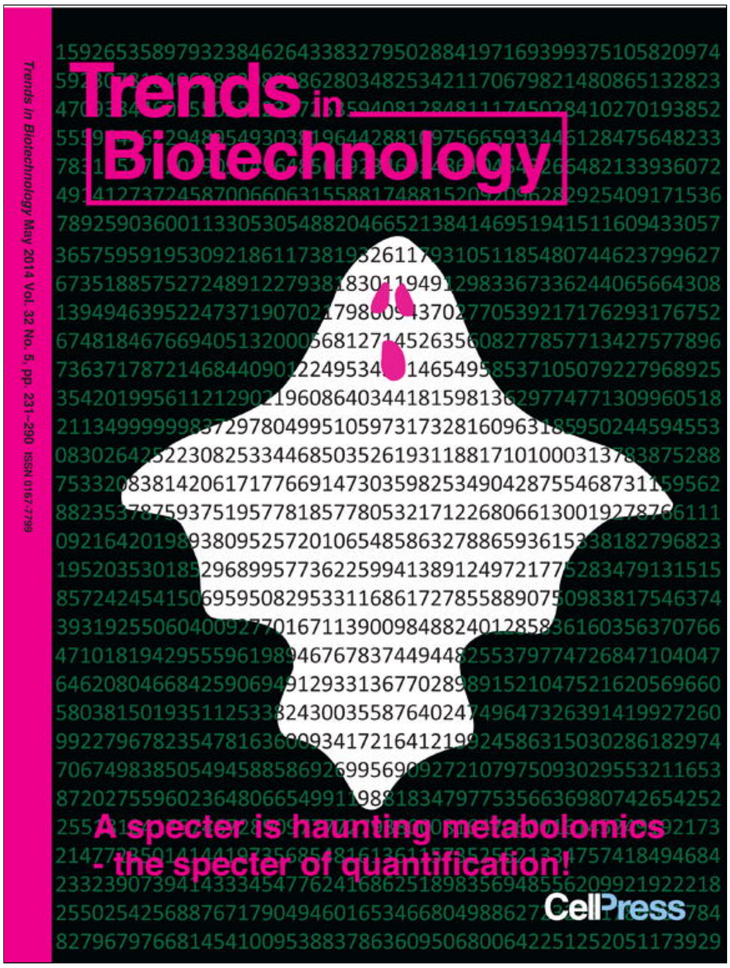
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Opportunities and challenges for seaweed in the biobased economy

Jaap W. van Hal[1], W.J.J. Huijgen[1], and A.M. López-Contreras[2]

[1] Energy Research Centre of The Netherlands (ECN), Biomass & Energy Efficiency, Westerduinweg 3, 1755 LE, Petten, The Netherlands
[2] Wageningen UR, Food and Biobased Research (WUR-FBR), Bornse Weilanden 9, 6708 WG, Wageningen, The Netherlands

The unique chemical composition of seaweeds and their fast growth rates offer many opportunities for biorefining. In this article we argue that cascading biorefinery valorization concepts are viable alternatives to only using seaweeds as carbohydrate sources for the fermentative production of biofuels. However, many challenges remain with respect to use of seaweeds for chemical production, such as the large seasonal variation in the chemical composition of seaweeds.

The history of seaweed use for chemicals

Kelps (brown seaweeds) were used in World War I to produce the acetone needed for the production of cordite-based gun and artillery shells [1]. The minerals from the seaweed were recycled as fertilizer. This is one of the first examples of a seaweed biorefinery used for the production of a chemical. Seaweeds were investigated as a raw material for digestive production of biogas in the US aquatic species research program from 1978 to 1996 [2]. Recent efforts in seaweed biorefining have focused on the production of biofuels, such as ethanol [3], butanol [4], and biogas [5]. A proposal to use seaweed and 'certain types of waste' as preferred biomass for biofuels fell two votes short in the European Parliament [6].

Advantages and opportunities

Seaweeds (or macroalgae) are fast-growing, highly photosynthetically efficient plants that live in most seas and oceans. Macroalgae are classified as brown (*Phaeophyta*), green (*Chlorophyta*), or red (*Rhodophyta*) seaweeds based on the composition of their photosynthetic pigments [7,8]. There is great potential for biomass production from seaweeds. We have estimated that The Netherlands can produce 25 Mton of seaweed biomass in 10% of the Dutch part of the North Sea [9]. Other European initiatives (i.e., from the Crown Estate in Scotland or the MAB3 initiative in Denmark) envision that large amounts of cultivated seaweed will be used for the production of energy [10].

Seaweeds can contain large amounts of protein and the variety of different carbohydrate molecules present in seaweed is large [11] (Table 1). There are thousands of as-yet-unexamined species, therefore, different structural and storage carbohydrates could be discovered. The protein present in seaweed can augment the protein supply needed for the growing human population, for instance as fish feed. The high amounts of ash in seaweeds (up to 40%) can contribute to closed-loop mineral fertilizer use, including the primary, secondary, and trace elements. One can thus recycle the minerals from fertilizer runoff by isolating them from seaweeds that have absorbed them. Furthermore, seaweeds are also envisioned as environmental remediation tool in large-scale fish and shellfish farming, using the 'integrated multi-trophic aquaculture' (IMTA) approach. This concept uses the ability of seaweeds to quickly absorb minerals needed for growth (1 year need in 1 day). In this approach, seaweeds absorb minerals from the excrements of the farmed fish. This absorbent ability of seaweed can reduce the waste run-off from fish farms significantly [8].

Unlike terrestrially produced biomass, seaweeds do not need any fresh water or fertilizers to grow and do not cause indirect land use change. *A priori*, they are thus a much more sustainable biomass in comparison to first- and even second-generation biomass sources. Compared to microalgae, seaweeds show higher volumetric production rates (biomass per volume per time) and biomass densities. Their chemical composition makes macroalgae a complimentary biomass source to microalgae (a lipid-based biorefinery platform) and lignocellulosic biomass (lignin- and cellulose-based biorefinery). Seaweeds also require relatively mild conditions for processing compared to lignocellulosic biomass. Lower temperatures, less severe acid conditions, and shorter reaction times are generally needed.

Challenges of seaweeds

The seasonal variation in the amount of carbohydrates in seaweeds is large. For example, variations between 17 and 23% for rhamnose in *Ulva* sp. in the period June–September [12], and even between 5 and 32% for mannitol in *Laminaria digitata* over a whole year have been reported [13]. This causes the need for seasonal harvesting and the development of storage technologies, because seaweed is known to decompose quickly. Seaweed contains generally only 20% dry matter, therefore, drying techniques before processing do not seem attractive from an energy perspective. Aqueous

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Corresponding author: van Hal, J.W. (vanhal@ecn.nl).

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Table 1. Example of the diversity of carbohydrates found in seaweeds [8]

Seaweed	Kelps	*Palmaria palmata*	Other red seaweeds	*Ulva* sp.
Carbohydrate molecules	Alginate	Xylose	(Anhydro) Galactose	Mannitol
	Mannitol	Glucose	Glucose	Glucuronic acid
	Laminaran	Galactose		Rhamnose
	Fucoidan			Xylose
				Glucose
				Arabinose

biorefinery technologies thus need to be developed, but inherently product concentrations tend to be limited. Even if no water is added, the starting concentration of, for instance, sugars is limited to about 14%, based on a total carbohydrate level of 70%. In addition, large-scale mechanized open sea farming techniques will also have to be developed. This should reduce the raw materials price of seaweed to competitive levels.

Seaweeds also contain recalcitrant polysaccharides. Alginates, for instance, are difficult to hydrolyze selectively either chemically or enzymatically to yield their monomers. In addition, genetically tractable microorganisms that can metabolize alginate polysaccharides have yet to be developed [3]. In contrast to the analysis of starch and lignocellulose-based biomass, there is no reliable standard analytical protocol for the analysis of carbohydrate molecules in seaweeds. Determining the biochemical composition of seaweeds, and thereby estimating their economic potential, is thus difficult. Some common methods for the identification and quantification of sugars, such as reduction and peracetylation, cannot differentiate between mannose and mannitol [12]. In this method, all sugars are reduced to their corresponding sugar alcohols and reacted with acetic anhydride to yield volatile sugar derivatives that can be analyzed by gas chromatography. Other challenges include the large chloride-containing salt fluxes that are likely to be present after most pretreatment schemes. These salt concentrations could both inhibit fermentation and corrode common alloys such as stainless steel used in fermentation vessels.

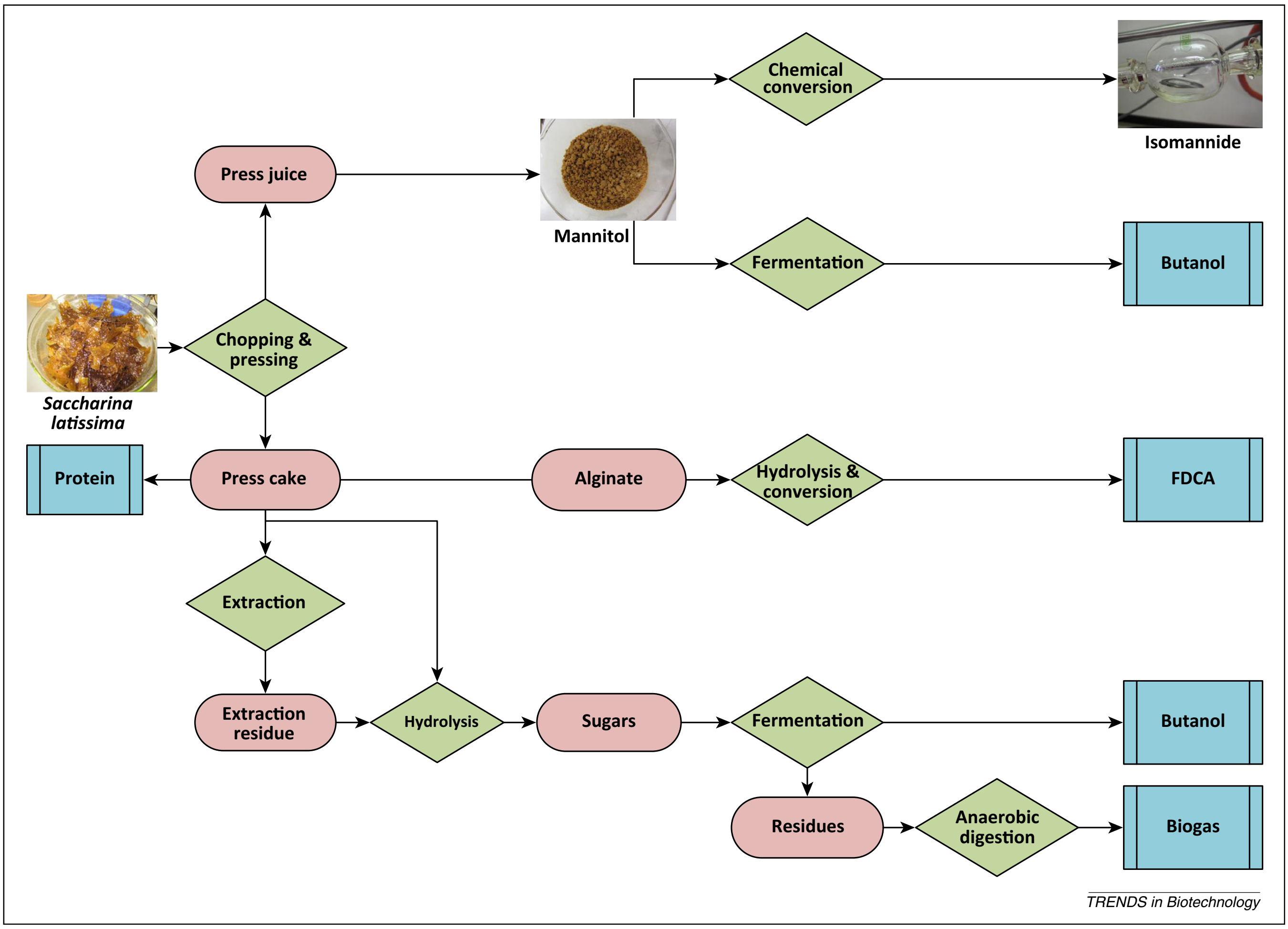

Figure 1. Schematic representation of a Kelp cascading seaweed biorefineries, showing the fresh *Saccharina latissima*, the intermediate products (pink ovals), the conversion steps (green diamonds), and final products [(blue)rectangles]. The pictures depict the fresh seaweed, the intermediate mannitol, and the end-product isomannide.

Why a cascading biorefinery?

Current production processes of chemicals from seaweed are focused on a single product, such as alginic acid, carrageenan, or colorants. The rest of the seaweed is treated as waste. Most of the current seaweed research programs also focus on producing a single product: predominantly, biofuels [5,7,14]. As an alternative to single-product approaches, cascading biorefinery approaches aim to maximize the inherent value of all components present in the biomass. In general, the cascading approach for seaweed is based on fractionating the carbohydrate molecules, proteins, and minerals, separating the different carbohydrate molecules from each other, and converting them into high-value chemical intermediates or using them as is. Seaweed is ideally suited for this approach because it contains, on the one hand, high-value components such as colorants, bioactive molecules, and specialty sugars, and, on the other hand, components often considered as raw materials for platform chemicals for the bio-based economy such as xylose and glucose. Next to seaweed biorefinery for the production of chemicals and fuel, one can also envision a cascading approach for the production of various food components from seaweed [15].

The Dutch Seaweed Biorefinery Program

The Dutch Seaweed Biorefinery Program started in 2009 [16]. Other initiatives looking into a seaweed biorefinery approach have been started such as the Danish MAB3 project [17]. Our approach was to develop cascading biorefinery approaches that maximize the value of the raw material, as shown in a scheme for brown seaweeds (Figure 1). In this scheme, a high mannitol syrup is obtained by shredding and pressing the seaweed. Further steps are the isolation of alginic acid as well as another fraction containing laminarin. The mannitol is converted to isomannide, the laminarin is fermented to acetone, butanol, ethanol (ABE), and the alginate fraction is converted to furan dicarboxylic acid (FDCA) or similar diacids that can be used for polyesters, for example.

Mannitol itself, aside from its food applications, can be used to produce rigid polyurethane foams. It can also be converted into intermediates for the production of detergents, as well as be converted to isomannide (an isomer of isosorbide). These isohexides have many applications, such as building blocks for polymers, fuel additives, and plasticizers [18]. The known isohexides can be interconverted into one another [19]. Thus, if one can produce isomannide from seaweed, one can also produce isosorbide and isoidide.

For the green and red seaweeds, hydrolysis-based processes were developed to produce carbohydrates that were fermented to ABE [*Palmaria palmata* (dulse)] or used to produce monomeric rhamnose [*Ulva lactuca* (sea lettuce)]. Adapting several pretreatment, fractionation, and conversion strategies to the different seaweed species has been the main focus of our seaweed biorefinery program, which by now has completed the proof of concept that demonstrates the technical viability of the seaweed biorefinery concept.

Aside from the technological challenges, many policy and societal aspects need to be addressed before seaweed can be widely adopted as a viable biomass source. Examples include legal and spatial planning aspects of large-scale farming of seaweeds in the North Sea, legal and environmental aspects of processing seaweed on vessels, and the impact of this new industry on the coastal economy. Integrating seaweed farming with other uses of the sea such as large-scale windfarms is also an unexplored area in the aforementioned terms.

Concluding remarks

Numerous challenges remain. Major breakthroughs are necessary in the area of cultivation and harvesting, understanding of the biology, genetics, and biochemistry of the seaweeds themselves. New cost-effective bioprocessing routes towards chemicals and fuel will also need to be developed. The legal, spatial planning, and societal aspects need to be addressed. However, with its large potential and unique chemical composition, seaweed can and probably will make a large contribution towards a sustainable environmentally benign chemical and fuel industry.

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