done to perform a prospective analysis. The uncertainty range is large, but hard to indicate. The design of the case-studies also affected the results; therefore follow-up studies could offer new insights. This study is one of the few studying both the environmental as the economic aspects of the macroalgae-based biorefinery (other examples are Reith et al., 2005; Florentinus et al., 2008). Also in these other studies, the uncertainty of the results seemed to be large.

In this study the important aspects of the macroalgae-based biorefinery were demonstrated. The extraction process is an energy-intensive process with potential improvements. In particular the plantlet cultivation for Saccharina latissima was energy demanding when considering the cultivation process. The alginate-and ulvan yield are very important for the economic feasibility of the project. The assumed costs for cultivation have a less pronounced effect on the economic performance. Further research should be focused on optimal ways for large-scale cultivation, the most economical harvesting method and other product mixes.

Concluding this, the research question posed in section 1.7 cannot be answered. After this study, the technical, environmental and economic potential is not yet demonstrated. Not all the possibilities could be studied due of a lack of data and the environmental and economic analysis was not reliable enough to draw absolute conclusions on. The analysis offered useful insights and demonstrated the required further research needs.

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Appendices

Appendix A – the knowledge gap

Selection of research on macroalgae-based biorefinery/ biofuels sorted in different categories.

Article title	*Year*	*Authors*	*Journal*	*Main contribution*	*Useful*	*Missing*
General studies: algae biorefinery						
Marine macroalgae: an untapped resource for producing fuels and chemicals	2013	Wei et al.	Trends in Biotechnolog y	Introducing advantages of macroalgae, broad review with some more specific parts. Mainly focussing on conversion of macroalgae into biofuels. Overview of biofuel projects	Conversion into biofuels, issues related to this	Very short on co-products
Green chemistry and the ocean-based biorefinery	2013	Kerton et al.	Green Chemistry	Broad, also adressing microalgae and fish waste. Adresses the products that can be produced from macroalgae	Co-products	Real design and practical issues of biorefinery
Case-studies						
Proposed design of distributed macroalgal biorefineries: thermodynamics, bioconversion technology, and sustainability implications for developing economies	2013	Golberg et al.	Biofuels, Bioproducts & Biorefining	Article focusses on conversion of Ulva spp. into bioethanol. With help of modeling equations, the optimal biorefinery scale and service area size. Attention is paid to the sustainability and cultivation of Ulva, and to conversion methods. All the findings	The use of a case-study, the study of a specific type of seaweed in a biorefinery approach	Only production of bioethanol is considered, while the biorefinery concept is studied
A visionary and conceptual macroalgae-based third-generation bioethanol biorefinery in Sabah, Malysia as an underlay for renewable and sustainable development	2010	Goh & Lee	Renewable and Sustainable Energy Reviews	Adresses practical issues of the selected case-study. Useful biorefinery scheme	Case-study	Main aim of study is to attract attention from researchers, not very thrustful statement
Studies by a non-academic institute						
A Review of the potential of Marine Algae as a Source of biofuel in Ireland	2009	Bruton et al.	Sustainable Energy Ireland	Very extensive analysis of the situation in Ireland, both on micro as macro algae. Scenario development	Much information on all the different processes for biofuel production	Non-scientific, but based on scientific literature
Bio-offshore; Grootschalige teelt van zeewieren in combinatie met offshore windparken in de Noordzee	2005	Reith et al.	ECN	Focussed mainly on cultivation and processing. A very extensive economic analysis, often referred to in other articles.	Economic analysis, policy analysis	Non-scientific, conversion to products briefly discussed

Selection of studies of specific products or species of macroalgae

Article title	*Year*	*Authors*	*Journal*	*Main contribution*	*Useful*	*Missing*
Specific studies						
Kinetics modeling of alginate alkaline extraction from Lamaria digitata	2009	Vauchel et al.	Bioresource Technology	Production methods and reaction conditions for one co-product from one species	Specific reaction conditions	No coupling to a broader perspective
Effect of extraction conditions on the yield and purity of ulvan extracted from *Ulva lactuca*	2013	Yaich et al.	Food Hydrocolloids	Production methods and reaction conditions for one co-product from one species	Specific reaction conditions	No coupling to a broader perspective
Specific studies, adressing the biorefinery concept						
Production of acetone, butanol, and ethanol from biomass of the green seaweed *Ulva lactuca*	2013	van der Wal et al.	Bioresource Technology	Description of specific experiments with one macroalgae specie. Reaction conditions included, yields.	Reaction conditions, multiple product study	-
Bioethanol production from Gracilaria verrucosa, a red alga, in a biorefinery approach	2013	Kumar et al.	Bioresource Technology	Specific experiments with one specie, reaction conditions. Yields, also compared with other species	Comparison with other species, mass balance, biorefinery scheme	-

Appendix B – medical and pharmaceutical applications of macroalgae

The different medical applications for carbohydrates present in macroalgae (Holdt & Kraan, 2011)**. This Table displays a summary of the different studies and activities, but is not exhaustive.**

Species		Component	Activity	Source
Saccharina	*lattisima*	Carbohydrates	Anti-tumour, anti-herpetic	Table 4
Saccharina	*pallidum*	Carbohydrates		
Saccharina	*lattisima*	Algins, alginic acid	Antibacterial, anticancer, lowering cholestrol in liver, anti-obesitas, anti-diabetes and more	Table 4
Laminaria	*spp.*			
Undaria	*pinnatifida*			
Sargassum	*vulgare*			
Ulva	*spp.*			
Kappafycus	*alvarezii*	Carrageenan	Anti-coagolant, stimulates collagen formation, treatment of diarrhoea, constipation and dysentery, anti-viral	Table 4
Kappafycus	*striatum*			
Eucheuma	*cottonii*			
Gracilaria	*spp.*	Agar	Decrease in blood glucose concentration, anti-tumour, anti-oxidant activity, absorption effect of UV rays	Table 4
Laminaria	*spp.*	Fucoidan	Anti-viral, anti-cancer, anti-coagolant, anti-oxidant	Table 5
Sargassum	*spp.*			
Undaria	*pinnatifida*			
Ulva	*pertusa*			
Porphyra	*haitaneses*			
Saccharina	*spp.*	Mannitol	Protects photosynthetic apparatus from low-salinity damage	Table 6
Laminaria	*spp.*			
Sargassum	*spp.*			
Saccharina	*lattisima*	Laminarin	Stimulates immune-system, anti-viral, anti-bacterial	Table 6
Laminaria	*spp.*			
Undaria	*pinnatifida*			
Ulva	*spp.*	Ulvan	Anti-influenza	Table 6

Appendix C – composition data

Detailed composition of the species studied in the case-studies (Jard et al., 2013).

Component	Unit	*Saccharina lattisima*	*Ulva lactuca*
TS fresh algae	g/kg	185	101
TS dried algae	g/kg	922	833
Mineral content	g/kgTS	436	179
Volatile solid (VS)	g/kgTS	564	821
Carbon content	g/kgTS	261	407
Total Kjeldahl nitrogen	g/kgTS	22	27
Ratio Carbon/ Nitrogen		11,8	15,1
Protein content	g/kgTS	110	131
Lipid content	g/kgTS	<10	16
Sugar content	g/kgTS	223	314
Fiber content	g/kgTS	359	421
Soluble fiber	g/kgTS	286	227
Insoluble fiber	g/kgTS	73	194
Mannitol	g/kgTS	14	4
Sodium	g/kgTS	60	20
Potassium	g/kgTS	109	11
Total sulphur	g/kgTS	11	44
Sulfates	g/kgTS	22	108
Chloride	g/kgTS	129	23
Phosphorus	g/kgTS	4	1
Ratio Sodium / Potassium		0,5	1,8

Biochemical composition, carbohydrates and polyphenols (Jard et al., 2013)**. Total alginates: 1,18*uronic acid. Total sugars: total alginates not included.**

Component (g/kgTS)	*Saccharina latissima*	*Ulva lactuca*
Uronic acid (guluronic + mannuronic)	206	
Ratio mannuronic to guluronic	1,4	
Total alginates (*1,18 uronic acid)	243	
Fucose	12	
Galactose		
Xylose		34
Glucose	<5	75
Rhamnose		104
Mannose	5	
Total sugars	223	314
Polyphenols	1,2	

Appendix D – life-cycle inventories

Life-cycle inventory for case-study 1A and 1B. All numbers are expressed per kg d.w. algae.

Process	Subsystem	Material inputs	Quantity	Unit
Plantlet production - materials	Nursery facilities	Concrete, for foundations	0,00000407	m3
		Cement	0,000651	m3
		Concrete blocks	0,00176	kg
		Agricultural shed	0,0000289	m2
	Plantlet cultivation in the nursery	Ammonium nitrate	0,04015	kg N
		Sodium phosphate	0,0324	kg Na3O4P
		EDTA	0,0177	kg
		FeCl3 (40%)	0,00268	kg
		Chemical inorganics	0,00266	kg
		Anhydrous boric acid	0,0155	kg
		Weaved polyamid	0,00717	kg
	Water treatment in the nursery	Water (filtered seawater)	4,6	l filtered seawater
Plantlet production - energy	Plantlet cultivation in the nursery	Electricity (circulation pump)	38,5	Wh
		Electricity (fluorescent lamps)	199,4	Wh
		Electricity (sparger)	65,9	Wh
	Water treatment in the nursery	Electricity (lamp UV)	8,7	Wh
		Electricity (circulation pump)	1,4	Wh
		Electricity (sand filter pump)	27,6	Wh
Offshore seaweed cultivation - materials	Offshore cultivation facilities	Steel	0,014	kg
		Moulded polypropylene	0,00423	kg
		Rigid foam polyurethane	0,0000136	kg
		Weaved polyamide	0,016	kg
		Concrete	0,5	kg
		Glass fibers	0,0102	kg
Harvesting - energy	Harvesting	Diesel	0,0152[14]	kg
Alginate extraction - materials	Biorefinery facilities	Chemical plants, organics	8,99E-09	p
	Alcoholic pre-treatment step[15]	Freshwater	10	L
	Alginate extraction - acid lixiviation	HCl (30%)	0,0243	kg
		Freshwater	3,98	L
	Alginate extraction - alkaline extraction	Alkalin (Na2CO3 1,5%)	0,2	kg
		Cellulose (only case 1A)	1[16]	kg
		Freshwater	10	L
	Alginate extraction - rectification	HCl (30%)	0,0243[17]	kg

[14] 0,11 L diesel use required per km*tonne (Langlois et al., 2012). Calculates to 166 km to the shore
[15] A high recycling rate for the ethanol is assumed here (Langlois et al., 2012)
[16] Quantity of 2,44 kg/kg d.w. used in Langlois (2012). A 1:1 ratio seemed to be more realistic.
[17] Quantity of 1601,6 kg 2M HCl/kg d.w. used in Langlois (2012). This quantity is unjustified, and also not reported by Vauchel et al. (2008)

		Freshwater	16,7	L
	Alginate extraction - conversion to sodium alginate	Alkalin (Na2CO3)	0,12	kg
Alginate extraction - energy	Alcoholic pre-treatment step	Electricity (crusher)	29[18]	Wh
		Electricity (strainer)	98	Wh
		Electricity (still)	339	Wh
	Alginate extraction - acid lixiviation	Electricity (strainer)	200	Wh
	Alginate extraction - alkaline extraction	Electricity (blender)	238	Wh
		Heating (Gas, 50-60 C)	482	Wh
		Electricity (filter press)	223,55	Wh
		Cooling (to 20 C)	639,54	Wh
	Alginate extraction - rectification	Electricity (blender)	66	Wh
		Electricity (strainer)	98	Wh
		Cooling (0-10 C)	83	Wh
	Alginate extraction - conversion to sodium alginate	Electricity (convective dryer)	67	Wh
Anaerobic digestion -materials	Anaerobic digestion facilities	Concrete blocks	0,00726	kg
		Concrete	0,00000089	m3
		Concrete, foundations	0,00000178	m3
		Extruted polyvinylchloride	0,000157	kg
		Unalloyed steel	0,0000482	kg
		Chromium steel	0,0000482	kg
		Extruted polyethylene high density	0,00000692	kg
	Anaerobic digestion	Lubricating oil	0,000119	kg
	Biomethane purification	Facilities, chemical production	0[19]	kg
		Water (water losses)	84	L
Anaerobic digestion - energy	Anaerobic digestion	Electricity	42,2	Wh
		Biomethane	629,5	Wh
	Biomethane purification	Electricity	5,35	Wh

[18] Energy requirement for a hammer mill (crushing straw): 29 kWh/tonne (Sun & Cheng, 2002)

[19] Quantity of 0,254 kg/kg d.w. used in Langlois (2012). Removed, since the environmental impacts are very large, which is not realistic for material requirements.

Life-cycle inventory for case-study 2A and 2B (Ulva lactuca). All numbers are expressed per kg d.w. algae.

Process	Subsystem	Material inputs	Quantity	Unit
Offshore seaweed cultivation - materials	Offshore cultivation facilities[20]	Steel	0,00123	kg
		Moulded polypropylene	0,00037	kg
		Rigid foam polyurethane	0,00000	kg
		Weaved polyamid	0,00140	kg
		Concrete	0,04387	kg
		Glass fibers	0,00090	kg
Harvesting - energy	Operating barge	Diesel[21]	0,0152	kg
Ulvan extraction - materials	Biorefinery facilities	Chemical plants, organics	1,51E-14	p
	Acid extraction	HCl (30%)	0,03866	kg
		Water	10	L
		Cellulose (only case 2A)	1	kg
	Neutralization	NaOH (50%)	0,0255	kg
	Precipitation	Ethanol (96%)[22]	0,0946	kg
Ulvan extraction - energy	Pre-treatment	Electricity (chrusher)	29[23]	Wh
		Electricity (strainer)	98	Wh
	Acid extraction	Natural gas (heating)	904	Wh
		Electricity (stirring)	98	Wh
	Cooling	Natural gas	665	Wh
	Centrifuging	Electricity (centrifuge)	16,7[24]	Wh
	Ulvan precipitation	Electricity (centrifuge)	16,7	Wh
	Drying	Natural gas (drying)	473	Wh
Anaerobic digestion - materials	Anaerobic digestion facilities	Concrete blocks	0,0012284	kg
		Concrete	0,000371	m3
		Concrete, foundations	1,19339E-	m3
		Extruted polyvinylchloride	0,0014039	kg
		Unalloyed steel	0,0438747	kg
		Chromium steel	0,0008950	kg
		Extruted polyethylene high density	0,000157	kg
	Anaerobic digestion	Lubricating oil	0,000119	kg
	Biomethane purification	Facilities, chemical production	0[25]	kg
Anaerobic digestion - energy	Anaerobic digestion	Electricity	42,2	Wh
		Biomethane	629,5	Wh
	Biomethane purification	Electricity	5,35	Wh

[20] All values from Langlois divided by 11,4; to account for the higher productivity of *Ulva lactuca*
[21] 0,11 L diesel use required per km*tonne (Langlois et al., 2012). Calculates to 166 km transport distance
[22] A 1:1 ratio of extract juice to ethanol is assumed (Paradossi et al., 1999). A 98% recycling rate of the ethanol is assumed.
[23] Energy requirement for a hammer mill (crushing straw): 29 kWh/tonne (Sun & Cheng, 2002)
[24] Energy requirement for centrifuging adapted from European Commission (2006)
[25] Quantity of 0,254 kg/kg d.w. used in Langlois (2012). Removed, since the environmental impacts are very large, which is not realistic for material requirements.

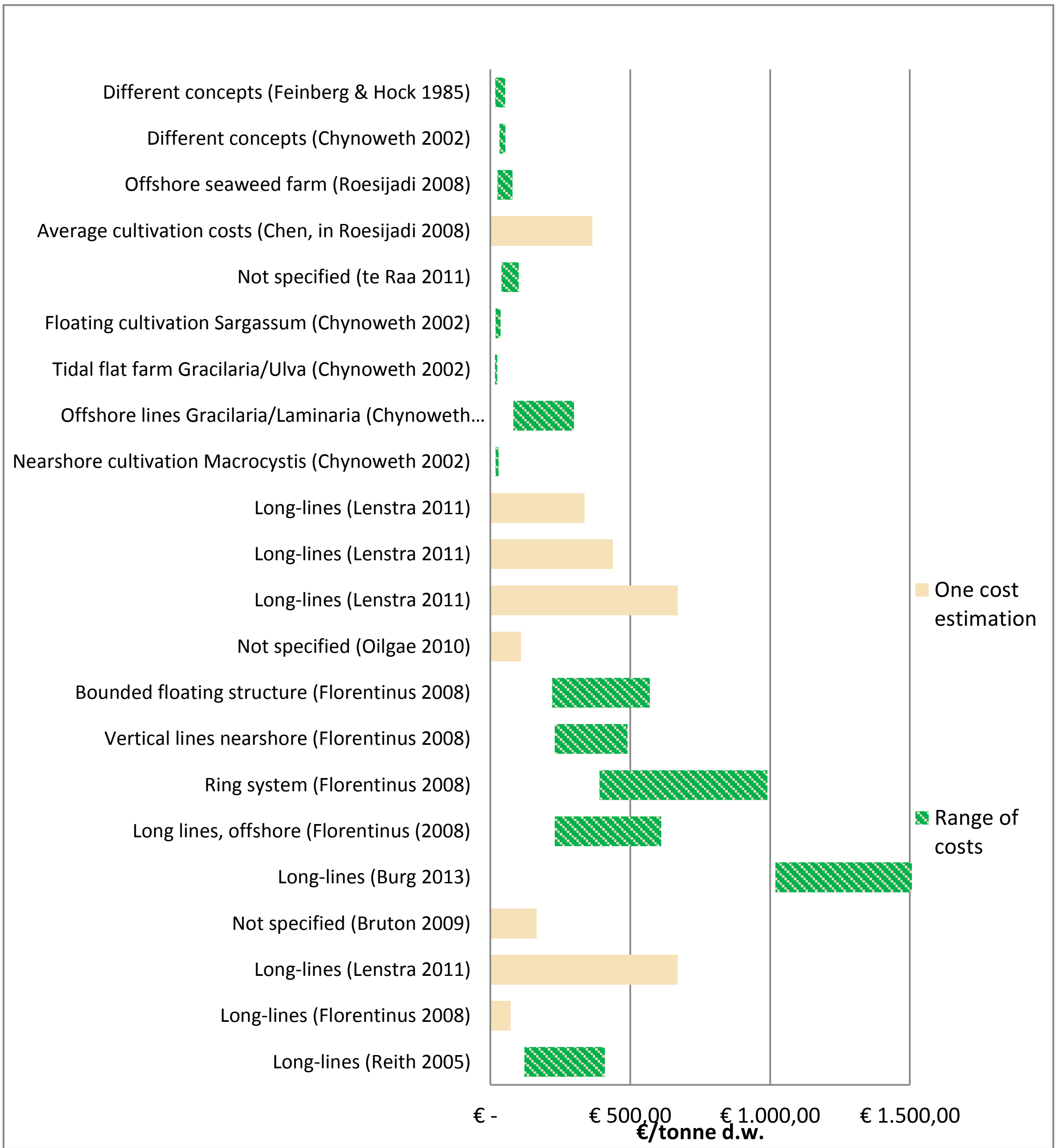
Life-cycle inventory for case-study 3 (Ulva lactuca). All numbers are expressed per kg d.w. algae.

Process	Subsystem	Material inputs	Quantity	Unit
Collecting biomass - energy	Operating barge	Diesel	0,0275	kg
Hydrolysis - materials	ABE fermentation facilities[26]	Concrete blocks	0,00362	kg
		Concrete	0,00000045	m3
		Concrete for foundation	0,00000089	m3
		Extruded PVC	0,0000779	kg
		Unalloyed steel	0,0000317	kg
		Chromium steel	0,000024	kg
		Extruded polyethylene high density	0,00000492	kg
	Hydrolysis of the biomass	Water	5,75	L
		Sulfuric acid (pure)	0,058	kg
	Neutralization	NaOH (50%)	0,047	kg
Hydrolysis - energy	Pre-treatment	Electricity (chrusher)	29[27]	Wh
		Electricity (strainer)	98	Wh
	Hydrolysis of the biomass	Natural gas (heating)	578	Wh
Fermentation - materials	Fermentation	Yeast (C saccharoper-butylacetonicum)	0,0012	kg
Fermentation - energy	Fermentation	Steam (agitator)	0,0	Wh
		Electricity (condensor)	78,6	Wh
		Electricity (gas pump)	1,5	Wh
		Electricity (gas stripper)	0,0	Wh
Separation products - materials	Facilities	Facilities, chemical production	0[28]	kg
Separation products - energy	Downstream processing[29]	Steam (adsorption feed pump)	0,0	Wh
		Steam (distillation column 1)	0,0	Wh
		Steam (distillation column 2)	465,2	Wh
		Steam (distillation column 3)	42,5	Wh
		Steam (distillation feed pump 2)	0,0	Wh
		Steam (distillation feed pump 3)	0,0	Wh
		Steam (adsorbent regeneration)	-5,4	Wh
		Electricity (adsorbent regeneration)	6,0	Wh

[26] Assumed that the material requirements are comparable with material requirements for the processing of whole seaweeds (Langlois et al., 2012).
[27] Energy requirement for a hammer mill (crushing straw): 29 kWh/tonne (Sun & Cheng, 2002).
[28] Quantity of 0,254 kg/kg d.w. used in Langlois (2012). Removed, since the environmental impacts are very large, which is not realistic for material requirements.
[29] All numbers adapted from Wu et al. (2007). Downscaled with a factor of 72,5 to account for the smaller scale of this case-study.

Appendix E – cultivation costs, costs of utilities and compounds

Long-list of price estimations of cultivation costs. Light bar indicates one value, green bar a range of values.



Assumed prices expressed in 2014 €/MWh (European Commission, 2014).

Category	€/MWh
Electricity case 1A	€95
Electricity case 1B	€100
Electricity case 2A	€120
Electricity case 2B	€135
Electricity case 3	€125
Natural gas (all cases)	€50

Assumed prices compounds expressed in 2014 € / tonne

Compound	Price		Source
Ammonium nitrate	€	148.00	Icis
Sodium phosphate	€	1,444.00	Icis
EDTA	€	811.00	Icis
FeCl3 (40%)	€	481.60	Icis
Anhydrous boric acid	€	719.00	Icis
HCl (30%)	€	77.40	Icis
Alkalin (Na2CO3)	€	430.00	Icis
Cellulose	€	200.00	Estimated
Lubricating oil	€	1,571.00	Icis
Water	€	1.36	Australian Government[30]
NaOH (50%)	€	335.00	Icis
Ethanol	€	719.00	Icis
H2SO4	€	81.00	Icis
Yeast	€	13,600.00	Sigma-Aldrich

[30] URL: http://www.dews.qld.gov.au/policies-initiatives/water-sector-reform/water-pricing/bulk-water-prices

Appendix F - cost-balance of the different case-studies

Case		Investment (€)			Costs (€/year)		Benefits (€/year)
Case 1A	Biorefinery	€	3,113,987.43	Cultivation	€ 3,766,800.00	Alginate	€ 23,263,848.71
	Biogas plant	€	1,659,026.06	Harvesting	€ 372,031.70	Biomethane	€ 127,966.82
				Utilities	€ 1,399,503.27	Compost	€ 133,716.36
				Compounds	€ 2,488,410.59		
				Labour	€ 35,438.13		
				O&M	€ 44,801.68		
Total		**€**	**4,773,013.48**		**€ 8,106,985.37**		**€ 23,525,531.88**
Case 1B	Biorefinery	€	2,579,781.20	Cultivation	€ 2,156,135.97	Alginate	€ 13,316,348.35
	Biogas plant	€	926,821.05	Harvesting	€ 212,952.89	Biomethane	€ 127,966.82
				Utilities	€ 832,486.57	Compost	€ 76,539.94
				Compounds	€ 2,143,091.19		
				Labour	€ 22,090.40		
				O&M	€ 23,727.60		
Total		**€**	**3,506,602.25**		**€ 5,390,484.61**		**€ 13,520,855.10**
Case 2A	Biorefinery	€	3,252,033.81	Cultivation	€ 2,237,181.79	Ulvan	€ 564,395.25
	Biogas plant	€	949,319.11	Harvesting	€ 19,388.91	Biomethane	€ 127,966.82
				Utilities	€ 525,448.13	Compost	€ 79,416.96
				Compounds	€ 794,831.66		
				Labour	€ 22,626.63		
				O&M	€ 24,303.58		
Total		**€**	**4,201,352.92**		**€ 3,623,780.69**		**€ 771,779.03**
Case 2B	Biorefinery	€	3,035,586.09	Cultivation	€ 1,549,651.79	Ulvan	€ 390,945.48
	Biogas plant	€	601,165.56	Harvesting	€ 13,430.32	Biomethane	€ 127,966.82
				Utilities	€ 375,820.48	Compost	€ 55,010.56
				Compounds	€ 1,067,114.84		
				Labour	€ 16,496.30		
				O&M	€ 13,314.20		
Total		**€**	**3,636,751.65**		**€ 3,035,827.92**		**€ 573,922.86**
Case 3	Pre-treatment	€	427,265.41	Cultivation	n.a.	Acetone	€ 79,641.50
	ABE facility	€	3,166,800.00	Harvesting	€ 529,806.06	Butanol	€ 347,922.91
				Utilities	€ 428,244.75	Ethanol	€ 26,891.12
				Compounds	€ 220,198.50		
				Labour	€ 182,700.00		
				O&M	€ 162,400.00		
Total		**€**	**3,594,065.41**		**€ 1,523,349.31**		**€ 454,455.53**