



Enabling Bioeconomy with Offshore Macroalgae Biorefineries

10

Alexander Golberg, Meiron Zollmann, Meghanath Prabhu,
and Ruslana Rachel Palatnik

Abstract

The bioeconomy provides a possible solution for the increasing demand on natural resources by substitution of the nonrenewable resources with resources derived from biomass, thus reducing the environmental impact of fossil fuels. A fundamental unit that will enable the bioeconomy implementation is biorefinery. The bioeconomy is a collective term for the complex system that includes biomass production, transportation, conversion into products, and product distribution. In this chapter, we introduce the concept of offshore marine biorefineries as potential drivers for the bioeconomy of the future. We discuss fundamental thermodynamics principles that determine the optimum scale of biorefineries and put the limit for the services area for a single-processing unit. We provide a review of the current methods to produce biomass offshore. Next, we exemplify the marine biorefineries, which show co-production of several products from the same biomass, thus reducing the waste and maximizing economic benefit from the unit. In addition, we discuss the economic and environmental challenges of marine biorefineries as an emerging platform for society transition to low-carbon economy.

Keywords

Biorefineries · Bioeconomy · Green technology · Renewable energy · Biofuel · Biomass

A. Golberg (✉) · M. Zollmann · M. Prabhu

Porter School of Environment and Earth Sciences, Tel Aviv University, Tel Aviv, Israel

R. R. Palatnik

Department of Economics and Management, and SEED – the Sustainable Economic and Environmental Development Research Center, The Max Stern Yezreel Valley College, Afula and Nazareth, Israel

NRERC- Natural Resource and Environmental Research Center, University of Haifa, Haifa, Israel

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173

10.1 Transition to Low-Carbon Societies with Bioeconomy

Growing population, increasing quality of life, and longevity impose new pressures on all industrial sectors involved in the production of food, chemicals, and fuels. This increasing pressure is expected to increase the use of land, potable water, fossil fuels, and other natural resources. This increased use of natural resources could lead to unpredictable changes in climate, loss of biodiversity, and reduction of the ability to maintain ecosystems sustainably. The bioeconomy provides a possible solution for this increasing demand to natural resources by substitution of the depletable resources with biomass-based commodities, thus reducing the environmental impact of fossil fuels. The bioeconomy describes the global industrial transition of sustainably utilizing renewable aquatic and terrestrial resources in energy, intermediates, and final products for economic, environmental, social, and national security benefits.

For bioeconomy implementation, the optimal supply chain should be designed in terms of procurement of feedstock (intermediate inputs), production and processing at the biorefinery, transportation, and marketing. The entrepreneurs must decide how much to produce, what segments of the supply chain to undertake in-house versus sourcing externally, and what institutions such as contracts and standards they will use to coordinate the suppliers assuring its external sourcing (Zilberman et al. 2019). These decisions are affected by the investor's financial situation, the political and social system, the technology available, etc. (Du et al. 2016).

As supply chains increasingly encompass far-flung markets and supply sources, manufacturers and retailers are susceptible to various types of supply chain risks. There are diverse supply chain risks associated with disruptions or delays that could be categorized into supply risks, process risks, demand risks, intellectual property risks, behavioral risks, and political/social risks. Supply chain contract uncertainties may occur due to asymmetric information (Du et al. 2016). That is, the innovator may not observe the ability of an effort being devoted by the contracted supplier, or the quality of his product. Entrepreneurs may invest in protective measures to increase the resilience of their supply chains to extreme weather risks. They may geographically diversify their external sources of feedstock to reduce exposure to weather shocks. Therefore, incorporating risk considerations may actually increase the cost of investment in implementing an innovation, especially if the enterprise is constrained by credit.

The supply chain design of industries in the bioeconomy may require determining strategies for the production and processing of the feedstock to produce multiple products (Zilberman et al. 2019). There are established supply chains for seaweed-based food production (Valderrama et al. 2015) and for bioethanol. Evidently, corn is used to produce ethanol as well as the residue product, Distillers Dried Grains (DDGs), which is being sold as animal feedstock (Taheripour et al. 2010). Many of the agrifood innovations increased the value added of agricultural resources either by identifying non-food uses of agricultural products and residues as part of the bioeconomy or producing differentiated products by increasing their convenience and quality (Zilberman et al. 2019).

10.2 Biorefineries as Essential Technological Platforms for Bioeconomy

A fundamental unit that will enable the bioeconomy implementation is biorefinery. The bioeconomy is a collective term for the complex system that includes biomass production, transportation, conversion into products at the biorefinery, and product distribution and marketing. Biorefineries convert renewable biomass into biofuels, food, chemicals, and other bio-based products. Some biorefinery technologies include power generation. Potentially, biorefineries create products with higher added value to the benefit of the economy and the environment.

The use of versatile, robust technologies is one of the key factors in biorefineries. The synergetic combination of process technologies can lead to the development of advanced biorefineries where non-food biomass is converted by a combination of mechanical, thermochemical, chemical, and biochemical processes into a range of bio-based chemicals, e.g., materials, chemicals, and energy. Hence, the maximum value is achieved from each feedstock (De Jong and Jungmeier 2015).

The main output of the biorefineries is bio-based chemicals. Bio-based chemicals can be defined as those classes of chemicals, which are produced by using natural feedstock and have minimal impact on the environment. Examples for bio-based chemicals include (but not limited to) carboxylic acids, polylactic acid, fatty acids, isoprene, biosolvents (e.g., bioethanol), amino acids, vitamins, bio-pesticides, bio-fertilizers, antioxidants, sterols, and even industrial enzymes (Golden et al. 2015; De Jong et al. 2012). The major market demand-driving factors that are expected to boost the demand include the availability of raw materials at a reduced cost, increasing consumer awareness toward and subsequent demand for bio-based products and government initiatives to promote green products among others.

The major drivers for the deployment of biorefineries are:

- (i) Sustainable and renewable energy supply – as biorefineries utilize renewable feedstock
- (ii) Saving foreign exchange reserves – required alternatively for importing fossil fuels and other chemicals
- (iii) Reduced dependency on imported crude petroleum and other chemicals – due to locally grown feedstock for biorefineries
- (iv) Establishment of carbon-neutral and circular economy – allowed by low-carbon footprint and net positive environmental impact of biorefineries

A comprehensive review of optimization-oriented biomass supply-chain designs shows numerous prior works that addressed various important conditions for a profitable supply chain (Ghaderi et al. 2016). Surprisingly, this review of 146 studies concluded that researchers have been mostly orientated toward single-feedstock, single-product, single-period, single-objective, and deterministic models without considering all the dimensions of sustainability. An alternative to this is a co-production of multiple products from the same biomass. Such processes are very common in the petrochemical industry and lead to almost complete use of the raw

material with close to zero waste and maximum valorization. However, for biomass feedstock-based biorefineries, integrated production of food, energy, and other valuable products with zero waste is a relatively new and novel idea and hence, limited literature is available. We discuss the co-production option for biorefineries in the following sections.

10.3 Offshore Marine Biorefineries

The choice of raw biomass material is critical to ensuring the efficient production of biofuels (Bentsen and Felby 2012). The currently used crops and cultivation methods supply raw biomass for the food and feed sectors for hundreds of years; however, most recently they also started to supply biomass for the transportation energy production. The first-generation liquid biofuel feedstock includes traditional agriculture crops (cereals, potatoes, sugar beet, and rapeseed), wood, and dedicated energy crops, while first-generation fuel products include ethanol and biodiesel (International Energy Agency 2011). The second-generation biomass feedstock includes animal fat and dedicated lingo-cellulosic crops and produces hydro-treated vegetable oil, cellulosic-ethanol, biomass-to-liquids (BtL)-diesel, bio-butanol, and advanced drop-in replacement fuels such as fatty acid ethyl esters, alkanes, alkenes, terpenes, and methyl ketones (Keasling and Chou 2008; Dunlop 2011; Lee et al. 2008; Bokinsky et al. 2011; Steen et al. 2010; Peralta-Yahya et al. 2011; Zhang et al. 2014). However, recent studies indicate that the future of biomass sector development is under a high degree of uncertainty mainly due to the limited crop yields and land availability (Bentsen and Felby 2012; Star-coliBRi 2011).

Alternative sources for biomass are offshore grown macroalgae. Macroalgae (or seaweeds) have been harvested throughout the world as a food source and as a commodity for the production of hydrocolloids for centuries. To date, macroalgae still present only a tiny percent of the global biomass supply ($\sim 17 \cdot 10^6$ wet weight macroalgae in comparison to $16 \cdot 10^{11}$ ton of terrestrial crops, grasses, and forests) (Roesijadi et al. 2010; Pimentel and Pimentel 2008; Pimentel 2012). However, world macroalgae biomass cultivation has continuously increased over the last 10 years at an average of 10% and is considered as new promising biomass for low-carbon economy (Jung et al. 2013; Balina et al. 2017).

Macroalgae are photosynthetic organisms living in damp places. As per classification, macroalgae are of three different kinds, green (*Chlorophyta*), brown (phaeophyta), or red (*Rhodophyta*) macroalgae, based on the composition of their photosynthetic pigments (Jung et al. 2013). In addition to photons, the algal plant needs nutrients (mostly nitrogen and phosphorus) and a carbon source to grow. These features are of major interest regarding two points. First, since algae fix carbon (annual cultivation and processing of 1 ton of dry weight of seaweed evaluated over a time horizon of 100 years result in a net reduction of 9.3 tons of atmospheric carbon, equivalent to 34 ton CO₂) (Seghetta et al. 2016a), it can be used as carbon storage and then as fuel. Second, waters polluted with excessive nutrient levels can be cleaned through growing and harvesting of algal biomass. Moreover, an

expanding body of evidence has demonstrated that marine macroalgae, which have unique chemical composition (Nunes et al. 2017; Patarra et al. 2011), have high growth rate (Jung et al. 2013; Chemodanov et al. 2017a), contain very little lignin, and do not compete with food crops for arable land or potable water, can provide a sustainable alternative source of biomass for sustainable food, fuel, and chemical generation (Roesijadi et al. 2010; Van Hal et al. 2014; Wei et al. 2013; Enquist-Newman et al. 2014; Potts et al. 2012; Hannon et al. 2010; Kraan 2013; Wargacki et al. 2012; van der Wal et al. 2013). The conceptual framework of offshore marine biorefineries is shown in Fig. 10.1.

10.4 Offshore Biomass Cultivation

Macroalgae feedstock for biorefineries cannot be based on the harvesting of wild stocks or on cultivation in onshore or nearshore farms. Wild-stock harvesting leads inevitably to over-exploitation, while on- or nearshore farming competes with food crops or coastal uses (Buschmann et al. 2017) and is limited by decreasing available areas (Möller et al. 2012). Two main solutions withstand the conditions above. One is envisioning of construction of very large seaweed farms in coastal unfertile deserts (Buschmann et al. 2017). The second, with a wider potential for global implementation, is the offshore cultivation.

Early reports of the offshore algae cultivation concept proposed to release juvenile *Sargassum* sp. 500 miles offshore the US-Canada border and harvest them

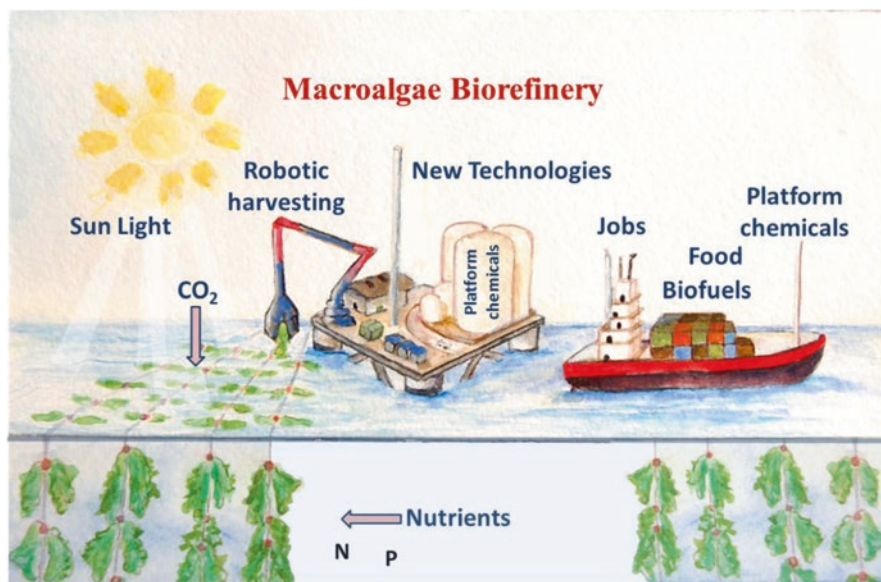


Fig. 10.1 The concept of offshore biorefineries for the production of food, platform chemicals, and biofuels in the ocean (Figure adapted from Lehahn et al. 2016 with permit)

offshore the USA-Mexico border, for the production of methane in onshore anaerobic digesters (Szetela et al. 1976). This proposal inspired in the late 1960s by Howard Wilcox from the San Diego Naval Undersea Center to envision and develop the first multi-product floating seaweed farm, called the “Ocean Food and Energy Farm Project” (Roesijadi et al. 2008). Due to the energy crisis of the 1970s, this project was stopped in favor of prioritized biofuel production programs. The “Marine Biomass Program” which operated during the 1970s and the early 1980s in California (Roesijadi et al. 2008) has made significant advances in understanding the complexity of the marine biological system and in enhancing growth data but failed to overcome the difficulties of working in the open ocean, especially the stability of the cultivation systems and of the attachment of the algae to the systems (Roesijadi et al. 2008).

Following the beginning of the new millennium, with increasing awareness of the environmental effects of the industrial era (Suutari et al. 2015), scientific engagement with offshore biomass cultivation has become significant again (Roesijadi et al. 2008, 2010; Suutari et al. 2015; Reith et al. 2005; Buck and Buchholz 2004, 2005; Buck et al. 2004; van den Burg et al. 2013; Hughes et al. 2012; Korzen et al. 2015a). Although previous techno-economic assessments were not favorable of offshore algae cultivation, four decades of technological evolution, casted into the current political-environmental context, has led to a reexamination of this idea (Feinberg and Hock 1985). This technological evolution includes experience gained through oil and gas exploration, advancements in the oceanographic and atmospheric sciences, and major improvements in both tensile strength and weight of materials that can be used at sea (Roesijadi et al. 2008). These new technologies include also the development of flexible and submersible offshore aquaculture structures, such as the SUBflex which is being operated offshore Israel since 2006 (Drimer 2019). Simultaneously, the establishment of offshore wind farms (Reith et al. 2005) and the inevitable distancing of aquaculture facilities from the coast (Troell et al. 2009) facilitated an additional potential reduction in cultivation costs via integration of infrastructure and operations (Reith et al. 2005; Buck and Buchholz 2004).

Traditional offshore algae cultivation systems include ropes, lines, nets, rafts, and cages, which are all popular due to inexpensive installation and maintenance (Table 10.1) (Fernand et al. 2017).

For example for the production of green macroalgae biomass, Liu et al. (2010) cultivated *Ulva prolifera* and *Ulva intestinalis* on rafts in the Yellow Sea offshore Jiangsu coastline, China, and measured yields of 198.6 and 89.2 kg ww ha⁻¹ 5 months⁻¹, respectively (Liu et al. 2010). The goal of this cultivation experiment was to examine the potential of these two species to exploit aquaculture rafts and cause green-tide events. Smaller-scale offshore experiments have demonstrated the cultivation of *Ulva rigida* in the Eastern Mediterranean Sea. Korzen et al. (2015b) used nylon net cages integrated with fish cages offshore Mikhmoret, Israel, and achieved maximal specific growth rates of 16.8% per day along 2 weeks cultivation periods (Korzen et al. 2015b). This maximal growth rate was measured 22 m downstream the fish cages where nutrients were sufficient. Chemodanov et al. (2017a) used flat double-layer net reactors at the nearshore location at the Reading Power

Table 10.1 Offshore-cultivated macroalgae biomass productivity yields (reports from 1980 to 2015)

Cultivation system	Species	Location	Yield	Units	Reference
Rope, vertical	<i>Undaria pinnatifida</i>	North western coastal bay of Spain	8.3	kg ww/m/139 days	Peteiro and Freire (2012)
			21 ^a	t ww/ha/year	Peteiro and Freire (2012)
Rope, horizontal	<i>Undaria pinnatifida</i>	North Western coastal bay of Spain	5.9	kg ww/m/147 days	Peteiro and Freire (2012)
Rope (concentrical)	<i>Laminaria saccharina</i>	German North Sea	4	kg ww/m/6 months	Buck and Buchholz (2004)
Ropes farm, horizontal	<i>Laminaria japonica</i>	Hokkaido, Japan	10 ⁶	t ww/41.2km ² /year	Yokoyama et al. (2007)
Rope, horizontal, transplanted ^b	<i>Saccharina latissima</i>	Northern Spain, Bay of Biscay	7.8	kg ww/m/106 days	Peteiro et al. (2014)
			45.6	t ww/ha/106 days	Peteiro et al. (2014)
Rope, horizontal	<i>Laminaria saccharina</i>	British Columbia, Canada	3–8	kg ww/m/8 months	Druehl et al. (1988)
Rope, horizontal	<i>Laminaria groenlandica</i>	British Columbia, Canada	2.6–20.5	kg ww/m/18 months	Druehl et al. (1988)
Rope, horizontal	<i>Cymathere triplicata</i>	British Columbia, Canada	1.1–2.7	kg ww/m/7 months	Druehl et al. (1988)
Rope, vertical ^c	<i>Palmaria palmata</i>	Northwest Scotland	1	kg ww/horizontal meter of top rope/year	Sanderson et al. (2012)
Rope, vertical ^c	<i>Saccharina latissima</i>	Northwest Scotland	28 ^d	kg ww/horizontal meter of top rope/year	Sanderson et al. (2012)
Rope, horizontal	<i>Alaria esculenta</i> ^e	Ard Bay, Carna, Co. Galway, Ireland	45.7	kg ww/m/year	(Kraan and Guiry 2001)
Rope, horizontal	<i>Saccharina latissima</i>	Isle of Man, Irish Sea	2.8	kg dw/m/year	Holt (1984)
Cage ^f	<i>Gracilaria tikvahiae</i>	Indian river lagoon, Florida	9.7 ^g	g dw/m ² /day	Hanisak (1987)

(continued)

Table 10.1 (continued)

Cultivation system	Species	Location	Yield	Units	Reference
Cage ^f	<i>Gracilaria tikvahiae</i>	Hutchinson Island, Florida	22.4	g dw/m ² /day	Hanisak (1987)
Nylon line attached to stakes fixed in sea bottom	<i>Eucheuma spinosum</i> (Bohol)	Zanzibar Island, Tanzania	5.4–7% ^h	Daily growth rate	Lirasan and Twide (1993)
Floating raft with rope	<i>Sargassum naozhouense</i> (Tseng et Lu)	Liusha Bay, Xuwen, Guangdong, China	1750	kg ww/km/95 days	Xie et al. (2013)
Rope net with two bamboo poles	<i>Ulva prolifera</i>	Jiangsu coastline, China	198.6 ⁱ	kg ww/ha/5 months	Liu et al. (2010)
Rope net with two bamboo poles	<i>Ulva intestinalis</i>	Jiangsu coastline, China	89.2 ⁱ	kg ww/ha/5 months	Liu et al. (2010)

Table adapted from Fernand et al. (2017) with permit

ww: wet weight; dw: dry weight.

^aEstimated value

^bTransplants were 2.1 kg fresh wt m⁻¹ rope

^cDroppers 1 m apart, with one 10 cm section of seeded string for every 1 m of dropper to 7 m depth

^dHighest mean yield obtained for a longline

^eHigh-yielding strain

^f2 cm plastic mesh on 2.5–5.0 cm diameter PVC pipe frames measuring 1 × 1 × 0.25 m deep (0.6 m² cage)

^gAverage between two stations (7.8 and 11.6 g dw/m²/day)

^hMinimum and maximum of five test plants at different locations

ⁱAverage of six stations

Station in Tel Aviv, Israel, and measured a mean daily growth rate of $4.5 \pm 1.1\%$, corresponding to an annual average productivity of 5.8 ± 1.5 g DW m⁻² day⁻¹ (Fig. 10.2) (Chemodanov et al. 2017a). More advanced systems are the offshore-rearing that was developed by Buck et al. (2004, 2005) (Buck and Buchholz 2005; Buck et al. 2004) and the moored multi-body seaweed farm that was developed by Olanrewaju et al. (2017), both supposed to withstand rough offshore conditions.

Different approaches have been suggested regarding future design of offshore cultivation systems. The commonly used extensive approach allows the algae to grow without adding nutrients or applying external mixing. Using a combination of climate models and seaweed metabolic models, global biomass potential for offshore cultivation was established if extensive approaches are used (Fig. 10.3). The main advantage of this approach is decreased labor, technology, and energy inputs, thus improving energy balance, while the main disadvantage is decreased biomass yields, leading to a large area-demand (Buck et al. 2008). Extensive cultivation can be performed on anchored platforms or on free-floating enclosures (Roesijadi et al. 2008).

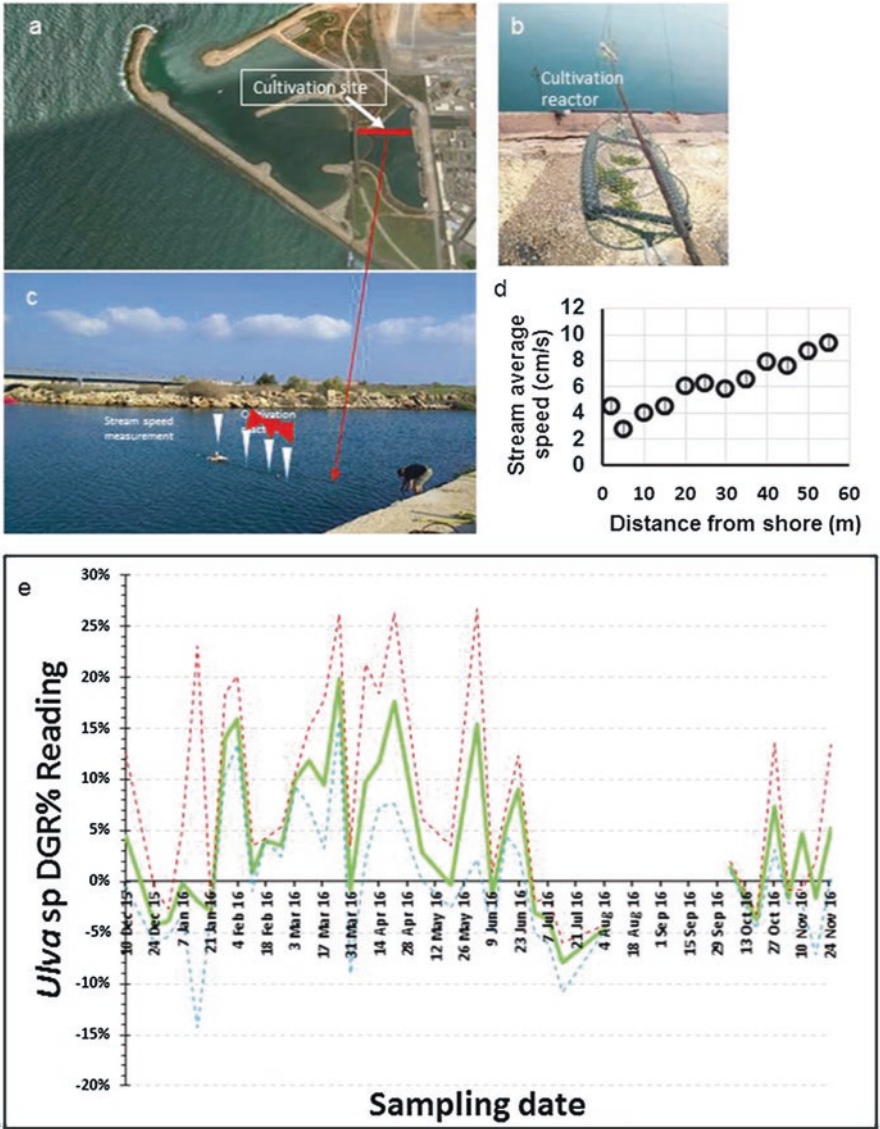


Fig. 10.2 Experimental setup for daily growth rate (DGR) measurements. (a) Macroalgae cultivation site at Reading Power Station in Tel Aviv, Israel. (b) Flat thin cultivation reactor with a signal cultivation depth and double net design. (c) Positions of cultivation reactors during 1 year measurements. (d) Water current speed profile at the cultivated area, measured at the same depths as the flat thin cultivation reactor ($N = 10$ for each point). (e) Measured annual daily growth rate (%DGR) of *Ulva* biomass at reading ($N = 3$ for each point). Green line shows an average value, red line shows a maximum value, and blue line shows the minimum value of % DGR. (Images adapted from Chemodanov et al. 2017a with permit)

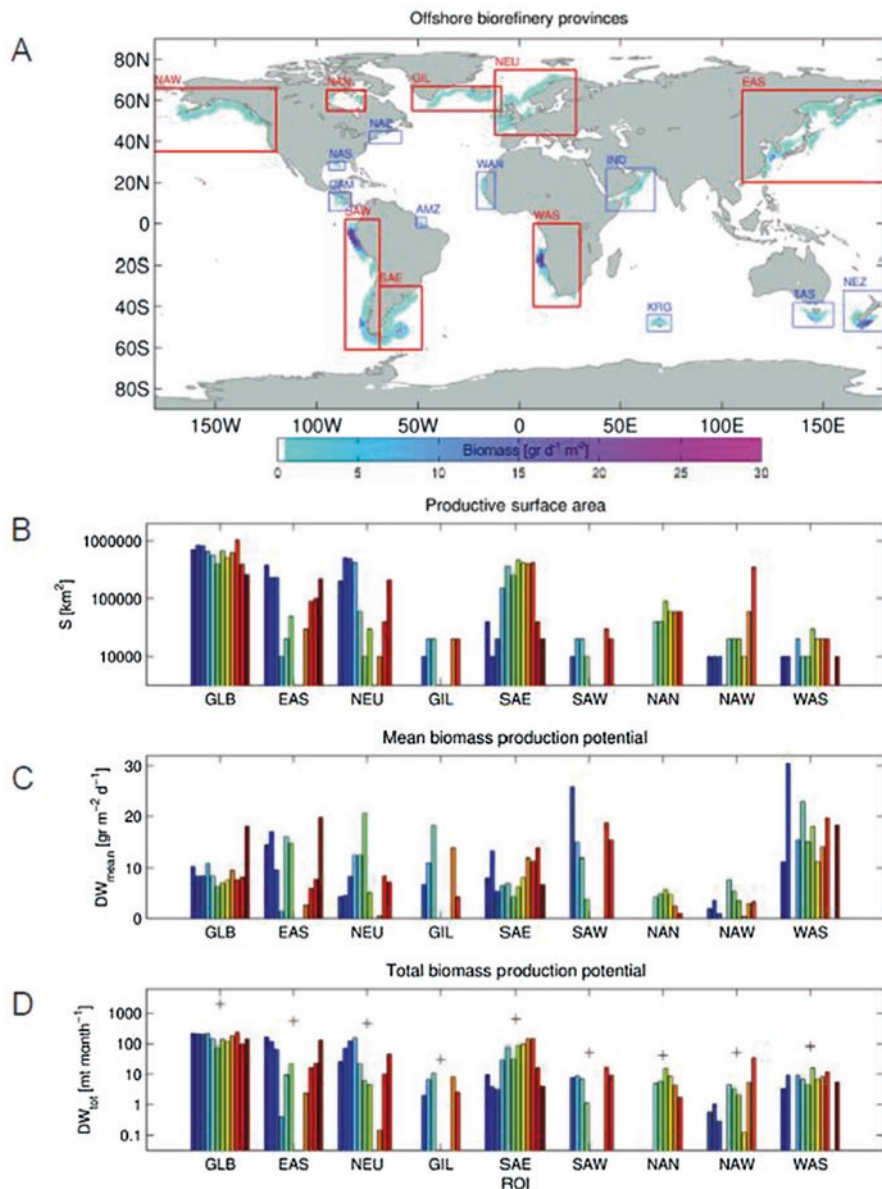


Fig. 10.3 Regional potential for offshore biomass production with extensive methods. (a) Potential for biomass production at a distance of less than 400 km from land. Boxes delineate major offshore biorefinery provinces, with that permitting biomass production at water depth of up to 100 m (defined as near-future deployable biorefinery provinces – NDBP) marked in red and that permitting biomass production only at deeper waters marked in blue. (b–d) Monthly estimates of (b) productive surface area, (c) mean biomass production potential, and (d) total production potential within the 8 NDBP (red boxes and associated abbreviations in panel A) and integrated globally (denoted GLB). Colors denote different months of the year. The analysis is

Free-floating enclosures can be released in areas with predicted currents, or alternatively followed with tracking devices, and finally collected and harvested when time and location are suitable and biomass weight is satisfactory. Such a system was suggested by Notoya (2010) that proposed to grow seaweed beds on 100 km² rafts, floating away from shipping lanes until ready to harvest. However, this concept is yet to be demonstrated. Anchored platforms can be sited in areas that are favorable for cultivation, aiming for optimal temperatures and sunlight, water motion which is sufficient to break down diffusion barriers, and natural supply of nutrients, for example, in natural upwelling zones (Roesijadi et al. 2008).

When the environmental concentration of nutrients are low, nutrients may be provided by artificial upwelling of deep nutrient-rich water as suggested already in the 1970s in the “Marine Biomass Program” (Roesijadi et al. 2008). The artificial upwelling solution can be potentially combined with Ocean Thermal Energy Conversion (OTEC) ventures, utilizing deep seawater for both nutrient enrichment and temperature difference-based power generation, thus reducing costs and environmental footprints while harnessing energy and nutrients (Roels et al. 1979). Another solution for supplying nutrients offshore is the polytrophic aquaculture, also known as integrated multi-trophic aquaculture (IMTA) (Ashkenazi et al. 2019; Neori et al. 2004). This approach can significantly increase system sustainability, inter alia by recycling waste nutrients from higher trophic-level species into the production of lower trophic-level crops of commercial value, such as macroalgae (Troell et al. 2009). Furthermore, co-cultivation of different species can increase productivity by increasing the light-harvesting efficiency. This can be done, for example, in a layered seaweed cultivation system, employing typical light absorption characteristics of green, brown, and red macroalgae, respectively, thus improving light use (Reith et al. 2005).

In contrast to the extensive approach, the intensive approach emphasizes the importance of achieving maximal biomass yields, even at the expense of energy costs. Following this approach, Golberg and Liberzon (2015), for example, have modeled smart mixing regimes to improve biomass productivity by enhancing light-harvesting and carbon fixation (Golberg and Liberzon 2015). Mixed water cultivation is commonly applied to onshore reactor cultivation of free-floating green algae (Chemodanov et al. 2017b). However, applying free-floating algae cultivation offshore, mixed or non-mixed, is challenging due to forceful ocean currents and increased loss risks, which may lead to uncontrolled macroalgal blooms (Liu et al. 2009).



Fig. 10.3 (continued) performed over locations associated with water depth of 100 m or shallower. The + signs mark annually integrated biomass production potential at each region. East Asia offshore waters (EAS); Northern Europe offshore waters (NEU); Greenland and Iceland offshore waters (GIL); North America offshore waters, north (NAN); North America offshore waters, west (NAW); South America offshore waters, east (SAE); South America offshore waters, west (NAW); West Africa offshore waters, south (WAS). Amazon River estuary (AMZ); Central America offshore waters (CAM); Indian Ocean (IND); Kerguelen (KRG); New Zealand (NEZ); Tasmania (TAS); North America offshore waters, south (NAS); North America offshore waters, east (NAE); West Africa offshore waters, north (WAN). Images adapted from ref (Lehahn et al., 2016) with permit.

10.5 Co-production of Multiple Products from Macroalgae

The global potential of the near-future achievable deployment offshore biomass production (i.e., in regions extending up to 400 km distance from the shore and with a water depth of up to 100 m) can provide $1.96 \cdot 10^9$ ton DW year⁻¹. This is equivalent to the 37 EJ year⁻¹ of primary energy potential (calculated as LHV). In comparison, the predicted bioenergy potential from agricultural land in 2050 is expected to be 64–161 EJ year⁻¹ (Haberl et al. 2011). Based on already available protocols in literature, this biomass can be converted to multiple products such as ethanol, butanol, acetone, methane, proteins, and others (Table 10.2).

A recent study developed a methodology to assess the performance of the integrated two-stage supply chain – feedstock farming and processing into multiple outputs. The results from the nonlinear dynamic model clarify that learning (by doing/researching) in a multistage supply chain creates a positive externality of co-outputs. Moreover, if the learning rate is faster than cost increase, then output grows faster than prices. Next, they demonstrated the application of the modeling framework on macroalgae (seaweed) farming and processing in the biorefinery into crude proteins and polysaccharide (carrageenan). The results indicated that for average prices of proteins and carrageenan, and for average costs of investment in cultivation farm and the biorefinery, macroalgae utilization is cost-efficient. The study indicated that using near-future aquaculture technologies, offshore cultivation of macroalgae has the potential to provide some of the basic products required for human society in the coming decades. However, the profitability of this supply chain is fragile due to the high volatility of outputs' prices, as well as a wide range of feedstock growth rate and chemical composition. Notably, the researchers identified the first stage of the supply chain, namely, macroalgae marine cultivation, as the main constraint for commercialization.

Studies have shown that the remaining pulp after extraction of high-value polysaccharides such as agar, alginates, and carrageenan still contain high amount of carbohydrates and other nutrients including protein, lipids, and ash, which may be used as a source of raw material for extraction of various other materials rather than treating as a waste (Kumar and Sahoo 2017; Alvarado-Morales et al. 2015). Utilization of all the organic content to useful, high-value products would make the biorefinery process most profitable and sustainable by maximizing the biorefinery's overall economic performance (Laurens et al. 2017). Notably, the outputs from macroalgae-based biorefinery vary with the species of the seaweed, as presented below.

Considering this, co-production of two or more products from green macroalgae in an integrated, cascading, biorefinery approach has been followed, thus maximizing the benefits of seaweed biomass (Postma et al. 2017; Trivedi et al. 2016; Ben Yahmed et al. 2016; Bikker et al. 2016a). Experimentally, sequential recovery of four economically important fractions, a mineral-rich liquid extract, lipid, ulvan (a sulfated polysaccharide, S-PS, of the genus *Ulva*), and cellulose from *Ulva fasciata*, was reported by Trivedi et al. (2016). The mineral-rich liquid extract was extracted by mechanical grinding and ulvan by a hydrothermal process. Bikker et al. (2016b)

Table 10.2 Potential for offshore production of biomass and derived products for various cultivation stocking densities. The notion “All waters” refers to all locations regardless of water depth and distance from the coast, while “shallow nearshore waters” refers to areas associated with water depths smaller than 100 m and located less than 400 km from the coast

Biomass stocking density	1 kg m ⁻²		2 kg m ⁻²		4 kg m ⁻²		6 kg m ⁻²		8 kg m ⁻²	
	All waters	Shallow near shore waters	All waters	Shallow near shore waters	All waters	Shallow near shore waters	All waters	Shallow near shore waters	All waters	Shallow near shore waters
Biomass (10 ⁶ t year ⁻¹) (DW)	67,500	591	81,000	710	108,000	946	54,000	473	40,500	355
Ethanol (10 ⁶ t year ⁻¹)	2025–15,525	18–136	2430–18,630	21–163	3240–24,840	28–218	1620–12,420	14–109	1215–9315	11–82
Butanol (10 ⁶ t year ⁻¹)	2025–4050	18–35	2430–4860	21–43	3240–6480	28–57	1620–3240	14–28	1215–2430	11–21
Acetone (10 ⁶ t year ⁻¹)	675–1350	6–12	810–1620	7–14	1080–2160	9–19	540–1080	5–9	405–810	4–7
Methane (10 ⁶ m ³ year ⁻¹)	675–6480	6–57	810–7776	7–68	1080–10,368	9–91	540–5184	5–45	405–3888	4–34
Protein (10 ⁶ t year ⁻¹)	3375–16,200	30–142	4050–19,440	35–170	5400–25,920	47–227	2700–12,960	24–114	2025–9720	18–85
Energy (10 ¹² kJ year ⁻¹)	1,282,500	11,234	1,539,000	13,481	2,052,000	17,974	1,026,000	8987	769,500	6740

Table adapted from Lehahn et al. (2016) with permit

demonstrated the co-production of a sugar-rich hydrolysate (38.8 g l^{-1}), used for the production of acetone, butanol, ethanol, and 1,2-propanediol by clostridial fermentation, and a protein-enriched (343 g kg^{-1} in dry matter) extracted fraction, used as animal feed, out of *Ulva lactuca* biomass. The extraction procedure included solubilizing the sugars by hot water treatment followed by enzymatic hydrolysis and separating solid and liquid fractions by centrifugation. Ben Yahmed et al. (2016) demonstrated the integrated biorefinery approach for co-production of bioethanol and biogas using fermentation and anaerobic digestion of *Chaetomorpha linum* hydrolysate obtained by thermochemical and enzymatic hydrolysis (Ben Yahmed et al. 2016). Postma et al. (2017) have co-extracted water-soluble proteins and carbohydrates from fresh *U. lactuca* biomass using osmotic shock, enzymatic hydrolysis, the pulsed electric field (PEF), and high shear homogenization (Postma et al. 2017). Glasson et al. (2017) reported the extraction of salts, pigments, ulvan, and monosaccharides from *Ulva ohnoi*, and more recently Gajaria et al. (2017) reported the extraction of five different chemical products: minerals, lipids, ulvan, protein, and cellulose, from *U. lactuca*, both in a cascading biorefinery process (Gajaria et al. 2017). Very recently, an additional work showed the liquid fraction obtained after homogenization of fresh *Ulva* biomass, and filtration can be processed for the effective extraction of starch in its native form (Prabhu et al. 2019). We also proposed that the starch extraction can be effectively integrated into the biorefinery, and the leftover biomass can be processed for the extraction of other various products. Based on various integrated biorefinery concepts mentioned above, a process design was developed for co-production of six different products and applications (Fig. 10.4).

Brown seaweeds are interesting feedstock for biorefineries as they contain a diverse array of metabolites including extracellular matrix polysaccharides such as alginates and fucoidans, storage polysaccharides such as laminarin and mannitol, and bioactive polyphenolic compounds and pigments such as fucoxanthin with potential applications in pharmaceutical, food, cosmetic, and biotechnology industries (Kostas et al. 2017). Using brown macroalgae *Laminaria digitata*, fucoidan, alginate, and bioethanol were extracted in a cascading biorefinery by Kostas et al. (2017). They also showed that the methanol fraction extracted using the waste stream after fucoidan extraction had antioxidant and antimicrobial activity. Yuan and Macquarrie (2015) indicated that *Ascophyllum nodosum* could be potentially used as feedstock for a cascading biorefinery process to produce valuable chemicals and fuels (fucoidan, alginates, sugars, and biochar). Van Hal et al. (2014) demonstrated extraction scheme for mannitol, alginate, laminarin, and sugars from *Saccharina latissima* in a cascading biorefinery. The mannitol was converted to isomannide; the laminarin was fermented to acetone, butanol, ethanol (ABE); and the alginate fraction was converted to furan dicarboxylic acid (FDCA) (Van Hal et al. 2014). Co-producing succinic acid, phenolic antioxidants, and fertilizer from *Saccharina latissima* indicate that the economic profit of the biorefinery is positive (Marinho et al. 2016).

Using red macroalgae, *Gracilaria corticata*, Baghel et al. (2016) demonstrated the simple process for recovery of mineral-rich liquid extract (MRLE), pigments,

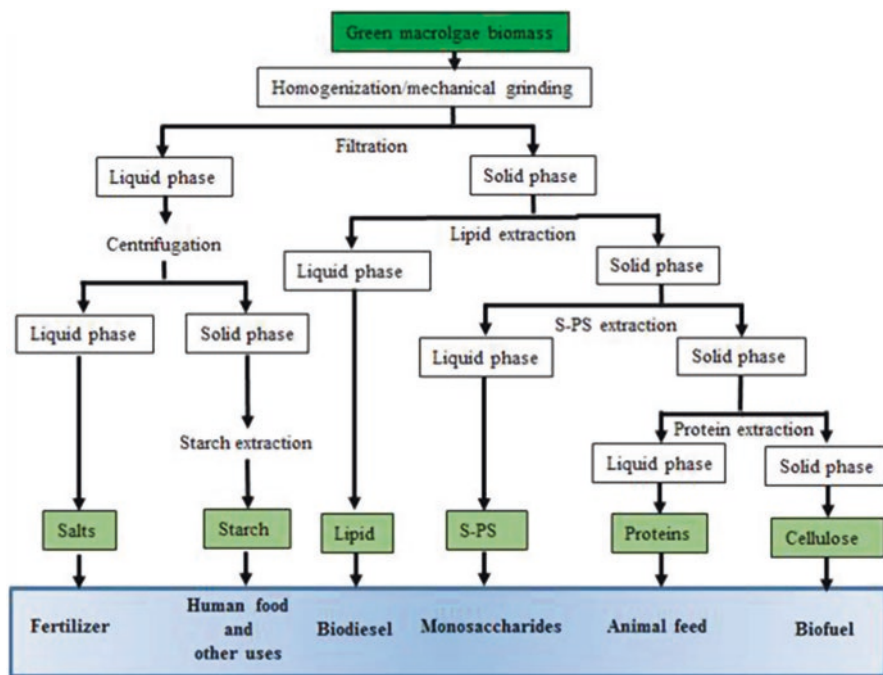


Fig. 10.4 Green macroalgae biorefinery process for co-production of a wide range of valuable products. (Figure adapted from Prabhu et al. 2019 with permits)

crude lipid, agar, soil conditioner, and bioethanol using various techniques such as homogenization, ultra-membrane filtration solvent extraction, enzymatic and thermal hydrolysis, and fermentation. An example of the biorefinery based on the currently widely cultivated red macroalgae *Kappaphycus alvarezii* being biorefined for the production of bioethanol, carrageenan, fertilizer, and biogas is shown in Fig. 10.5. Such studies enable to realize the full potential of marine macroalgal feedstock for production of fuel and chemicals. Such a production of high-value multiple products at a time, in the integrated process, is necessary in order to meet current bioeconomy challenges (Chandra et al. 2019). Various integrated biorefinery studies producing various streams of products in cascading fashion involving green, brown, and red macroalgae species are shown in Table 10.3. Various products and by-products can be derived from integrated alga (Chandra et al. 2019; Sahoo et al. 2012; Milledge et al. 2016). The most important biomass products in algal biorefineries are:

- Biomass – health food, functional food, feed additive, aquaculture, biofertilizer
- Phycocolloids – agar, carrageenan, alginates
- Pigments/carotenoids – astaxanthin, phycocyanin, phycoerythrin, fucoxanthin
- Vitamin – A, B1, B6, B12, C, E, biotin, riboflavin, nicotinic acid, pantothenate, and folic acid

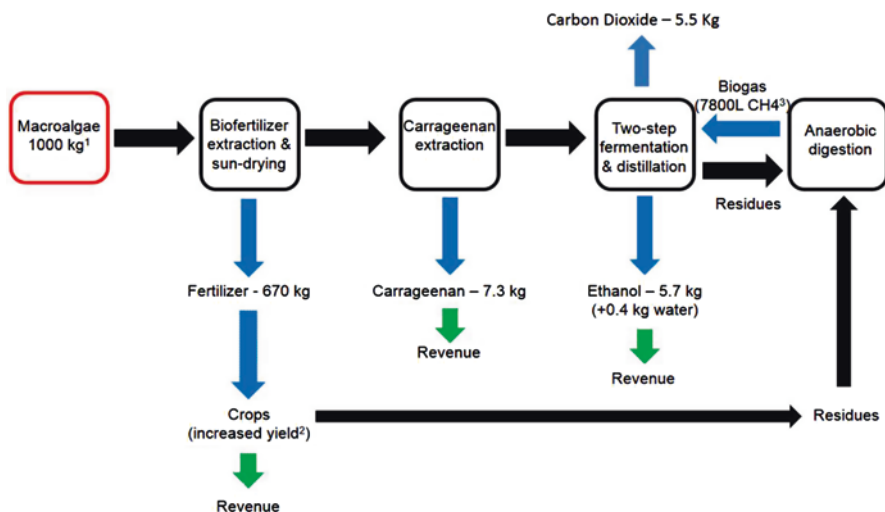


Fig. 10.5 Red seaweed *Kappaphycus*-based biorefinery for the co-production of fertilizers, carrageenan, ethanol, and biogas. (1) 1 kg of freshly harvested algae (fresh weight), (2) (Eswaran et al. 2005), (3) yield from digestion of algal biomass only (Park et al. 2012). Calculations were done using the following yield and assumption: fertilizer yield (67%), residue moisture content (25%), carrageenan yield (12% g/kg dry algae), ethanol yield (minimum scenario of 77.6 g/kg dry algae), ethanol purity after distillation (95:5 v:v ethanol-water mixture), 1 mol of produced ethanol = 1 mol of produced CO₂, 141 L CH₄/kg of algal dry matter before ethanol production. (Figure adapted from Ingle et al. 2017 with permits)

- Antioxidants – β -carotene, tocopherol
- Antioxidant extracts – PUFA extracts (polyunsaturated fatty acids), arachidonic acid (ARA polyunsaturated omega-6 fatty acid, docosahexaenoic acid) (DHA omega-3 fatty acid)
- Other/pharmaceuticals – antifungal, antimicrobial, antiviral, toxins, amino acids, proteins, and sterols
- Biofuels – bioethanol, biodiesel, bio-butanol, biomethane, and biochar

10.6 Economic Challenge of Offshore Marine Biorefineries

There are numerous challenges associated with the successful deployment of marine biorefinery operations as summarized in Fig. 10.6. The profitability of marine biorefinery is subject to various sources of uncertainty such as that of feedstock supply, processing technology, investment, contracting, and demand (Palatnik and Zilberman 2017).

Selection of right biomass is critical as there are numerous species of macroalgae. As presented in Table 10.3, each of them differs for chemical structure and therefore differs for bio-based chemicals to be produced (Jung et al. 2013). The

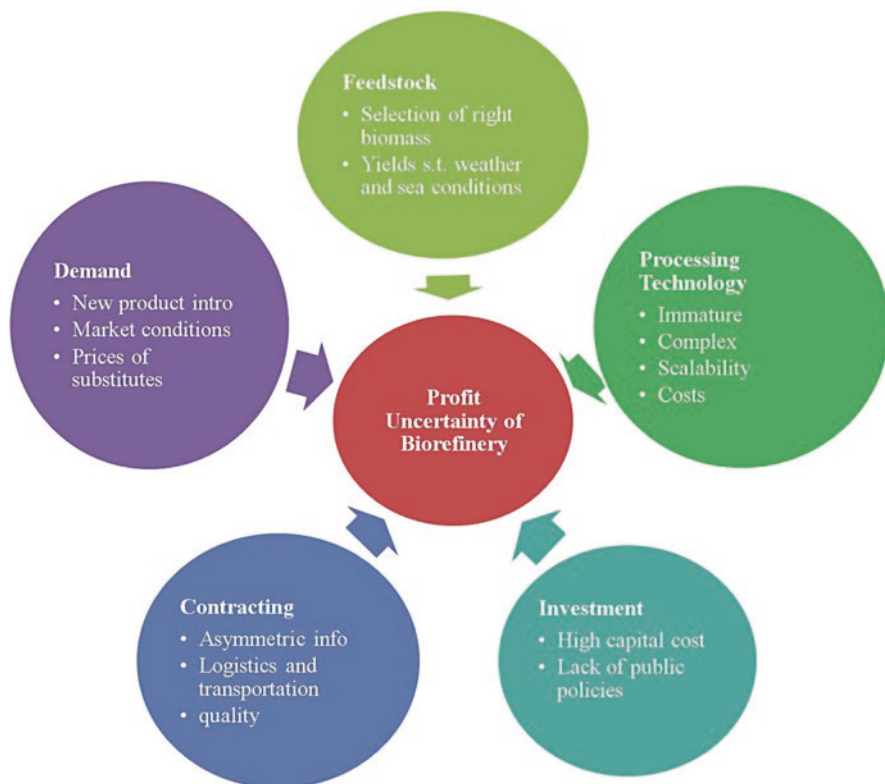


Fig. 10.6 Major sources of uncertainty for marine biorefinery deployment

entrepreneur should determine which algae-based activities are profitable under multidimensional uncertainty outlined below.

The rate of feedstock growth shows a wide range of values. Studies report the range of 6–108 tonnes/ha per year (Valderrama et al. 2015). This uncertainty in feedstock yield has a major impact on the cost-effectiveness of the technology. Feedstock growth depends on saturation kinetics by light intensity, ambient dissolved inorganic nutrient concentrations, and temperature (Lehahn et al. 2016). Cultivation uncertainty is exacerbated by stochastic weather, seasonal variability between regions, within years, and between years. Studies point at the biomass productivity as the main constraint against being competitive with other energy- and protein-producing technologies (Seghetta et al. 2016b).

Anaerobic digestion, fermentation, transesterification, liquefaction, and pyrolysis can convert algal biomass into proteins and sugars that can result in food, chemicals, and biofuels. At each stage of the production process, the entrepreneur should decide between various options that ultimately affect the irreversible (sunk) and variable costs of the production, the productivity, and the output, therefore affecting the total profitability. Yet, the biorefinery yields are highly uncertain (Lehahn et al.

Table 10.3 Green, brown, and red macroalgae species-based biorefinery studies carried out for production of various products

Species	Biorefinery products	Technologies/methods	Reference
Green macroalgae			
<i>U. lactuca</i>	Proteins and carbohydrates	Osmotic shock, enzymatic hydrolysis, PEF or high shear homogenization	Postma et al. (2017)
<i>U. lactuca</i>	Animal feed (343 g protein kg ⁻¹ dry matter), acetone, butanol, ethanol, and 1,2-propanediol	Thermal and enzymatic hydrolysis and fermentation	Bikker et al. (2016c)
<i>Chaetomorpha linum</i>	Bioethanol and biogas	Thermochemical and enzymatic hydrolysis, fermentation, and anaerobic digestion	Ben Yahmed et al. (2016)
<i>Ulva fasciata</i>	MRLE, lipid, ulvan, and cellulose	Mechanical grinding, thermal and chemical extraction, and water extraction	Trivedi et al. (2016)
<i>Ulva ohnoi</i> and <i>Ulva tepida</i>	Mainly salt (demonstrating the use of leftover biomass for protein, fertilizer, animal feed and fuel)	Aqueous washing and drying	Magnusson et al. (2016)
<i>U. lactuca</i>	MRLE, lipid, ulvan, protein and cellulose	Mechanical pressing and crushing, heat treatment and organic solvent, and alkali extraction	Gajaria et al. (2017)
<i>U. lactuca</i>	Acetone, butanol and ethanol (ABE)	Pretreatment, enzymatic saccharification and fermentation	van der Wal et al. (2013)
<i>Ulva rigida</i>	Liquid stream with carbohydrate and salt; remaining stream with concentrated protein	Ionic liquid deconstruction	Pezoa-Conte et al. (2015)
<i>U. ohnoi</i>	Salt, pigment, ulvan, and protein	Aqueous pretreatment, thermal and chemical extraction	Glasson et al. (2017)
<i>U. lactuca</i>	MRLE, ulvan, protein, and methane	Aqueous, thermal and chemical extraction, and anaerobic digestion	Mhatre et al. (2018)
Brown macroalgae			
<i>Laminaria digitata</i>	Succinic acid, feed and energy	Enzymatic hydrolysis, fermentation, anaerobic digestion	Alvarado-Morales et al. (2015)
<i>Laminaria digitata</i>	Alginate, fucoidan, alginate, bioethanol	Acid hydrothermal, enzymatic scarification, fermentation	Kostas et al. (2017)
<i>Ascophyllum nodosum</i>	Fucoidan, alginates, sugars, and biochar	Thermal, acid hydrolysis	Yuan and Macquarrie (2015)

(continued)

Table 10.3 (continued)

Species	Biorefinery products	Technologies/methods	Reference
<i>Saccharina latissima</i>	Isomannide, butanol, furan dicarboxylic acid, biogas	Shredding and pressing, fermentation	Van Hal et al. (2014)
<i>Saccharina latissima</i>	Succinic acid, fertilizers, and antioxidants	Enzymatic hydrolysis and fermentation, solvent extraction	(Marinho et al. 2016)
<i>Durvillaea potatorum</i>	Alginate, fucoidan, and laminarin	Mechanical grinding, acid and alkali extraction	Abraham et al. (2019)
Red macroalgae			
<i>Gracilaria verrucosa</i>	Agar, bioethanol, and biofertilizer	Thermochemical, enzymatic hydrolysis, and fermentation	Kumar et al. (2013)
<i>Gracilaria corticata</i>	MRLE, pigments, lipid, agar, soil conditioner, and bioethanol	Homogenization, ultra-membrane filtration solvent extraction, enzymatic and thermal hydrolysis, fermentation	Baghel et al. (2016)
<i>Porphyra umbilicalis</i>	Proteins, carrageenan, pectin, and cellulose	Cold alkali extraction, thermochemical, solvent extraction	Wahlström et al. (2018)

2016) signaling the immaturity of the technology. The upper value of yields can be ten times larger than the lower one (Table 10.4), significantly affecting the potential profitability of the process.

Numerous studies are focusing on the effort to evaluate future costs of the process that is currently available mostly in small (lab) scale (e.g., Seghetta et al. 2016b; Korzen et al. 2015c). These studies, however, do not report a structured production function that leads to a cost function. The common assumption is a linear approximation. This assumption should be treated cautiously and verified against actual data when production is scaled up.

The development of a new biorefinery, its design, and construction requires huge investments (Stichnothe et al. 2016). The strategy about the capacity of the biorefinery may change over time; the innovator may experiment by starting at a small scale. Once the production system is established, the innovator may either expand operations or reach out to cooperatives to provide it with inputs.

Moreover, introducing and perfecting innovations is a random process, and the economic conditions that face technology vary over time. Learning takes time, and the dynamics of knowledge accumulation affect the timing of introduction of innovations, their refinement, and their commercialization. Timing can also affect the decision regarding both the capacity of innovation and the extent of reliance on external sources.

Lack of public policies supporting biorefinery sector limits the long-term investment decision required. There are various strategies, but there are no distinct policy drivers for the utilization of bio-based chemicals, in direct contrast to the biofuels industry where various national regulations are driving rapid growth.

Table 10.4 Examples for costs of macroalgae production and commodities' prices

Description	Average value	Range	Source
First unit cost of <i>carrageenan</i>	USD 4500/ton 2014	USD 4000–6500/ton 2010	Brown (2015)
First unit cost of feedstock seaweed <i>Kappaphycus</i>	USD 1600/ton 2016	USD 600–7000/ton 2010	Calculated based on Ricardo et al. (2015)
Price of protein	USD 5000/Ton	USD 1000–15,000/ton 2016	Price calculated from value and quantity world 2016 <i>Source</i> : UN COMTRADE; commodity 210610 protein; concentrates and textured protein substances
Annual growth of the price of protein	7%	–43 to 92% in 1991–2016	Price calculated from value and quantity of Philippines and US export 1991–2016 <i>Source</i> : UN COMTRADE; commodity 210610 protein; concentrates and textured protein substances
Price of <i>carrageenan</i>	USD 5500/ton	USD 3000–6000/ton 2016	https://www.alibaba.com/trade/search?fsb=y&IndexArea=product_en&CatId=&SearchText=carrageenan
Annual growth of the price of <i>carrageenan</i>	4%	–11 to 53% in 1991–2016	Price calculated from value and quantity of Philippines export <i>Source</i> : UN COMTRADE; commodity HSI30239 (mucilages and thickeners ones)

The impact of price variation should be analyzed in several aspects: price uncertainties that face the aqua-farmer, price uncertainties of feedstock for the biorefinery, and the price uncertainty of competitive outputs (backstop technology). A seaweed industry that contains many small-scale price-takers is especially prone to boom-bust cycles. For example, the strong demand from China drove the price of dry cottonii in the Philippines from USD 900/ton in 2007 to almost USD 3000/ton in 2008 causing the Philippines production to double from 1.5 million tons (wet weight) in 2007 to 3.3 million tons in 2008. The “seaweed rush” lasted only 1 year – the price dropped to USD 300/ton in 2009 (Ricardo et al. 2015). Table 10.4 exemplifies the range of prices as well as annual growth rates for one of the macroalgae species – *Kappaphycus* – and for two possible biorefinery outputs: *carrageenan* and proteins in the years 1991–2016. Generally, when strong demand for dry seaweeds drives up the price, seaweed farmers tend to increase their planting efforts and/or harvest immature crops. However, if the price is low, seaweed farmers tend to reduce production, which creates sourcing difficulties for the biorefineries. On the other hand, biorefineries would tend to reduce demand as prices of feedstock rise by substituting cheaper alternatives. A likely result would then be that feedstock supply exceeding demand and consequently a collapse in price.

The economics of biorefinery based product depends heavily on drop-in versus non-drop-in (existing demand and infrastructure). Therefore, demand may be very strong or very weak, leading to general uncertainty. It is difficult to know, for example, if an investment in the bio-based supply chain will make economic sense. It might not be possible to sell the produced bio-based chemicals at a price necessary to make the investment profitable. Of course, these are the kinds of decisions that all businesses face, but the reliance of biomass markets on policy measures and the lack of long-term signals in, for example, EU policy regarding biomass means that uncertainties are unusually high. In addition to the production cost, the value of biorefinery products when reaching end users may also reflect the expenses on research and development (R&D), formulation, marketing, etc. (Ricardo et al. 2015). Specific information on these aspects is generally lacking.

10.7 Sustainability and Environmental Impacts

The sustainability of seaweed biorefineries was assessed in various life cycle assessment (LCA) studies (Seghetta et al. 2016b, Seghetta et al. 2017; Alvarado-Morales et al. 2013; Czyrnek-Delêtre et al. 2017; Langlois et al. 2012; van Oirschot et al. 2017; Aitken et al. 2014). Overall, seaweed cultivation was found to contribute to the environmental restoration and climate mitigation. However, several parameters have been pointed out to have significant effects on the environmental performance of the complete biorefinery process and should be optimized.

Large-scale macroalgae cultivation can be responsible for positive and negative impact on coastal and marine ecosystems (Hughes et al. 2012). Therefore, the balance is necessary to attain in between food, chemicals, and fuel production and its environmental cost (Wei et al. 2013). Although scale-up reduces production costs of

macroalgae, the offshore cultivation is challenging because of the harsh environment and also could possess risks to the environment. Risk management framework should be developed for each individual case to address these factors.

The overall risk management framework is generally used for the decision-making process and provides a more clear idea to make a decision about any technological term and includes and comprises defining the challenge or problem; stakeholders involved; consideration of almost possible concerns; identification of actual risk, review, and judgment; and finally the decision (Singh et al. 2016; Keswani and Singh 2019). The proposed framework of risk management for offshore macroalgae cultivation is shown in Fig. 10.7. The framework is divided into three sections as follows. Section 10.1 shows the possible risks, which can be prevented before the cultivation or during the cultivation and are related to the requirement of macroalgae cultivation. Section 10.2 shows the risks that might be controlled in the process production of biomass and harvesting. Section 10.3 shows the risks that will need to be mitigated, as these are the potential impacts of cultivation of macroalgae on the marine environment.

To summarize, we show that offshore macroalgae biorefinery concepts are emerging for co-production of multiple products, which could reduce the environmental burden of fossil fuels and agriculture. Technologies for offshore biomass

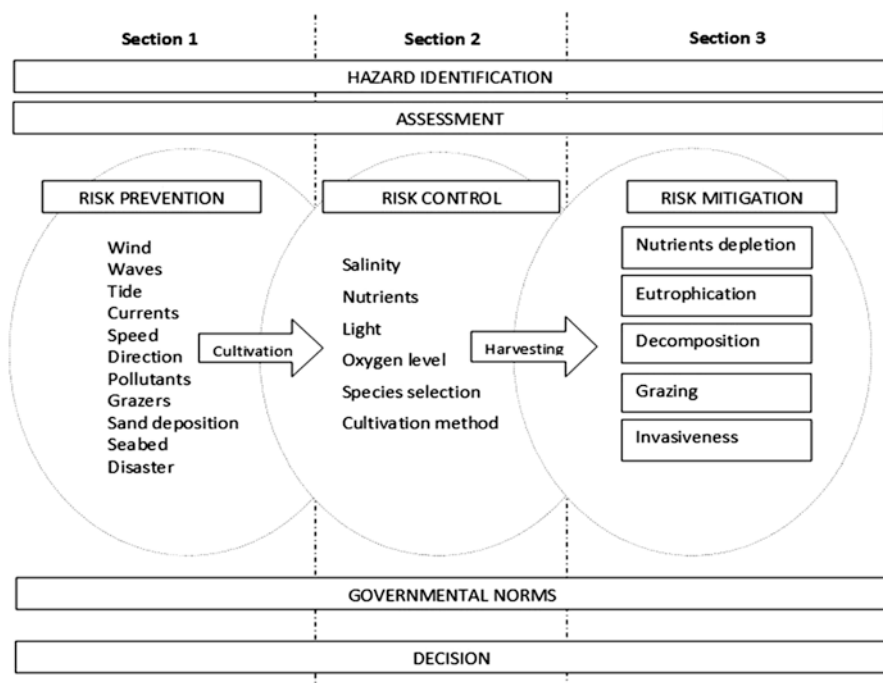


Fig. 10.7 The entire framework of the risk management for offshore macroalgae cultivation. (Figure adapted from Lehahn et al. 2016 with a permit)

cultivation are being developed worldwide. Biomass fractionation technologies are emerging and provide a broad spectrum of products. Yet the challenging, high-energy sea environment and unusual composition of the biomass still result in high levels of uncertainty of technological and economic feasibility of these projects. To decrease this uncertainty, demonstration units with different scales, technologies, species, and products are needed.

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