

Kelp2Plastics

Converting sugar kelp into biobased plastics

Paulien Harmsen

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Colophon

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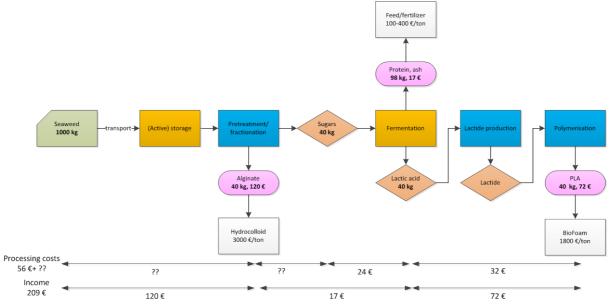
Abstract

Ocean Forest is a partnership between Leroy Seafood Group ASA and the Bellona Foundation. The aim of Ocean Forest is to develop and establish new forms of biomass production tied to aquaculture. The company wants to reduce the costs of biomass production at sea, as well as to develop products for food, feed, energy and raw materials for industry and aquaculture. In open water aquaculture there is increasing focus on the nutrient load (N+P) into the environment from the fish farming activities. An option to reduce this nutrient load is to use the extractive properties of seaweeds and bivalves (e.g. clams, oysters, mussels) to remove these nutrients. This concept is known as Integrated Multi-Trophic Aquaculture (IMTA) and is gaining a lot of attention at the moment. IMTA has great potential for both aquaculture and coastal areas for the production of new products from seaweeds. The Ocean Forest site in Norway has facilities to produce salmon, blue mussels and b<u>rown seaweed</u> together in one system. Aim of this study was to get insight in the options of <u>converting seaweed</u> into valuable products like bioplastics in order to fully recycle materials generated by the salmon production.

Brown seaweeds are interesting sources of biomass as they contain both fermentable sugars and alginates. Species common to Norway are *Laminaria hyperborea, Laminaria digitata, Ascophyllum nodosum* and *Saccharina latissima*. These seaweeds are currently used as feedstocks for the production of alginate for food and pharma applications and seaweed meal as feed or fertilizer. Biochemical composition is influenced by type, environmental conditions, maturity, gender and season. Within brown seaweeds variations in storage carbohydrates (laminarin, mannitol) is large, whereas variation in structural carbohydrates (alginic acid, cellulose) is less pronounced. Highest yields of laminarin and mannitol coincides with the lowest yields in ash, protein, moisture and polyphenols and vice versa. Due to these variations, selecting the right seaweed and time of harvest seems necessary for optimal exploitation of the seaweed biomass.

In this study rough calculations were performed to estimate the potential income in \notin /ton wet seaweed. *Saccharina latissima* was selected as model seaweed, main constituents were identified and market values were estimated. 3 Different cases were described with different output: Multiple products, Alginate and sugars, and Sugars. From the calculations it was clear that currently the application of alginic acid as alginate generates the highest income. For the calculations we assumed $3 \notin$ /kg for technical grade alginate, but depending on the quality it can be even more than $10-12 \notin$ /kg. In such a situation the only real value of brown seaweed is as source of alginic acid. Also fucoidan was regarded as potential high added value product, but the amount of fucoidan in seaweed was estimated low and has as such no large impact. Using all seaweed carbohydrates as sugars for fermentation or chemical conversion was the least profitable option due to the low price and large scale availability of sugars from terrestrial crops like maize, tapioca or sugar cane (0.3-0.4 \notin /kg).

The most profitable case was used for the design of a value chain for Ocean Forest. The value chain included the conversion of brown seaweed to alginate as main product, remaining sugars to be fermented to lactic acid for the production of the bioplastic polylactic acid (PLA), and a residual stream for feed or fertilizer.



This case generated an estimated income of $209 \notin$ /ton wet seaweed. Viability of this case depended on the price of the seaweed and processing costs. Estimation of the processing costs was difficult as it often confidential information. We estimated processing costs of sugars to PLA of 56 \notin , costs of alginate and sugars extraction from seaweed were unknown to us but are essential to assess the viability of the value chain. Production of alginate is common practice, but the use of seaweed sugars for the production of PLA is innovative. Also the combined production of alginate and sugars from seaweed is new. This value chain is promising as it makes use of residual streams from alginate production, which is existing technology. It is essential that the process of alginate but also other valuable components.

In the case of higher production levels of alginate there is a risk of market saturation and drop of prices. In such a situation new market applications for seaweed products are necessary. Numerous initiatives on seaweed cultivation and harvesting are running at the moment, aiming at higher production levels required to widen the application area of seaweed, especially to non-food applications. Emerging market applications of seaweed are foreseen in the bioplastics area where hydrocolloids like alginate can replace petrochemical plastics with similar characteristics. Also chemical building blocks with acid and/or alcohol functionalities can be well produced from seaweed biomass since the oxygen atoms needed for these building blocks are already present in the biomass. Examples are mannitol as polyol for polyesters or polyurethanes, and mannuronic acid and guluronic acid from alginates for the production of 2,5-FDCA for replacement of PET.

Sugars from seaweed are potential feedstock for biofuels and chemical building blocks but competition with terrestrial crops is strong.

Seaweeds are fast growing sea plants and do not require arable land or fresh water for cultivation. They have the unique property to be able to remove (in)organic nutrients from water. This makes them valuable plants for open water fish aquaculture as they can be applied for bioremediation. In addition, they contain ingredients not found in terrestrial plants like hydrocolloids. To widen the application area of seaweeds it is essential that the seaweed biomass is fully exploited.

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1 Introduction

1.1 Aim of this study

There is increasing concern about the negative environmental effects in open water fish aquaculture related to nutrients discharged from fish cage aquaculture. One possible solution for this is to use the extractive properties of seaweeds and bivalves (e.g. clams, oysters, mussels) to remove these nutrients. This concept is known as Integrated Multitrophic Aquaculture (IMTA) and is gaining a lot of attention at the moment. IMTA has great potential for both aquaculture and coastal areas for the production of new products from seaweeds.

Leroy Seafood Group ASA (salmon producer) and the Bellona Foundation (NGO) have been collaborating for years to find sustainable solutions for the fish farm industry. The production of salmon together with seaweeds and mussels is the basis for Ocean Forest, a partnership between Leroy and the Bellona Foundation established on August 2013. The aim of Ocean Forest is to develop and launch new forms of biomass production tied to aquaculture by cooperation with researchers and technology providers to reduce costs of biomass production at sea, as well as to develop products for food, feed, energy and raw materials for industry and aquaculture.

The Ocean Forest site in Norway has R&D-facilities and equipment to produce salmon, blue mussels and brown seaweed (*Saccharina Latissima* and *Laminaria Digitata*) together in one system. So besides salmon, also mussels and seaweeds are produced. The mussels are planned to be applied as fish feed (tests are running at the moment) and small part of the seaweed is applied as seasoning, but large volumes of seaweeds are left over. Aim of this study is to get insight in the conversion of seaweed into valuable products like bioplastics in order to fully recycle the materials generated by the salmon production.

Leroy has indicated that the polystyrene boxes they use at the moment form an environmental issue as they take in a lot of space and reuse of the boxes is not possible. Compostable poly(lactic acid) (PLA, produced from starch (corn, tapioca) or saccharide (sugar cane)) boxes would solve this problem. This project intents to provide information on the value chain of seaweed to PLA foam boxes. Is this a promising business case? Another topic of interest is the non-food application of alginates. Alginates are known for their water-binding capacity and are potential substitutes for poly acrylates used in incontinence products (super-absorbing polymers or SAP's), as thickening agent and/or as part of coating systems. Also in this case the question is how the business case works out based on current or future technology.

1.2 Approach

Brown seaweeds are interesting sources of biomass as it contains both fermentable sugars and alginates. Within this project we want to examine the possibility of converting brown seaweed to valuable (non-food) products. In chapter 2 background information is provided on seaweed properties and current uses, with focus on Norwegian seaweed species. Also current applications and future developments of products from brown seaweeds are described. Chapter 3 deals with Ocean Forest as case study. Three different cases are evaluated to determine the most promising value chain. Also including emerging market applications and a SWOT analysis is provided. This report is finalized with main conclusions and some recommendations.

2 Background

2.1 Introduction

This chapter provides some general information on seaweeds like classification, current uses, and composition. Also a short description of the Norwegian seaweed industry is provided and the species growing in Norway.

2.2 Seaweed classification and current uses

Seaweeds can be classified into three major classes: brown (*Phaeophyceae*), red (*Rhodophyceae*) and green (*Chlorophyceae*). This classification is based on the presence or lack of certain pigments⁽¹⁾. In general seaweeds are characterised by⁽²⁾:

- High water content (70-90 wt% fresh weight)
- High carbohydrate content (brown 30-50 wt% dry weight, red 30-60 wt% dry weight, green 25-50 wt% dry weight
- High mineral content such as alkali metals (10-50 wt% dry weight)
- Low protein content (7-15 wt% dry weight)
- Low lipid content (1-5 wt% dry weight)

Current seaweed production is estimated to be 16-20 million tons of wet biomass⁽³⁾. The seaweed industry is primarily focused on food products for human consumption, which account for 83–90% of the global value of seaweed ⁽³⁾(\$5 billion worldwide). Algal hydrocolloids extracted from macroalgae, such as alginate, agar and carrageenan, account for most of the remaining value. Other applications include therapeutic materials, fertilizer, and animal feed. World market volume of alginate is around 30.000 tons⁽⁴⁾.

2.3 Short description of the Norwegian seaweed industry

Seaweed species common to Norway are the brown species *Laminaria hyperborea*, *Laminaria digitata*, *Ascophyllum nodosum*, *Saccharina latissima*. Also a green species (*Ulva lactuca*) is cultivated on small scale for food applications but is excluded from this study. Detailed information on these seaweed species is provided in Appendix 1.



Ascophyllum nodosum

Laminaria Digitata

Laminaria hyperborea

Saccharina latissima

Information on the Norwegian seaweed industry included here is obtained from the desk study conducted by Meland and Rebours from Bioforsk in the European project Netalgae⁽⁵⁾:

- The algae industry in Norway has long tradition of exploiting natural resources. Seaweed constitutes an important part of the ecosystem and is of important commercial value. Seaweed has been used as fertilizer, feed and food.
- Annual alginate production is around 5.000 tons dry weight by FMC Biopolymer AS (owned by the FMC Corporation, formerly known as Protan AS). In the past, alginate production was based on drift kelp and hand-cut *Laminaria digitata*, but since 1963 *Laminaria hyperborea* has been the most important raw material due to mechanization of harvest and high volumes.
- From 1930, seaweed meal from *Ascophyllum nodosum* for animal food and fertilizer was an important product from the Norwegian industry. Algea AS, established in 1937 is the only remaining company and is owned by the Italian Valagro Group.
- Area of seaweed harvest and processing in Norway (see Figure 1):
 - Laminaria hyperborea (150.000 tons/year) is harvested between Rogaland and Sør-Trøndelag. First hand value is under 23 €/ton wet weight (FMC Biopolymer AS 2011). It is is processed to alginates (5.000 tons/year) for pharma- and nutraceutical products.
 - Ascophyllum nodosum (10.000-20.000 tons/year) is harvested between Møre og Romsdal and Nordland. First hand value delivered to factory is 50 €/ton wet weight (Algea AS)¹. It is processed to seaweed meal (by drying and milling) for agricultural, nutraceutical and cosmetic products.
 - *Ulva lactuca* (140 kg/year) is harvested by hand in Rogaland yearly and sold to restaurants. First hand value is 50 €/kg wet weight.
- Laminaria hyperborea has been harvested for years with a seaweed trawl (see Figure 2). The trawl (150 tons daily) tears plants larger than 20 cm from the substrate and leaves smaller plants for re-growth. The seaweed is delivered to transport ships, collecting stations or directly to the factory. *Ascophyllum nodosum* is harvested either with paddlewheel or water jet driven seaweed cutters, which both leave at least 10 cm of the plant for re-growth (Algea AS). The harvested material is transported in bags or nets to the factory.

¹ http://www.algea.com/

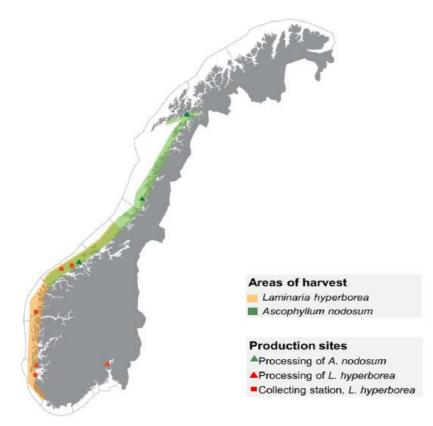


Figure 1: Area of harvest and processing of *Laminaria hyperborea* and *Ascophyllum nodosum* in Norway⁽⁵⁾

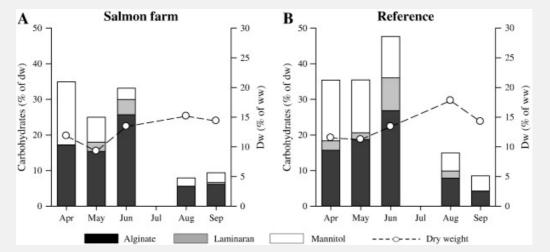


Figure 2: Harvesting methods for a) *Lamniaria hyperborea*, the seaweed trawl and for b) *Ascophyllum nodosum* the paddlewheel cutter. Photos: a) FMC Biopolymer AS, b) Sander Andersen⁽⁵⁾

2.4 IMTA Ocean Forest

Ocean Forest is a partnership between the Bellona Foundation and the Leroy Seafood Group ASA. The aim of Ocean Forest is to develop and establish new forms of biomass production tied to aquaculture. The company wants to reduce the costs of biomass production at sea, as well as to develop products for food, feed, energy and raw materials for industry and aquaculture². In open water aquaculture there is increasing focus on the nutrient load (N+P) into the environment from the fish farming activities. One possible solution for this is to use the extractive properties of seaweeds and bivalves (e.g. clams, oysters, mussels) to remove these nutrients. This concept is known as Integrated Multi-Trophic Aquaculture (IMTA).

In a study by Handa *et al.*, the cultivation of macroalgae (*S. latissima*) in integration with salmon farming in cages in Norway is described ⁽⁶⁾. The results in the study states that "IMTA with salmon can be a sound strategy to obtain enhanced growth in length of macroalgae in Norwegian coastal waters. On the other hand, depth- and seasonal-dependent growth response emphasises that the potential for IMTA with salmon and macroalgae as well as the potential for bioremediation services needs to be assessed holding the seasonality of the macroalgae (with a rapid spring growth) up against the salmon production pattern (with higher fish biomass and feed use with a corresponding increase in nutrient discharge in late summer an autumn). This suggest a seasonal mismatch regarding direct recycling of nutrient effluents from salmon aquaculture by macroalgae". The study by Handa also illustrated the variations in carbohydrate content and dry weight of the seaweed at the salmon farm or at the reference station.



Content of alginate, laminaran and mannitol and dry weight of whole sporophytes of juvenile S. latissima deployed at the salmon farm and at the reference station 4 km south of the farm in August 2010 ⁽⁶⁾.

The integrated system of Ocean Forest is illustrated in Figure 3. Salmon is cultivated in cages and their deposits are taken up by blue mussels (undissolved particles) and micro- and macro-algae (dissolved components (phosphate, nitrogen)). Blue mussels are filter feeders but also catch

² http://bellona.org/news/uncategorized/2013-08-bellona-launches-ocean-forest

copepods (small crustaceans). These copepods spread the sealice that the salmon suffers from. Blue mussels can then serve as feed for the salmon and the shells can be used for oyster cultivation. But what to do with the large amounts of seaweeds that are produced?

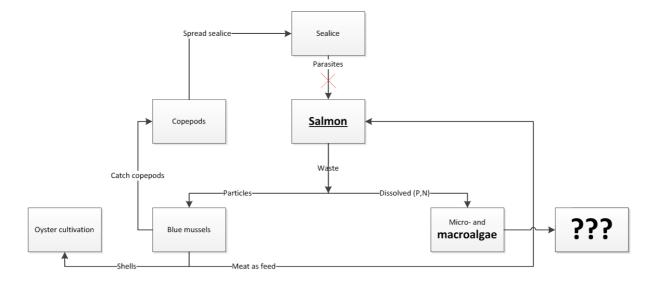


Figure 3: IMTA Ocean Forest

2.5 Seaweed properties

Seaweeds are known for their variation in properties depending on type, location, season etc. Especially brown seaweeds show large variations in chemical compositions.

2.5.1 Seasonal variability

Seasonal variability is a well-recognized part of the cycle of seaweed growth. Black ⁽⁷⁾measured the changes in seaweed composition over the yearly cycle for various seaweed species. Figure 4 is very illustrative for the seasonal variability regarding the content of various components in *Laminaria saccharina*.

Studies like this are key data in understanding economic considerations around value chains. The chemical nature of the seaweed varies with both species and time of year. Due to these variations, selecting the right seaweed and time of harvesting seems necessary for optimal exploitation of the seaweed biomass ⁽⁸⁾.

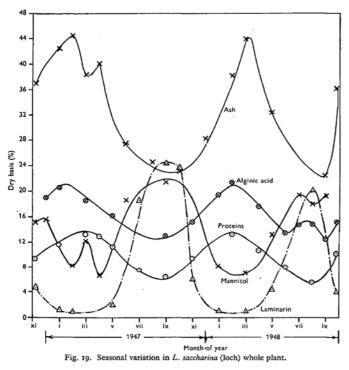


Figure 4: Concentration of various components measured over a 2-year period for *Laminaria* species ⁽⁷⁾

2.5.2 Chemical composition

The chemical composition of seaweed is well documented but quantitative data are difficult to report due to large variations in seaweed type, seasonality, harvesting location and age of the plant. For our study on economic and technical feasibility of converting seaweed into bioplastics or other materials it is prerequisite to have a rough estimation on the chemical composition of brown seaweeds.

Carbohydrate content in brown seaweed is around 30-50 wt% of the dry weight. The carbohydrates can be divided in storage carbohydrates, which function as food reserve, and structural carbohydrates, which are found in the cell wall and give mechanical strength and prevent the seaweed from dehydration. In Table 1 the carbohydrates present in brown seaweeds is presented and the characteristics of each carbohydrate are described below. A schematic illustration of the carbohydrates found in seaweed is given in Figure 5⁽⁹⁾. Some of these carbohydrates are also found in terrestrial plants (*i.e.* cellulose) but others are exclusively found in seaweeds (*i.e.* alginic acid, laminarin, fucoidan).

Storage ca	rbohydrates	Structural carbohydrates			
Carbohydrate	Building block	Carbohydrate	Building block		
Laminarin	Glucose	Cellulose	Glucose		
Mannitol	Mannitol	Alginic acid	Uronic acids (guluronic acid, mannuronic acid)		
		Fucoidan	Fucose (sulphated)		

Table 1: Carbohydrates present in brown seaweed

- Storage carbohydrates^(9, 10)
 - Laminarin is the main storage carbohydrates in brown seaweed. It is a water-soluble polymer containing 20-25 glucose units and its content can vary from 0 to 30 % dry weight. It accumulates during summer and autumn and is utilized during winter as an energy source for new tissue growth (see Figure 4). It is a potential source of glucose.
 - Mannitol is a water soluble sugar alcohol which functions as a food reserve.
 Concentrations in brown seaweed vary from 5 to 30 % dry weight. Like laminarin it is accumulated during summer and autumn and is utilized during winter as energy source for tissue growth (see Figure 4).
 - Large variations in carbohydrate content exists and depends on season, location and type of seaweed.
- Structural carbohydrates ^(9, 10)
 - Cellulose is the structural component of the cell wall of terrestrial plants and seaweeds (brown, red and green). It is a linear polysaccharide of several hundred to more than 10.000 glucose units. In brown seaweed the cellulose content is around 8 % of the dry weight with limited variation during the seasons.
 - Alginic acid is a linear polymer consisting of mannuronic acid (M) and guluronic acid (G) blocks in varying sequences. Alginic acid is present as salt of different metals, primarily sodium and calcium, and functions are principally of structural and ion exchange type. Content in brown seaweed can be as high as 30-40 % dry weight.
 - Fucoidan is a heterogeneous polysaccharide in brown seaweed consisting primarily of 1,2-linked α-l-fucose-4-sulfate units with very small amounts of d-xylose, d-galactose, d-mannose, and uronic acid. Content in brown seaweeds is around 5 % dry weight.

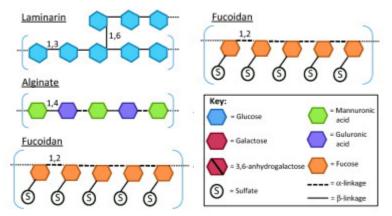


Figure 5: Structural information on polysaccharides in seaweed biomass (9)

Protein content in brown seaweed (3-15 wt% dry) is generally lower compared to red and green seaweed. Contrary to the carbohydrate profiles, protein contents were found to be highest in winter and lowest during summer, where it has been suggested that this build-up of nitrogen reserves is to sustain rapid growth rates into the summer months.

Another significant part of brown seaweed biomass is its **ash** content which can be as high as 50% of its dry weight. Ash in *Laminaria Digitata* consists largely of the ions sodium, potassium, calcium and magnesium with chloride and sulphate as the main counter ions⁽¹¹⁾.

Finally, the **polyphenol** content in brown seaweed is limited but it its known for their inhibitory action towards microbial activities. This makes the polyphenol content in seaweed an important parameter when the seaweed is used for biological processes such as fermentation to *e.g.* ethanol or lactic acid ⁽¹²⁾.

2.6 Current applications and future developments of carbohydrates, protein and ash from brown seaweed

2.6.1 Sugars (e.g. glucose)

Nowadays, application of sugars is not restricted to food. The chemical sector is currently using more and more renewable biomass (sugars, vegetable oils) as raw material to replace increasingly scarce mineral oil. Sugars are regarded as the 'oil of the future' and are applied on large scale for the production of ethanol as biofuel. In the near future this will not be restricted to biofuels as the chemical industry is developing chemical building blocks from renewable resources for various applications⁽¹³⁾.

Current

Sugars are currently not produced from seaweed on commercial scale but from terrestrial sugar rich crops (sugar cane, sugar beet), starch rich crops (grains) or from cellulose-rich biomass (2nd generation).

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<u>Future</u>

Availability of terrestrial crops is large compared to seaweed, and the current established market conditions for glucose production implies that recovery of fermentable sugars as byproduct from seaweed harvesting is unlikely to be attractive⁽⁸⁾. However, if easily extracted from seaweed and available as *e.g.* residues from alginate production, these sugars can be used for fermentation to alcohols or acids, or for conversion to other chemical building blocks.

2.6.2 Mannitol

Mannitol is a sugar alcohol (polyol) which is currently being used mainly in the food and pharmaceutical industry. Since uptake of mannitol is independent of insulin, it is also applicable in diabetic food products.

Current

Commercial production of mannitol is mainly done by reduction of fructose leading to mannitol and sorbitol (isomers) in equal parts. Hydrolysis of sucrose (disaccharide) followed by catalytic hydrogenation also leads to mannitol and sorbitol in a molar ratio of 1:3.

Production of mannitol from fructose or sucrose is always accompanied by the production of sorbitol. Extraction of pure mannitol from natural resources like seaweeds is also an option and this is done on commercial scale in China.

<u>Future</u>

Due to the current drawbacks of mannitol production, research efforts have been directed towards developing new techniques in the production of pure mannitol like biological processes and extraction of natural resources ⁽¹⁴⁾. Mannitol extraction from seaweed is now done only in China but this might be expanded in the future.

2.6.3 Fucoidan

Fucoidan is a group of polysaccharides primarily composed of sulphated fucose with <10% of other monosaccharides. They are found in the cell walls of brown seaweeds. This polysaccharide protects the plant from dehydration and retains water. A certain proportion of fucoidan can be extracted from seaweed with water or dilute acid.

Current

Current market value is unknown and commercial activities are very limited. Fucoidans have been noted to have a wide variety of biological activities of which anticoagulant properties are most commonly studied. Fucoidans are due to the sulphate groups similar to heparin. Biological activity is strongly dependent on the structure of the polysaccharide ⁽¹⁵⁾ and as such also on the method of isolation/extraction.

A Tasmanian company, Marinova³, supplies commercial volumes of fucoidan extracts and their derivatives. The company has developed a cold water extraction process which maintains the integrity of fucoidans and produces nature-equivalent high-molecular weight molecules with optimal bioactivity ⁽¹⁶⁾. However, although fucoidan shows marked anticoagulant activity *in vitro*, it does not appear to demonstrate any anticoagulant activities in human studies (*in vivo*)⁽¹⁷⁾.

<u>Future</u>

Future applications for fucoidan are most likely as high added-value products. In addition, it is a naturally occurring negatively charged polysaccharides with possibly broad applications (see chapter 3).

2.6.4 Alginate (and hydrocolloids in general)

Hydrocolloids are non-crystalline high molecular weight polymers that dissolve in water to increase viscosity and are classified as agar, alginates and carrageenan:

- Agar is extracted from red seaweeds. About 90% of the agar is used for food applications (bakery, confectionary, meat, fish, dairy products), the other 10% for bacteriological applications.
- Alginates are extracted from brown seaweeds. Alginate is the term referring to salts of alginic acid. Alginates are used for three distinct properties: thickening of aqueous solutions, formation of gels by the replacement of monovalent cations by calcium, and film formation.
- Carrageenan is extracted from red seaweeds. It is further subdivided as kappa, lambda and iota types and is used in food, air freshener gels and toothpaste.

Current

Hydrocolloids are mostly applied in food, and they form the major part of all of the non-food products derived from seaweed⁽⁸⁾. Current sales value of hydrocolloids exceeds 1 billion \$ (see Table 2). The extraction process of alginate from brown seaweed is described in Appendix 2.

Hydrocolloid	Sales volu	ume (ton)	Average pr	ices (\$/kg)	Sales val	lue (M\$)
	1999	2009	1999	2009	1999	2009
Agar	7500	9600	17	18	128	173
Alginates	23000	26500	9	12	225	318
Carrageenan	42000	50000	7	10.5	291	527
Total	72500	86100			644	1018

Table 2: Sales volume, average prices and sales value of hydrocolloids from seaweed⁽¹⁸⁾

³ http://www.marinova.com.au/

Bixler ⁽¹⁸⁾ highlighted the changes in the hydrocolloid market over the period 1999-2009. Prices have been increasing and these higher prices have been driven by higher energy, chemicals and seaweed costs. The higher seaweed costs reflect seaweed shortages, particularly for the carrageenan-containing species. Increased sales volume is coming from emerging markets applications, not from newer products. Most of the expansion in alginates over the last decade has been due to China entering the market.

Future

The alginate sales volume in 2009 was around 30.000 ton. Assuming that for each ton of alginate approximately 25 ton of wet seaweed is required (20% dry matter seaweed, 20% yield), then approximately 750.000 ton of wet seaweed is needed for the world alginate production. Production volume of cultivated brown seaweed worldwide is approximately 6.5 Mton⁽¹⁹⁾, and the fraction needed for alginate production is then 12%. In the long term market saturation is a possibility and emerging market applications are necessary. Given the unique properties of alginate it is imaginable that application does not remain restricted to food.

2.6.5 Feed additives and fertilizer

Seaweed in dried form (seaweed meal) is a commercial product and is currently applied as feed supplement or soil conditioner, for example by Algea AS)⁴ in Norway or Arramara TEO⁵ in Ireland. Product prices are unknown to us.

2.7 Summary

- Algae industry in Norway has long tradition of exploiting natural resources. Seaweed constitutes an important part of the ecosystem and is of important commercial value. It has been used as fertilizer, feed and food.
- Seaweed species common to Norway are Laminaria hyperborea, Laminaria digitata, Ascophyllum nodosum, Saccharina latissima
 - Alginate production by FMC Biopolymers is around 5.000 tons with *Laminaria Hyperborea* as main raw material
 - o Seaweed meal is produced by Algea AS with Ascophyllum nodosum as main raw material
- Biochemical composition of seaweed is influenced by type, environmental conditions, maturity, gender and season
 - Concerning brown seaweeds, variations in storage carbohydrates (laminarin and mannitol) are large, variation in structural carbohydrates (algninic acid, cellulose) and proteins is less pronounced.
 - Highest yields of laminarin and mannitol coincides with the lowest yields in ash, protein, moisture and polyphenols and vice versa.

⁴ http://www.algea.com/

⁵ http://www.arramara.ie/

- The chemical nature of seaweed varies with both species and time of year. Due to these variations, selecting the right seaweed and time of harvesting seems necessary for optimal exploitation of the seaweed biomass.
- Commercial activities of seaweed products (besides food) include production of hydrocolloids, mannitol and seaweed meal. In an expanding seaweed market it is necessary to search for alternative uses of hydrocolloids, as market saturation is a possibility.
- Sugars of seaweed are an option as future feedstock for biofuels and chemical building blocks but competition with terrestrial crops is strong.

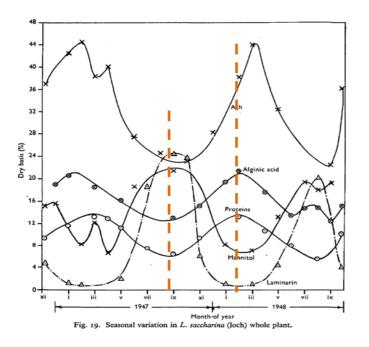
3 Case study Ocean Forest

3.1 Introduction

In this chapter we perform rough calculations in order to estimate the potential income in €/ton wet seaweed. For this we chose a model seaweed and 2 scenario's for the harvest period. Main components are identified and market values estimated. Based on these results we describe 3 cases with different output: <u>Multiple products</u>, <u>Alginate and sugars</u> and <u>Sugars</u>. The most promising case is used for the design of a value chain for the production of bioplastics from seaweed. This chapter is finalized with a SWOT analysis.

3.2 Assumptions

Given the large variations in chemical composition of seaweeds we selected *Saccharina latissima* as our model seaweed. For the economic evaluation we chose two scenario's based on the graph of Black⁽⁷⁾:



- <u>Scenario 1(high carbohydrates)</u> is around September with high values of laminarin and mannitol and low values of alginic acid, proteins and ash.
- <u>Scenario 2 (low carbohydrates)</u> is around February with low levels of mannitol and laminarin and high values of ash, proteins and alginic acid.

• Chemical composition

The chemical composition as input for the calculations is shown in Table 3, where estimations for cellulose and fucoidan content are added.

Table 5: Chemical composition	Drown	i seaw	eeu a	is mpu	it for	econo	omic	evalua	111
	C	hemio	cal c	ompo	sitio	n (wt	% dry	/)	
Scenario	Laminarin	Mannitol	Cellulose	Alginic acid	Fucoidan	Protein	Ash	Other	
Scenario 1: high carbohydrates	24	22	8	12	5	6	23	0	
Scenario 2: low carbohydrates	1	6	8	20	5	13	36	11	

Table 3: Chemical composition brown seaweed as input for economic evaluation

• Dry matter content

Dry matter content of seaweed may vary between 10-30 wt% of the fresh seaweed. For this study the dry matter content of fresh seaweed was set at 20 wt%.

- Calculations show the theoretical max yield of (intermediate) products based only on the chemical composition of the seaweed. Isolation efficiencies and other losses are not included.
- Costs of handling, processing etc are not included.
- All envisioned processes are assumed technical feasible.
- The calculated income in €/ton fresh seaweed is a rough estimation based on product prices from Table 4.

(Intermediate) product	Source	Price (€/kg)	Remarks
Sugars	Laminarin, cellulose	0.3	Price comparable to sugars from food crops
Mannitol	Mannitol	1.0	Estimation
Fucoidan	Fucoidan	2.9	As value added product ⁽²⁰⁾
Alginate (technical g r ade)	Alginic acid	3.0	Price depending on quality. Can be as high as 10 €/kg or more.
Feed additive	Proteins	0.4	Estimation
Fertilizer	Ash	0.1	Estimation

Table 4: Product prices

3.3 Economic evaluation 3 cases

3.3.1 Theoretical yield main components

For the 2 scenario's (high carbohydrates and low carbohydrates) the theoretical maximum yield of the main components in kg/ton wet seaweed is calculated. This includes laminarin, mannitol, cellulose, alginic acid, fucoidan, protein and ash. These data are required for calculation of theoretical income per ton wet seaweed, and the results are presented in Figure 6.

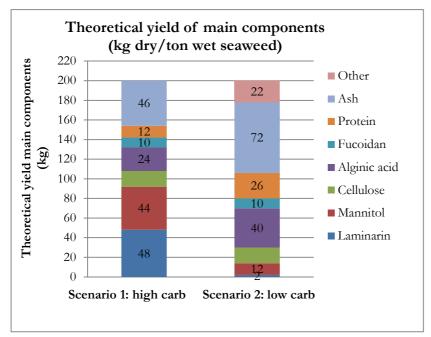


Figure 6: Theoretical yield (kg dry) of main components based on 1 ton fresh seaweed

We assumed 20 wt% dry matter of the seaweed, resulting in 200 kg of dry matter from 1 ton of wet seaweed. Processing of the chemical composition (see Table 3) of the seaweed for the 2 scenarios gives then the absolute amount of main components from wet seaweed. Large differences are observed, especially in the amount of ash, mannitol and laminarin. These data are used as input for the economic evaluation of the 3 different cases.

3.3.2 Calculated income for 3 different cases

Case 1: Multiple products (174-184 €/ton wet seaweed)

For this case all components are isolated from the seaweed with 100% yield and efficiency and sold as (intermediate) products. After extraction, laminarin and cellulose are further hydrolysed to glucose to be sold as fermentable sugars. With the estimated product prices from Table 4 it is rather straightforward that the most valuable product is alginate, and the scenario with the highest alginate yield is the most profitable one (Figure 7). For scenario 1 the total income per ton of wet seaweed is estimated at $174 \notin$, for scenario 2 at 184 \notin .

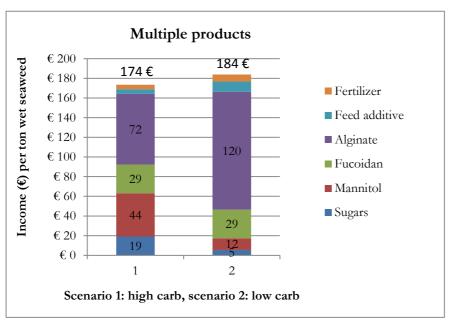


Figure 7: Case 1: income in € per ton fresh seaweed when all main components are isolated and sold.

Case 2: Alginate and sugars (117-150 €/ton wet seaweed)

For case 2, the carbohydrates from laminarin, cellulose and fucoidan are sold as monomeric sugars, including mannitol. Alginic acid is sold as alginate and protein and ash as feed additive and fertilizer. Again, the scenario with the highest alginic acid content is the most profitable one. For scenario 1 the total income per ton of wet seaweed is estimated at $117 \in$, for scenario 2 at $150 \in$.

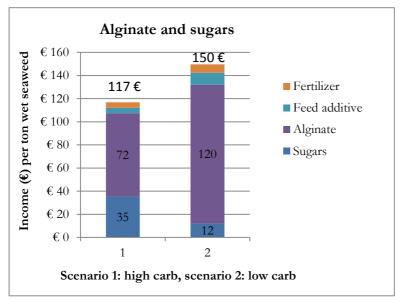


Figure 8: Case 2: Income in € per ton fresh seaweed when main products are alginate and sugars from laminarin, cellulose, fucoidan and mannitol.

Case 3: All carbohydrates to sugars (42-52 €/ton wet seaweed)

In this case all the carbohydrates present in the seaweed are converted to sugars, including mannitol, fucoidan and alginic acid. Protein and ash are sold as feed additive and fertilizer. For this case the total income is $52 \notin$ per ton of fresh seaweed for scenario 1 and $42 \notin$ for scenario 2. This can be increased when the sugars are further converted to higher added value products like ethanol (estimated price $700 \notin$ /ton) or lactic acid (estimated price $800 \notin$ /ton):

- For conversion of fermentable sugars to ethanol the income increases to 60 € for scenario 1 and 46 € for scenario 2
- For conversion to lactic acid the income increases to 123 € for scenario 1 and 82 € for scenario 2. Lactic acid results in a higher income due to a higher product price and a higher theoretical yield from fermentable sugars (51% for ethanol and 100% for lactic acid).

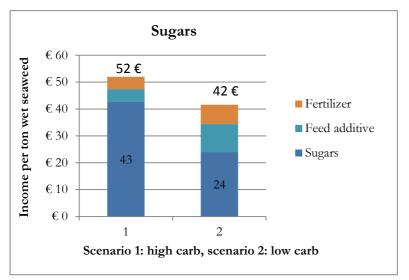


Figure 9: Case 3: Income in € per ton fresh seaweed when all carbohydrates are converted to sugars.

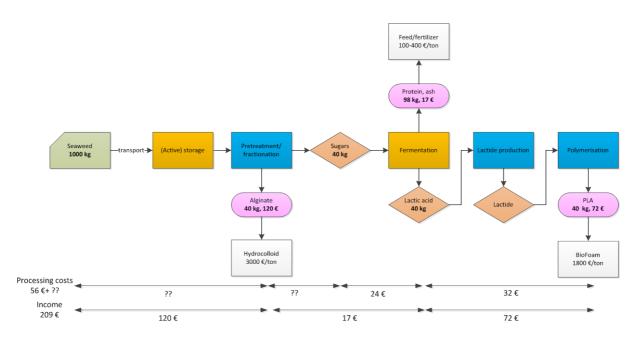
3.3.3 Conclusions

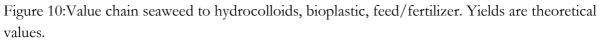
The chemical composition of the seaweed is very relevant in relation to the value of seaweed products. From the estimated product prices it is clear that in the current situation the application of alginic acid as alginate generates the highest income, and the scenario with the highest alginic acid content is the most profitable one. For the calculations we assumed $3 \notin kg$ for technical grade alginate, but depending on the quality it can be even more than $10-12 \notin kg$. In such a situation the only real value of seaweed is as source of alginic acid. Also fucoidan is regarded as potential high added value product, but the amount of fucoidan in seaweed is estimated low and has as such no large impact. Using all seaweed carbohydrates as sugars for fermentation or chemical conversion is the least profitable option due to the low price and large scale availability of sugars from terrestrial crops like maize or sugar cane.

3.4 Design value chain

For design of the value chain we chose <u>Scenario 2-case 2 (Alginate and sugars)</u> as most promising one. Although case 1 (Multiple products) generates in theory the highest income, the estimated processing cost will be high when all seaweed components are isolated (highest number of unit operations).

The value chain includes the conversion of brown seaweed to alginate, sugars for PLA and a residual stream containing protein and ash as feed/fertilizer. In the scheme below product prices are included, with an estimated price for PLA of 1800 €/ton. All processing steps are described below:





Harvesting, logistics, storage

Seaweed is collected from the cases and brought to land. After harvesting the seaweed must be dewatered or stored in a proper way to increase shelf life and improve handling. Often this is done by drying.

Shelf life of brown seaweeds is comparatively long compared to other seaweed species as they resist microbial degradation due to polyphenols present. They can be stored at ambient temperature for hours or even days without deterioration. This is considered to be beneficial for conventional manufacturing or extraction processes. However, this resistance to fermentation becomes an inhibitory factor for downstream microbial processes⁽⁴⁾.

Active storage of seaweeds like ensiling is under investigation in the project MacroBioCrude⁶ where they try to establish an integrated supply and processing pipeline for the sustainable manufacture of liquid hydrocarbon fuels from seaweeds.

Pretreatment and fractionation

In this step the separation of alginate and other carbohydrates is required. Commercial alginate production comprises several acid and alkaline processing steps, and especially during the acid hydrolysis steps, sugars are extracted from the seaweed biomass (see Appendix 2). These liberated sugars can be used as feedstock for fermentation to lactic acid. Alginate producers like Cargill have shown their interest to look at alginate residues streams as feedstock for other applications besides energy (e.g. biogas).

In the future alginate may be extracted by milder separation techniques. By hydrolysis of easily extractable sugars from laminarin, fucoidan and possibly cellulose the remainder is the recalcitrant alginate structure.

Fermentation to lactic acid, processing to PLA and Biofoam

Lactic acid fermentation

Fermentation of sugars from terrestrial plants to lactic acid is common technology, from seaweeds it is new. In a study by Hwang, the potential of seaweed sugars for lactic acid production was examined ⁽²¹⁾. From comparative analysis of predicted lactic acid production yields it was found that "seaweeds are comparable to lignocellulosics at the current state of technology". In a European Project named Seabioplas⁷ (2013-2015) the fermentation of seaweed sugars to lactic acid for PLA production is being studied. Model sugars resembling seaweed hydrolysates can be fermented to lactic acid; the next step is to ferment seaweed hydrolysates. Real seaweed hydrolysates contain besides fermentable sugars also other components that can be inhibitory to lactic acid producing micro-organisms (*e.g.* salts). To increase lactic acid yield these inhibitory components need to be identified and removed prior to fermentation. This is comparable to the situation for lactic acid from lignocellulosic biomass, where also inhibitory components are formed during the isolation of fermentable sugars⁽²²⁾.

Fermentation of sugars (C6-sugars, glucose or fructose) to lactic acid on commercial scale is done by *Lactobacillus*. Theoretical yield is 100%, as 2 molecules lactic acid are formed from 1 molecule of glucose. For our value chain we estimated 100 % efficiency from sugars to lactic acid.

Production of PLA

Downstream processing of lactic acid, i.e. the isolation of the lactic acid from the fermentation broth, is complex and costly. Further conversion of lactic acid to PLA is quite efficient (no major losses). Industrial production costs of PLA from maize starch are estimated 1300-1600 €/ton of

⁶ http://community.dur.ac.uk/p.w.dyer/page2/styled-2/index.html

⁷ http://www.seabioplas.eu

which 520-800 \notin is lactic acid production (including raw materials) and 780-800 \notin /ton PLA production⁽²³⁾. PLA is sold on the market for approximately 1800 \notin /ton.

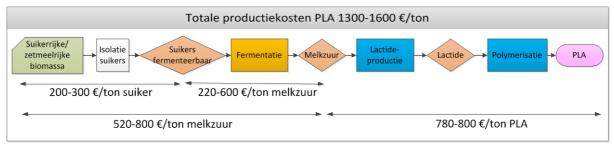


Figure 11: Production costs of PLA⁽²³⁾.

PLA is well known as packaging material for food. For food packaging PLA has an advantage over other polymers since it does not contain, and thus will not leak, any potential harmful chemical building blocks. PLA is compostable as the ester linkage can be hydrolysed under well-defined conditions.

<u>Biofoam</u>

PLA is known for their clear, crisp appearance but it can also be transformed to a material comparable to polystyrene foam. The Dutch company Synbra Technology BV⁸ has succeeded in producing a biobased version of polystyrene foam (EPS, expandable polystyrene) by making the foam from PLA. This foam is called BioFoam, can be composted and is considered as green waste.

BioFoam is already on the market as packaging material for fish. In general, BioFoam boxes are twice as expensive as EPS boxes. Compostability of the material is an advantage if the proper infrastructure is available.

3.5 Processing costs

Processing costs for the Ocean Forest value chain as presented in Figure 10 were estimated as follows:

- Seaweed is delivered at the gate 'free of charge'
- Processing costs of alginate from seaweed are unknown to us, and also the value of residual streams from alginate production are not known.
- Processing costs sugars to lactic acid is 0.60 €/kg lactic acid, yielding 24 € for 40 kg of lactic acid.
- Processing costs lactic acid is 0.80 €/kg PLA, yielding 32 € for 40 kg of lactic acid.

Total processing costs are 56 € plus extraction costs of alginate and sugars from the seaweeds.

⁸ http://www.biofoam.nl/index.php

Financial models for seaweed to alginate and PLA are hard to generate as it is often confidential information. Available financial models made for cases like alcohols from seaweed can be used to get an idea. Lewis⁽⁸⁾ concluded the following for ethanol from seaweed:

- "Economic analysis of a seaweed-to-ethanol medium scale plant (30.000 m³/year) based on available data suggest that the only likely viable model that can be operated is when the seaweed is delivered to the plant essentially free of charge.
- Economics are dominated by the commodity pricing of the desired product, the yields of ethanol that can be obtained from a feedstock together with the problem of a limited season for seaweed use when it is high in fermentable carbohydrate content. Alginate is assumed not to contribute to the ethanol yield.
- Processing of corn in an ethanol plant benefits from year round operation due to ability to store this grain for more than 12 months. Similar storage techniques are not in evidence for seaweeds."

For the case of butanol as biofuel from seaweed similar conclusions were made, including:

- "The capital required to build a plant is not the stumbling block. Rather it is the cost of the seaweed used as the raw material, the yield of the product obtained and the commodity price of the products."
- Butanol is less attractive due to the lower theoretical yield of butanol (41%) compared to ethanol (51%).

3.6 Emerging applications of seaweed products

Current market size of alginate is small. In a growing seaweed market all the alginate produced cannot be sold for 10 €/kg or more and other applications are required. Also residues streams from the alginate production can be made of value. In this paragraph some ideas are listed.

Hydrocolloids

Hydrocolloids from seaweed are special polymers with specific properties. They can only be extracted from seaweeds and not from terrestrial plants. Draget ⁽²⁴⁾showed that alginate represents a very high diversity with respect to chemical composition and monomer sequence, giving the alginate family a large variety of physical and biological properties. They foresee a future trend in which the exploitation of alginate gradually shifts from low-tech applications to more advanced applications in "food, pharmaceutical and biomedical areas". We would like to add <u>biobased plastics</u> as well.

Seaweeds contain large amounts of polysaccharides including charged polysaccharides like alginate and fucoidans. Anionically charged polysaccharides can serve as starting materials to replace widely used petrochemical polymers <u>polyacrylate</u> and <u>polyacrylamide</u>. The annual production of ionically charged polymers amounts to several million tons per year. These polymers are applied in adhesives, coatings, detergent formulations, water-treatment chemicals,

superabsorbents in diapers, oil and gas drilling fluids and a multitude of other applications. Synthetic polymers like polyacrylate and polyacrylamide are based on toxic monomers like acrylate esters or acrylamide. Although, after polymerisation of the monomers, the polymers as such are non-toxic, their non-biodegradability is considered a drawback in numerous applications. It is very difficult to introduce a high degree of anionic groups in for example starch, a commonly available and cheap renewable resource, while maintaining the required polymeric structure of the starch. Naturally occuring charged polysaccharides like alginate and fucoidan, that already contain anionic charges, are under explored as renewable substitutes to polyacrylates and polyacrylamide. Based on the technical specifications, hydrocolloids from seaweeds can be applied <u>beyond</u> food, pharmaceutical and biomedical areas.

Chemical building blocks

In the plastics sector many developments are taking place to replace petrochemical resources with renewable resources. Chemical building blocks with acid and/or alcohol functionalities can be well produced from biomass since the oxygen atoms needed for these building blocks are already present in the biomass. Versatile building blocks that can be applied in many applications due to their chemical structure are promising and are expected to undergo substantial growth.

- Mannuronic acid and guluronic acid, i.e. the monomers of alginic acid, as chemical building blocks for the chemical industry. Mannuronic acid and guluronic acid are, based on their chemical structure, interesting building blocks for polyesters. Hydrolysis, oxidation and dehydration of alginate yields 2,5-FDCA. Ethyleneglycol and 2,5-FDCA are polymerised to the polyester PEF which is similar to PET (market volume of 50 Mton/y)⁽¹³⁾.
- Mannitol as a polyol is interesting as a chemical building block for the production of polyesters and polyurethanes. Dehydration of mannitol leads to isomannide which might also be an interesting building block for bioplastics like polyesters and polycarbonates.

Strengths	Weaknesses
• No seaweed costs as feedstock. It is a by-	• Seasonal variability, no consistent feedstock
product from salmon production	• No suitable storage (except for drying) to allow
• Make use of seaweed that is available, no	year round processing
disposal costs	Possible technical bottlenecks
• Infrastructure for processing seaweed is	
available in Norway	
Opportunities	Threats
Green image: making biodegradable	• Competition with other (cheaper) resources
plastics	from terrestrial crops or petrochemical nature
• Closing the loop: packaging of salmon in	• Volume of seaweed is too small for envisioned
BioFoam boxes made of seaweed from	processes
the fish farms	Investment costs and processing costs too high

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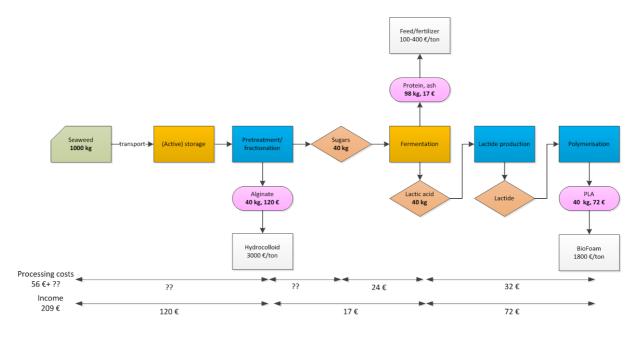
3.8 Summary and conclusions

- *Saccharina Latissima* was used as model species for brown seaweed. For the economic evaluation two scenarios based on harvesting period were applied: <u>high carbohydrates</u> and <u>low carbohydrates</u>. Three different cases were described with different output: <u>Multiple products</u>, <u>Alginate and sugars</u>, and <u>Sugars</u>.
- Income per ton of wet seaweed ranged from 42 to 184 €, with <u>Multiple products</u> as highest value and <u>Sugars</u> the lowest value. Based on estimated product prices it was clear that alginate is by far the most valuable product > 3 €/kg, whereas sugars are estimated at 0.3 €/kg.
- Sugars from seaweed can be converted to ethanol, lactic acid or a range of other chemical building blocks. Lactic acid results in higher income than ethanol due to higher product price and higher theoretical yield. However, isolation of lactic acid is more costly than ethanol.
- In our value chain for Ocean Forest, brown seaweed is converted to alginate, protein and ash, and the remaining sugars are fermented to lactic acid for the production of the bioplastic PLA. This case generates an income of 209 €/ton wet seaweed. Viability of this case depends on the price of the seaweed and processing costs. Estimation of the processing costs is difficult as it often confidential information. We estimated processing costs of sugars to PLA of 56 €, costs of alginate and sugars extraction from seaweed are unknown to us but are required to assess the viability of the value chain.

4 Main conclusions and recommendations

4.1 Conclusions

- In Norway all infrastructure is available for processing of seaweeds. Seaweed in Norway is used as fertilizer, feed and food.
- Seaweeds are known for their variation in properties depending on type, location, season etc. Especially brown seaweeds show large variations in chemical composition, making it hard to supply consistent feedstock. No suitable storage techniques are available, except for drying, to allow year round processing. Selecting the right seaweed and time of harvesting seems necessary for optimal exploitation of seaweed biomass.
- Numerous initiatives on seaweed cultivation and harvesting are running at the moment, aiming at higher production levels required to widen the application area of seaweed, especially to non-food applications. In such a situation the market for alginate is easily saturated and prices will drop, and new market applications for seaweed products are necessary.
- For our study we took a rough estimation on the chemical composition of *Saccharina Latissima* (our model seaweed) based on data found in literature. We estimated product prices and processing costs for the value chain of seaweed to alginate, bioplastic PLA and protein/ash.



• Production of alginate is common practice, but the use of seaweed sugars for the production of PLA is innovative. Also the combined production of alginate and sugars from seaweed is new. This value chain is promising as it makes use of residual streams from alginate production, which is existing technology. Looking at the technical aspects of alginate production, it is essential that the process is being evaluated and redesigned if possible to yield not only alginate but also other valuable components.

- Emerging market applications of seaweed are foreseen in the bioplastics area
 - Hydrocolloids as replacement for petrochemical plastics. Seaweeds contain large amounts of polysaccharides including charged polysaccharides like alginate and fucoidans. Anionically charged polysaccharides can serve as starting materials to replace widely used petrochemical polymers polyacrylate and polyacrylamide.
 - Chemical building blocks. In the plastics sector many developments are taking place to replace petrochemical resources with renewable resources. Chemical building blocks with acid and/or alcohol functionalities can be well produced from seaweed biomass since the oxygen atoms needed for these building blocks are already present in the biomass. Examples are mannitol as polyol for polyesters or polyurethanes, and mannuronic acid and guluronic acid from alginates for the production of 2,5-FDCA for replacement of PET.

4.2 Recommendations

- Design of the value chain was based on model seaweed and estimated chemical composition. To get more accurate data this should be repeated with data from seaweed harvested at the Ocean Forest site.
- Get estimation of processing costs of production of alginate and sugar-rich residues from alginate industry
- Look at technical feasibility of using residue streams from alginate industry as feedstock for fermentation to lactic acid
- Look at technical feasibility of alginate as feedstock for the production of 2,5-FDCA for the polyester PEF (as replacement of PET)
- Look at structure/function relationships of alginates in relation to polyacrylates; can they be a substitute in current applications?

References

- 1. Samaraweera AM, Vidanarachchi JK, Kurukulasuriya MS, *Industrial Applications of Macroalgae*, Handbook of Marine Macroalgae: Biotechnology and Applied Phycology2011. p. 500-21.
- 2. Jung KA, Lim S-R, Kim Y, Park JM, Potentials of macroalgae as feedstocks for biorefinery, *Bioresource Technology*, **135**(0):182-90 (2013).
- 3. Roesijadi G, Jones SB, Snowden-Swan LJ, Zhu Y, *Macroalgae as a biomass feedstock: a preliminary analysis,* Pacific Northwest National Laboratories- US department of Energy (PNNL-DOE) (2010).
- 4. Bruton T, Lyons H, Lerat Y, Stanley M, Bo Rasmussen M, *A review of the potential of marine algae as a source of biofuel in Ireland*, Sustainable Energy Ireland (2009).
- 5. Meland M, Rebours C, *The Norwegian Seaweed Industry. Netalgae WP1 and 2,* Bioforsk-Norwegian Institute for Agricultural and Environmental Research (2012).
- Handå A, Forbord S, Wang X, Broch OJ, Dahle SW, Størseth TR, et al., Seasonal- and depthdependent growth of cultivated kelp (Saccharina latissima) in close proximity to salmon (Salmo salar) aquaculture in Norway, 414-415:191-201 (2013).
- Black WAP, The seasonal variation in weight and chemical composition of the common British Laminariaceae, *Journal of the Marine Biological Association of the United Kingdom*, 29(01):45-72 (1950).
- 8. Lewis J, *Product options for the processing of marine macro algae-summary report,* The Crown Estate The Centre for process innovation (2011).
- 9. Wei N, Quarterman J, Jin Y-S, Marine macroalgae: an untapped resource for producing fuels and chemicals, *Trends in Biotechnology*, **31**(2):70-7 (2013).
- 10.Percival E, The polysaccharides of green, red and brown seaweeds: Their basic structure, biosynthesis and function, *British Phycological Journal*, **14**(2):103 17 (1979).
- 11.Adams JMM, Toop TA, Donnison IS, Gallagher JA, Seasonal variation in Laminaria digitata and its impact on biochemical conversion routes to biofuels, *Bioresource Technology*, 102(21):9976-84 (2011).
- 12.Schiener P, Black KD, Stanley MS, Green DH, The seasonal variation in the chemical composition of the kelp species Laminaria digitata, Laminaria hyperborea, Saccharina latissima and Alaria esculenta, (2014).
- 13.Harmsen PFH, Hackmann MM, Bos HL, Green building blocks for bio-based plastics, *Biofuels, Bioprod Bioref*, **8**(3):306-24 (2014).
- 14. Ghoreishi SM, Shahrestani RG, Innovative strategies for engineering mannitol production, *Trends in Food Science & Technology*, **20**(6–7):263-70 (2009).
- 15.Bilan MI, Grachev AA, Shashkov AS, Kelly M, Sanderson CJ, Nifantiev NE, et al., Further studies on the composition and structure of a fucoidan preparation from the brown alga Saccharina latissima, *Carbohydrate Research*, **345**(14):2038-47 (2010).
- 16.Holdt SL, Kraan S, Bioactive compounds in seaweed: functional food applications and legislation, *Journal of Applied Phycology*, **23**(3):543-97 (2011).

- 17.Irhimeh MR, Fitton JH, Lowenthal RM, Pilot clinical study to evaluate the anticoagulant activity of fucoidan, **20**(7):607-10 (2009).
- 18.Bixler HJ, Porse H, A decade of change in the seaweed hydrocolloids industry, *Journal of Applied Phycology*, **23**(3):321-35 (2011).
- 19.FAO, Fishery and Aquaculture Statistics 2010, (2012).
- 20.Bjerre A-B, The Macroalgae Biorefinery (MAB3)- with focus on cultivation, bioethanol production, fish feed and sustainability assessment, Danish technological institute (2013).
- 21.Hwang HJ, Lee SY, Kim SM, Lee SB, Fermentation of seaweed sugars by Lactobacillus species and the potential of seaweed as a biomass feedstock, *Biotechnology and Bioprocess Engineering*, **16**(6):1231-9 (2011).
- 22.Harmsen PFH, Lips S, Bakker RRC, Productie groene grondstoffen (BO-03-007-012); van biomassa tot PLA; economische aspecten, WUR-FBR (2011).
- 23.Draget KI, Smidsrod O, Skjak-Braek G, *Alginates from algae*, In: Rhee Sa, editor. Polysaccharides and polyamides in the food industry Properties, production and patents. Weinheim: Wiley-VCH Verlag GmbH; 2005.
- 24.Edwards M, Hanniffy D, Heesch S, Hernandez-Kantun J, Moniz M, Queguineur B, et al., *Macroalgae Fact-Sheets*, Ryan Institute ISRG (2012).
- 25.McHugh DJ, A Guide To The Seaweed industry, FAO Fisheries Technical Paper, 44 (2003).
- 26. Vauchel P, Kaas R, Arhaliass A, Baron R, Legrand J, A new process for extracting alginates from Laminaria digitata: Reactive extrusion, *Food and Bioprocess Technology*, **1**(3):297-300 (2008).

Appendix 1: Brown seaweed species common to Norway

<u>Ascophyllum nodosum⁽²⁵⁾</u>

Habitat: grow	vs in mid-littoral zor	Egg Wrack Growing up to 1,5 Application as feed transport Allowed for huma vitamins and trace Has been describe inflammatory pro	n consumption in Fran e elements d to have anti-coagular perties	s of 1 cm wide g material for shellfish nce as source of nt and anti-
Splash zone shor		Lower shore	Low tide Subtidal	
Seasonality				
	Winter	Spring	Summer	Autumn
Biomass				
Fertility			And the second second	

<u>Laminaria digitata ⁽²⁵⁾</u>

 Common names: Kombu, Oarweed, Tangle Generally 1-2 m long, but may be larger Stipe is long, flexible, smooth, oval in cross-section The blade is broad, commonly 5-20 fingers Of agricultural interest for its growth enhancing pr Source of bioactive compounds with hypotensive a antibacterial properties Used for alginate production. alginates are used this stabilizer and gelling agent. 	coperties and
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Laminaria hyperborea ⁽²⁵⁾

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 Generally 1-3 m long, but may be larger Stipe is inflexible, rough and circular in cross-section (in contrast to <i>Laminaria digitata</i>) The blade is broad, commonly with 5-20 fingers Long-lived species, generally lives for 3-4 years Forms extensive subtidal forests which supports a huge diversity of other flora and fauna Used for alginate production Habitat: rocky shores on exposed to very exposed coasts. Always found in full salinity sites. It occupies the zone below <i>Laminaria digitata</i> , usually from 0-10m depth but extending to 30 m in very clear water. Upper shore Middle shore Lower shore Subtidal Scasonality Winter Spring Summer Autumn Biomass Fertility			•	Common names:	Kombu, Oarweed, Fo	orest Kelp			
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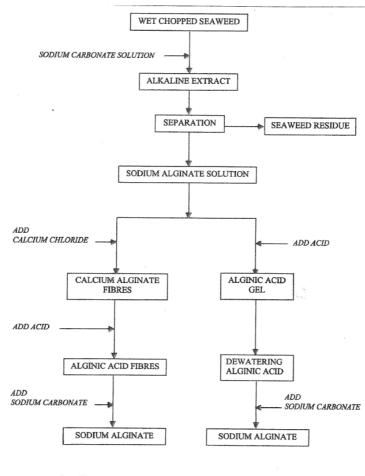
<u>Saccharina latissima (25)</u>

		kelpBrown alga with length	a short stipe and long	a, sweet kombu, sugar g fronds up to 4 m French and Irish cuisine
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Appendix 2: Production of alginate

Alginate is the term usually used for the salt of alginic acid. Alginate is difficult to extract or hydrolyse as it consists of unbranched chains comprising blocks of α -1,4-linked D-mannuronic acid and blocks of α -1,4-linked L-guluronic acid. In addition, alginate binds selectively to divalent cations (egg-box model)⁽²⁴⁾.

It is present in the cell walls of brown algae as the calcium, magnesium and sodium salts of alginic acid. Calcium and magnesium salts do not dissolve in water, but the sodium salt does. The rationale behind extraction of alginate from seaweed is to convert all alginate salts to sodium salt, dissolve this in water and to remove the seaweed residue by filtration. <u>Alginic acid</u> or <u>calcium alginate</u> can be precipitated from the extract solution of sodium alginate, and converted back to sodium alginate in a mixture of water and alcohol in which the sodium salt does not dissolve ⁽²⁶⁾. The two methods are illustrated in Figure 12.



CALCIUM ALGUNATE PROCESS ALGUNIC ACID PROCESS Figure 12: Flow chart for the production of sodium alginate ⁽²⁶⁾.

In the EOS LT project 'Seaweed Biorefinery' Food and Biobased Research (WUR-FBR) was involved among others in the pretreatment and fractionation of seaweed. In this project we extracted alginate from fresh *Laminaria Digitata* by a reactive extrusion process described by Vauchel⁽²⁷⁾ and sodium alginate was isolated by the <u>alginic acid process</u> (see Figure 12) described by McHugh⁽²⁶⁾. These experiments were done to see in practice how alginate extraction works and to analyse the side streams on sugar content. The process scheme is illustrated in Figure 13.

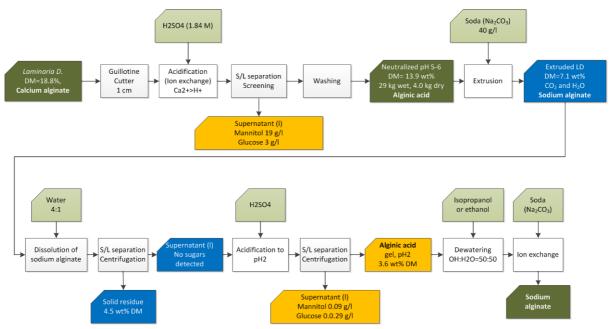


Figure 13: Process scheme of sodium alginate extraction from Laminaria Digitata (WUR-FBR)

From the whole extraction process samples were taken after each step and a rough mass balance was constructed based on dry matter content and monomeric sugar content. These experiments illustrated the complexity of alginate extraction; it is a procedure with multiple pH-shifts and loss of valuable sugars in the side streams. Overall alginate yield was approximately 10 wt% of the seaweed biomass.

Sodium alginate is the main product but side streams generated during alginate extraction may also contain valuable products. For optimal use of seaweed biomass and the design of a biorefinery scheme, knowledge on side streams provides valuable information.